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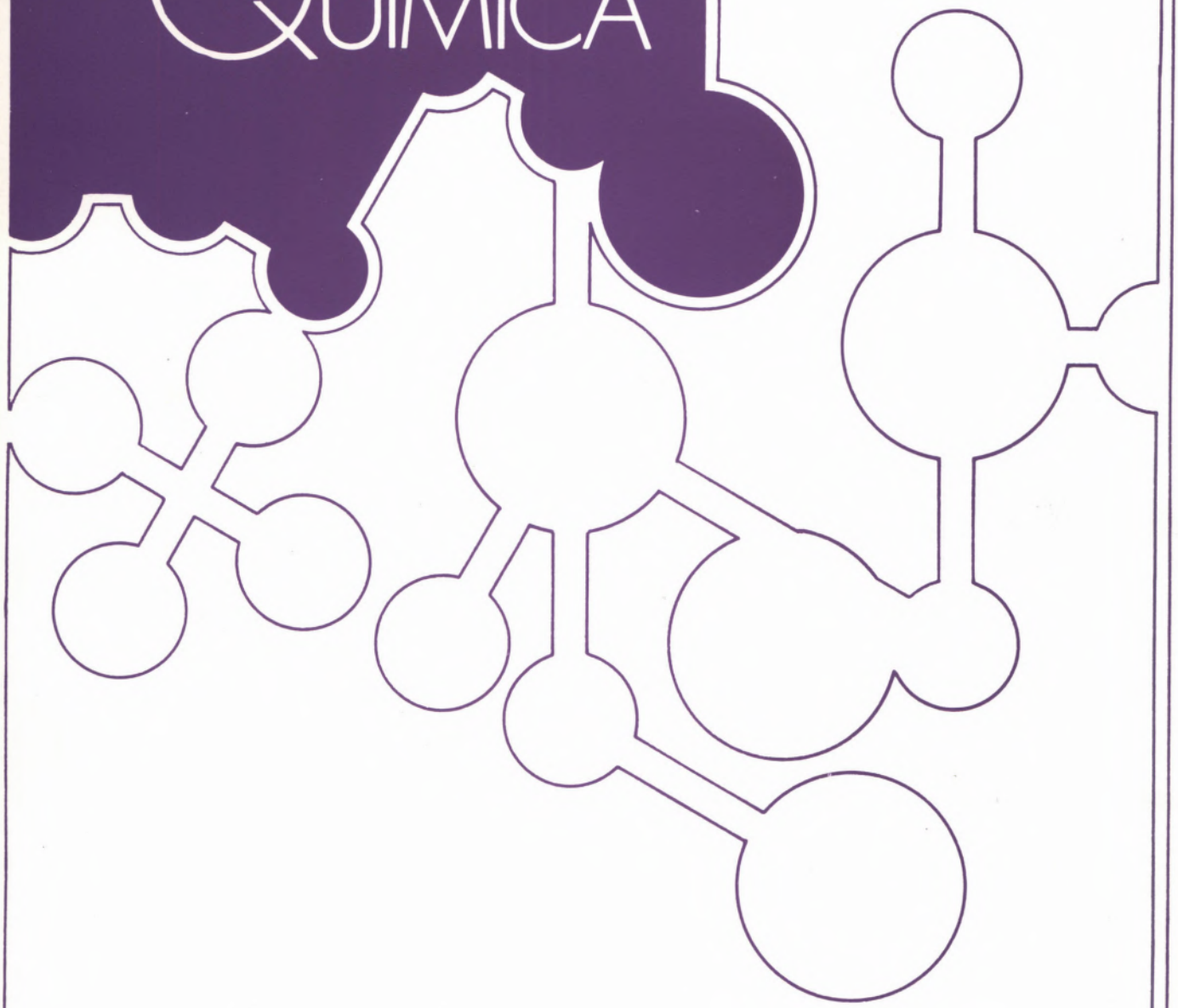

SOCIEDADE PORTUGUESA DE QUÍMICA

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DIVISÃO DE QUÍMICA ANALÍTICA

A Delegação Norte da SPQ estabeleceu recentemente contactos com o Colégio Oficial de Químicos e Associação Nacional de Químicos de Espanha - - Delegação da Galiza, tendo em vista promover o intercâmbio científico e técnico entre as duas associações.

Em resultado destes contactos, foi decidido organizar anualmente um Encontro, alternadamente na Galiza e na Região Norte. O "1º Encontro Anual de Química Galaico-Portucalense" realizar-se-á na Galiza em Janeiro de 1985 e o seu tema será a água: - Águas naturais, águas residuais e controle de qualidade.

Também de particular interesse para a Divisão de Química Analítica é o intercâmbio no domínio da Normalização e Controle de qualidade. Desde já se convidam os colegas interessados neste tema a contactarem com esta Divisão, indicando o seu ramo de actividade a fim de se poder elaborar e permutar um ficheiro de especialistas que facilitará futuros contactos pessoais.

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NOTA DO EDITOR

Este número da Revista Portuguesa de Química está a ser editado no período de transição entre a saída do Editor Carlos M. Pulido e a entrada em funções da nova equipa editorial.

Relativamente às características de uma publicação como a Revista Portuguesa de Química muitas podem ser as opiniões e todas elas são respeitáveis. Pelo nosso lado, temos defendido que é importante a manutenção do bom aspecto gráfico (dentro das limitações dos nossos orçamentos).

É certo que numa revista científica, é contudo dos textos e não o seu aspecto gráfico aquilo que determina a qualidade do trabalho. No entanto, nós defendemos que uma boa apresentação pode facilitar bastante a leitura do texto, contribuindo assim para melhorar a comunicação entre os autores e os seus leitores.

Infelizmente, muitos artigos submetidos à Revista nestes últimos anos, têm sido publicados com um enorme atraso em relação à data de recepção dos trabalhos. Peço desculpa aos autores que foram prejudicados por tais atrasos e agradeço a compreensão que revelaram relativamente às dificuldades que tivemos de ultrapassar.

Quero também expressar os meus agradecimentos ao ex-Editor da Revista Carlos M. Pulido pelos conselhos e palavras de encorajamento com que me apoiou, a M. Helena D. Santos a rapidez com que sempre executou os trabalhos de preparação de texto e revisão de provas e ao pessoal da tipografia Proença o esforço e a boa vontade com que se empenharam na rápida execução deste número.

Finalmente, queria deixar expressos os meus mais cordiais votos de felicidades á nova equipa editorial.

Luís Vilas-Boas

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RESÍDUOS METÁLICOS CEDIDOS POR UTENSÍLIOS DE COZINHA

III. CEDÊNCIA DE CHUMBO, CÁDMIO E ALUMÍNIO POR LOUÇA DE CERÂMICA PARA CRIANÇAS

Faz-se o estudo de alguns serviços de cerâmica destinados normalmente a servir alimentos a crianças, no respeitante a cedências de chumbo, cádmio e alumínio.
Foram analisadas 38 peças de várias marcas e, através dos metais cedidos, estabelece-se uma correlação entre a tecnologia das diferentes casas fabricantes e a qualidade das peças no respeitante a cedências.

1 — INTRODUÇÃO

O cádmio e o chumbo, pela toxidade e bioacumulação no organismo (períodos de semi-vida biológicos da ordem dos 10 a 30 anos e dos 1900 dias, respectivamente) adicionadas às interacções dietético-nutricionais com elementos essenciais (o chumbo interfere com o cálcio e o ferro, o cádmio com o zinco, etc.) estão desde longa data consagrados como perigosos para a saúde [1-6]. Daí que os vários investigadores continuem a previlegiá-los como matéria de estudo e que as autoridades sanitárias, no último decénio, venham estabelecendo doses limites de ingestão admissíveis e teores de tolerância na biosfera à medida dos dados disponíveis [7,8].

Pelo contrário, a toxicidade do alumínio ainda não foi rigorosamente averiguada. O estudo da sua prevalência na atmosfera e nos alimentos tem sido igualmente descurado, provavelmente a pretexto duma pressuposta baixa toxicidade decorrente da sua abundância na crusta terrestre (ocupa entre os elementos, o terceiro lugar com uma representatividade de 8 % [9,10] e presumível reduzida absorção em consequência da sua pequena solubilidade ao pH deste meio. Porém, estudos recentes vêm demonstrando que este metal está longe de ser inócuo [11-13]. Por estes factos e atendendo ao continuado e crescente uso que destes metais se vem fazendo por toda a parte, acompanhando em todos os países o desenvolvimento industrial e económico, teme-se uma crescente contaminação da biosfera, o que traria consequências graves no futuro e quiçá imprevisíveis.

A particular vulnerabilidade das crianças aos efeitos deletérios destes metais torna o problema de extrema acuidade relativamente a este grupo etário. De facto, e no que respeita ao ***chumbo***, para além da clássica sintomatologia a que o saturnismo conduz nos adultos, reconhecem-se-lhe efeitos teratológicos de certa gravidade no período embrionário [14] e efeitos neurológicos de maior gravidade nos primeiros anos de vida [1,6,15]. Encefalites graves podem ocorrer em crianças, por contaminação com baixas quantidades de chumbo e revelando plumbémias muito inferiores às que produzem idêntica patogenia nos adultos. Sustentam alguns investigadores que para elas uma plumbémia clinicamente infratóxica é responsável por atrasos mentais

e por diminuições dos seus coeficientes intelectuais [16,17]. Para além desta particular susceptibilidade, as crianças que praticam "pica", isto é, ingestão contínua de produtos não alimentares, roendo objectos variados (terra, unhas, tintas, etc.) [18-20] podem ingerir este metal e outros em teores imprevisíveis e extremamente difíceis de quantificar, o que poderá revestir-se de particular gravidade atendendo à elevada capacidade de absorção que as crianças têm para o chumbo (calculada em 40 a 50% contra 5 a 10% para o adulto) [21]. Pelas razões apontadas em 1971, KING sugeriu como dose de ingestão admissível máxima para as crianças a quantidade de 300 μg/dia [22]. Posteriormente, em 1977, MAHAFFEY restringiu a dose para valores inferiores a 100 e 150 μg/dia para as crianças com idade até seis meses e entre os seis meses e os dois anos, respectivamente [15].

Não obstante a importância de que se reveste o problema, são escassos os estudos de avaliação do grau de contaminação dos alimentos infantis [23-25]. Pensamos que na base deste desinteresse esteja a suposição que sejam mais temíveis, por mais significativas, as contaminações secundárias dos alimentos, por migração do chumbo das embalagens e dos recipientes que com eles contactam (utensílios de cozinha, pratos de cerâmica, etc.) do que a contaminação primária dos mesmos. Por isso, algumas Organizações Internacionais, Food Drug Administration, Comunidades Europeias e a Organização Mundial de Saúde estabeleceram como limites de cedênca nas cerâmicas destinadas a ser utilizadas no serviço a crianças a taxa limite de 2,5 mg/l de volume por elas contido. Nesta matéria, muitos países possuem legislação própria e em certos casos ainda mais restritiva (a Suécia, por ex., tolera somente a cedência de 1 mg/l).

A intoxicação crónica pelo *cádmio* é ainda mais perigosa do que pelo chumbo, não só a despeito da sua patogenia, como do seu mais longo período de semi-vida biológico. Além disso, o seu diagnóstico precoce não é muito fácil por ser a sintomatologia pouco objectiva (insuficiência renal, acção hipertensiva, interferência com o metabolismo do cálcio, etc.) [3].

É de salientar, pelo perigo que representa para as crianças, a sua bioacumulção a nível ósseo e renal e a sua interferência nas fases metabólicas mediadas pelas enzimas com zinco e no metabolismo mineral do sistema ósseo. Neste domínio parece existir uma influência directa da absorção do Ca/P a nível gastro-intestinal ou, indirectamente, por influência na actividade da vitamina D, da actividade parotídica e pela regulação da excreção renal Ca/P. Transtornos renais com proteinúria são também clássicos na intoxicação crónica pelo cádmio [26]. Importante pelos graves malefícios que provoca é o impacto do cádmio no desenvolvimento fetal, produzindo fenómenos teratológicos, morte fetal e necroses placentárias [14]. Uma possível acção carcinogenética por este metal também não está fora de cogitação [4].

Sendo a via de intoxicação principal a digestiva [27], não se deve ignorar os perigos a que o homem se expõe de contaminação pulmonar ao respirar numa atmosfera fabril fortemente poluída com pó fino de cádmio ou ao fumar os seus cigarros. Estima-se que a ingestão média diária de cádmio seja de 72 μg (média) ou 33 μg (mediana) ressalvando, obviamente, não só as variações regionais como as dos diversos países.

Que tenhamos conhecimento, para as crianças, ainda não foram fixados internacionalmente limites de ingestão admissíveis, porém, para os adultos, a OMS estima como tolerável a quantidade de 400 a 500 μg/semana.

Tal como foi dito em relação ao chumbo, por maioria de razão, a contaminação secundária dos alimentos pelo cádmio pode ser mais expressiva e mais perigosa para as crianças e, por esse facto, a CEE, a FDA e OMS fixaram já como limite de cedência pelas cerâmicas para este metal a taxa de 0,25 mg/l.

Até muito recentemente não se descreveu na literatura qualquer caso de intoxicação humana pelo *alumínio*, apesar de ser elevada na dieta a quantidade de metal ingerido (estima-se em 10 a 100 mg/dia ou mesmo mais conforme o uso que se faça dos utensílios de alumínio nas operações culinárias). Porém, já em 1934, TCHIJEVSKY e TCHIJEVSKAYA [28] admitiram haver relação entre a mortalidade por cancro e o uso que se vinha fazendo dos artigos de alumínio, hipótese não comprovada até ao momento.

Em termos hipotéticos, em 1970, BERLYNE [29] atribuiu as elevadas taxas de aluminémia que observara em doentes renais crónicos, submetidos a diálise, à frequente ingestão de geles de alumínio e ao alumínio contido na água usada na diálise. Em 1972, as

experiências levadas a cabo por este investigador vieram confirmar a sua hipótese, ao observar intoxicações por este metal quando administrava a ratos sais de alumínio quer por via oral quer por via parenteral [11]. Neste mesmo ano, ALFREY[30] observou pela primeira vez casos de demência em dialisados renais e LAUGHLIN e Col. [31] relataram manifestações tóxicas por via pulmonar de etiologia aluminica. Posteriormente, CRAPPER e Col., em 1973 [12] e BOUKARI e Col., em 1978 [32] interpretam a doença de ALZHEIMER como uma sindroma encefalopática de etiopatogenia pelo alumínio.

A interpretação que actualmente se encontra para esta aparente discrepância entre as intoxicações actualmente constatadas e a toxidade antigamente prevista é a de que, em situações muito pouco esclarecidas e imprevisíveis, a absorção deste metal possa ser bastante facilitada. Pensa-se, no entanto, não ser de rejeitar o efeito interactivo deste metal com outras moléculas exógenas provenientes da dieta, as alterações da flora microbiológica intestinal para além de outros factores individuais [10].

Considerando: 1. A tendência crescente do uso de louça policolorida para servir os alimentos às crianças; 2. Que não foi assunto estudado em Portugal; 3. Que também entre nós venham a ser estabelecidos limites de cedência admissíveis para este tipo de louça; 4. Ser nossa obrigação dar contributo para a melhoria tecnológica das indústrias que têm a cargo o fabrico deste tipo de louça, fomos sensibilizadas a proceder ao estudo que a seguir se relata.

2 — PARTE EXPERIMENTAL

2.1 — *AMOSTRAS ENSAIADAS*

As amostras constaram de 38 peças de louça de cerâmica para criança, comercialmente conhecidas por "serviços de criança" e normalmente formados por um conjunto de 3 peças cada (caneca, prato e prato de sopa). Estes serviços foram adquiridos no comércio local (Porto) e foram distribuídos por cinco grupos que representamos nos Quadros de resultados por A, B, C, D e E. Quatro deles foram perfeitamente identificados com a casa fabricante e de acordo com a lei vigente em Portugal. Um outro, o representado pela letra B, que não pudemos identificar por falta de marcação das peças, não se cumprindo para este caso aquela formalidade legal.

Todas as peças eram de fundo branco, vidradas, com desenhos variados e de grande policromia.

2.2 — *MÉTODOS*

As extracções dos metais migrados das peças foram executadas segundo a norma da CEE [36] e já referidas em trabalho anterior [33].

Todas as peças ensaiadas foram sujeitas a tratamentos idênticos. Primeiramente, foram lavadas com abundante água desionizada e secas. Seguidamente, foram cheias com solução de ácido acético a 4%, cobertas e deixadas durante 24 horas à temperatura ambiente ($22 \pm 2°C$). Após este contacto, cada solução extractiva foi evaporada em goblé até volume reduzido. Após arrastamento e lavagem quantitativa do conteúdo do goblé, completou-se o volume de 25 ml, em balão volumétrico aferido, com água desionizada.

As determinações foram feitas em todas as soluções extractivas, usando o ácido acético a 4% como branco e fazendo a calibração da escala com a solução padrão de concentração conveniente. Em alguns casos foi necessário proceder a uma diluição apropriada da solução extractiva, adaptada à calibração previamente realizada.

Todo o material auxiliar das experiências foi previamente fervido em ácido azótico a 20% e lavado com água desionizada.

No *caso dos pratos* repetiu-se a extracção com idêntica metodologia, intervalando as duas extrações por lavagem com água desionizada.

Para *as canecas* procedeu-se do seguinte modo:

1.ª extracção — contacto interior com a solução extractiva de modo análogo ao praticado para as restantes peças.

2.ª extracção — contacto exterior com a solução extractiva (em consequência de serem coloridas exteriormente).

2.2.1 — REAGENTES

Os produtos empregados na preparação de padrões (nitrato de chumbo, sulfato de cádmio e sulfato duplo de alumínio e potássio bem como os solventes ácido acético e ácido azótico) apresentavam pureza (p.a.) e foram fornecidos pela Merck. A água utilizada em todos os ensaios era desionizada e previamente testada.

2.2.2 — APARELHAGEM

Utilizou-se um espectrofotómetro de absorção atómica "Varian Techtron 1000" e um Spectronic 21 Baush e Lomb.

2.2.3 — CONDIÇÕES EXPERIMENTAIS

O *chumbo* e o *cádmio* foram determinados por espectrofotometria de absorção atómica nas condições experimentais que se seguem e já referidas em trabalhos anteriores [33,34]:

	Lâmpada	Int. da corr. (mA)	Comp. de onda (nm)	Abertura da fenda	Gases	Chama	Limite de sensibil. (μg/ml)
CHUMBO	Cátodo oco	6	217,0	1,0	Ar/Acetileno	Oxidante	0,05
CÁDMIO	»	3	228,8	0,5	»	»	0,01

Quadro 1
Cedência de chumbo em louça de criança (μg/l)

Marcas	A	B	C	D	E
Média da 1.ª ext. ±SEM	140±37 (n=9)	35600±21100 (n=6)	7900±6900 (n=6)	1000±700 (n=7)	3100±1700 (n=10)
Média da 2.ª ext. ±SEM	47±8,6 (n=6)	9600±5300 (n=4)	7300±6900 (n=4)	550±370 (n=5)	1800±1200 (n=7)
Amplitude (1.ª extr.)	0−290	20−100000	34−39000	0−4700	10−14200
% de peças com cedência superior ao limites da CEE e FDA	0	66,7	33,3	14,3	20

SEM representa o erro padrão da média

Para o *alumínio* usámos um método colorimétrico clássico de complexação com aluminon e segundo a técnica descrita pormenorizadamente em [35]. Para este metal o limite de sensibilidade é de 0,02 μg/ml.

3 — RESULTADOS

Os Quadros 1, 2 e 3 referem as médias dos resultados das cedências, em μg/litro, para os três metais estudados, Pb, Cd e Al, respectivamente. As peças encontram-se agrupadas por casas e os resultados são respeitantes aos dois tratamentos efectuados. Indica-se a dispersão das cedências em cada grupo estudado. Faz-se referência também às percentagens de peças que ultrapassam os limites estabelecidos para este tipo de louça quer pela CEE, FDA e OMS no referente a Pb e Cd.

O Quadro 4 apresenta as cedências pela superfície exterior das canecas ao ácido acético a 4% onde foram imersas e os valores são expressos também em μg/l da solução de contacto externo e para os três elementos estudados.

3.1 — *CHUMBO*

O Quadro 1 mostra que, na globalidade das peças, o chumbo migrado para o ácido acético variou de 0 a 100 mg/l.

Facilmente se constata a diferença de qualidade, em termos de inércia química, dos 5 fabricos analisados. De facto, as nove peças da casa A cedem ao ácido acético a 4%, quantidades muito baixas de chumbo, longe mesmo do valor considerado limite pelos Organismos Internacionais (2,5 mg/l). Todas as outras marcas apresentam peças que cedem teores de chumbo considerados elevados e perigosos para este tipo de louça. Mas é sem dúvida o grupo de peças assinalado pela letra B o de pior qualidade, sendo a cedência em média, para a primeira extracção, de 35,6 mg/l.

Na segunda extracção, o chumbo cedido pelas peças é sempre mais baixo mas, em muitos casos ainda perigoso, particularmente nos grupos de peças B e C que, em média, cedem ainda 9,6 e 7,3 mg/l, respectivamente.

Quanto aos teores de chumbo cedidos pelo exterior das canecas (Quadro 4), de novo o grupo B é o de pior qualidade com uma cedência, em média, de 42,5 mg/l. Este ensaio exterior permite-nos avaliar do perigo das decorações exteriores das peças de mesa, em particular das vulgarmente usadas por crianças, dada a frequente prática de "pica" [37].
Um aspecto que nos parece relevante e digno de registo é a cedência muito baixa de chumbo nas peças sem decoração interior, que neste nosso estudo abrangeu apenas as canecas. De facto, os valores de chumbo migrados no ensaio que efectuámos nas 12 canecas situaram-se entre 0 e 45 μg/l, havendo apenas um valor de cedência elevado, situado para além daqueles limites e que foi de 1600 μg/l.
Os valores de cedência obtidos permitem-nos concluir da forte relação entre as cores garridas dos motivos apresentados pelas peças e a quantidade de chumbo cedido, sendo, como é óbvio, de marcante importância a qualidade do vidrado e a tecnologia usada nos diferentes fabricos [34]. Donde seja de sugerir a utilização de louça branca preferencialmente à colorida no sentido de minorar as migrações de chumbo.

3.2 — *CÁDMIO*

A amplitude dos valores cedidos na primeira extracção varia de 0 a 8000 μg/l, como se mostra no Quadro 2.
À excepção da marca D que, no que se refere ao cádmio é de qualidade aceitável, a situação é semelhante à do chumbo e que já discutimos anteriormente em 3.1.

Os limites admitidos pela CEE, FDA e OMS para cedência de cádmio por louça de criança são muito mais apertados comparativamente aos do chumbo (apenas 250 μg/l).
As peças de pior qualidade pertencem ao grupo B e as marcas A e D são as melhores, sendo os valores de cádmio cedidos sempre baixos.
As canecas não cederam cádmio em nenhum caso (n = 12) à solução acética o que evidentemente se deve ao facto daquelas peças serem brancas e sem qualquer motivo colorido.
No Quadro 4 estão apresentados os resultados do ensaio exterior feito para as canecas de todos os serviços analisados. Também no respeitante a este metal há casos de cedências consideráveis e podemos então concluir de mais uma causa de perigo para as cianças que praticam "pica".

Quadro 4
Ensaio exterior

Peça n.º	Marca	Al	Pb	Cd
1	A	30	44	1,3
4	»	43	25	1,3
9	»	20	50	4,0
10	B	—	43200	790
15	»	—	41700	310
16	C	410	930	110
21	»	17	59	3,0
22	D	91	1800	35
26	»	35	52	9,0
29	E	83	9700	93
32	»	93	560	31
38	»	120	2800	320
		n = 10	n = 12	n = 12

Quadro 2
Cedência de cádmio em louça de criança (μg/l)

Marcas	A	B	C	D	E
Média da 1.ª ext. ±SEM	11,5±3,6 (n = 9)	2300±1400 (n = 6)	720±620 (n = 6)	80±40 (n = 7)	170±74 (n = 10)
Média da 2.ª ext. ±SEM	5,9±1,0 (n = 6)	800±430 (n = 4)	570±520 (n = 4)	51±22 (n = 5)	140±71 (n = 7)
Amplitude (1.ª extr.)	0—26	0—8000	0—3500	0—200	0—730
% de peças com cedência superior aos limites da CEE e FDA	0	66,7	33,3	0	20

SEM representa o erro padrão da média

Verificámos que às cores garridas vermelho, laranja e amarelo dos motivos de decoração se associam elevadas cedências de cádmio como já vem sendo documentado em estudos feitos por outros autores.

3.3 — *ALUMÍNIO*

No Quadro 3 registam-se os resultados do Alumínio. Também para este metal as peças analisadas se revelaram de diferente qualidade no respeitante à sua migração para a solução extractiva, tendo sido encontrados valores que variam entre 23 e 18800 μg/l. Os grupos de peças com cedência mais significativa são o B e o C. Os valores cedidos externamente variam entre 17 e 410 μg/l, o que não nos parece preocupante para este metal e para este tipo de ensaio [43].

A cedência do alumínio por artigos de louça de cerâmica, do ponto de vista tecnológico, parece-nos dever ser encarado de diferente modo relativamente ao chumbo e ao cádmio. De facto, a presença do alumínio é devida à constituição natural da argila de que as peças são feitas. A sua migração é provavelmente devida à fragilidade do vidrado que, quando não é convenientemente preparado, aplicado e cozido, se torna quebradiço e permite assim que os constituintes do barro situados sob aquela superfície protectora fiquem facilmente acessíveis aos alimentos e, neste nosso estudo, à solução extractiva [37].

Não temos conhecimento de qualquer legislação regulamentadora da cedência de alumínio em utensílios de cozinha. Tal facto pode ter relação com a circunstância de não estarem perfeitamente averiguadas as suas acções toxicológicas nem as doses que poderão constituir perigo. No entanto, do que nos foi possível averiguar, há já estudos feitos no sentido de apurar a cedência deste metal aos alimentos quando cozinhados em utensílios de alumínio, donde podemos concluir da importância dada ao problema [43,44).

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BIBLIOGRAFIA

[1] G. Goodman, L.S. Goodman, A. Gilman, "The Pharmacological Basis of Therapeutics", MacMilan Publishing, Co., Inc, sixth edition, 1980.

[2] B. Holmstedt, R. Lauwerys, M. Mercier, M. Roberfroid, "Mecanisms of Toxicity and Hazard Evaluation", Elsevier North-Holland, 1980.

[3] L. Friberg, M. Piscator, G.F. Nordberg, T. Kjellstrom, "Cadmium in the Environment", 2.ª edição, CRC Press, 1976.

[4] F.E. Guthrie, J.J. Perry, "Introduction to Environmental Toxicology". Elsevier New York, 1980.

[5] P.B. Hammond, "Exposure of Humans to Lead", *Ann. Rev. Pharmacol. Toxicol.*, **17**, 197-214 (1977).

[6] Burgat-Sacaze, "Contamination par les Metaux Lourds" em "La Sécurité du consommateur face a l'alimentation d'aujourd'hui", Paris, 21-22 de Maio de 1981, *Annales Symposium International*, 149-160.

[7] "Liste de concentrations maximales de contaminants recommandées par la commission mixte FAO/OMS du Codex Alimentarius", CAC/FAL, 4-1978, troisieme série, OMS.

[8] E. di Ferrante, A. Berlin, "Research and Regulatory Actions on Heavy Metals in the European Community, International Conference Heavy Metals" in: The Environment, Amsterdam, September 1981, CEE/OMS.

[9] M.W. Skougstad, M.J. Fishman, *Toxicological and Environmental Chemistry Reviews*, **2**, 219-236 (1978).

[10] Cl. Boudene, "Donnes Recentes sur la Toxicité des Contaminantes Metalliques Apportés a L'Aliment Conservé par son Emballage", *Méd. et Nut.*, T. XV. n.° 6, 425-430 (1979).

[11] G.M. Berlyne, J.B. Ari, E. Knopf, R. Yagil, G. Weinberger, G.M. Danovitch, "Aluminum Toxicity in Rats", *The Lancet*, 564-567 (1972).

[12] D.R. Crapper, S.S. Krishnan, A.J. Dalton, "Brain Aluminium Distribution in Alzheimer's Disease and Experi-

Quadro 3
Cedência de alumínio em louça de criança (μg/l)

Marcas	A	B	C	D	E
Média da 1.ª ext.±SEM	320±250 (n=9)	1600±850 (n=6)	4000±3300 (n=6)	180±40 (n=7)	290±120 (n=10)
Média da 2.ª ext.±SEM	50±11 (n=6)	1800±1500 (n=4)	4400±4900 (n=4)	940±970 (n=5)	110±37 (n=5)
Amplitude (1.ª extr.)	41−2200	100−4300	37−18800	49−330	23−1100

SEM representa o erro padrão da média

rimental Neurofibrillary Degeneration", *Science*, **180**, 511--513 (1973).

[13] D.P. PERL, A.R. BRODY, "Alzeimer's Disease: X-ray Spectrometric Evidence of Aluminum Accumulation in Neurofibrillary Tangle- Bearing Neurons", *Science*, **208**, 297-299 (1980).

[14] L.W. CHANG, P.R. WADE, J.G. POUNDS, K.R. REUHL, "Prenatal and Neonatal Toxicology and Pathology of Heavy Metals", *Advances in Pharmacology and Chemotherapy*, **17**, 195-231 (1980).

[15] K.R. MAHAFFEY, "Relation Between Quantities of Lead Ingested and Health Effects of Lead in Humans", *Pediatrics*, **59**, n.° 3, 448-459 (1977).

[16] O. DAVID, B. MCGANN, S. HOFFMAN, J. SVERD, "Low Lead Levels and Mental Retardation", *The Lancet*, 1376--1379 (1976).

[17] E. HODGSON, J.R. BEND, R.M. PHILPOT, "Reviews in Biochemical Toxicology", 2, Elsevier North-Holland, Inc., 1980.

[18] D. BARLTROP, "The Prevalence of Pica", *Amer. J. Dis. Child.*, **112**, 116-123 (1966).

[19] D.G. MITCHELL, "Increased Lead Absorption: Paint is not the only Problem", *Pediatrics*, **53**, 142-144 (1974).

[20] P. ROBISCHON, "Pica Practice and Other Hand-Mouth Behaviour and Children's Developmental Level", *Nursing Research*, **20**, n.° 1, 4-16 (1971).

[21] K. KOSTIAL, I. SIMONOVIC, M. PISONIC, "Lead Absorption from the Intestine in Newborn Rats", *Nature*, **233**, 564 (1971).

[22] B.G. KING, "Maximum Daily Intake of Lead Without Excessive Body Lead-Burden in Children", *Amer. J. Dis. Child.*, **122**, 337-340 (1971).

[23] D.C. KIRKPATRICK, H.B.S. CONACHER, J.C. MÉRANGER, R. DABEKA, B. COLLINS, A.D. MCKENZIE, G.M.A. LACROIX, G. SAVARY, "The Trace Element Content of Canadian Baby Foods and Estimation of Trace Element Intake by Infants", *Can. Inst. Food. Sci. Technol. J.*, **13**, n.° 4, 154-161 (1980).

[24] H. WOIDICH, W. PFANNHAUSER, "Spurenelemente in der Kleinkindernahrung: Arsen, Blei, Cadmium", *Z. Lebensm. Unters. Forsch.*, **170**, 95-98 (1980).

[25] P.J. BARLOW, "Micro-Determination of Lead and Cadmium in Pasteurized Market Milks by Flameless Atomic Absorption Spectroscopy using a Base Digest", *Journal of Dairy Research*, **44**, 377-381 (1977).

[26] E. HODGSON, J.R. BEND, R.M. PHILPOT, "Reviews in Biochemical Toxicology", 1, Elsevier North-Holland, Inc., 1979.

[27] F. PANEBIANCO, "Residui di Metalli e non Metalli Tossici Negli Alimenti di Origine Animale", *Atti Societá Italiana Scienze Veterinarie*, **30**, 116-138 (1976).

[28] A.L. TCHIJEVSKY, T.S. TCHIJEVSKAYA, "L'aluminium comme facteur contribuant au surgissement ou au progrés de divers processus pathologiques dans l'organisme", *Gaz. Hop.*, **853** (1934).

[29] G.M. BERLYNE, J. BEN ARI, D. PEST, J. WEINBERGER, M. STERN, G.R. GILMORE, R. LEVINE, "Hyperaluminiaemia from aluminium resins in renals failure", *The Lancet*, **94** (1970).

[30] A.C. ALFREY, G.R. LEGENDRE, W.D. KAENY, "The dialysis encephalopathy syndrome: possible aluminum intoxication", *N. Engl. J. Med.*, **294**, 184 (1976).

[31] A.I.G. MC LAUGHLIN, G. KAZANTZIS, E. KING, D. TEARE, R.J. PORTER, R. OWEN, "Pulmonary fibrosis and encephalopathy associated with the inhalation of aluminum dust, *Brit. J. Ind. Med.*, **19**, 253 (1972).

[32] M. BOUKARI, J. ROTTEMBOURG, M.C. JAUDON, J.P. CLAVEL, M. LEGRAIN, A. GALLI, "Influence de la prise prolongée de gels d'alumine sur les taux sériques d'aluminium chez les patients atteints d'insuffisance rénale chronique", *Nouv. Presse Méd.*, **7**, 85 (1978).

[33] M. LOURDES ALMEIDA BASTOS, MARGARIDA A. FERREIRA, M.I. CARDOSO, "Resíduos Metálicos cedidos por Utensílios de Cozinha. I — Cedências de chumbo, ferro, cobre, crómio e cádmio pela louça de barro vidrado de Barcelos", *Rev. Port. Farm.*, XXXII, n.° 2, 55-71 (1982).

[34] M. LOURDES ALMEIDA BASTOS, MARGARIDA A. FERREIRA, RUI A. PINTO, "Resíduos Metálicos Cedidos por Utensílios de Cozinha. II — Cedências de Pb, Cu, Zn, Fe, Cr, Mn, Cd e Co pela louça de faiança regional das Caldas da Rainha", em publicação.

[35] J. RODIER, "L'analyse de l'eau", 6.ª edição, Bordas, 1978.

[36] "Proposal for a Council on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with food (limitation of extractable quantities of lead and cadmium)", *OJ of the EC*, n.° C46 of 27-2-75.

[37] P.J. HILE (FDA), D. SCHMELTZER (CPSC), W. MUIR (EPA): Task Force Members — "Lead and Cadmium in Decorated Glass Tumblers — Interagency Task Force Report", November 13, 1978.

[38] R.A. EPPLER, "Formulation and processing of ceramic glazes for low lead release", *L'Industrie Céramique*, **706** (1977).

[39] P. HENRY, "Chemicals used in the Manufacture of Ceramic Colors", *Ceramic Bulletin*, **36**, n.° 11, 1957.

[40] P. LAUGEL, D. WENCKER, B. WEILL, M. HASSELMANN, "Contribution a l'étude de la contamination des aliments par le cadmium. I — Evaluation des apports de cadmium par la vaisselle", *Ann. Fals. Exp. Chim.*, **69**, n.° 741, 473--487 (1976).

[41] I. BECKMAN, J. MOVITZ, N. MONICA, S. SLORACH, "Utlosning av bly och Kadmium i Keramiskt och emaljerat hushallsgods", *VarFoda*, Volym 31, Supplement 1, 1-80, 1979.

[42] C.L. HACKLER, R.E. CARPENTER, "Which is the Yellow for You?", *Ceramic Bulletin*, **59**, n.° 8, 1980.

[43] P. MATTSSON, B. HOPSTEN, "Rapport Fran Konferens on Aluminium", *VarFoda*, **33**, n.° 6, 227-230, 1981.

[44] S.E. LEVICK, "Demencia from Aluminum pots", *The New England Journal of Medicine*, p. 164, July, 1980.

SUMMARY

This report refers a study about lead, cadmium and aluminum leached from some Portuguese ceramic tablewares for children. 38 utensils made by several factories were analysed. From the levels of metals leached, a very clear correlation could be established about the technology carried on in each factory.

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DETERMINACION ESPECTROFOTOMETRICA DE CROMO(III) CON ACIDO ETILENDIAMINO-*N,N'*-DIPROPIONICO (AEDDP). APLICACION A LA DETERMINACION DE CROMO EN ACEROS*

Se propone un nuevo método para la determinación espectrofotométrica de cromo con ácido etilendiamino-N-N'-dipropiónico (AEDDP). Este metal reacciona con el AEDDP para dar un complejo con dos máximos de absorción a 520 y 405 nm. A 520 nm la ley de Beer se cumple en un intervalo de concentraciones de 20 a 240μg de cromo/ml, y el intervalo óptimo de aplicación según la curva de Ringbom está comprendido entre 60 y 230 μg de Cr/ml. La absortividad molar es igual a 140 l mol^{-1} cm^{-1} y la sensibilidad 0,3513 μg/cm^2. Se investigaron la estequiometría, interferencias, así como la reproducibilidad y precisión del método. Se compara el nuevo método con otros similares hallados en la bibliografía, y se aplica el método a la determinación de cromo en una muestra patrón de acero.

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1 — INTRODUCCION

En trabajos anteriores [1,2] se ha utilizado el AEDDP para la determinación espectrofotométrica de cobalto y cobre(II).
En el presente trabajo se estudia el espectro en la zona visible, del complejo coloreado que el ácido etilendiamino-*N,N'*-dipropiónico (AEDDP) forma con el cromo(III).

2 — PARTE EXPERIMENTAL

REACTIVOS

Cromo(III), disolución patrón. — Tritisol Merck conteniendo 1000 μg de Cr(III)/ml, que corresponde a una concentración 0,01923 M.
AEDDP, disolución al 2%. — Se preparó disolviendo en agua destilada la cantidad adecuada de AEDDP.
Disolución patrón de AEDDP 0,01923 M — Se preparó por pesada de 0,78336 g de ácido puro, se disolvió en agua destilada y se llevó a 200 ml en un matraz aforado.
Hidróxido sódico, disolución acuosa 1 M.
Acido clorhídrico, disolución acuosa 1 M.

APARATOS

Espectrofotómetro "Spectronic 700" Bausch & Lomb, equipado con cubetas de 1,00 cm de espesor. Medidor de pH "Beckman Electromate" con electrodos de sensibilidad ±0,02 pH.

ESPECTRO DE ABSORCIÓN

Se realizó el espectro de absorción del sistema cromo(III)-AEDDP a distintos valores de pH con el fin de encontrar la longitud de onda a la cual la absorción es máxima. Para ello se pasaron partes alícuotas de la disolución de cromo(III) de concentración conocida a matraces aforados de 25 ml, añadiendo 5 ml de disolución de AEDDP al 2% y ajustando el pH con disolución de hidróxido sódico o ácido clorhídrico hasta alcanzar un pH de 3,1; 7 y 11. Se calentaron en un baño de agua hirviendo, se enfriaron a temperatura ambiente y se llevaron a 25 ml con agua destilada; la concentración resultante fue de 120 μg de Cr/ml.
Las medidas se realizaron en el espectrofotómetro en el intervalo de 360 a 750 nm, utilizando agua destilada como blanco; se observa que las longitudes de onda de los máximos de absorción son las

mismas a pH ácido y neutro. Observándose dos máximos uno a 520 nm y otro mucho más débil a 405 nm. Los resultados obtenidos se representan en la fig. 1.

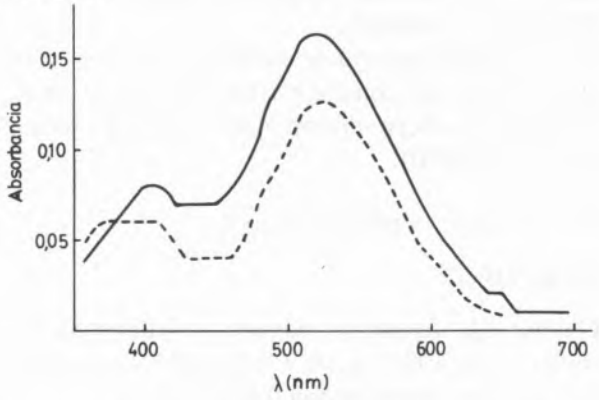

Fig. 1

Espectros de absorción de las disoluciones del complejo Cr(III)-AEDDP a pH 3,1 y 7. Concentración: 120μg de cromo(III)/ml. —— pH = 3,1; ---- pH = 7,0

EFECTO DEL pH

Se estudió la influencia del pH en la formación del complejo Cr(III)-AEDDP, preparando una serie de disoluciones según el procedimiento anteriormente descrito y cuyos valores de pH estuvieron comprendidos en un intervalo lo más amplio posible. A medida que la disolución se va alcalinizando se intensifica su color, permaneciendo constante la absorbancia en el intervalo de pH 4,6-5,9 a 520 y 405 nm, decayendo luego debido a la precipitación del cromo en forma de hidróxido. Los valores obtenidos se hallan representados en la fig. 2; se eligió como pH adecuado de trabajo el intervalo de 5 a 5,5.

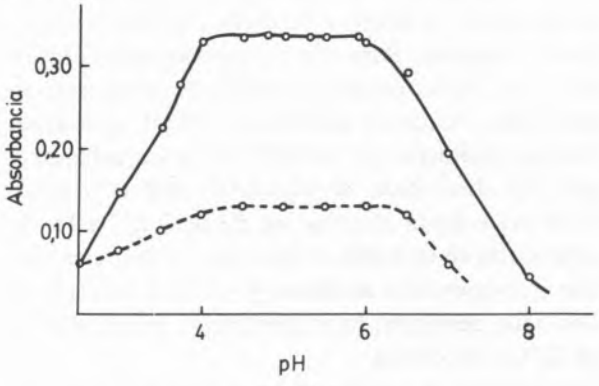

Fig. 2

Variación de la absorbancia de las disoluciones del complejo Cr(III)-AEDDP con el pH. Concentración: 120 μg de cromo(III)/ml. —— 520nm; ---- 405 nm

INFLUENCIA DEL TIEMPO DE CALENTAMIENTO

Para determinar la influencia del tiempo de calentamiento sobre la absorbancia del complejo Cr(III)-AEDDP, se prepararon una serie de disoluciones del modo indicado anteriormente, se introdujeron simultáneamente en un baño de agua hirviendo, y fueron retiradas a distintos tiempos comprendidos entre 0 y 60 minutos. Enfriados a temperatura ambiente se enrasaron con agua destilada y se midieron las absorbancias a 520 y 405 nm. De los resultados obtenidos se deduce que el tiempo óptimo de calentamiento es de 50 minutos para las longitudes de onda de trabajo.

INFLUENCIA DE LA CANTIDAD DE REACTIVO Y TIEMPO

Con el fin de estudiar el efecto que produce la cantidad de reactivo sobre la absorbancia y formación del complejo Cr(III)-AEDDP, se pasaron a una serie de matraces aforados de 25 ml partes alícuotas de la disolución patrón de cromo(III), de modo que la concentración de cromo sea siempre constante, se adicionaron cantidades variables de AEDDP al 1% y se ajustó el pH entre 5 y 5,5; los matraces se calentaron en un baño de agua hirviendo durante 50 minutos, se enfriaron a temperatura ambiente y se añadió agua destilada hasta el enrase. Encontrándose que por cada 120 μg de Cr/ml deben adicionarse 10 ml de AEDDP al 1%, y que cantidades superiores no influyen en la absorbancia del complejo. La formación del complejo es inmediata y la absorbancia no varía por lo menos en 32 horas.

CUMPLIMIENTO DE LA LEY DE BEER E INTERVALO ÓPTIMO DE RINGBOM

Para comprobar el cumplimiento de la ley de Beer se prepararon una serie de disoluciones según el procedimiento ya conocido, estando la concentración de cromo comprendida entre 20 y 280 μg de Cr/ml, se midió la absorbancia en las condiciones anteriormente establecidas encontrándose que a 520 y 405 nm esta ley se cumple entre 20 y 240 μg de Cr/ml. Se calculó la absortividad molar y la sensibilidad del complejo Cr(III)-AEDDP encontrándose los valores de 140 l mol^{-1} cm^{-1} y 0,3513 μg/cm^2 respectivamente a 520 nm y 56 l mol^{-1} cm^{-1} y 0,9285 μg/cm^2 a 405 nm. El intervalo óptimo de Ringbom

está comprendido entre 60 y 230 μg de Cr/ml a 520 nm y entre 100 y 230 μg de Cr/ml a 405 nm.

REPRODUCIBILIDAD Y PRECISIÓN

El estudio estadístico para las concentraciones de cromo(III) de 40, 80, 120, 160, 200, 240 μg Cr/ml en series de 10 muestras dió las siguintes desviaciones normales o típicas de 0,0035; 0,0024; 0,0047; 0,0101; 0,0062; 0,0106; a 520 nm y 0,0000; 0,0021; 0,0032; 0,0034; 0,0035; 0,0016 a 405 nm. En cuanto al error relativo medio los valores hallados fueron de: 2,13; 0,75; 0,79; 1,66; 0,79; 1,70% respectivamente a 520 nm y 0,00; 1,70; 1,75; 1,44; 1,20; 0,49% a 405 nm.

IDENTIFICACIÓN DE LA FÓRMULA DEL COMPLEJO

Para establecer la fórmula del complejo, se utilizaron tres métodos: el de "la razón molar" de YOE y JONES [3], el de "las variaciones contínuas" de JOB [4] y el de "la razón de las pendientes" de HARVEY y MANNING [5]. La disolución de cromo fue 0,01923 M. La disolución de AEDDP era 0,01923 M. Los resultados obtenidos se representan en las figs. 3, 4, 5, 6, deduciéndose que la relación molar Cr(III)-AEDDP es 1:4. Efectuados los cálculos con los valores extraídos de las gráficas 3 y 4 se obtiene un valor aproximado de la constante de formación del complejo Cr(III)-AEDDP de 32.10^{32}.

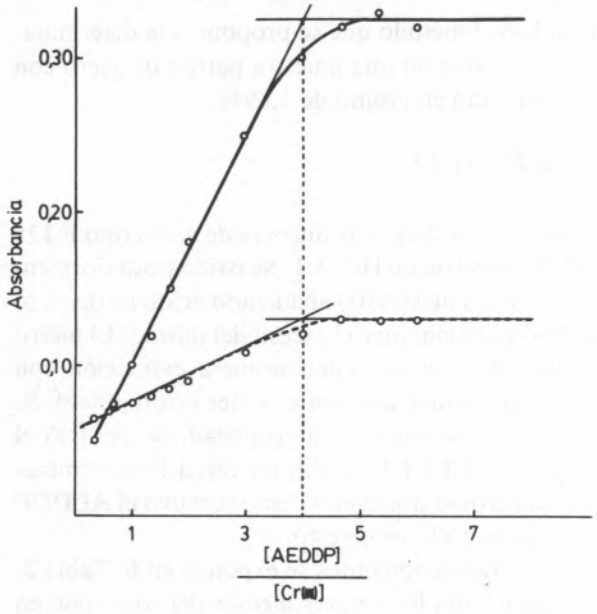

Fig. 3

Aplicación del método de "la razón molar" para la determinación de la estequiometría del complejo Cr(III)-AEDDP a pH 5-5,5. —— a 520 nm; ---- a 405 nm

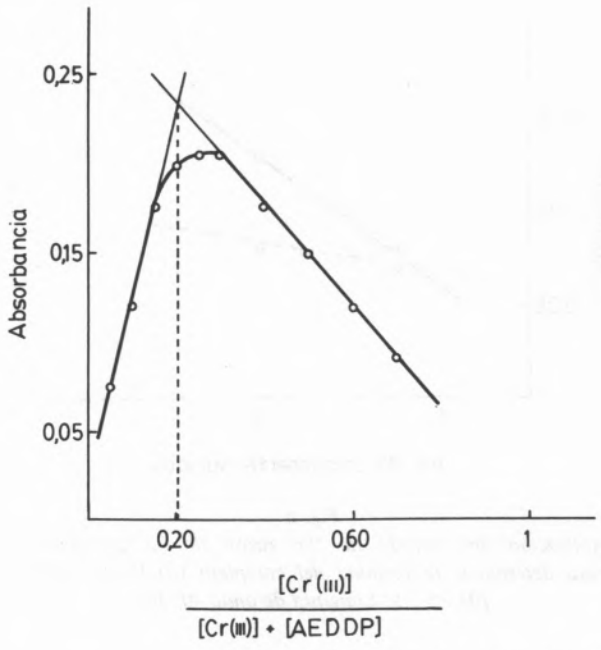

Fig. 4

Aplicación del método de "las variaciones contínuas" para determinar la fórmula del complejo Cr(III)-AEDDP a pH 5-5,5. Longitud de onda 520 nm

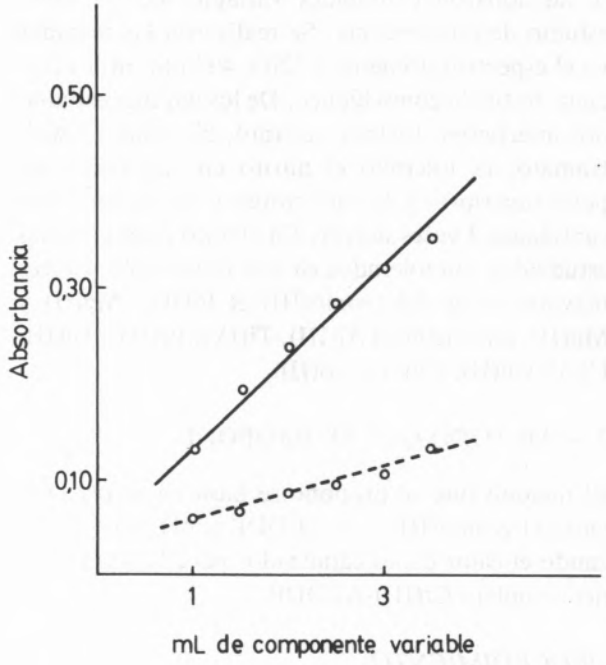

Fig. 5

Aplicación del método de "la razón de las pendientes" para determinar la fórmula del complejo Cr(III)-AEDDP a pH 5-5,5. Longitud de onda 520 nm

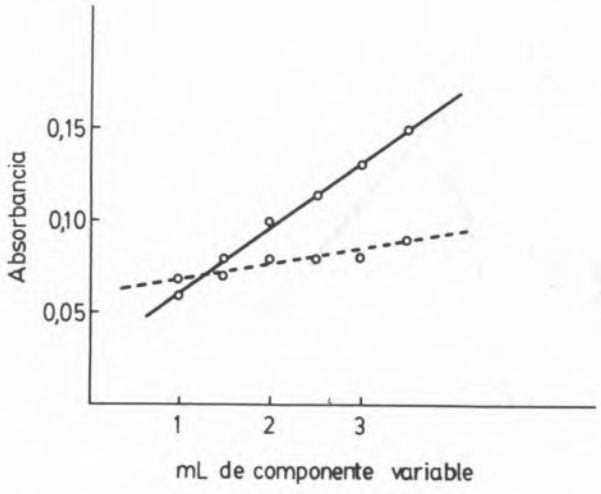

Fig. 6
Aplicación del método de "la razón de las pendientes" para determinar la fórmula del complejo Cr(III)-AEDDP a pH = 5-5,5. Longitud de onda 405 nm

EFECTO DE LOS IONES EXTRAÑOS

Se estudió la interferencia que puede ocasionar la presencia de otros iones en la formación del complejo cromo(III)-AEDDP, para lo cual se prepararon en las condiciones anteriormente fijadas, disoluciones de cromo de concentración 120 μg Cr/ml y se adicionaron cantidades variables de los iones estudio de interferencia. Se realizaron las medidas en el espectrofotómetro a 520 y 405 nm, utilizando agua destilada como blanco. De los aniones estudiados interfieren: fosfato, tartrato, dicromato y wolframato, es tolerado el nitrito en cantidades un poco superiores a las del cromo y el tiocianato en cantidades 3 veces mayor. En cuanto a los cationes estudiados son tolerados en una proporción 4 veces mayores a las del cromo(III) el Bi(III), Mg(II) y Mn(II), interfieren el Al(III), Ti(IV), Fe(III), Sn(II), UO_2^{2+}, Cu(II), Cu(I) y Co(II).

3 — METODO QUE SE PROPONE

El método que se propone se basa en la reacción entre el cromo(III) y el AEDDP a pH 5-5,5, utilizando el calor como catalizador para la formación del complejo Cr(III)-AEDDP.

PROCEDIMIENTO

Tomar una parte alícuota de la disolución problema de cromo(III) de tal modo que la concentración resultante al diluir a 25 ml esté comprendida dentro del intervalo óptimo de aplicación de la ley de Beer (desde 60 a 230 μg Cr/ml), añadir 5,5 ml de disolución de AEDDP al 2%, llevando a pH 5-5,5 con disolución de hidróxido sódico 0,1 M. Calentándose a continuación en un baño de agua hirviendo durante 50 minutos, se enfria y enrasa a 25 ml con agua destilada. Para el cálculo de la concentración de la disolución problema utilizar la curva de calibrado preparada con una disolución patrón de cromo.
Las medidas de absorbancia se realizan a 520 nm puesto que a esta longitud de onda el método es mucho más sensible.

4 — ESTUDIO COMPARATIVO

Con el objeto de estimar el valor del nuevo procedimiento para la determinación de cromo(III), se hace un estudio de los métodos absorciométricos propuestos para la determinación de cromo(III) con quelones. En la Tabla 1 se encuentran descritas las características de los diversos quelatos del cromo(III), de lo que se deduce que a pesar de que el método propuesto no es el más sensible de los estudiados, tiene a 520 nm una absortividad bastante aceptable.

5 — APLICACION A LA DETERMINACION DE CROMO EN ACEROS

Se aplicó el método que se propone a la determinación de cromo en una muestra patrón de acero con un contenido en cromo de 1,09%.

PROCEDIMIENTO

Se disolvieron 2,00 g de muestra de acero tipo F-125 I.H.A. en 50 ml de HCl 1:1. Se oxidó posteriormente el hierro a hierro(III) añadiendo ácido nítrico y se calentó para eliminar el exceso del mismo. El hierro es extraído con éter (una primera extracción con éter etílico y una segunda con éter isopropílico). Se evaporó la fase acuosa a sequedad, se disolvió el resíduo en HCl 1:1, y se prodedió a la determinación del cromo utilizando como reactivo el AEDDP según el método propuesto.
Los resultados obtenidos se exponen en la Tabla 2, indicando sólo los valores medios del contenido en cromo para cada una de ellas. Se comparan estos resultados con los dados por el certificado de análisis.

Tabla 1
Características de algunos quelatos de Cromo(III)

Quelato	pH	Máximo de absorción (nm)	Intervalo ley Beer (μg/ml)	Absortividad molar	Refer.
Cr(III)-AEDT	4,5	545	5-150	200	[6]
Cr(III)-ADCT	2-6	540	4-80	198	[7]
Cr(III)-ADCT*	—	395	—	82	[8]
Cr(III)-ADCT*	—	555	—	142	[8]
Cr(III)-ADTP	2,3-5,5	545	10-150	153	[9]
Cr(III)-ADTP	2,3-5,5	385	10-150	109	[9]
Cr(III)-ATTH	3-5	390	20-300	109	[10]
Cr(III)-ATTH	3-5	540	20-300	154	[10]
Cr(III)-ANT	2-4	555	—	106	[11]
Cr(III)-ANT	2-4	405	—	110	[11]
Cr(III)-APDT	4,5	540	—	200	[12]
Cr(III)-AUD	4,8	420	95-2565	24,4	[13]
Cr(III)-AID	4-6	385	30-1100	82	[14]
Cr(III)-AID	4-6	520	30-1100	80	[14]
Cr(III)-AHDT	2,2-5	390	—	122	[11]
Cr(III)-AHEDT	2,2-5	545	—	153	[11]
Cr(III)-AEDDP	5-5,5	520	20-240	148	Propuesto

* Indica que el medio es sulfóxido de dimetilo.

Tabla 2
Análisis de acero F-125 I.H.A. con 1,09% de Cromo

Muestra n.°	% de Cr	Error relativo %
1	1,03	5,50
2	1,06	2,75
3	1,05	3,67
4	1,03	5,50
5	1,03	5,50
6	1,03	5,50
7	1,10	0,92
8	1,03	5,50
	$\bar{x} = 1,05$	$\bar{x} = 4,35$

Se aplica el cálculo estadístico basado en la prueba "t de Student" para un muestreo en una población en que la media es conocida [15], llegando a la conclusión de que no hay diferencia significativa entre los valores encontrados y los dados por el certificado de análisis.

Se estudió en la misma muestra la recuperación del procedimiento propuesto, obteniéndose resultados satisfactorios.

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BIBLIOGRAFIA

[1] M.ª DEL CARMEN CASAIS LAIÑO, ROSA A. LORENZO FERREIRA, F. BERMEJO MARTÍNEZ, *Acta Quím. Compostelana*, **3** (4), 134-43 (1979).

[2] M.ª DEL CARMEN CASAIS LAIÑO, ROSA A. LORENZO FERREIRA, F. BERMEJO MARTÍNEZ, *Acta Quím. Compostelana*, **2**, 25-35 (1981).

[3] H.J. YOE, A.C. JONES, *Anal. Chem.*, **16**, 111-15 (1944).

[4] P. JOB, *Ann. Chim.*, **10** (9), 113-203 (1928).

[5] A.E. HARVEY, D.L. MANNING, *J. Am. Chem. Soc.*, **74**, 4744-6 (1952).

[6] S. ARRIBAS JIMENO, R. MORO GARCIA, M.L. ALVAREZ BARTOLOME, C. GARCIA BAO, *Inform. Quím. Anal.*, **27** (5), 201-8 (1973).

[7] M.R. VERMA, V.M. BHUCHAR, K.L. AGRAVAL, R.K. SHARMA, *Mikrochim. Acta*. **766-9** (1959)-C.A. **56**, 4087b (1962).

[8] A. CONCHEIRO NINE, J.A. RODRIGUEZ VAZQUEZ, F. BERMEJO MARTINEZ, *Afinidad*, **34** (345), 197-9 (1977).

[9] F. BERMEJO MARTINEZ, J.A. RODRIGUEZ CAMPOS, *Quím. e Industria*, **16** (6), 13-18 (1970).

[10] F. BERMEJO MARTINEZ, A. LONGARELA PENA, *Acta Cient. Comp.*, **8** (2), 85-104 (1971).

[11] G. DEN BOEF, B.C. POEDER, *Anal. Chim. Acta*, **30** (3), 261-8 (1964).

[12] S. VICENTE PEREZ, L. HERNANDEZ, J. ROSAS, *Quím. Anal.* **28** (6), 283-8 (1974).

[13] A. ALVAREZ DEVESA, C. BALUJA SANTOS, L. CES VIQUEIRA, *Quím. Anal.*, **30** (5), 267-70 (1976).

[14] A. BERMEJO BARRERA, F. BERMEJO MARTINEZ, *Acta Quím. Compostelana*, **2** (4), 118-26 (1978).

[15] JEAN PHILIPPE, "Les methodes Statistiques en Pharmacie et en Chimie", Masson et cie Editeurs, Paris VI° (1967), pag. 29 y 33-35.

SUMMARY

A new method for the spectrophotometric determination of chromium whith ethylenediamine-N,N′-dipropionic acid (EDDPA) as reagent is proposed. This metal reacts with EDDPA to form a complex with two absorption maxima (520 and 405 nm). The Beer's law is followed for 20 to 240 μg Cr/ml at 520 nm, and the optimal interval of application according with Ringbom is between 60 and 230 μg de Cr/ml. The molar absorptivity is 140 mol^{-1} cm^{-1} and the sensitivity 0,3513 $\mu g/cm^2$. The composition of chromium complex, interferences, as well as reproducibility and precision were studied. The new method is compared with other similar methods, and this method is used for the determination of chromium in a standard sample of steel.

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A MARKOV CHAIN METHOD FOR SIMULATING THE TIME EVOLUTION OF DRUGS IN PHARMACOKINETICS SYSTEMS

A stochastic method based on discrete Markov chains is employed to simulate numerically the time course of drugs, without either solving differential equations or supplying closed form rate equations. The method is general, simple, accurate and fast. The method is applied to several linear and nonlinear pharmacokinetic models.

INTRODUCTION

The time evolution of the concentrations of molecular species during a chemical reaction can be formulated in a probabilistic or in a deterministic framework. Deterministic approaches are generally favoured, because, in chemical kinetics, the stochastic master equation is very often mathematically intractable [1]. However, recently, methods have been developed that allow exact numerical calculations within stochastic formulations without having to deal explicitly with the master equation [2-4]. One of such methods employs discrete Markov chains for the numerical integration of coupled chemical reactions. This Markov chain method (MCM) has proved to be a simple, accurate and general technique for the study of homogeneous and nonhomogeneous [3] systems. Here MCM is applied to the study of several models of interest in pharmacokinetics, to reveal the possibilities of the method in this field.

MARKOV CHAIN METHOD

MARKOV CHAINS

The concept of a Markov chain is associated with systems whose states change with time in a random manner, such that the outcome of any trial depends only on the outcome of the directly preceding trial [4]. Hence the probability, p_{ij}, of the system going from a state a_i at a time t (discrete variable) to a state a_j at a time $t+1$ depends only on the states at t, but is independent of the states of the system at times prior to t. The probability that a_i will remain unchanged between t and $t+1$ is p_{ii}. The transition probabilities can be presented in a matrix form

$$\widetilde{T} = \begin{bmatrix} p_{11} & p_{12} & \cdots & p_{1m} \\ p_{21} & p_{22} & \cdots & p_{2m} \\ \vdots & \vdots & & \vdots \\ p_{m1} & p_{m2} & \cdots & p_{mm} \end{bmatrix} \quad (1)$$

the so-called transition matrix. If we assume that the process begins at some particular state at time t, characterized by independent variables, X_1, X_2, X_3 ..., represented also in a matrix form

$$\widetilde{C}_t = [X_1(t), X_2(t), X_3(t), \ldots] \quad (2)$$

then the state after one step of time is given by the matrix $\widetilde{C}_{t+1}$ where

$$\widetilde{C}_t \times \widetilde{T} = \widetilde{C}_{t+1} \quad (3)$$

The $\widetilde{C}$ matrixes represent the absolute probabilities of the system being in its different possible states $i = 1,...m$. In addition to the so called one-step transition probabilities p_{ij}, it is of interest to consider n-step probabilities $p_{ij}^{(n)}$. These express the probability of a transition from a state i to a state j in n steps. A relationship between these different kinds of probabilities can be established recursively through the "Chapman-Kolmogorov functional equation"

$$\widetilde{T}^{m+n} = \widetilde{T}^m \times \widetilde{T}^n \quad (4)$$

where $\widetilde{T}^n$ represents the matrix of the n-step transition probabilities.

A Markov chain is stationary when $\widetilde{C}_{t+1} = \widetilde{C}_t$ and in this case the absolute probability of being at any state is the same for all steps of the process. Stationary situations occur after a large number of steps, as long as $\widetilde{T}$ is a stochastic regular matrix, i.e.,

$p_{ij} \geq 0$ $\sum_{j=1}^{m} p_{ij} = 1$ and $\sum_{n=1}^{\infty} p_{ij}^{(n)}$ converges.

On the other hand if the series $\sum_{n=1}^{\infty} p_{ij}^{(n)}$ diverges the state i is called recurrent. In general the divergence of this series implies the divergence of $\sum_{n=1}^{\infty} p_{jj}^{(n)}$ [4].

It is of interest in statistical applications to consider the relationship between the mean and the variance of a variable $X^{(n)}$ once the mean, m, and the variance, σ, of $X^{(1)}$ are known. For a simple branching process

$$\begin{aligned} &\text{mean } X^{(n)} = m^n \\ &\text{variance } X^{(n)} = n\,\sigma^2. \end{aligned} \quad (5)$$

TRANSITION PROBABILITIES FOR CHEMICAL REACTIONS

In homogeneous chemical reactions time is a continuous variable, but Markov chains discrete in time can be employed to study the time evolution of chemical systems, so long as the discreteness in the time variable does not hinder an accurate interpolation of molecular concentrations between any two instants. In order to apply MCM to reaction kinetics rate constants must be related to the Markovian transition probabilities [3]. For a first order process characterized by a rate constant k_1

$$A \xrightarrow{k_1} B$$

the probability of conversion of A into B during a single step is

$$p_{AB} = k_1\,\Delta t, \quad (6)$$

where Δt is the duration of each step, such that $p_{AB} \ll 1$. The probability that A will remain unchanged during one step is $p_{AA} = 1\text{-}k_1\,\Delta t$. For a second order process

$$A + B \xrightarrow{k_2} C$$

The probability of conversion of A into C is

$$p_{AC} = k_2\,[B]\,\Delta t$$

and $p_{AA} = 1\text{-}k_2\,[B]\,\Delta t$, $p_{BC} = k_2[A]\,\Delta t$ and $p_{BB} = 1\text{-}k_2\,[A]\,\Delta t$. In the definition of these transition probabilities care must be exercised to preserve the stoichiometry of the reaction. For example if C is considered to be formed simultaneously from A and from B then p_{AC} and p_{BC} should be multiplied by $\frac{1}{2}$ [3].

Concentrations or doses of drugs at different times can be determined through an iterative process by eq (3). The matrix C_t represents the concentrations or doses of the different substances at time t and through eq. (3) the concentrations after one step, i.e., at $t + \Delta t$, can be determined. For example the concentration of $[X_i(t + \Delta t)]$ is related to the molecular concentrations at time t by

$$\begin{aligned} &[X_i(t + \Delta t)] = p_{1i}\,[X_1(t)] + p_{2i}\,[X_2(t)] + \ldots \\ &\ldots + p_{mi}\,[X_m(t)] \end{aligned} \quad (7)$$

For any substance the area, A, under the concentration curve is given by

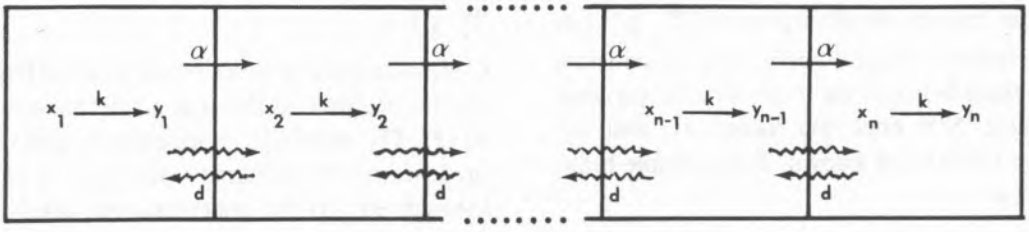
$$A = \sum_{t=0}^{t=n\Delta t} [X_i(t)] \quad (8)$$

The properties of matrices ensure that MCM verifies the Rule of Corresponding Areas [5].

The use of one-step transition matrix $\widetilde{T}$ can sometimes lead to a time consuming iterative process. However such iteration can be much faster if one employs an n-step transition matrix $\widetilde{T}^n$. The use of $\widetilde{T}^n$ is always possible when the transition probabilities are time-independent. When this is not so, e.g. in nonlinear kinetics, the use of such matrices is permissible under certain conditions that will be discussed later on.

NONHOMOGENEOUS SYSTEMS

To study spatial nonhomogeneous kinetic systems Markov chains discrete in time and in space must be employed [3]. The spatial coordinates of the system are represented as discrete variables. The reaction system is considered to be divided into several compartments. Molecular concentrations are the same at all points of any compartment but vary in a discrete manner from compartment to compartment. Molecular concentrations are therefore space, l, and time, t, $[X_i(l,t)]$ dependent. The Markov chain transition probabilities contain not only the probabilities of transitions between different substances through chemical reaction, but also the conversion of a substance in a compartment i to a compartment j through mass transfer.



The probability of mass transfer in a flow system of velocity v is

$$\alpha = \frac{v\,\Delta t}{\Delta l} \qquad (9)$$

where Δl is the dimension of the compartments in a given direction. The probability through diffusion is

$$d = \frac{D\,\Delta t}{(\Delta l)^2} \qquad (10)$$

where D is the diffusion coefficient. Chemical conversion is only considered within each compartment. The transition matrix $\widetilde{T}$ for a nonhomogeneous system contains the one-step spatial and temporal transition probabilities, but obviously n-step transitions in space and in time can also be considered.

NUMERICAL ERRORS

To assess the errors involved in the numerical simulation of concentrations through MCM let us consider a first order reaction $A \xrightarrow{k_1} B$ which can be represented by a simple branching process. The errors can be calculated for different transition probability values, $p = k_1\,\Delta t$, through eqs. (5). With $k_1\Delta t = 0.1$ the error in [A] is 10% after 3 periods and 16% after 5 periods, an error which is similar to the experimental errors in pharmacokinetics. The error decreases linearly with the decrease in the transition probability $k_1\,\Delta t$, and consequently with the decrease in Δt. The error in the area under the curve (eq. (8)), after 5 periods, is only 1%, with $k_1\Delta t = 0.1$ and also decreases linearly with a decrease in Δt.

The accuracy of MCM is dependent on the time scale of iteration, with respect to the magnitude of rate constants, and depends consequently on the number of iteration steps that one is prepared to carry out. For time-independent transition probabilities the accuracy of the method depends only on the one-step transition probabilities, but is independent of the order of the multistep transition probabilities. For most purposes the accuracy provided by the transition probabilities $k\Delta t = 0.1$ or $k[A]\Delta t = 0.1$ is good enough and, therefore, in the examples considered in the following section Δt is chosen such that $k\Delta t = 0.1$ for the highest kinetic rate constant.

Time dependent transition probabilities are required to simulate non-linear kinetics and for time-dependent first order rate constants. An example of such kinetics is provided by some models of

enzyme induction [6]. For a first-order process whose rate constant varies between k_o at $t=0$ to k_∞ at $t=\infty$ with $k=k_\infty-(k_\infty-k_o)e^{-\gamma t}$ the concentration is given by

$$C(t)=C_o \exp-\{k_\infty t-\frac{k_\infty-k_o}{\alpha}[1-\exp(-\gamma t)]\} \quad (11)$$

where γ is a constant and C_o the concentration at time zero. The MCM equation for this process is

$$C(t_{i+1})=C(t_i)\,(1-k_i)$$

where $k_i=(k_\infty-(k_\infty-k_o)e^{-\gamma t_i})\,\Delta t$.

Fig. 1 compares C(t) given by eq. (11) with the results of MCM, with $k_o\,\Delta t=0.01$, $k_\infty\,\Delta t=0.1$ and $\gamma=0.2$ time^{-1}. The agreement is excellent with an error of 12% after five periods of reaction. Multistep transition probability matrices can also be employed in the calculation. However for time-dependent probabilities the matrices $\tilde{T}^n$ introduce an additional error in the calculation. This error is reasonable as long as the survival probabilities do not vary, by more than 5% during each multistep transition. Fig. 1 illustrates the employement of a five-step transition which, after the first step, gives an error $\leqq 25\%$; the error decreases along the course of reaction since the variation with time decreases with increase in time. The error of the numerical simulation can be decreased by decreasing Δt and increasing, in the same proportion, the multistep transition. For example at $t=10$ the error is 25% with $\Delta t=1$ and $n=5$, but decreases to 6% if $\Delta t=0.1$ and $n=50$. Consequently in MCM, the judicious employment of multistep transition matrices can considerably decrease the time of computation without any significant loss of accuracy.

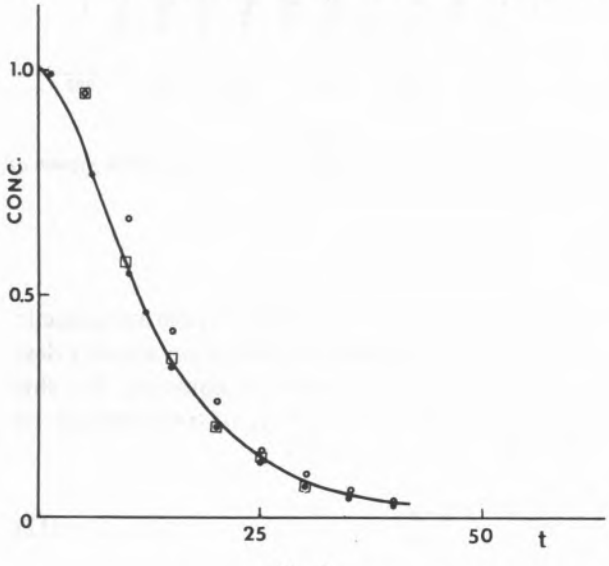


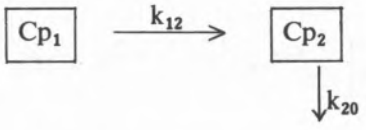
Fig. 1

First-order time-dependent induction kinetics $k=k_\infty-(k_\infty-k_o)e^{-\gamma t}$; $k_o=0.01$, $k_\infty=0.1$ and $\gamma=0.2$: ——— exact solution; ○ $\Delta t=1$ 1-step transition; • $\Delta t=1$ 5-step transition; □ $\Delta t=0.1$ 50-step transition

APPLICATIONS

MULTI-EXPONENTIAL KINETICS

In contrast with the analytical and numerical integration techniques, MCM provides a general method to deal with any kind of linear pharmacokinetics model [7]. To illustrate the applicability of MCM let us consider a two compartment model



Where Cp_i is the concentration in compartment i. This system [7] has an exact analytical solution, the so called "Bateman function". The one-step transition matrix for this kinetic scheme is

$$\begin{array}{c} \\ Cp_1 \\ Cp_2 \\ \text{elim.} \end{array}\begin{bmatrix} 1-k_{12}\,\Delta t & k_{12}\,\Delta t & 0 \\ 0 & 1-k_{20}\,\Delta t & k_{20}\,\Delta t \\ 0 & 0 & 1 \end{bmatrix}$$

Equation (7) leads to the one-step recurrence equations for the concentration of drug in any of the compartments. For example for the central compartment

$$[Cp_2]_{t+\Delta t}=[Cp_1]_t\,k_{12}\Delta t+[Cp_2]_t(1-k_{20}\Delta t)$$

Fig. 2 compares the computed time dependence of the drug in the central compartment with the theoretical one for a system where $\frac{k_{12}}{k_{20}}=100$. The fit is very good throughout, with an error that does not exceed 5%. The calculation at the earlier stages used a step $n=1$, at the middle stages $n=23$ and for the later stages $n=1024$. Multicompartment models do

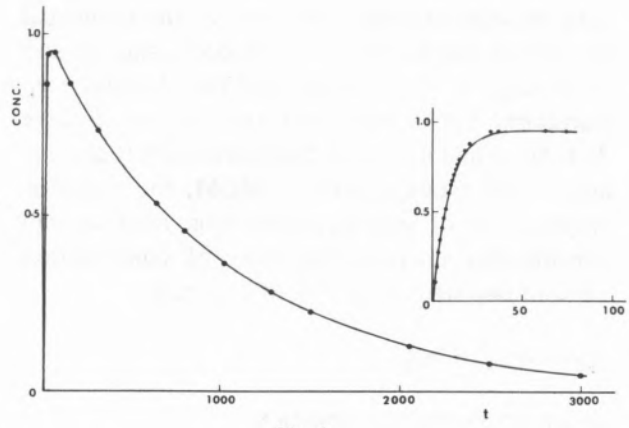
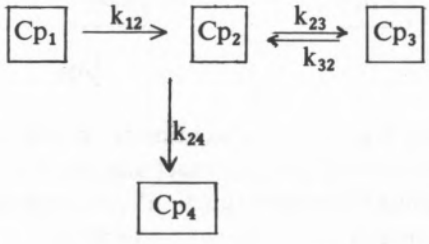


Fig. 2

Concentrations as a function of time for a two-compartment first-order model ($k_{12}=100$ $k_{20}=1$ and $\Delta t=10^{-3}$): ——— exact solution; • MCM solution

not add any special difficulty to the method, except by the requirement of a larger computer memory. A reasonable complex system of 4 compartments such as



leads to a transition matrix

$$\begin{bmatrix} 1-k_{12} & k_{12} & 0 & 0 \\ 0 & 1-k_{23}-k_{24} & k_{23} & k_{24} \\ 0 & k_{32} & 1-k_{32} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

with the rate constants expressed in units of Δt. Fig. 3 illustrates the time evolution of the drug in some of the compartments. Although MCM provides a discrete set of concentration values, such values allow the evaluation of the continuous functions of concentration *versus* time, as fig. 3 shows. To speed up the computation 1-step and 8-step transitions were considered. The effect on the dose in the central compartment of a repeated administration of an unitary dose in compartment 1, at every 20 units of time, is illustrated in fig 4. Within the model this effect can be easily simulated by the addition of a dose of 1, in Cp_1, every 20 units of time.

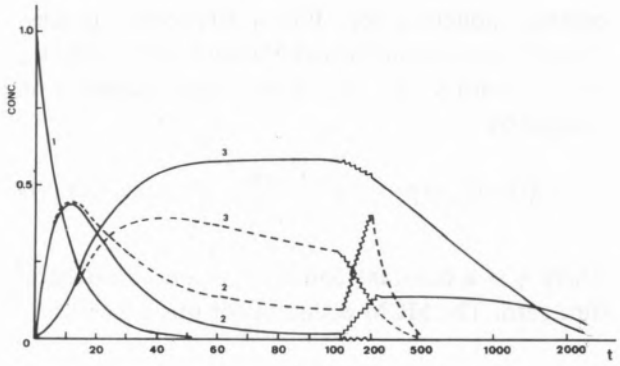


Fig. 3

Time evolution of a drug in a 4-compartment model: $k_{12}\,\Delta t=0.1$, $k_{23}\Delta t=0.05$, $k_{24}\Delta t=0.03$; ---- linear $k_{32}\Delta t=0.025$; ——— nonlinear $k_{32}\Delta t=\dfrac{0.00125}{0.05+[Cp_3]}$

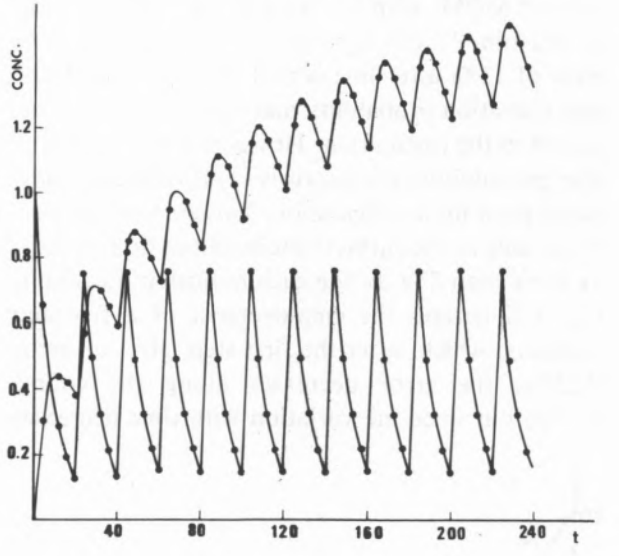


Fig. 4

Multidose administration in the linear 4-compartment system of fig. 3

NONLINEAR KINETICS

As an illustration of a nonlinear pharmacokinetic model we will consider the saturation kinetics described by the Michaelis-Menten equation. For this kind of kinetics the probability of transition can be given by

$$p_{ij}=\frac{V_M\,\Delta t}{K_M+[S]} \qquad (12)$$

where V_M is the maximum rate of reaction or elimination, [S] the substrate concentration and K_M the Michaelis constant, which is the concentration at which the rate of elimination is one-half of the ma-

ximum possible value. Let us consider a process with a rate law

$$-\frac{d[A]}{dt} = \frac{V_M[A]}{K_M + [A]} \tag{13}$$

for which the recurrence equation is

$$[A]_{t+\Delta t} = (1 - \frac{V_M \Delta t}{K_M + [A]_t})[A]_t \tag{14}$$

Eq. (13) can be integrated and gives

$$K_M \ln \frac{[A]_o}{[A]} + [A]_o - [A] = V_M t \tag{15}$$

where $[A]_o$ is the initial concentration of the substance A. Eq. [15] reveals that ln [A] is a linear function of $V_M t + [A] - [A]_o$. Markov chain data conform well with this prediction, with an error $<1.5\%$ after 3 periods of reaction and an error of 7.5% when 20-step transitions are employed (fig. 5).

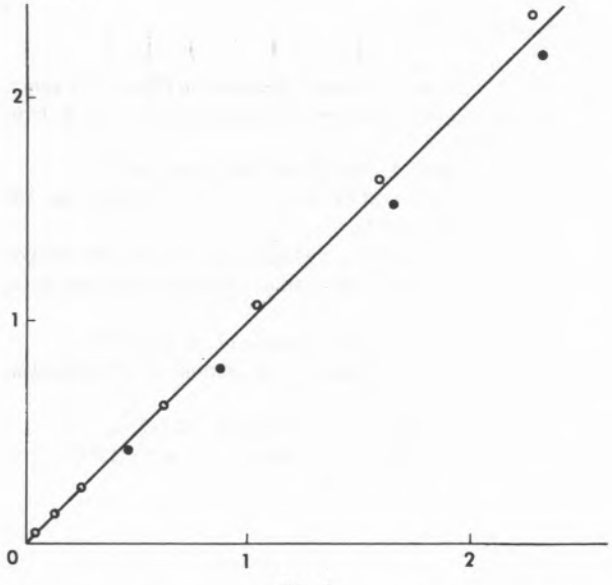


Fig. 5

Plot according to eq. (15) for the disappearance of a substance following Michaelis-Menten kinetics: $[A]_o = 1$, $K_M = 0.5$, $V_M = 0.05$, $\Delta t = 1$; ○ $n = 1$; • $n = 10$

To illustrate a drug interaction process, saturation kinetics were considered in the 4-compartment level of the last section for the intercompartmental transition rate k_{32}; the first order rate constant, at low $[Cp_3]$, is identical to the rate in the linear system. Fig. 3 illustrates this system and comparison with the linear system reveals the drug retention in Cp_3 in the nonlinear situation, with the consequent decrease of the drug concentrations in the central compartment. After the initial stages, the concentrations do not vary strongly with time and consequently n-step transitions can be employed without loss of accuracy. In the calculation, for $t > 50$, 16-step transitions were employed.

GASTROINTESTINAL ABSORPTION

Gastrointestinal absorption introduces new factors into the kinetic systems. In the models that are going to be considered we will take into consideration the gastrointestinal filling and emptying and the effect of blood flow. MCM can be applied to the different phases of gastrointestinal absorption by considering the intestine divided into several segments of length Δl. In each segment the concentration of drug is the same at all points, but varies in a discrete manner from segment to segment. Absorption into blood occurs from a portion of the intestine tube and is characterized by a rate constant k_{abs}; the flow of the chyme has a rate v_c. The probability of mass transfer through flow in the intestine is α_c (eq. (9)). In a situation where absorption occurs only from the central segment the transition matrix is

$$\begin{array}{l} \text{entrance} \\ \text{middle} \\ \text{exit} \\ \text{blood} \end{array} \begin{bmatrix} 1-\alpha_c & \alpha_c & 0 & 0 \\ 0 & 1-\alpha_c-k_{abs} & \alpha_c & k_{abs} \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1-k_{el} \end{bmatrix}$$

where k_{el} is the rate constant for the elimination process. Fig. 6 presents the curves for the absorption of the drug into the blood. The chyme is filling the intestine up to a time tg, such that the total dose is unity.

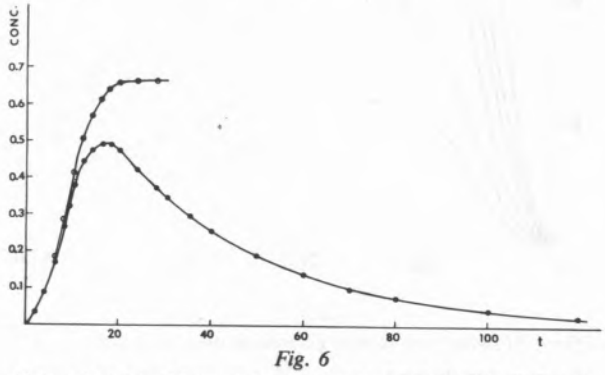
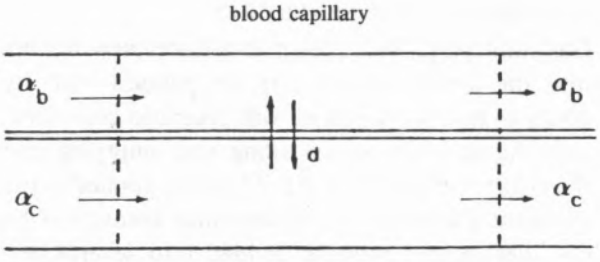


Fig. 6

Absorption (•) and invasion (○) curves gastrointestinal absorption with $\alpha_c = 0.1$, $k_{abs} = 0.1$, $k_{el} = 0.03$, dose = 1 and $\Delta t = 1$

In this model of gastrointestinal absorption the mixing of the drug in the blood compartment is considered to be very fast. However such models do not take into consideration the effect of blood flow rate [8] when this is comparable to the absorption or the chyme flow rate. A model such as the following one can simulate this effect



A reversible diffusion, d, between chyme and blood is considered. The probability of mass transfer through flow in the blood is α_b and elimination is only considered from the exit blood compartment with a rate k_{el}. Fig. 7 presents a family of computed curves which clearly show that when the blood flow rate approaches the rate of diffusion, there is a decrease in drug absorption.

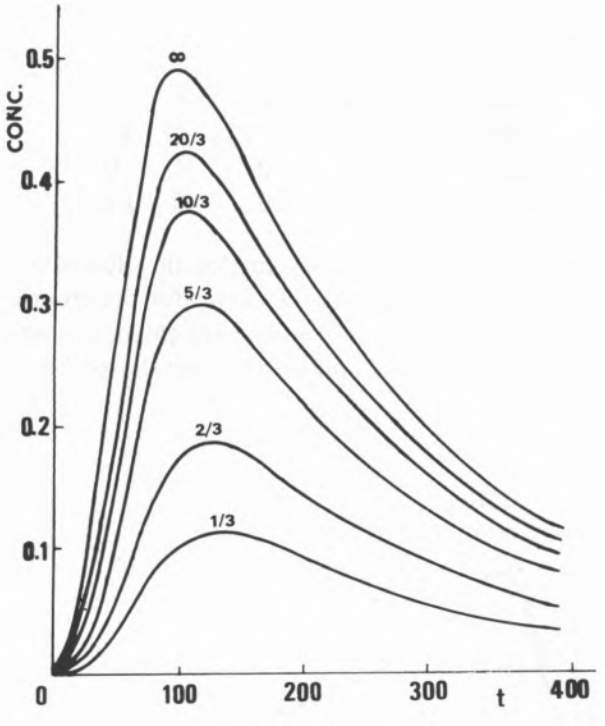


Fig. 7

Effect of blood flow rate on gastrointestinal absorption. Family of curves for different ratios $\frac{\alpha_b}{d}$; $k_{el}=5\times10^{-3}$, $d=3\times10^{-2}$; $\alpha_c=1.5\times10^{-2}$, $\Delta t=1$

In conclusion we have shown that MCM can be applied to several situations of relevance in pharmacokinetics. The method is universal, can be made as accurate as one wishes, but can also be a fast method of numerical integration. This allows MCM to be employed in model search. For any given model the method can be used for constructing families of curves of doses or concentrations as a function of time, which may allow estimation of kinetic rate constants.

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REFERENCES

[1] D.A. McQuarie, *Stochastic Approach to Chemical Kinetics, Methuen Review Series in Applied Probability*, vol. **8**, Jerusalem, 1967.
[2] D.T. Gillespie, *J. Phys. Chem.*, **81**, 2340 (1977).
[3] S.J. Formosinho, M.G. Miguel, *J. Chem. Educ.*, **56**, 582 (1979); **59**, 281 (1982).
[4] A.T. Bharucha-Reid, "Elements of Theory of Markov Processes and Their Application", McGraw-Hill, New York, 1960, Chap. 1.
[5] E. Nüesch, *Eur. J. Clin. Pharmacol.*, **6**, 33 (1973).
[6] R.H. Levy, M.S. Dumain, J.L. Cook, *J. Pharmacokin. Biopharm.*, **7**, 557 (1979).
[7] H. Akaike, *SIAM J. on Control*, **13**, 162 (1975).
[8] D. Winne, *J. Pharmacokin. Biopharm.*, **6**, 55 (1978).

RESUMO

Aplicação do Método das Cadeias de Markov à Evolução com o Tempo de Medicamentos em sistemas Farmacocinéticos

O método estocástico das Cadeias de Markov é aplicado ao estudo da evolução temporal de medicamentos em situações de cinética linear e não-linear. O método que é um processo de integração numérica, é simples, rápido e tão exacto quanto se queira.

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CYCLOMETALLATION REACTIONS OF Pd(II) WITH *N*-(α-NAPHTHYLIDENE)-*o*-TOLUIDINE **

Reaction of N-*(α-naphthylidene)-o-toluidine with palladium(II) acetate yields a bridged acetato complex, [(nf-N,C)PdAc]$_2$. Metathetical reactions with sodium chloride or bromide give bridged chlorine or bromine complexes, [(nf-N,C)PdX]$_2$ (X = Cl, Br). Halogen bridge splitting reactions have been carried out with triphenylphosphine in 1:2 and 1:4 molar ratio to obtain the corresponding cyclometallated and non-cyclometallated monomers. The elemental analyses, IR and NMR spectra are in accordance with the structures given for the present compounds, and they allow us to distinguish the bridged complexes from the monomers, and among the latter between the cyclometallated [(nf-N,C)PdLX)] and non-cyclometallated ones [(nf-C)PdL$_2$X], in which the five membered ring disappears due to the presence of two triphenylphosphine ligands bonded to the central atom.*

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INTRODUCTION

Cyclometallation reactions have been widely studied [1,2] most of all with aromatic *N*-donor ligands, although other ligands with group VB and VIB donor atoms have been used [2]. In the course of our investigations regarding the formation of orthometallated complexes we have already studied the reactions of a typical *N*-donor ligand [3] and we now report the synthesis and characterization of the complexes derived from *N*-(α-naphthylidene)-*o*-toluidine. The acetato, chloro and bromo bridged complexes have been prepared first. Halogen bridge splitting reactions with triphenylphosphine yielded the cyclometallated and non-cyclometallated monomers when a 1:2 and 1:4 molar ratio was used, respectively. Our aims were to study the different types of complexes formed on the basis of the spectroscopical data, specially in the cases of the non-cyclometallated compounds in which the ν(C=N) stretching frequency appears unusually low for this type of compounds.

EXPERIMENTAL

MATERIALS

o-toluidine and α-naphthaldehyde were distilled before use. Palladium(II) acetate (Fluka) and triphenylphosphine (Merck) were not further purified. *N*-(α-naphthylidene)-*o*-toluidine was synthesized by refluxing equimolar amounts of *o*-toluidine and α-naphthaldehyde in chloroform solution during 1 hour. The solvent was distilled "in vacuo" after which a yellow solid was obtained. Solvents were purified by the standard methods. The reaction between palladium acetate and the Schiff base was carried out in a N_2 atmosphere.

ANALYSES

C, H, N, analyses were carried out in a Perkin-Elmer model 240-B elemental analyzer. IR spectra were recorded on a Perkin-Elmer model 180 spectrophotometer as nujol mulls or polyethylene pellets. The NMR spectra were recorded with a Varian CFT-20 in deuterochloroform using tetramethylsilane as an internal standard. Pd was determined polarographically. The analytical results are reported in Table 1.

Table 1
Analyses and colour of the complexes

Complex	Colour	% C*	% H*	% N*	% Pd*
$[(nf\text{-}N,C)PdAc]_2$	Light Orange	58,8(58,6)	4,7(4,2)	3,1(3,4)	25,65(25,97)
$[(nf\text{-}N,C)PdCl]_2$	Yellow	56,1(56,0)	3,8(3,7)	3,5(3,6)	27,35(25,55)
$[(nf\text{-}N,C)PdBr]_2$	Yellow	48,9(50,2)	3,3(3,3)	2,9(3,2)	24,25(24,70)
[(nf-N,C)PdLCl]	Pale Yellow	66,9(66,7)	4,6(4,5)	1,7(2,2)	16,36(16,41)
[(nf-N,C)PdLBr]	Pale Yellow	61,6(63,4)	4,4(4,2)	1,7(2,0)	14,81(15,35)
$[(nf\text{-}C)PdL_2Cl]$	Pale Yellow	69,8(71,2)	4,9(4,9)	1,4(1,5)	12,13(11,68)
$[(nf\text{-}C)PdL_2Br]$	Pale Yellow	67,5(67,9)	4,7(4,7)	1,3(1,5)	11,50(11,14)

* The calculated analyses are in parentheses.
nf-N,C and nf-C = N-(α-naphthylidene)-*o*-toluidine bi- and monodentate, respectively.
L = $P(C_6H_5)_3$

$[(nf\text{-}N,C)PdAc]_2$

In a 100 ml round-bottomed flask 0.3 g (1.36 mmol) of palladium acetate and 0.34 g (1.4 mmol) of *N*-(α-naphthylidene)-*o*-toluidine were dissolved in 25 ml of acetic acid. The dark-red solution turns orange-red upon heating. After refluxing for 1 hour the solution is cooled, diluted with water and extracted with dichloromethane. The extract was concentrated and cromatographed on silica gel. With benzene a yellow green band was eluted, which once analyzed showed to be the initial Schiff base. With dichloromethane containing 1 % ethanol a yellow-red band was eluted. After being concentrated it was again cromatographed on silica gel. A green band eluted with dichloromethane produced an oil that was not further investigated. The title complex was eluted with dichloromethane containing 1 % ethanol and recrystallized from chloroform/*n*-hexane to give a light orange solid.

$[(nf\text{-}N,C)PdX]_2$

To a solution of 0.1 g (0.12 mmol) of $[(nf\text{-}N,C)PdAc]_2$ in acetone an aqueous solution of sodium chloride (X = Cl) or sodium bromide (X = Br) was added, and a yellow precipitate was obtained in each case. The solids were filtered off, washed with water and dried.

[(nf-N,C)PdLX]

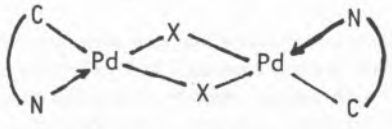
To a suspension of 0.050 g (0.065 mmol) of $[(nf\text{-}N,C)PdX]_2$ (X = Cl) and to another one of 0.05 g (0.058 mmol) (X = Br), both in acetone (5 ml), 0.034 g (0.13 mmol) and 0.030 g (0.116 mmol) of triphenylphosphine were added, respectively. In both cases a yellow solution forms. Addition of *n*-hexane to the solution gave a precipitate that was filtered off, washed with *n*-hexane and dried in vacuum.

$[(nf\text{-}C)PdL_2X]$

To a suspension of 0.050 g (0.065 mmol) of $[(nf\text{-}N,C)PdX]_2$ (X = Cl) and to another one of 0.050 g (0.058 mmol) (X = Br), both in acetone (5 ml), 0.068 g (0.26 mmol) and 0.061 g (0.23 mmol) of triphenylphosphine were added, respectively. In both cases a yellow solution forms. Addition of *n*-hexane to the solution gave a precipitate that was filtered off, washed with *n*-hexane and dried in vacuum.

RESULTS AND DISCUSSION

The bridged complexes are of the type



(X = Ac, Cl, Br)

the organic ligand being bonded to the metal atom by a σ carbon bond and a coordinated nitrogen bond. In the cyclometallated monomers the five-membered ring remains, with the halogen atom "*trans*" to the carbon atom. In the non-cyclometallated monomers the organic moiety is linked to the metal atom only through the carbon atom. All this is confirmed by the IR data, which are reported in Table 2.

The acetato bridged complexes exhibit two IR bands at 1565 and 1410 cm^{-1} that correspond to $\nu_{as}(CH_3COO)$ and $\nu_s(CH_3COO)$, respectively.

Table 2

Complex	ν(C=N)	ν_{op}(Pd-C)	ν_{ip}(Pd-C)	ν(Pd-C)	ν_{op}(Pd-N)	ν_{ip}(Pd-N)	ν(Pd-N)	ν(Pd-P)	ν_{as}(Pd-X_b)	V_s(Pd-X_b)	ν(Pd-X_t)
Ligand	1628m										
[(nf-N,C(PdAc]$_2$	1615m	580m	562w		418m	370vw					
[(nf-N,C)PdCl]$_2$	1615s	580m	563w		415m	360vw			308m	248m	
[(nf-N,C)PdBr]$_2$	1617s	580m	564w		417m	360vw			192m	160w	
[(nf-N,C)PdLCl]	1612m			582vw			350w	180w			295m
[(nf-N,C)PdLBr]	1614s			582m			365w	176w			202w
[(nf-C)PdL_2Cl]	1611m			582vw				184w			290m
[(nf-C)PdL_2Br]	1609m			578m				166w			196m

L = $P(C_6H_5)_3$

They also show absorptions between 460 and 540 cm^{-1}, which can be assigned to Pd-O vibrations.

The bridged halogen complexes exhibit two ν(Pd-X) frequencies due to ν_{as}(Pd-X_b) (308 cm^{-1}, X = Cl; 192 cm^{-1}, X = Br) and ν_s(Pd-X_b) (248 cm^{-1}, X = Cl; 160 cm^{-1}, X = Br). By their position the higher ones belong to the ν(Pd-X) "*trans*" to the nitrogen atom and the lower ones to the ν(Pd-X) "*trans*" to the carbon atom, as is expected by the lower "*trans*" influence of the nitrogen atom [11], and as CROCIANI *et al.* have observed with similar types of complexes [12]. In the monomers there is only one band assignable to ν(Pd-X_t), as is expected. Thus, the second monomers (Table 2) are non ionic, which is in accordance with the fact that they are only slightly soluble in water and with the absence of precipitation by treatment with silver nitrate. Also by their position [7,12] we may conclude that the halogens are "*trans*" to atoms of high "*trans*" influence, *i.e.*, "*trans*" to the carbon atom or to one of the phosphine ligands in the second two monomers. The "*cis*" or "*trans*" positions of the two phosphine ligands can be ascertained, according to MASTIN [14], by the intensity of a band near 550 cm^{-1}; the weak intensity of this band in the spectra of the second two monomers leads to a "*trans*" disposition of the phosphine ligands in these compounds, so that the halogen atom must be "*trans*" to the carbon atom.

The spectra of all these compounds show weak to medium intensity bands between 580 and 560 cm^{-1}, which are characteristic of Pd-C vibrations [7], indicating the presence of Pd-C bonding. So, in the bridged complexes there are two Pd-C bands at 580 and *ca.* 560 cm^{-1} due to the out-of-phase and in-phase vibrations, respectively, whereas in the four monomers there is only one *ca.* 580 cm^{-1}.

For the Pd-N vibrations we find in the specta of the dimers bands at *ca.* 415 and *ca.* 360 cm^{-1}, corresponding the the out-of-phase and in-phase motions. Between 450 and 350 cm^{-1} only the spectra of the first two monomers show a band, which can be attributed to a ν(Pd-N) mode with the nitrogen atom "*trans*" to a high "*trans*" influence ligand, that is, a phosphine ligand; so, these complexes are cyclometallated. The absence of such a band in the spectra of the second two monomers indicates that these cannot be cyclometallated.

The shift towards lower wavenumbers of the band assigned to the ν(C=N) frequency in the complexes in comparison with the original Schiff base has been claimed to be a sign of coordination through the nitrogen atom [4,5]. A lower frequency shift can be expected in the formation of an ordinary coordination complex, where the Schiff base is bonded to the central atom by the nitrogen atom only. But in our case we must not forget a possible conjugation of the C=N double bond not only with the phenyl ring bonded to the carbon atom, but also with the one linked to the nitrogen atom. In the -C=C-C=N-C- system there are two conjugated double bonds and it is possible that there may be strong coupling between ν(C=N), ν(C=C), ν(N-C), and δ(C-H), so it is quite difficult to foresee the modification that will take place when a simultaneous coordination by the carbon and nitrogen atoms is produced in the formation of a chelate ring. Furthermore, the electron pair of the M-C bond is bonding as it was in the Schiff base, while the electron pair of the M-N bond, initially non bonding, is now slightly bonding. On the other hand, the possible presence of metal-to-ligand back bonding should cause a partial occupation of the >C=N- π^* orbitals. In our complexes the ν(C=N) frequency shifts are all

towards lower wavenumbers, -12 cm^{-1} in the bridged complexes, -15 cm^{-1} in the cyclometallated monomers and -18 cm^{-1} in the non-cyclometallated ones. With these results we can only conclude that the formation of a complex, whether cyclometallated or not, results in lower wavenumbers of the $\nu(C=N)$ frequency.

The assignment of metal-phosphine vibrations has been a subject of controversy [6-10], but the criterium most widely accepted nowadays is that they lie below 200 cm^{-1}. In the spectra of our complexes we find bands for ν(Pd-P), whose wavenumbers can be seen in Table 2.

The ^1H NMR spectrum of the Schiff base shows a singlet at 8.98 ppm (azomethine proton). The high field chemical shift of an azomethine proton indicates that the coordination of the palladium atom is through the nitrogen atom and not through the C=N double bond [13], and that the Pd-N bond is effectively established. In the bridged complexes there are singlets at 8.21 ppm ($X=CH_3COO$), 8.60 ppm (X=Cl), and 8.64 ppm (X=Br), all of them shifted to higher field.

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REFERENCES

[1] I. OMAE, *Chem. Rev.*, **79**, 287 (1979).
[2] M.I. BRUCE, *Angew Chem. Internat. Ed. English*, **73**, 16 (1977).
[3] A. SUAREZ, J.M. VILA, E. GAYOSO, M. GAYOSO, *An. Quím.*, in press.
[4] S.P. MOLNAR, M. ORCHIN, *J. Organomet. Chme.*, **16**, 196 (1969).
[5] H. ONOUE, I. MORITANI, *J. Organomet. Chem.*, **43**, 431 (1972).
[6] D.M. ADAM, D.J. CHANDLER, *Chem. Commun.*, 69 (1966).
[7] K. NAKAMOTO, "IR and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed. Wiley Interscience (1978).
[8] P.L. GOGGIN, R.J. GOODFELLOW, *J. Chem. Soc., A*, 1462 (1966).
[9] G.D. COATES, C. PARKIN, *J. Chem. Soc.*, 421 (1963).
[10] M.A. BENNETT, R.J.H. CLARK, A.D.J. GOODWIN, *Inorg. Chem.*, **6**, 1625 (1967).
[11] F. BASOLO, R.G. PEARSON, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley (1967).
[12] B. CROCIANI, T. BOSCHI, R. PIETROPAOLO, U. BELLUCO, *J. Chem. Soc., A,*, 53A (1969).
[13] Y.A. USTYNYUK, V.A. CHERTKOV, I.V. BARINOV, *J. Organomet. Chem.*, **29**, C53 (1971).
[14] S.H. MASTIN, *Inorg. Chem.*, **13**, 1003 (1974).

RESUMO

Reaccións de Ciclometalación de Pd(II) con *N*-(α-naftiliden)-*o*-toluidina.

A reacción de N-(α-naftiliden)-o-toluidina con acetato de paladio(II) produce un complexo cas pontes acetato $[(nf\text{-}N,C)PdAc]_2$. As reaccións de matáteses con cloruro e bromuro de sodio dan complexos con pontes cloro e bromo, $[(nf\text{-}N,C)PdX]_2$ (X=Cl, Br). A reacción dos dímeros con pontes halógeno con trifenilfosfina, en relación molar 1:2 e 1:4, conduce aos monómeros ciclometalados e non ciclometalados, respectivamente. As análises elementais e os espectros de IR e RMN concordan cas estruturas que se propoñen e permíten distinguir entre os complexos dímeros e os monómeros, e nos derradeiros, entre os monómeros ciclometalados [(nf-N,C)PdLX] e os non ciclometalados $[(nf\text{-}C)PdL_2X]$, nos que o anel de cinco membros desaparece por mor da unión de dous ligandos trifenilfosfina ao metal central.

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THERMODYNAMICS OF THE IDEALLY POLARIZED INTERFACE BETWEEN TWO IMMISCIBLE SOLUTIONS OF ELECTROLYTES. THE ELECTRO-CAPILLARY EQUATION AND SURFACE EXCESSES

The electrocapillary equation for an ITIES is derived. Surface excesses relative to the solvent in each phase are defined and a precise definition of surface charge density on each side of the interface is presented. The residual entropy S is defined and a way to be calculated as a function of surface charge density is indicated.*

1 — INTRODUCTION

Polarized interfaces between two immiscible electrolyte solutions are attracting the attention of electrochemists [1-4]. The structure and properties of the electrical double layer existing at such interfaces are being investigated but, so far, no detailed thermodynamic treatment has been published. In this paper we present the electrocapillary equation for an ITIES (Interface between Two Immiscible Electrolyte Solutions) giving the proper definition of the surface charge density and all the surface excesses on both sides of the interface.

2 — THE ELECTROCAPILLARY EQUATION

To simplify, the cell considered will be one with reference electrodes reversible respectively to the cation on the organic phase and to the anion on the aqueous phase. It can be represented by

Cu′	RE Er(X^+)	solution of XY in organic solvent	solution of CA in water	RE Er(A^-)	Cu
		δ	α	δ'	

where salts XY and CA are considered to exist solely in the organic and aqueous phases respectively.
The only polarized interface is α while δ and δ' are considered non polarized and therefore the potential drop across them are exclusively determined by the activities of X^+ (δ) and A^- (δ') ions. The analog of the Gibbs Duhem equation for the interphase is

$$-d\gamma = S^\alpha dT - V^\alpha dp + \Gamma_{X^+} d\bar{\mu}_{X^+} + \Gamma_{Y^-} d\bar{\mu}_{Y^-} + \Gamma_{C^+} d\bar{\mu}_{C^+} + \Gamma_{A^-} d\bar{\mu}_{A^-} + \Gamma_w d\mu_w + \Gamma_O d\mu_O \quad (1)$$

where the symbols have the following meaning
w — water, O — organic solvent, and all extensive variables are expressed per unit area of the interface and Γ_j is surface excess of species j.
The first step in the derivation is to eliminate single ion electrochemical potentials in eq. (1) using the equilibria existing in the organic and aqueous phases.

For the aqueous phase

$$d\bar{\mu}_{A^-} + d\bar{\mu}_{C^+} = d\mu_{CA}$$

or

$$\Gamma_{C^+} d\bar{\mu}_{C^+} = \Gamma_{C^+} d\mu_{CA} - \Gamma_{C^+} d\bar{\mu}_{A^-} \quad (2)$$

while for the organic phase

$$d\bar{\mu}_{X^+} + d\bar{\mu}_{Y^-} = d\mu_{XY}$$

or

$$\Gamma_{Y^-} d\bar{\mu}_{Y^-} = \Gamma_{Y^-} d\mu_{XY} - \Gamma_{Y^-} d\bar{\mu}_{X^+} \quad (2)'$$

After substitution eq. (1) becomes:

$$-d\gamma = S^\alpha dT - V^\alpha dp + (\Gamma_{X^+} - \Gamma_{Y^-}) d\bar{\mu}_{X^+} + (\Gamma_{A^-} - \Gamma_{C^+}) d\bar{\mu}_{A^-} + \Gamma_{C^+} d\mu_{CA} + \Gamma_{Y^-} d\mu_{XY} + \Gamma_w d\mu_w + \Gamma_O d\mu_O \quad (3)$$

The terms $(\Gamma_{X^+} - \Gamma_{Y^-})$ and $(\Gamma_{A^-} - \Gamma_{C^+})$ represent the net amount of charge accumulated respectively on the organic and aqueous sides of the interface.
Defining

$$\sigma^w = F(\Gamma_{C^+} - \Gamma_{A^-})$$

and considering that the interphase must be electrically neutral

$$\sigma = \sigma^w = F(\Gamma_{C^+} - \Gamma_{A^-}) = -\sigma^O = = -F(\Gamma_{X^+} - \Gamma_{Y^-}) \quad (4)$$

These relations define the surface charge density at an ITIES and identify its value with the amounts of ions accumulated at each side of the interface.
After substitution eq. (3) becomes

$$-d\gamma = S^\alpha dT - V^\alpha dp + (\sigma/F)(-d\bar{\mu}_{X^+} - d\bar{\mu}_{A^-}) + \Gamma_{C^+} d\mu_{CA} + \Gamma_{Y^-} d\mu_{XY} + \Gamma_w d\mu_w + \Gamma_O d\mu_O$$

or

$$-d\gamma = S^\alpha dT - V^\alpha dp + (\sigma/F)\, d\epsilon^{\pm} + \Gamma_{C^+} d\mu_{CA} + \Gamma_{Y^-} d\mu_{XY} + \Gamma_w d\mu_w + \Gamma_O d\mu_O \quad (5)$$

where $\epsilon^{\pm}$ is a generalized electrochemical potential to be considered later.

It remains to eliminate in eq. (5) the chemical potentials of the solvents in each phase which requires the Gibbs-Duhem relations for each phase.
Given the miscibility of each solvent in the other such relations are

$$x_O^w d\mu_w + x_O^O d\mu_O + x_O^{XY} d\mu_{XY} + S_O dT + V_O dp = 0 \quad (6)$$

$$x_w^w d\mu_w + x_w^O d\mu_O + x_w^{CA} d\mu_{CA} + S_w dT + V_w dp = 0 \quad (6)'$$

where x_j^i are the molar fractions of component i in solvent j and S_j and V_j are, respectively, the molar entropies and molar volumes of the phase with solvent j.
Eqs. (6) and (6)′ are a system of two equations with two unknowns, $d\mu_w$ and $d\mu_O$ the solutions of which are

$$d\mu_O = \frac{x_w^w x_O^{XY}}{\beta} d\mu_{XY} - \frac{x_O^w x_w^{CA}}{\beta} d\mu_{CA} + \left(\frac{x_w^w S_O - x_O^w S_w}{\beta}\right) dT \quad (7)$$

$$d\mu_w = \frac{x_w^O x_O^{XY}}{\beta} d\mu_{XY} - \frac{x_O^O x_w^{CA}}{\beta} d\mu_{CA} + \left(\frac{x_O^O S_w - x_w^O S_O}{\beta}\right) dT \quad (7)'$$

where

$$\beta = x_O^w x_w^O - x_w^w x_O^O \quad (8)$$

Substituting these values in eq. (5) and after rearrangement

$$-d\gamma = \Gamma_S dT - \Gamma dp + \Gamma_{C^+/w} d\mu_{CA} + \Gamma_{Y^-/O} d\mu_{XY} + q d\epsilon^{\pm} \quad (9)$$

where

$$\Gamma_{C^+/w} = \Gamma_{C^+} + \frac{\Gamma_w x_O^O - \Gamma_O x_O^w}{x_O^w x_w^O - x_w^w x_O^O} x_w^{CA} \quad (10)$$

$$\Gamma_{Y^-/O} = \Gamma_{Y^-} + \frac{\Gamma_O x_w^w - \Gamma_w x_w^O}{x_O^w x_w^O - x_w^w x_O^O} x_O^{XY} \quad (11)$$

are the surface excesses in the aqueous phase relative to the water and in the organic phase relative to the organic solvent and

$$\Gamma_S = S^\alpha + \frac{\Gamma_w x_O^O - \Gamma_O x_O^w}{x_O^w x_w^O - x_w^w x_O^O} S_w + \frac{\Gamma_O x_w^w - \Gamma_w x_w^O}{x_O^w x_w^O - x_w^w x_O^O} S_O \qquad (12)$$

is the surface excess of entropy.

It is needed now to clarify the meaning of the generalized electrochemical potential ϵ_-^+. Let us consider the equilibrium existing at each reference electrode assumed to be

i) in the aqueous phase

$$NA + e_{Cu} = N_{\downarrow}^- + A^-$$

and

$$d\bar{\mu}_{A^-} = d\mu_{NA} + d\bar{\mu}_{e_{Cu}} - d\mu_N$$

ii) in the organic phase

$$X^+ + e_{Cu'} \rightleftharpoons X$$

and

$$d\bar{\mu}_{X^+} = d\mu_X - d\bar{\mu}_{e_{Cu'}}$$

Replacing these values in eq. (9), it becomes

$$-d\gamma = \ldots + (\sigma/F)\{(-d\mu_X - d\mu_{NA} + d\mu_N) + (d\bar{\mu}_{e_{Cu'}} - d\bar{\mu}_{e_{Cu}})\} + \ldots \qquad (13)$$

or

$$-d\gamma = \ldots (\sigma/F)(dK + (d\bar{\mu}_{e_{Cu'}} - d\bar{\mu}_{e_{Cu}})) \qquad (14)$$

If ϕ'' and ϕ' are the inner potentials of the two chemically identical copper wires connected to both reference electrodes then

$$d\bar{\mu}_{e_{Cu'}} - d\bar{\mu}_{e_{Cu}} = F(d\phi'' - d\phi') = F\, dE_-^+ \qquad (15)$$

where E_-^+ refers to the potential of the right hand side of the cell with respect to the left hand side. At constant temperature $dK = 0$ because it only refers to solid phases of the reference electrodes.

The generalized potential ϵ_-^+ is, therefore, given by

$$\epsilon_-^+ = E_-^+ + \frac{\mu_N - \mu_{NA} - \mu_X}{F} \qquad (16)$$

3 — PHYSICAL IMPLICATIONS OF THE ELECTROCAPILLARY EQUATION

As it can be noted in eq. (9-12) the relations for an ITIES are similar to those obtained for the mercury-solution interface. Determination of the surface excess of an ion in one of the phases requires the use of a reference electode reversible to the ion of opposite charge in the same phase, keeping constant the activity of the salt on the other phase. This obviously means to keep constant the potential of the reversible reference electrode in the other phase. It is clear that any choise of a reference electrode reversible to an ion in solution is possible and there are 4 possible combinations.

However it is more usual to use an Ag/AgCl reference electrode in both sides of the interface as represented

$$\begin{array}{ccccccccccc} Cu' & | & Ag & | & AgCl & | & X\,Cl & | & X\,Y & | & Z\,Cl & | & AgCl & | & Ag & | & Cu \\ & & & & & & \text{water} & & \text{nitrobenzene} & & \text{water} & & & & \\ & & & & & & \delta & & \beta & & \alpha & & & & \delta' \end{array}$$

X, Z cations

The reference electrode on the right hand side is reversible to Cl^- anion present in the aqueous phase and thus, keeping constant the composition of the organic phase and the potential at the other reference electrode it is possible to determine the surface excess of ion Z^+.

To make the potential drop across interface β with a Nernstian response to the activity of X^+ in the organic phase requires the use of appropriate conditions which are not in the scope of this paper.

It must be emphasized that the relative surface excesses of the ions each phase are effected by the degree of miscibility of both solvents. When such miscibility is very small eq. (10,11) can be approximated by

$$\Gamma_{C^+/w} = \Gamma_{C^+} + \frac{x_w^{CA}}{x_w^w}\Gamma_w$$

$$\Gamma_{Y^-/O} = \Gamma_{Y^-} + \frac{x_O^{XY}}{x_O^O}\Gamma_O$$

which are the values found for the case of two completely immiscible phases.

It is easy to show that the charge densities on each side of the interphase defined as

$$\sigma^{w} = \Gamma_{C^+} - \Gamma_{A^-}$$

and

$$\sigma^{O} = \Gamma_{X^+} - \Gamma_{Y^-}$$

are also given by

$$\sigma^{w} = \Gamma_{C^+/w} - \Gamma_{A^-/w}$$

and

$$\sigma^{O} = \Gamma_{X^+/O} - \Gamma_{Y^-/O}$$

These quantities are easily generalised for any number of cations or anions adsorbed.

4 — THE ENTROPY OF FORMATION OF THE ITIES

A non-thermodynamic excess of entropy, S* has been defined for the Hg/solution interface which has proved to be very useful in assessing the properties of the solvent monolayer in such interphases [5-8]. An identical quantity is here defined for an ITIES.
S* is defined as the residual

$$S^* = \Gamma_S - \sum_i \Gamma_{i/w} \hat{s}^{i}_{w} - \sum_j \Gamma_{j/O} \hat{s}^{j}_{O} \qquad (17)$$

where Γ_S is the thermodynamic surface excess of entropy, $\Gamma_{i/w}$ and $\Gamma_{j/O}$ are relative surface excesses as defined by eqs. (10) and (11) and s^{i}_{w} and s^{j}_{O} are respectively the partial molar entropies of components i and j and in the aqueous and organic phases.
Using the definition of surface charge densities eq. (17) becomes

$$S^* = \Gamma_S - (\sigma/F)\, \hat{s}^{+}_{w} - \Gamma_{-/w} \hat{s}^{salt}_{w} + \\ + (\sigma/F)\, \hat{s}^{+}_{O} - \Gamma_{-/O} \hat{s}^{salt}_{O} \qquad (18)$$

where $\hat{s}^{salt}_{j}$ is the partial molar entropy of the salt existing in the phase of solvent j.
After rearranging eq.(18) becomes

$$S^* = \Gamma_S - \sigma/F\, (\hat{s}^{+}_{w} - \hat{s}^{+}_{O}) - \Gamma_{-/w} \hat{s}^{salt} - \\ - \Gamma_{-/O} \hat{s}^{salt}_{O} \qquad (19)$$

or in general terms

$$S^* = \Gamma_S - \sigma/F\, (\hat{s}^{\pm}_{w} - \hat{s}^{\pm}_{O}) - \Gamma_{\pm/w} \hat{s}^{salt}_{w} = \\ = \Gamma_{\pm/O} \hat{s}^{salt}_{O} \qquad (20)$$

where the superscripts in $\hat{s}$ correspond in the same order to the subscripts in Γ.
If the reference electrodes used are as assumed in part 2, eq.(20) takes the form

$$S^* = \Gamma_S - \sigma/F\, (\hat{s}^{+}_{w} - \hat{s}^{-}_{O}) - \Gamma_{-/w} \hat{s}^{salt}_{w} + \\ + \Gamma_{+/O} \hat{s}^{salt}_{O} \qquad (21)$$

Substituting in eq.(9) the value of Γ_S as obtained from eq.(21) it becomes

$$-d\gamma = (S^* + \sigma/F\, (\hat{s}^{+}_{w} - \hat{s}^{-}_{w}) - \Gamma_{-/w} \hat{s}^{salt}_{w} + \\ + \Gamma_{+/O}\, \hat{s}^{salt}_{O}) dT + \sigma d\epsilon^{+}_{-} + \\ + \Gamma_{-/w} d\mu^{salt}_{w} + \Gamma_{+/O} d\mu^{salt}_{O} \qquad (22)$$

Therefore at constant composition in both phases eq.(22) can be written

$$-d\gamma = (S^* + \sigma/F(\hat{s}^{+}_{w} - \hat{s}^{-}_{O}))dT + q d\epsilon^{+}_{-} \qquad (23)$$

because

$$d\mu^{salt}_{w} = -\hat{s}^{salt}_{w} dT$$

and

$$d\mu^{salt}_{O} = -\hat{s}^{salt}_{O} dT$$

Eq.(23) establishes the route to obtain values of S* directly from the temperature coefficients of the interfacial tension, or indirectly through the temperature coefficients of the differential capacities. The meaning of S* in the case of an ITIES is not as simple as in the case of two completely immiscible phases and is given by

$$S^* = \Gamma_w(\dot{S}^{w}_{\alpha} - \hat{s}^{w}_{w}) + \Gamma_O(\dot{S}^{O}_{\alpha} - \hat{s}^{O}_{O}) + \\ + \Gamma^{-}_{w}(\dot{S}^{-}_{\alpha} - \hat{s}^{-}_{w}) + \Gamma^{+}_{w}(\dot{S}^{+}_{\alpha} - \hat{s}^{+}_{w}) + \\ + \Gamma^{-}_{O}(\dot{S}^{-}_{\alpha} - \hat{s}^{-}_{O}) + \Gamma^{+}_{O}(\dot{S}^{+}_{\alpha} - \hat{s}^{+}_{O}) - \\ - b\, x^{w}_{O}\, (\hat{s}^{w}_{w} - \hat{s}^{w}_{O}) - a\, x^{O}_{w} (\hat{s}^{O}_{O} - \hat{s}^{O}_{w})$$

where

$$b = \frac{\Gamma_O x^{w}_{w} - \Gamma_w x^{O}_{w}}{x^{w}_{O} x^{O}_{w} - x^{w}_{w} x^{O}_{O}}$$

$$a = \frac{\Gamma_w x^{O}_{O} - \Gamma_O x^{W}_{O}}{x^{w}_{O} x^{O}_{w} - x^{w}_{w} x^{O}_{O}}$$

$\Gamma^{-,+}_{j}$ are the surface excesses of the anion or cation existing in solvent j.

REFERENCES

[1] J. KORYTA, P. VANYSELE, "Advances in Electrochemistry and Electrochemical Engineering", Vol. 12, John Wiley & Sons Inc., New York (1982).

[2] H. GIRAULT, D.J. SCHIFFRIN, *J. Electroanal. Chem.*, **150**, 43 (1983).

[3] J.D. REID, O.R. MELROY, R.P. BUCK, *J. Electroanal. Chem.*, **147**, 71 (1983).

[4] Z. SAMEC, V. MARECEK, J. WEBER, *J. Electroanal. Chem.*, **100**, 841 (1979).

[5] G.J. HILLS, FERNANDO SILVA, *Can. J. Chem.*, **59**, 1835 (1981).

[6] M.H. CHARLES, M. MULENGA, A. JENARD, H.D. HURWITZ, *Can. J. Chem.*, **59**, 2053 (1981).

[7] J.A. HARRISON, J.E.B. RANDLES, D.J. SCHIFFRIN, *J. Electroanal. Chem.*. **48**, 359 (1973).

[8] NGUYEN HUU CUONG, A. JENARD, H.D. HURWITZ, *J. Electroanal. Chem.*, **103**, 399 (1979).

RESUMO

Termodinâmica da interface idealmente polarizável entre duas soluções imiscíveis de electrólitos.

A equação electrocapilar e os excessos superficiais.

Apresenta-se a equação electrocapilar para uma interface idealmente polarizada entre duas soluções imiscíveis de electrólitos. Definem-se os excessos superficiais relativos ao solvente de cada fase assim como a densidade de carga superficial em ambos os lados da interface. Define-se uma entropia residual S e estabelece-se uma forma do seu valor ser calculado em função da densidade superficial da carga.*

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PROPERTIES OF TRANSITION METAL CENTRES IN NITROGEN FIXATION

This work presents an attempt for the characterization of the dinitrogen-binding transition metal centres and a proposal for the way the activation of N_2 depends on their properties.

Although a few recent rivews are known [1-4] on dinitrogen complexes, the concept of the present work develops under a new perspective which relates properties and types of behaviour previously described individually in more detail.

Following a brief introduction on the current importance of the nitrogen fixation, the composition and structure of the transition metal centres which bind N_2 are presented, as well as their electronic properties (electron richness, σ acceptance and π back-bonding capacities, and polarisability) which play a fundamental role in the coordination of dinitrogen. The dependence of these properties on the periodic group of the central metal and on the effect of co-ligands is discussed.

The chemical behaviour of these centres (which is dependent mainly on electronic and structural factors such as the unsaturated character derived from the lability of the dinitrogen ligand) is then described, followed by the types of activation of N_2 upon coordination in poli- or mono-nuclear complexes. It is then analysed the dependence of this activation on the periodic group of the transition metal and on the presence of ions of the less electronegative non-transition metals.

The application of isocyanides as potential models for the coordination and reactivity of dinitrogen is also proposed, and structural models for the enzimatic nitrogen fixation centre are presented.

INDEX

1 — INTRODUCTION

Definition and interest

The current interest on the reactivity of dinitrogen, the most abundant gas of the earth atmosphere (formerly considered as an inert species) is justified mainly by the importance of the applications of its fundamental derivative, ammonia.

The reductive transformation of dinitrogen into ammonia is known as "nitrogen fixation", although in a broad sense all the types of studies which somehow may contribute to a better understanding of this process may be included under this topic.

Within the biological field, ammonia constitutes the basis of biosynthetical inclusion (assimilation) of the nitrogen element in organic molecules which form fundamental celular components with proteins or nucleic acids.

The direct assimilation of N_2 from the air is not possible by upper organisms and plants get nitrogen from the soil usually after the formation of ammonia, whereas that element becomes available to animals (namely to Man) through the feed (plants or other animals).

The abovementioned reduction, in a catalytic way, may be performed biologically by the enzyme nitrogenase under ambient conditions, or in industry under drastic conditions. Moreover, the nitrogen fixation constitutes usually the limiting factor of the biological productivity; only in regions of high nitrogen concentration (due to decomposition processes or to the exaggerated application of nitrogen fertilizers) other nutrients, such as potassium, phosphorus or sulphur, become the limiting factors.

Within the industrial field, ammonia constitutes the starting material for the production of most of the nitrogen compounds: nitric acid, nitrogen fertilizers, acrylonitrile, amines and explosives.

Historical background

Although since a few thousand years Man discovered that the yield of the crops could be increased by the addition of legumes to the soil, only by the end of last century this problem started to be enlightened when, in 1887, Hellriegel and Wilfarth proved the nitrogen fixation capacity of nodulated legumes. In the following year, the first nodule bacterium was isolated by Beijerinck and, in 1893, Winogradsky isolates the first soil bacterium which can fix nitrogen (it was later called *Clostridium pasteurianum*).

Meanwhile, by the end of last century and beginning of the current one, there occured an increasing demand on nitrogen fertilizers (due to feed requirements) and on nitric acid (mainly after the invention of dinamite by Alfred Nobel in 1866). Nitrates from Chile were then the main natural resource for the starting materials, but they were insufficient for the requirements of an increasing consumption.

Dinitrogen, with a huge natural stock in the atmosphere, appeared as a potential alternative candidate, but the known industrial processes (oxidation to NO and reduction to calcium cyanamide), with high energy requirements, deserved only a weak popularity.

The problem appears to be solved in 1908 through the development of a distinct route: taking advantage of the use of high pressures and in the presence of a metal catalyst, Haber promotes the synthesis reaction of ammonia from dinitrogen and dihydrogen which becomes commercially profitable.

However, the industrial synthesis of ammonia requires a high energy consumption, not only by the synthesis reaction (which requires high pressures and temperatures) but also in the production of dihydrogen (which consumes reserves of fossil energy such as petroleum derivatives, natural gas or coal). It was estimated [5] that the production of nitrogen fertilizers corresponds roughly to $1 \sim 1.6\%$ of the world consumption of fossil energy.

Hence, the nitrogen fixation appears as a fundamental chemical reaction to satisfy the increasing feed demands (due to the demographic expansion), but requiring a high and increasing energy consumption which is not compatible with the decrease of the fossil energy stocks. The required nitrogen supply to the biosphere has then to be balanced with the energy cost.

Excluding, for this problem, a drastic solution of control or reduction of the population, a few interdisciplinary proposals may be presented:

— Increasing the efficiency of the Haber synthesis with a decrease in the energy cost;

— Production of a new type of catalyst, model of the enzymatic activity, which may operate (preferably in the soil) in ambient conditions without

requiring fossil energy resources (water and sun ligh may behave as the hydrogen and energy sources, respectively);

— Promotion of the biological fixation namely through a wider distribution of nitrogen fixation bacteria and the extension, by genetic manipulation, of the fixing capacity to plants, such as cereals, with a high agricultural interest.

The first two routes, chemically in nature, require a better understanding of the metal centres which may activate dinitrogen, as shown below.

Although in 1930 it was shown by BORTELS [6] the essential role of molybdenum in the enzymatic fixation (*e.g.*, *A. vinelandii* does not fix nitrogen in a medium without Mo and the growing is stimulated by the presence of this element), the explanation based on the recognition of the presence of Mo in a protein of the enzyme was based [7] only in 1966 when the two components of nitrogenase were separated and one of them was shown to present this element.

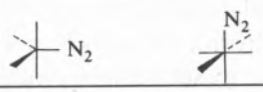
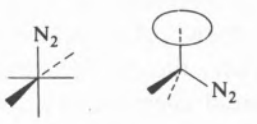
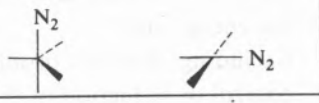
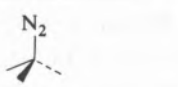
Meanwhile, in 1964, the reduction of N_2 in solution by a transition metal system is reported by VOL'PIN [8] an the occurrence of a stable metal-dinitrogen bond is demonstrated (ALLEN and SENOFF [9]) in 1965 through the preparation of the first transition metal dinitrogen complex. It is, in this way, evidenced the possibility of occurrence of a similar metal-dinitrogen interaction in the natural system and in the industrial synthesis, *i.e.*, the probable involvement of dinitrogen complexes as intermediates in the production of ammonia.

2 — STRUCTURAL AND ELECTRONIC PROPERTIES

The knowledge of the properties of a dinitrogen-binding metal centre is hampered by the common difficulty of isolation. It is usually present in the

Table 1

Common metal oxidation state and d^n electronic configuration, geometry, charge and examples of co-ligands in transition metal dinitrogen complexes

		d^n	Geometry	Charge	Co-ligands
IVB	Ti^{II} Zr^{II}	d^2		0	$\eta^5-C_5R_5^-$, R^-
VB	$Nb^{III(V)}$ $Ta^{III(V)}$	$d^{2(o)}$		0	CHR(2−),R^-, X^-
VIB	M^o	d^6		0	PR_3,$\eta^6-C_6R_6$,CO,PhS$(CH_2)_2$SPh
VIIB	M^I	d^6		0	PR_3,$P(OR)_3$ Cl^-, $S_2PR_2^-$,$S_2CNR_2^-$, H^- CO,$\eta^5-C_5H_5$
VIII	Fe^{II} Ru^{II} Os^{II}	d^6		+1 +2	PR_3 H^-,Cl^-,R^-,$\eta^5-C_5H_5^-$,SR^- NH_3,H_2O thf, porphinato
	Co^I Rh^I Ir^I	d^8		0	PR_3 H^-,Cl^-
	Ni^o	d^{10}		0	PR_3 Electropositive metal (polynuclear structures)
	Co^{-I}			−1	

composition of coordinatively saturated complexes, and its properties are deduced from their expression in these complexes where the influence of other ligand(s) is present.

2.1. *COMPOSITION*

2.1.1. METAL AND LIGANDS

Fully characterized dinitrogen complexes prepared by conventional techniques are already known for the majority of transition metals as shown below:

IVB	VB	VIB	VIIB	VIII		
Ti		Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
	Ta	W	Re	Os	Ir	Pt

Moreover, some of the gaps may be filled if one considers species prepared by low temperature matrix isolation techniques — *e.g.*, $V(N_2)_6$ [10], $M(N_2)_n(O_2)$ (M = Pd, Pt; n = 1,2) [11] and $Cu_n(N_2)_m$ [12].

Usually the dinitrogen complexes obey the 18-electron rule (except in the extreme groups), they are diamagnetic and neutral (with exceptions for those of the iron sub-group which are often cationic). They present the metal in a low oxidation state and co-ligands which are considerable electron donors and commonly weak π acceptors, namely tertiary phosphines and halides, or ammonia and amines in the case of Ru and Os (Table 1). The last two general features (low metal oxidation states and the presence of electron donor co-ligands) evidence an important property of the dinitrogen-binding transition metal centres: their high (or, at least, considerable) electron richness; this point will be treated below in more detail.

Examples of ligating atoms of co-ligands are known for any of the IVA to VIIA groups, the most common being underlined in Table 2.

Sulphur ligands are very rare although in the enzymatic system sulphur is an element which is present in the vicinity of molybdenum. The only well characterized examples are the Re(I) complexes *mer*-[Re (S-S) (N_2) $(PMe_2Ph)_3$] (S-S$^-$ = $S_2PPh_2^-$, $S_2CNR_2^-$, $S_2(OEt^-)$ [13] and derived mixed dinitrogen-isocyanide species such as *mer*-| $Re(\eta^1\text{-}S_2PPh_2)$ (N_2) $(CNMe)_x(PMe_2Ph)_{4-x}$|(x = 1 or 2) [14], the Os(II) complex *mer*-[$OsCl(SC_6F_5)$ (N_2) $(PMe_2Ph)_3$] [15] and the less well defined 1,2-bis(phenylthio)ethane complex of Mo(0) *trans*-[$Mo(N_2)_2$ $(PMe_2Ph)_2$(S-S)] (S-S = $PhSCH_2CH_2SPh$) [16]. However, no reaction involving the N_2 ligand (apart from possible displacement) has yet been reported.

Lighter metals (Fe, Co, Ni) appear to present a higher tendency to bind hydride relative to the heavier ones (Re, Os, Ir) which ligate preferentially halides as co-ligands in N_2 complexes.

A few other general observations are presented below, but the best choice of co-ligands, in N_2 complexes, is still guided by experience, their stabiility being strongly dependent on the composition. Hence, *e.g.*, although $[IrCl(N_2)(PPh_3)_2]$ is a known stable species, the analogues with PMe_2Ph or $P(C_6H_4CH_3\text{-}4)_3$ are not enough stable to be isolated without decomposition.

2.1.2. GEOMETRY

The geometry of the dinitrogen complexes appears to be determined by the d^n electronic state of the metal (see Table 1) which, for d^6-d^{10} species (VIB — VIII groups), may be rationalised by extended Hückel theoretical calculations [17] based on the following assumptions: the N_2 bonding results mainly from the π-backbonding component; the molecular orbitals of the N-N_2 bond derived from overlap of the metal d orbitals with the dinitrogen $1\pi_g^*$ orbitals are fully occupied.

The former proposal may, however, fail in complexes of the group VIII (where the σ component may

Table 2
Ligand bonding atoms in dinitrogen complexes

Group	Bonding atom	Ligand
IVC	*C*	$\eta^5\text{-}C_5H_5^-$, $\eta^6\text{-}C_6H_6$ CO,CNR CHR(2−),R^-
VA	N *P* As	NH_3, $H_2N(CH_2)_2NH_2$, edta *PR_3* (and chelating diphosphines), $P(OR)_3$ AsR_3
VIA	O S	H_2O,thf, edta $S_2PPh_2^-$, $S_2CNR_2^-$,SR^-,$PhS(CH_2)_2SPh$
VIIA	*X*	Halide(Cl^-)
IA	*H*	*Hydride*

have a fundamental role, as shown below), whereas the latter assumption may not be followed by the group IVB metals since the expected strong π interaction with N_2 (see below) may result in a considerable stabilization of the M-N_2 bond even for an incomplete fulfilment of the π(M-N_2) orbitals.

Group IVB d^2 metal complexes present either a trigonal — *e.g.*, $[\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2(\mu\text{-}N_2)]$ [18] — or a tetrahedral geometry — *e.g.*, $[\{(\eta^5\text{-}C_5H_5)_2Zr(N_2)(\mu\text{-}N_2)\}]$ [19].

However, group VB d^2 (or d^0, depending on the formal charge on the ligand N_2, as shown below) metal compounds display a trigonal bipyramid structure — *e.g.*, $[\{Ta(CH_2CMe_3)(CHCMe_3)(PPh_3)\}_2(\mu\text{-}N_2)]$ [20] where the axial positions are occupied by the two phosphines — or an octahedral-type geometry as in $[\{TaCl_3(Pbz_3)(thf)\}_2(\mu\text{-}N_2)]$ (bz = $CH_2C_6H_5$) [21] where thf is in *trans* position relative to the bridging N_2 ligand.

Dinitrogen complexes of groups VIB and VIIB and of the iron sub-group usually present a metal d^6 centre (which corresponds to metal oxidation states of 0, +1 and +2, respectively) with either an octahedral-type geometry — such as $[M(N_2)_2L_4]$ (M = Mo, W; L = tertiary monophosphine or $\frac{1}{2}$ diphosphine [22], *trans*-$[ReCl(N_2)L_4]$ [23], *trans*-$[FeH(N_2)(tetraphos)]$ Br {tetraphos = $= Ph_2PC_2H_4P(Ph)C_2H_4P(Ph)C_2H_4PPh_2$} [24] and $[Ru(NH_3)_5(N_2)]$ Cl_2 [25] — or, if a cyclic arene ligand is bound, a trigonal pyramid geometry is observed where this ligand coordinates the apical position — *e.g.*, $[\{Mo(\eta^6\text{-}C_6H_3Me_3)(dmpe)\}_2(\mu\text{-}N_2)]$ [26] (where dmpe = $Me_2PC_2H_4PMe_2$) and $[\{Mn(\eta^5\text{-}RC_5H_4)(CO)_2\}_2(\mu\text{-}N_2)]$ [27].

Group VIB metal complexes with an electronic state different from d^6 (metal oxidation state other than zero) are also known and they may present a distinct geometry: $[WH(N_2)_2(dppe)_2]^+$ (where dppe = $Ph_2PC_2H_4PPh_2$) which is pentagonal bipyramid [28] (coordination number seven) with metal d^4 and $[\{Cl_4Mo\}_2(\mu\text{-}N_2)]$ [29] with a d^2 metal and coordination number five.

Metal d^8 complexes of the Co sub-group display either a trigonal bipyramid geometry — *e.g.*, $[CoH(N_2)(PPh_3)_3]$ [30] — or a square planar arrangement such as in $[RhH(N_2)(PPhBu_2)_2]$ [31] (in both cases, the hydride ligand is *trans* to N_2).

Metal d^{10} complexes of group VIII present either a trigonal planar geometry — $[\{(PCy_3)_2Ni\}_2(\mu,\eta^2\text{-}N_2)]$ [32] and $[\{Ph(NaOEt_2)_2\{Ph_2Ni\}_2(\mu,\eta^2\text{-}N_2)NaLi_6(OEt)_4OEt_2\}_2]$ [33] — or a trigonal pyramid structure as in the hexameric cluster $K[Co(N_2)(PMe_3)_3]$ [34] and in $[\{Co(PMe_3)_3(N_2)\}_2Mg(thf)_4]$ [35].

Polyhydridic complexes deviate from the above-mentioned geometric patterns, as observed, *e.g.*, for the double metal-metal bonded dinuclear compound $[\{RuH_2(PPh_3)_2\}(\mu\text{-}H)_4\{Ru(N_2)(PPh_3)_2\}]$ [36].

2.2. *DINITROGEN BONDING*

2.2.1. BONDING MODES

A wide versatility of coordination to a transition metal is known for the dinitrogen ligand, and the modes shown in fig. 1 have already been clearly evidenced.

The terminal mode of coordination is the most common, either in mononuclear or in dinuclear complexes; in the latter, N_2 behaves as a di-hapto (η^2) ligand.

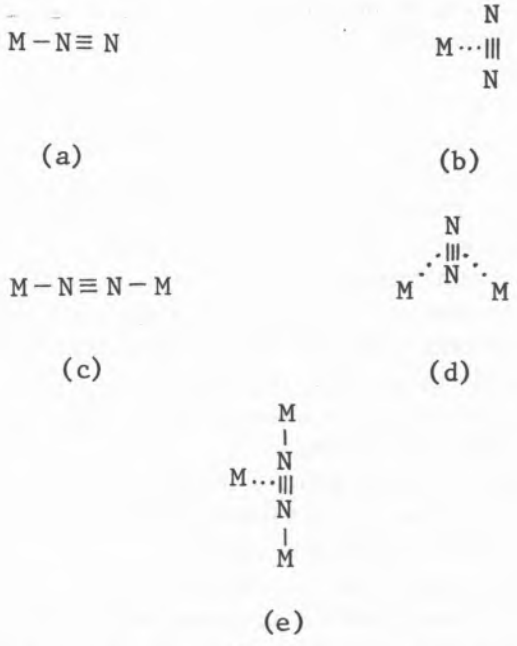


Fig. 1

Modes of dinitrogen bonding to transition metals. (a) η^1-terminal. (b) η^2-lateral. (c) μ^2,η^2-bridging terminal. (d) μ^2,η^2-bridging lateral. (e) μ^3,η^2-bridging terminal-lateral

Only scant examples are known for the lateral (side-on) coordination and they may involve polinuclear species with high complexity.

The simplest known compound with a side-on N_2 ligand is $Co(\eta^2\text{-}N_2)$, prepared by co-condensation reaction of atomic cobalt with dilute nitrogen-argon matrices at 10K, the type of N_2 bonding being evidenced by i.r. studies with $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$ (only one stretching band is observed for the $^{29}N_2$ isotopic ligand) [37].

ESR electron-nuclear spin coupling studies on $[Zr(\eta^5\text{-}C_5H_5)_2(N_2)\{CH(SiMe_3)_2\}]$ with $^{28}N_2$ and $^{30}N_2$ and the absence, in the i.r. spectrum, of any band assigned to $\nu(N\equiv N)$, suggest a sideways--bound (type *b*) dinitrogen, although a fast zirconyl oscillation between the two nitrogen atoms of a corresponding end-on bonded N_2 complex cannot be ruled out [38].

Type (d) bonding is present, *e.g.*, in the following complexes of Ni(0): $[\{(LiPh)_3Ni\}_2(\mu, \eta^2\text{-}N_2)(OEt_2)_2]$ [39], prepared by reaction of [Ni(CDT)] (where CDT = cyclododecatetraene) with LiPh in Et_2O, and $[\{Ph(NaOEt_2)_2\{Ph_2Ni\}_2(\mu,\eta^2\text{-}N_2)NaLi_6(OEt)_4OEt_2\}_2]$ [33] which is formed when the reaction occurs also in the presence of NaPh; a partial view of the latter is depicted in fig. 2, the N_2 ligand lying in the intersection of two distorted trigonal planar $\{Ph_2Ni(\eta^2\text{-}N_2)\}$ units with each Ni atom above (by 0.05 Å) the plane approaching the

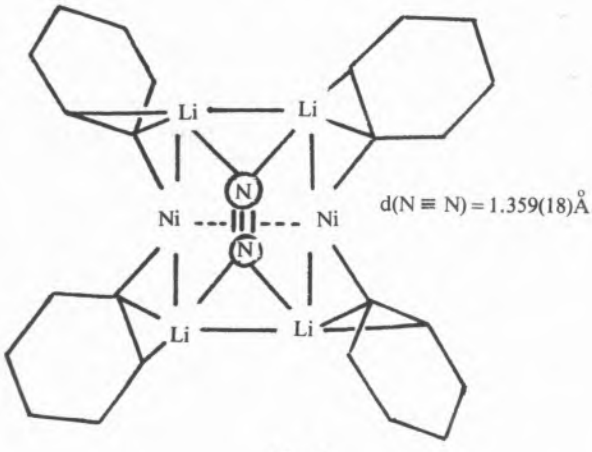


Fig. 2
Partical view of the internal skeleton of complex $[\{Ph(NaOEt_2)_2\{Ph_2Ni\}_2(\mu,\eta^2\text{-}N_2)NaLi_6(OEt)_4OEt_2\}_2]$

other transition metal atom. Each Ni atom and the ***N_2 ligand also interact with a few ions of electropositive non-transition metals*** (lithium and sodium) through multicentered electron-deficient bondings; the negative charge at the N_2 ligand is stabilized by its interaction with these metal atoms. Such a stabilization with a promoting effect on the metal to dinitrogen back-bonding is also observed in other complexes where N_2 bridges a transition and non--transition metals such as K^+ in the hexameric K^+ $[Co(N_2)(PMe_3)_3]^-$ complex [34] and Mg^{2+} in $[\{Co(PMe_3)_3(N_2)\}_2Mg(thf)_4]$ [35].

The effect of the cation of the electropositive species on the activation of dinitrogen will be considered later on.

Dinitrogen bridges three transition metal atoms (mode *e* of fig. 1) in $[(\mu_3\text{-}N_2)\{(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)_2Ti_2\}\{(\eta^1\text{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2\}]$. $[(\eta^5\text{-}C_5H_5)_2Ti(C_6H_{14}O_3)]$. $C_6H_{14}O_3$ which is prepared by reaction of $[\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)\}(\eta^5\text{-}C_5H_5)_3Ti_2]$ with N_2 in DME/diglyme; it is composed of two complex units (one with N_2 and the other without this species and presenting a molecule of diglyme, $H_3COC_2H_4OC_2H_4OCH_3$, bonded through two oxygen atoms) and diglyme of crystallization [40]; it is unknown if the two complex units are distinct molecules co-crystallized in the unit cell or if the compound is a complex ionic salt. The complex unit with N_2 and a fulvalene $(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ and cyclopentadienyl ($\eta^5\text{-}C_5H_5$ and $\eta^1\text{:}\eta^5\text{-}C_5H_4$) co-ligands is depicted in fig. 3.

Dinitrogen may also bridge three atoms in a terminal mode, but they are not all transition metals: $[\{WCl(PMe_2Ph)_3P_y(\mu_3\text{-}N_2)(AlCl_2)\}_2]$, formed in

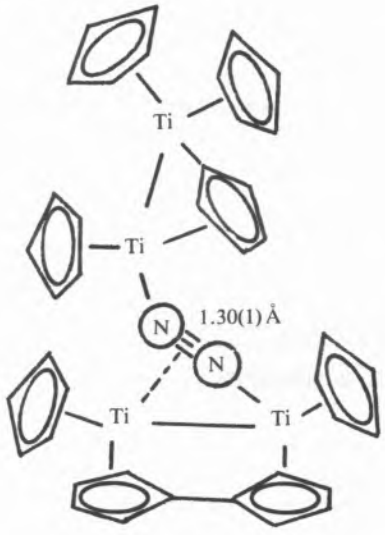
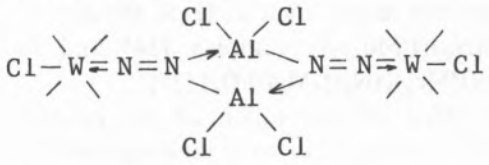


Fig. 3
Complex unit with a bridging terminal-lateral dinitrogen ligand, $[(\mu_3\text{-}N_2)\{(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)_2Ti_2\}\{(\eta^1\text{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2\}]$ *(see text fot the complete formulation of the complex)*

the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with $AlCl_3/P_y$ in C_6H_6, and presenting two $AlCl_2$ bridges between the N_2 ligands [41]:



2.2.2. BONDING PARAMETERS

A slight increase of the N-N bond length (relative to the value in the free ligand) [42] usually occurs upon ligation of dinitrogen to a mononuclear metal centre (Table 3), as observed, *e.g.*, in complex *mer*-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$ [44]. However, in some mulfinuclear complexes, a strong lengthening may result leading to a N-N distance which lies in the expected range intermediate between the values for a double (1.23 Å) [46] and a single (1.46 Å) [48] bond. This behaviour is observed, *e.g.*, in the abovementioned Ti complex [40] with a triple N_2 bridge (see fig. 3) where d(N-N) = 1.30(1) Å, and in the dinuclear Ni species [33] with a bridging edge-on (side-on) N_2 (fig. 2) [d(N-N) = = 1.359(18) Å]. A long N-N distance [1.30(1) Å] also occurs in the known group VB dinuclear N_2 complexes, *e.g.*, $[[Ta(CH_2Bu^t)(CHBu^t)(PPh_3)_2]_2(\mu\text{-}N_2)]$ which displays a short metal-nitrogen bond corresponding to a considerable double bond character [20].

In these complexes with a long N-N distance, the ν(NN) stretching vibration, when it is observed, occurs at values which are also intermediate between the expected ones for a N-N double and single bond (Table 3). Moreover, at least a considerable lowering of ν(NN) upon N_2 coordination is always observed in agreement with a substantial participation of the metal to π^* dinitrogen backbonding as shown below.

2.2.3. BONDING ORBITALS

The *terminal* mode of bonding of N_2 to a metal centre may be described as for CO by the Chatt-Dewar-Duncansson model; it is the result of a N_2 to metal σ electron donor component with concomitant π backbonding from a filled metal t_{2g} orbital to a π_g^* N_2 antibonding orbital (fig. 4).

Table 3

Bonding parameters and i.r. (or Raman) ν (NN) data for dinitrogen ligand

Compound	d(N-N) Å	d(M-N) Å	ν (NN) cm^{-1}	Ref.
N ≡ N(free)	1.0976(1)		2331[a]	[42,43][b]
$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$	1.13(1)	1.83(1)	1980	[44]
$[\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2(\mu\text{-}N_2)]$	1.16(1)[c]	2.017(10)[c]		[45]
Ph−N=N−Ph	1.23		1441[a]	[46,47][b]
$[(\mu_3\text{-}N_2)\{(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)_2Ti_2\}\ \{(\eta^1\text{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2\}]\cdot$ $[(\eta^5\text{-}C_5H_5)_2Ti(C_6H_{14}O_3)]\cdot C_6H_{14}O_3$	1.30(1)	1.91(1) t 2.14(1) l	1282	[40]
$[\{Ta(CH_2Bu^t)(CHBu^t)(PPh_3)_2\}_2(\mu\text{-}N_2)]$	1.30(1)	1.837(8) 1.842(8)		[20]
$[\{Ph(NaOEt_2)_2\{Ph_2Ni\}_2(\mu\text{-}N_2)NaLi_6(OEt)_4OEt_2\}_2]$	1.359(18)	2.01(5)		[33]
$H_2N\text{-}NH_2$	1.46		1111	[48,49][b]

a) In Raman spetroscopy
b) Corresponding to d(N-N) and ν (N-N), respectively
c) Average values for two independent molecules

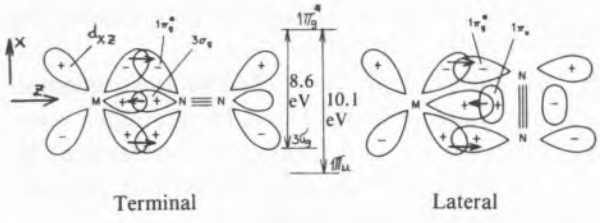


Fig. 4
Terminal and lateral (side-on) modes of N_2 bonding to a transition metal

The *side-on* N_2 bonding may be accounted for by the same model, but one of the π_u N_2 bonding orbitals is now the dinitrogen to metal donor orbital; the other π_u N_2 orbital which lies perpendicularly to the former may bind a second metal forming a dinuclear complex with side-on bonded N_2, the two M-N_2 bonds being roughly perpendicular to one another, as known for the abovementioned dinuclear Ni complexes.

Although both π_g^* N_2 orbitals may π accept from filled metal t_{2g} orbitals when N_2 binds in a terminal mode, only one of the π_g^* orbitals can be involved in the bonding for a mononuclear side-on N_2 complex (fig. 4), in agreement with the rare occurrence of the latter type of complexes (another argument based on energy considerations will be mentioned below). Since the π backbonding occurs to a ligand antibonding orbital, a weakening of the N-N bond results leading to a decrease in ν(NN) relative to the value in free N_2.

2.3. *ELECTRON π-DONOR AND σ-ACCEPTOR CHARACTER OF THE METAL CENTRE*

2.3.1. DEPENDENCE ON THE TRANSITION METAL PERIODIC GROUP

The high stability of the N_2 molecule towards coordination to a metal centre results mainly from the exceptionally low energy of the donor orbital (specially in the case of the side-on mode of bonding — see fig. 4) and the high energy difference relative to the acceptor π_g^* orbital.

Hence, in order to bind N_2, a metal centre should present an empty σ orbital with low energy *and* filled t_{2g} orbitals at a high energy level to overlap with the correspondent ligand orbitals.

In other words, due to the weak σ donor character of N_2, the binding metal centre should display a considerable σ-acceptor character and/or a high π donor ability in order to compensate the weak σ component of the bond.

A high electron richness is also a common feature of the metal centre which favours the π backbonding. This component of the bond is also promoted by an energy increase of the metal filled d_{xz} and d_{yz} orbitals which are involved in the bond, since they become closer to the high energy acceptor π_g^* orbital of N_2. However, the σ acceptance of the metal centre is favoured by an energy decrease of the metal acceptor orbital.

Hence, due to the known decrease of the energy level of the d orbitals along any transition series, the *σ acceptor character is favoured by an increase in the atomic number of the metal whereas the π backbonding capacity is promoted by a decrease of this number*, thus occurring preferably in the first groups (IVB and VB) which are also those which present orbitals with a more difuse character; however, the latter groups present a low number of filled d orbitals. The increase of σ acceptance along a transition series also agrees with the known similar trend followed by the *effective nuclear charge* (as a result of the imperfect shielding of one *d* electron by another) and the *electronegativity* of the metal.

These general features are summarized in fig. 5 where typical examples are shown, namely the dinuclear group VB centres with a high π backbonding capacity; as a result of the strong electron π-donation from these metals, an oxidation may result with reduction of the N_2 ligand and, *e.g.*, in complexes of the type $[\{TaCl_3(PR_3)(thf)\}_2(\mu\text{-}N_2)]$, ligating N_2 appears to behave formally as diimido [or dinitrito(4-)] species (N_2^{4-}) whereas the metal atoms display the +5 high oxidation state, as evidenced by chemical studies which will be mentioned later on (section 3.2.1.i).

In agreement with the general trends metioned above, the transition metals of the first groups present common hight oxidation states in their usual compounds, whereas low oxidation states are usual for high group transition metals.

The presence of a positive charge at the metal results in an increase of the electron acceptor ability

and in dicationic complexes of the iron sub-group (with Ru(II) and Os(II)) the N_2 ligand may bind a site which presents only σ donor co-ligands.
In the abovementioned dinuclear Ni (group VIII) complexes with a high σ-acceptor character, N_2 may bind in the more unfavourable side-on mode; in these complexes, both N_2 π_g^* orbitals are involved in π backbonding which is enhanced by the interac-

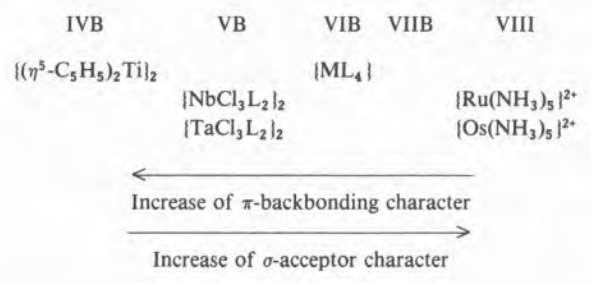


Fig. 5
Dependence of the π-backbonding and the σ-acceptor characters of a metal centre on the periodic group (L = tertiary phosphine)

tion of the N_2 ligand with cations of electropositive elements such as lithium and sodium, as it was mentioned earlier.
The implications of the abovementioned electronic properties of metal centres on the chemical reactivity of the N_2 ligand will be discussed in sections 3.2. and 5.

2.3.2. DEPENDENCE ON THE TRANSITION SERIES (ALONG EACH GROUP)

Although general correlations between the electronic properties of the transition metals (and, hence, the resulting stability of their N_2 complexes) and their position along each group are difficult to detect, a few comments may be mentioned.
For *high transition metal groups* with a weak π-and a strong σ-component in the metal-dinitrogen bond (see fig. 5), *the stability of binary dinitrogen complexes may follow the order of the Allred-Rockow electronegativity* (which corresponds to the electrostatic force exerted by the nucleus on the valence electrons, being proportional to the ratio between the effective nuclear charge and the covalent radius): first transition series > third transition series > second transition series metal (within each periodic group); the reversal of the second and third transition series order results from the known lanthanide contraction.
Hence, *e.g.*, the stability of the dinitrogen complexes $M(N_2)_n$ ($n = 1-3$) of the Ni subgroup (prepared by matrix co-condensation techniques) follows the order Ni > Pt > Pd [50].
In agreement with these observations, unambiguously characterized Pd and Pt dinitrogen complexes are unknown at ambient temperature, although dinitrogen complexes of Ni (see previous sections) have been prepared.
However, in dinitrogen complexes with ligands other than N_2 or with metals of lower periodic groups (hence, with an important π-component in the M-N_2 bond), other factors (such as the energy of the t_{2g} metal orbitals and the dependence of the metal *d* orbitals energy on the co-ligands) may play a fundamental role and the abovementioned correlation fails often.
Hence, *e.g.*, within the Fe sub-group, although the stability of the complexes *trans*-$[MH(N_2)(dppe)_2]^+$ (M = Fe, Ru, Os) [51] follows the order of the Allred-Rockow electronegativity (Fe > Os > Ru), the monophosphinic species $[MH_2(N_2)L_3]$ [52] and the amino complexes do not obey the same trend (the former follow the order Fe > Ru > Os, whereas in the latter the observed order is Os > Ru $\gg$ Fe, the aminocomplexes of iron being even unknown).
As discussed in the previous section, the transition metal basicity decreases along each series.
However, an *increase of the transition metal basicity on going down each periodic group* was proposed [53] on the basis of studies of the reactivity of transition metal complexes with Lewis acids. For N_2 complexes, this trend appears to be followed at least by some metals of the VIB and VIIB groups as evidenced by chemical studies which will be discussed in sections 3.2. and 5.

2.3.3. DINITROGEN COMPLEXES WITH REPRESENTATIVE METALS

From the considerations mentioned on sections 2.2.3. and 2.3., it is understandable the paucity of examples known with N_2 ligating a representative metal due to the unavailability of filled *d* orbitals to participate in metal to ligand π backbonding.
However, a few cases are known, the representative metal centre behaving as an electron acceptor (Lewis acid) towards N_2 or as a stabilizer of the negative charge at this ligand which may bind concomitantly a transition metal centre whose π backbonding donor capacity to N_2 is enhanced by the elec-

tron acceptor character (or the positive charge) of the representative metal site. The bond of N_2 to this site has a proeminent σ character; however, electrostatic representative metal-reduced N_2 (nitride) interactions are possible.

Hence, *group IA* cations of electropositive metals (Li^+, Na^+, K^+) may ligate N_2 in polynuclear structures with electron deficient multicentered bonds also involving transition metals. Examples were already quoted (section 2.2.1.): the hexameric cluster $K[Co(N_2)(PMe_3)_3]$ and $[\{Ph(NaOEt_2)_2\{Ph_2Ni\}_2$ $(\mu,\eta^2\text{-}N_2)$ $NaLi_6(OEt)_4OEt_2\}_2]$.

Ionic nitrides of electropositive IA and IIA elements are known and some of them may be formed by direct reaction with N_2. Hence, *e.g.*, the dinitride(1-) $Li^+N_2^-$ [$\nu(N_2) = 1800$ cm^{-1}] and the dinitride(2-) $Li_2^{2+}N_2^{2-}$ [$\nu(N_2) = 1535$ cm^{-1}] are formed by low-temperature matrix co-deposition of Li atoms and dinitrogen [54].

Scant examples of dinitrogen compounds with a *group IIA* metal involve $Mg(NH_2)_2$ [$\nu(N_2) = 2160$ s, 2040 sh cm^{-1}] (prepared by thermolysis of the azide-hydrazine compound $Mg(N_3)_2(N_2H_4)_2$) [55] and some N_2 species of calcium, strontium and barium obtained by acid decomposition and oxidation (CH_3COOH or H_2O) of the corresponding pernitrides of metal(II), M_3N_4 [56].

Table 4

Values of P_L ligand parameter for a variety of ligands (see text)

L	P_L(volt)[a]	L	P_L(volt)[a]
NO^+	1.40	NH_3	−0.77
CO	0.00	CF_3COO^-	−0.78
N_2	−0.07	NCS^-	−0.88
$P(OPh)_3$	−0.18	CN^-	−1.00
$CNC_6H_3Cl_2$−*2,6*	−0.33*	NCO^-	−1.16
PPh_3	−0.35	I^-	−1.15
CNC_6H_4Cl−*4*	−0.37*	Br^-	−1.17
CNPh	−0.38	Cl^-	−1.19
$CNC_6H_4CH_3$−*2*	−0.38*	H^-	−1.22
$CNC_6H_4CH_3$−*4*	−0.39*	N_3^-	−1.26
$CNC_6H_4OCH_3$−*4*	−0.40*	OH^-	−1.55
NCPh	−0.40		
CNMe	−0.43		
CNBu	−0.44*		
NCMe	−0.58		
Py	−0.59		

a) Values in volt (*versus* s.c.e.), measured in thf-$[NBu_4]$ BF_4 at a Pt electrode. All values taken from reference [59] except those denoted by * which are given by reference [60].

Dinitrogen may also bridge a transition metal and a Mg(II) moiety such as in $[\{Co(PMe_3)_3(N_2)\}_2$ $Mg(thf)_4]$ [35] and in various titanium and vanadium species, $[Ti(\eta^5\text{-}C_5H_5)_2(NNMgCl)]$ [$\nu(N_2) = 1255$ cm^{-1}] and possible [(thf)ClM(NNMgCl)] (M = Ti or V), which are intermediate in the reduction of N_2 to hydrazine, ammonia or organonitrogenated compounds (see section 3.2.1.i).

Electrophilic attack of a *group IIIA* Lewis acid to a dinitrogen ligand may lead to dinitrogen bridging species as shown in section 3.2.3.

Dinitrogen may also ligate a *group IVA* metal centre as in $[MX_2N_2]$ prepared in low temperature matrix studies by condensation of N_2 with the unsaturated dihalides MX_2 (M = Sn, Pb; X = halide) (an analogous reaction occurs for HgX_2 [57]. The prominent σ character of the metal-N_2 bonds evidenced by the positive shift of ν(CO) which occurs on coordination of carbon monoxide to form the analogous compounds $[MX_2(CO)]$.

2.4. — *ELECTRON RICHNESS*

2.4.1. ELECTROCHEMICAL QUANTIFICATION

The common high electron richness of a mononuclear dinitrogen binding metal centre (resulting, *e.g.*, from the low metal oxidation state and the presence of electron donor co-ligands) is patent since its genetion. Hence, the most general preparative route of dinitrogen complexes from direct reaction with N_2 consists in the reduction of a metal species by a strong reducting agent until N_2 binds in a late stage of the reduction when an electron-rich centre is available — see, *e.g.*, the synthesis of *trans*-$[Mo(N_2)_2$ $(dppe)_2]$ by reduction of $[MoCl_5]_2$ by Na(Hg) or Mg in the presence of dppe and under N_2 [58].

Although the i.r. $\nu(N_2)$ value may be considered as an indicator of the electron rich character of the binding metal centre [which is favourable to π backbonding and, thus, to a decrease in $\nu(N_2)$], the coupling of the N≡N to other group stretching vibrations and other effects (*e.g.*, dependence on the σ component) lead to a somewhat unreliable character in the use of this parameter.

The ready chemical or electrochemical oxidation of the dinitrogen complexes also results from the high electron richness of the metal centre and on the basis of the half-wave oxidation potential ($E_{1/2}^{ox}$) values, a criterium for the quantification of the elec-

tron rich character of the centre was proposed [59]. Square pyramid 16-electron metal sites $\{M_s\}$ were considered and their *electron-richness* (E_s) was defined [59] by the half-wave oxidation potential of the carbonyl complex:

$$E_s = E^{ox}_{1/2}[M_s(CO)] \quad (1)$$

The greater the electron rich character of the site, the easier its oxidation and hence the lower the E_s value will be.

A linear correlation was observed [59] between $E^{ox}_{1/2}$ of the elements of a series of 18-electron octahedral-type complexes $[M_sL]$ (where L varies along the series) and $E^{ox}_{1/2}$ of their homologues in a isoelectronic and isostructural series of pentacarbonylchromium complexes:

$$E^{ox}_{1/2}[M_sL] - E^{ox}_{1/2}[M_s(CO)] = \beta.\{E^{ox}_{1/2}[Cr(CO)_5L] - E^{ox}_{1/2}[Cr(CO)_6]\} \quad (2)$$

The slope, β, of the line is a measure of the sensitivity of the energy of the HOMO orbital to a change of L ligand is called *polarisability* of the metal centre.

The difference between $E^{ox}_{1/2}[Cr(CO)_5L]$ and $E^{ox}_{1/2}[Cr(CO)_6]$ is a measure of the net electron donor character of the ligand and is denoted by P_L (*ligand parameter*) (equation 3): the higher this character, the lower $E^{ox}_{1/2}[Cr(CO)_5L]$ is and, hence, the lower (usually the more negative) the P_L value becomes; high P_L values correspond to ligands which behave as strong net electron acceptors.

$$P_L = E^{ox}_{1/2}[Cr(CO)_5L] - E^{ox}_{1/2}[Cr(CO)_6] \quad (3)$$

Hence, since $E^{ox}_{1/2}[M_s(CO)]$ is the E_s electron-richness parameter of the metal site, equation (2) becomes, upon rearrangement:

$$E^{ox}_{1/2}[M_sL] = E_s + \beta.P_L \quad (4)$$

P_L values have already been quoted [59,60] for a variety of ligands (see Table 4) and, *e.g.*, CO, N_2 and CNR (isocyanides) behave, in this order, as strong net electron acceptors (high P_L values) whereas the anionic ligands such as thiocyanate (NCS^-), halides, hydride and hydroxide present a strong net electron donor character (low P_L values).

Linear relationships of the type of equation 4 have been experimentally observed [59,60] for a variety of 16-electron dinitrogen binding metal centres and the estimated E_s and β values are shown in Table 5.

Table 5

Values of E_s and β for a variety of 16-electron square pyramid dinitrogen-binding metal sites

$\{M_s\}$	E_s(volt)[a] (*vs* s.c.e.)	β
$\{Mo(NO)(dppe)_2\}^+$	+0.91	0.51
$\{Mo(CO)(dppe)_2\}$	−0.11	0.72
$\{Mo(N_2)(dppe)_2\}$	−0.13	0.84
$\{Mo(NCPh)(dppe)_2\}$	−0.40	0.82
$\{Mo(N_3)(dppe)_2\}^-$	−1.00	1.0
$\{FeH(dppe)_2\}^+$	+1.04	1.0
$\{Re(N_2)(dppe)_2\}^+$	+1,20	0.74
$\{ReCl(dppe)_2\}$	+0.68*	3.4*

a) Values in volt (*versus* s.c.e.), measured in thf-$[NBu_4]BF_4$ at a Pt electrode. All values taken from reference [59] except those denoted by * which are given by reference [60].

The Mo(0) centres present a higher electron richness (lower E_s values) than the Fe(II) and Re(I) sites and, within a group with a common metal, the anionic centres are more electron rich than the neutral ones. On the basis of these electrochemical parameters, it is possible to propose dinitrogen coordination and chemical reactivity criteria; the latter will be exemplified along the text but the former may now be considered.

Hence, metal sites with a high electron richness (low E_s values) bind strong electron acceptor ligands (with high P_L values) such as N_2, CO or CNR as it is observed for the $\{Mo(N_2)(dppe)_2\}$ metal centre ($E_s = -0.13$ V).

However, N_2 may bind sites with E_s values falling in the -1.3 to $+1.3$ V range, but when the centre presents a high E_s value, the ligand which is *trans* to N_2 behaves as a strong net electron donor (such as halide or hydride) thus presenting a low P_L value; it is then experimentally observed that such a metal site has a high polarisability (β). A typical example is given by $\{ReCl(dppe)_2\}$ (with high E_s and β values of $+0.68$ V and $+3.4$, respectively) [60] which may bind N_2 in *trans*-$[ReCl(N_2)(dppe)_2]$ where the strong net electron donor chloride ligand ($P_L = -1.19$ V) is *trans* to N_2.

Based on these observations, one may propose that *high electron-richness (low E_s value) and high polarisability (high β value) of a metal centre favour dinitrogen coordination* [59].

2.4.2. CO-LIGAND EFFECT

The dinitrogen bonding to a metal centre may be favoured by the presence, in *trans* position, of a strong net electron donor co-ligand.

The electron donating power of the ligand *trans* to N_2 enhances the metal to dinitrogen π backbonding, thus stabilizing the M-N_2 bond and promoting the coordination of dinitrogen.

Chloride and *dithiophosphinate* ($S_2PPh_2^-$) *trans* to N_2 are strong M-N_2 bond stabilizers as evidenced, *e.g.*, by the stability of the complexes *trans*-[ReCl(N_2) (dppe)$_2$], *mer*-[ReCl(N_2) (CNMe){P(OMe)$_3$}$_3$] [61] and *mer*-[Re(η^1-S_2PPh_2) (N_2) (CNMe)$_x$(PMe_2Ph)$_{4-x}$] (x = 1 or 2) [14], the N_2 ligand binding a site which may present up to two strong competitors (CNMe) for the π backbonding.

Chloride is a known *π donor and a weak field ligand:* interaction of a filled *p* chloride orbital with a t_{2g} metal orbital results in a destabilization of the latter with a decrease of the energy difference (Δ) relative to the empty e_g^* orbitals; the increase in energy of the t_{2g} metal orbitals favours the electron π donor capacity (π backbonding ability) of the metal centre to the $\pi_g^*N_2$ orbitals. This stabilizing effect on the M-N_2 bond by a π donor ligand in *trans* position may also be rationalized by some simplified π-molecular orbital schemes: an increase of the number of filled M-N_2 bonding (and N-N antibonding) character orbitals results from the electron π release from the π donor ligand [62].

Hydride is also a ligand which tends to be in a *trans* position relative to N_2 in hydridic dinitrogen complexes such as the trigonal bipyramid [CoH(N_2) (PPh_3)$_3$] [30] and the square planar [RhH(N_2) ($PPhBu_2$)$_2$] [31] species.

It is a strong net electron donor ligand [$P_L(H^-)$ = $= -1.22$ V], comparable to chloride [$P_L(Cl^-)$ = $= -1.19$ V], although without a π donor capacity. It presents a high *trans* effect (through a σ mechanism) which favours the bonding, in *trans* position, of a weak σ donor (and strong π acceptor) ligand rather than a strong σ donor (and weak π acceptor) species which may compete with the hydride by the metal σ orbitals.

The higher tendency of the hydride ligand to be *trans* to N_2 rather than to a phosphine (see the abovementioned Co(I) and Rh(I) complexes) evidences the weaker σ donor (and stronger π acceptor) character of dinitrogen relative to a phosphine ligand.

The σ-donor hydride ligand may promote, through a synergic effect, the π-backbonding ability of the metal centre to the *trans* N_2 ligand.

In a high electron rich metal centre dinitrogen may also bind to the metal even in the presence, in *trans* position, of a strong electron acceptor competitor, such as carbonyl; however, the metal-dinitrogen bond then presents a high lability.

This behaviour is observed for the {Mo(CO) (dppe)$_2$] site ($E_s = -0.11$ V) which can bind reversibly N_2 to afford the labile *trans*-[Mo(N_2) (CO) (dppe)$_2$] species (the N_2 ligand is evolved by just bubbling argon through a solution of this complex) [63].

The effect of other co-ligands, such as the strong net electron donor methoxide anion (from methanol solvent dissociation), on the activation towards protonation of dinitrogen derived ligands (*e.g.*, the hydrazido(2-) species, NNH_2) will be mentioned in later sections (3.2.).

3 — CHEMICAL PROPERTIES

The chemical behaviour of dinitrogen-binding metal centres is usually mainly dependent on their electronic properties which were discussed in the previous sections.

However, structural features related, *e.g.*, to the geometry or to the unsaturation of the binding centre due to the lability of N_2, may also play a role, as well as some stereochemical factors as shown by the following example.

Although the bis(diphosphinic) complexes [FeHX (depe)$_2$] and [FeHX (dppe)$_2$] are known, the pentacoordinated tetraphosphinic species [FeH (tetraphos)]X [tetraphos = $Ph_2PC_2H_4P(Ph)C_2H_4P(Ph)C_2H_4PPh_2$; $X^- = Br^-$, I^-] is ionic and does not bind the X^- halide although N_2 may ligate the metal site to afford [FeH(N_2) (tetraphos)]X. As evidenced [24] by X-ray data the unability of the halide to bind is due to a stereochemical hindrance of the phenyl rings and N_2 (with an atomic radius which is smaller than the halide ionic radius) may ligate the metal site in preference to the halide.

3.1. — *CHEMICAL REACTIVITY OF DINITROGEN BINDING METAL SITES*

The evolution of N_2 from a dinitrogen complex (*e.g.*, by photolysis) may constitute a convenient way to generate a dinitrogen binding metal centre;

this may also be formed by following the synthetic steps for a dinitrogen complex in the absence of N_2, under argon atmosphere.

However, the direct study of the metal centre is usually hampered by its high reactivity which prevents its isolation, although a very limited number of examples are known where this isolation was achieved.

3.1.1. SIMPLE ADDITION REACTIONS

Simple addition reactions to a metal centre following N_2 evolution correspond to the replacement of this ligand in a dinitrogen complex.

In metal centres which present a *high π-backbonding capacity* (groups IVB to VIIB(Re)), the known examples of N_2 replacement involve preferably strong π acceptor ligands such as CO, CNR, NCR or C_2H_4, as observed in the N_2 substitution reactions of $[M(N_2)_2L_4]$ (M = Mo or W; L = tertiary m o n o -

phosphine or $\frac{1}{2}$ dppe) by isocyanides [64,65] or carbon monoxide [66].

The mechanism of this type of reactions was studied [67] at the Mo(0) and W(0) phosphinic metal sites and N_2 loss was shown to be the rate limiting step followed by addition of the incoming ligand (L') to the unsaturated pentacoordinated $[M(N_2)L_4]$ centre; the replacement of the second N_2 ligand also

$$[M(N_2)_2L_4] \xrightarrow{k_1} [M(N_2)L_4] + N_2$$
$$[M(N_2)L_4] + L' \longrightarrow [M(N_2)L'L_4]$$
$$[M(N_2)L'L_4] \xrightarrow{k_2} [ML'L_4] + N_2$$
$$[ML'L_4] + L' \longrightarrow [ML'_2L_4] \qquad (5)$$

follows a dissociative mechanism with dinitrogen loss being the rate controlling step (equations 5).

Although N_2 is readily replaced by a strong π acceptor in complex $[Mo(N_2)_2(dppe)_2]$, the σ donor NH_3 species behaves as a labile ligand affording the unstable aminocomplex $[No(N_2)(NH_3)(dppe)_2]$ which was only detected in solution by electrochemical techniques [59].

However, when the metal centre presents a *lower electron π releasing character but a high σ-acceptor capacity* [mainly for groups VIIB (Mn) and VIII, although examples for group VIB are also known), N_2 may be replaced by σ-donor ligands without π withdrawing ability.

Hence, the pentaminoruthenium(II) moiety in $[Ru(NH_3)_5(N_2)]^{2+}$ may readily bind a sixth molecule of NH_3 to give $[Ru(NH_3)_6]^{2+}$ through an irreversible replacement of N_2 (reaction 6) [68].

$$[Ru(NH_3)_5(N_2)]^{2+} + L \longrightarrow [Ru(NH_3)_5(L)]^{2+} + N_2 \qquad (6)$$

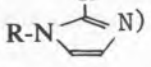
The N_2/NH_3 competition for a metal site presents some catalytic meaning since NH_3, a product of reduction, has to be replaced by N_2 in order to complete the catalytic cycle of N_2 reduction to NH_3.

The unsaturated metal centres involved in these reactions were not isolated, but in the following examples the *isolation* was possible.

The square pyramid [63] pentacoordinated carbonyl species $[Mo(CO)(dppe)_2]$, generated, *e.g.*, by N_2 evolution from the dinitrogen parent complex, undergoes addition reactions with a variety of (electron donor) Lewis bases not only with π-acceptor ability (carbon monoxide, nitriles) but also without this capacity (ammonia, amines) or even with a π-donor character (amides*, imidazoles) (reactions 7) [69].

The presence of the strong electron π-acceptor CO ligand renders the Mo(0) metal centre susceptible to π-acceptance from convenient π-donor ligands, although without complete loss of the π-backbonding ability and of the σ-acceptor character which, as shown previously, appear to be important features of the N_2 binding transition metal sites.

$$[Mo(CO)(dppe)_2] + L \longrightarrow \textit{trans}\text{-}[Mo(CO)L(dppe)_2] \qquad (7)$$

(L = CO, N_2, C_2H_4, NCR, NH_3, amines, pyridines, amides RR'NC(R")O, imidazoles 

Another rare example of structural characterization of an unsaturated intermediate involved in N_2 substitution reactions, or related ones, was recently reported [70]. It is a trigonal bipyramid Re(I) species, $[ReCl(dppe)_2]$, prepared by photolysis of the octa-

* The low i.r. ν(CO) values (~1680 ~1720 cm^{-1}) observed in the amide complexes suggest that these ligands are behaving not only as σ-donors but also as π-donors:

hedral parent N_2 complex, through N_2 loss and a structural change (equation 8). The reaction is

$$trans\text{-}[ReCl(N_2)\,(dppe)_2] \xrightarrow{h\nu} [ReCl(dppe)_2] + N_2 \qquad (8)$$

irreversible and it demonstrates another *fundamental requirement for binding of dinitrogen:* the *geometry* of the metal centre, *i.e.*, the presence of convenient co-ligands at a metal with a favourable oxidation state is not enough for N_2 coordination.

Although the {$ReCl(dppe)_2$} centre is not susceptible to bind N_2, it presents a high reactivity and can coordinate stronger ligands than N_2 such as isocyanides [70].

3.1.2. OXIDATIVE ADDITION REACTIONS

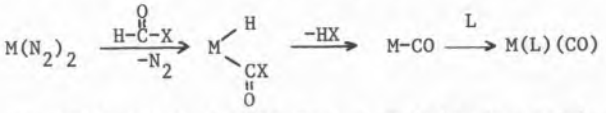
The N_2 binding metal centres are particularly susceptible to oxidative addition reactions, leading, *e.g.*, to the formation of metal-carbon or metal-hydrogen bonds. *These reactions are favoured by the electron-rich character and the unsaturation of the metal centres.

(i) *Addition of C-H bond*

Orthometalation reactions are known since long in the chemistry of dinitrogen complexes and they are believed to be involved, *e.g.*, in the [$CoH(N_2)(PPh_3)_3$] plus D_2 system with exchange between deuterium atoms and the hydrogen atoms of the hydride ligand and of the *ortho* positions in the phosphinic phenyl rings. The postulated [72] mechanism involves a reversible oxidative addition of the *ortho* C-H bond of the phenyl groups to the unsaturated metal centre derived from N_2 evolution. This type of study may be of biological significance since HD formation occurs during the enzymatic N_2 reduction under an N_2/D_2 atmosphere.

Other more recent examples of orthometalation reactions of N_2 binding centres have been reported: the {$Mo(PMe_3)_5$} site (generated by loss of PMe_3 from [$Mo(PMe_3)_6$] with a high stereochemical tension among the phosphine ligands) which may ligate N_2 can undergo two reversible orthometalation reactions (the second one upon loss of another phosphine ligand) [73]; the postulated [$ReH(dppe)_2$] species, derived by N_2 evolution from the parent dinitrogen complex, undergoes orthometalation and other oxidative addition reactions such as C-D addition from C_6D_6 to yield [ReH(D)(C_6D_5) $(dppe)_2$] which, under N_2, affords [ReD(N_2) $(dppe)_2$] upon C_6D_5H loss [74].

Oxidative addition of C-H bond is probably also involved in *decarbonylation* reactions of aldehyde-tipe species by *trans*-[$Mo(N_2)_2(dppe)_2$]: formamides (HCONRR′), formate esters (HCOOR) and aldehydes (RCHO) are decarbonylated to amines (RR′NH), alcohols (ROH) and alkanes (RH), respectively, with formation of carbonyl complexes [75]. The proposed [75] reaction scheme is shown by equations (9), and it involves loss of N_2 and oxidative addition of C-H followed by reductive elimination of the decarbonylated species. The C-H bond addition is evidenced by the unreactivity of acetamides MeC(CO)NRR′ (which do not present such a bond) and the evolution of a small amount of H_2, during the reactions, in agreement with the possible involvement of a hydridic species.



M = {Mo(dppe)$_2$}. X=NRR',OR,R. L=HCOX(X=NMe$_2$,NEt$_2$), N_2(X=OR) (9)

Primary alcohols may also undergo decarbonylation by the same Mo(0) metal centre and by the postulated [76] {$ReCl(dppe)_2$} species derived by N_2 loss from the parent dinitrogen complex. The mechanism was not studied but may involve dehydrogenation of alcohol to aldehyde which then undergoes decarbonylation.

Decarbonylation and dehydrogenation of hydroaromatic compounds may also be achieved [75] by the [$Mo(N_2)_2$ $(dppe)_2$] complex and, *e.g.*, [$Mo(CO)_2$ $(dppe)_2$] and [MoH_4 $(dppe)_2$] are formed from reaction of the dinitrogen complex with thf under heating; this reaction probably occurs *via* saturated carbon-hydrogen bond activation.

(ii) *Hydrogenation*

The ready hydrogenation of unsaturated centres with formation of polyhydridic species, illustrated by reaction (10) [74,76], corresponds to the known

* Other types of addition reactions are known and *e.g.*, *trans*-[Mo(NO) (NCO) $(dppe)_2$] is formed from the reaction of *trans*-[$Mo(N_2)_2$ $(dppe)_2$] with *N*-methyl-*N*-nitrosourea, $MeN(NO)C(O)NH_2$, which is postulated to occur via the intermediate [Mo(NO){$N(Me)C(O)NH_2$}$(dppe)_2$] which, upon loss of NH_2Me, yields the final product [71].

oxidative substitution (which may be reversible) of N_2 by H_2, exemplified by reaction (11) [66,77].

$$[ReX(dppe)_2] + H_2 \longrightarrow [ReXH_2(dppe)_2] \quad (10)$$
$$(X = H, Cl)$$

$$[Mo(N_2)_2(dppe)_2] + 2H_2 \longrightarrow$$
$$[MoH_4(dppe)_2] + 2N_2 \quad (11)$$

This type of study may present some biological interest since H_2 is a competitive inhibitor of the enzymatic nitrogen fixation. Moreover, since NH_3 is industrially synthesized from N_2 and H_2, it would be interesting to study the interaction between N_2 and hydride ligands bonded at a metal site with possible hydrogenation of the former which, however, was not yet achieved.

(iii) *Oxidation reactions by protic acid or organohalide*

Dinitrogen complexes usually react with protic acids which attack the metal centre (leading, *e.g.*, to protonation or halogenation). Dinitrogen evolution occurs commonly as the result of the metal oxidation, and oxidative addition reactions are often involved as shown in equations (12) [78] and (13) [79].

$$trans\text{-}[IrCl(N_2)(PPh_3)_2] +$$
$$+ HCl \longrightarrow [IrHCl_2(PPh_3)_2] + N_2 \quad (12)$$

$$trans\text{-}[W(N_2)_2(dppe)_2] \xrightarrow{HCl}$$
$$[WH(N_2)_2(dppe)_2]Cl \xrightarrow[-2N_2]{HCl}$$
$$[WCl_2H_2(dppe)_2] \quad (13)$$

If the metal centre presents a high reducing power as in *trans*-$[Mo(NCS)(N_2)(dppe)_2]^-$ with the strong net electron donor thiocyanate ligand [$P_L(NCS^-) = -0.88$ V], solvated protons may be reduced to dihydrogen with oxidation of the centre leading, in this example, to unidentified and unstable oxidized species [80].

Mechanistic studies performed on the reactions of *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) with weak acids in thf evidence the initial outer-sphere association of the acid electrophile to the metal centre which is followed by protonation at the N_2 ligand. However, since these reactions lead to attack at ligating dinitrogen they will be mentioned in section 3.2.1.ii.

Organohalides also present an oxidizing effect on the metal centre, *e.g.*, $\{ML(dppe)_2\}$ (M = Mo or W; L = NCS^-, N_2, NCR, N_3^-), the oxidation occurring through an outer-sphere electron transfer process if the centre presents a high reducing power (*e.g.*, for L = NCS^-) or *via* an inner-sphere electron transfer mechanism for metal centres with a lower reducing power and presenting a labile L ligand (*e.g.*, for L = N_2 or NCR); however these reactions involve the N_2 ligand and will be treated in section 3.2.2.i.

3.1.3. CATALYTIC REACTIONS

Due to the common high lability of the N_2 ligand, its complexes may behave as precursors for unsaturated metal centres; their chemical properties were already mentioned and they account for their active role in catalytic reactions such as hydrogenation, isomerization, oligomerization and polimerization of olefins. The subject has been reviewed [81] and only a few examples are now cited briefly.

$[RuH_2(N_2)(PPh_3)_3]$ catalyses the double bond migration of 1-pentene to 2-pentene, $[RuH_2(PPh_3)_3]$ being the active species; N_2 presents an inhibiting effect due to the competition with the olefin for this unsaturated site [82]. The reaction may possibly proceed through a hydrogen β-elimination to give an η^3-allyl ligand or through a migratory insertion of hydride into the olefin double bond followed by an hydrogen β-elimination.

The lability of a co-ligand may also induce the catalytic activity and the *cis* to *trans* isomerization of 2-pentene by $[CoH(N_2)(PPh_3)_3]$ may involve the proposed active $[CoH(N_2)(\eta^2\text{-}cis\text{-2-pentene})(PPh_3)_2]$ species; the catalytic activity of the system is promoted by the presence of N_2 which favours dinitrogen coordination, the N_2 ligand presenting a labilizing effect on the *trans*-2-pentene ligating product [88,83]. The mechanism may conceivably involve a migratory insertion of hydride into the olefin double bond followed by a rearrangement and an hydrogen β-elimination.

Supported titanocene-type species (on a styrene-divinylbenzene polymer) which can reduce N_2 (at *ca.* 100 atm) to NH_3, although in a non-catalytic low yield (< 0.55 mol NH_3/mol Ti) exhibit catalytic activity in the hydrogenation, isomerization and epoxidation of olefins, which appears to be promoted by the bonding, through substituted cyclopentadienyl moieties, of the Ti centres to the polymer

which prevents the formation of inactive dimers [84]. The activation of N_2 is postulated [84] to result from bonding to two Ti centres which are held in position by a methylene bridge between two cyclopentadienyl-type ligands (one at each Ti centre).

H-D exchange reactions between D_2O and aromatic hydrogens [of aromatic hydrocarbons PhX where X = F, CH_3, OCH_3, $COCH_3$, $N(CH_3)_2$] (equation 14) and between D_2O and H_2 (equation 15) are catalysed by $[RhH(PPr^i)_3]$ — which is isoelectronic and related to $[RhH(N_2)(PR_3)_2]$ — and $[Rh_2H_2(PCy_3)_4(\mu\text{-}N_2)]$ [85].

$$ArH + D_2O \longrightarrow ArD + DHO \qquad (14)$$

$$H_2 + D_2O \longrightarrow HD + DHO \qquad (15)$$

These reactions involve O-D and aromatic C-H (or H-H) bond activation and the mechanism, which was not studied in detail, is suggested [85] to be initiated by O-D oxidative addition to an unsaturated centre (formed by N_2 or phosphine loss) to give $[RhHDL_2]^+OD^-$ which, upon reductive elimination of DHO, affords $[RhDL_3]$; this species may then undergo oxidative addition of C(Ar)-H or of H-H bond (for reations with ArH or H_2, respectively) to give $[RhHD(Ar)L_2]$ or $[RhDH_2L_2]$; reductive elimination of the exchange products, ArD or HD, respectively, regenerate the active $[RhHL_3]$ centre [85].

Aryldiazonium species $ArN_2^+Cl^-$ (Ar = Ph, *p*-ClC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$) may be catalytically *reduced to hydrocarbons* ArH by primary or secondary alcohols ROH (R = Me, Et, Pr^i) in the presence of the catalyst precursor *trans*-$[W(N_2)_2(dppe_2]$ [86]. The α-hydrogens of the alkyl group of the alcohol are the hydrogen source as evidenced by studies with deuterated alcohols and the C-H bond rupture appears to be the rate limiting step; a carbonyl group is formed and ketone was detected in the reaction with isopropanol (equation 16).

$$ArN_2^+ + MeCH(OH)Me \longrightarrow ArH + MeC(O)Me + N_2 + H^+ \qquad (16)$$

The reaction proceeds at ambient temperature and is selective; in the absence of catalyst, it only occurs with heating and also leads to the formation of phenolic ethers [86].

It is also possible to recognize, in various effective catalytic systems, the *involvement of N_2 binding* (or related species) *intermediates*.

Hence, the Rh(I) Wilkinson catalyst for the hydrogenation of olefins involves the active unsaturated centre $[RhClL_2]$ — formed, *e.g.*, by ligand evolution from $[RhClL_3]$ (L = monophosphine such as PPh_3) — which may bind N_2 (reaction 17) [87a].

$$[RhCl(PCy_3)_2] + N_2 \longrightarrow [RhCl(N_2)(PCy_3)_2] \qquad (17)$$

The $[RhClL_2]$ centre undergoes an oxidative addition reaction of H_2 to afford a dihydride complex which binds the olefin; a migratory insertion of hydride into the olefin double bond (to give an alkyl derivative) is followed by a reductive elimination of the alkane product with regeneration of the active $[RhClL_2]$ site [87b].

3.2. *ACTIVATION AND REACTIVITY OF DINITROGEN*

Although the free N_2 molecule is non-polar, on coordination it undergoes an *electronic polarization* (as a result of the different intensities of the σ and π components and of the distinct orbitals involved in the bond) as evidenced by the high intensity of the i.r. $\nu(N_2)$ band and by ESCA spectroscopic studies [88], *e.g.*, in $[ReCl(N_2)(dppe)_2]$ where the two nitrogen atoms exhibit distinct N-ls emissions at 397.9 and 399.9 eV (whereas the free N_2 molecule presents a single emission at 411 eV), suggesting a charge difference of 0.4 e between the two N atoms of the dinitrogen ligand.

When binding a *transition metal centre with a high π-backbonding* capacity [with a group IVB to VIB metal or with Re(I)], the N_2 molecule acquires a negative electronic charge density and is activated towards *attack by electrophiles* which occur at the *exo* nitrogen atom; i.r. $\nu(N_2)$ then occurs at a *low value* (typically below 1980 cm^{-1}) and the oxidation of the complex is observed at a *low* $E^{ox}_{1/2}$ (below *ca.* 0 Volt *vs.* s.c.e., at a Pt electrode, in thf-$[NBu_4]$ $[BF_4]$); the electrophilic attack may also involve the metal centre [89,59].

However, when the metal site presents a *weak π-backbonding ability*, N_2 may be susceptible to attack by a *nucleophile* at the *endo* N atom, the i.r. $\nu(N_2)$ occuring at values (*e.g.*, > 2100 cm^{-1}) which lie above those reported for the previous type of activation and the complexes presenting higher $E^{ox}_{1/2}$ (above *ca.* +0.8 V); the nucleophilic attack may also occur at the metal centre [89,59].

These reactions may lead to the formation of N-H (hydrides of nitrogen) and N-C (organonitrogenated species) bonds which, generally, will be mentioned separately.

Our attention will be focussed mainly on the systems where intermediate species were isolated or which have been subject to mechanistic studies since they present the richest information on the involved metal sites.

Hence, aqueous systems (which have been reviewed) [90] will not be treated due to the yet so speculative nature and controversy of the hypotheses which have been put forward; no N_2 complex and no intermediate reduced species was isolated. The most effective catalytic systems at ambient temperature and pressure involve molybdenum (metal present in nitrogenase) and may be cited: MoO_4^{2-}/peptide chain component of bovine insuline/$NaBH_4$ (yield of *ca.* 70 mol NH_3/Mo) [91] and, more recently, Mo(III)/Na(Hg)/Mg^+/phospholipid in alcoholic medium (yield of *ca.* 80 mol $NH_3 + N_2H_4$/Mo) [92].

3.2.1. FORMATION OF HYDRIDES OF NITROGEN

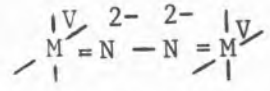
(i) *Polynuclear complexes*

A high activation of dinitrogen towards protonation may result from its simultaneous coordination to two, or even more, metal centres. This behaviour appears to be observed typically for *the extreme transition metal groups (IVB, VB and VIII), and cations of the less electronegative elements* (Li^+, Na^+, K^+ and even Mg^{2+} or MgX^+) may be involved in the activation since they may stabilize the negative charge accumulated at dinitrogen from the transition metal electron π-release.

Hence, *e.g.*, a high yield of ammonia (*ca.* 90%) and some hydrazine are formed by aqueous hydrolysis of complex $[(\mu_3\text{-}N_2)\{(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)\ (\eta^5\text{-}C_5H_5)_2Ti_2\}\{(\eta^1\text{:}\eta^5\text{-}C_5H_4)\ (\eta^5\text{-}C_5H_5)_3Ti_2\}].[(\eta^5\text{-}C_5H_5)_2Ti(C_6H_{14}O_3)].C_6H_{14}O_3$ (see section 2.2.1. and fig. 3) in diglyme [40]; the N_2 ligand bridges three Ti centres and presents a long N-N bond.

Hydrazine (86% yield) is also obtained from the reaction of $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ with HCl in toluene at $-80°C$ an by using ^{15}N labelled terminal N_2 ligand it was shown that both terminal and N_2 generate the hydrazine [93].

Bridging N_2 in group VB dinuclear complexes present a high N-N bond elongation (which corresponds to a bond length which is intermediate between a single and a double bond, as mentioned in section 2.2.) and, *e.g.*, hydrazine is formed on protonation of $[\{Cl_3L_2M\}_2(\mu\text{-}N_2)]$ (M = Nb, Ta; L = thf, PR_3); the same complexes react with acetone to give dimethylketazine, $Me_2C=N\text{-}N=CMe_2$*, and these results evidence the localization of four formal negative charges at the bridging N_2 ligand which is reduced as a result of the extensive π-backbonding from the metal atoms which then present a formal high oxidation state (+5) [94]. The ligating N_2 may then be viewed [94] as a diimido (or dinitride(4-)) species:



and the bonding and activation of N_2 may be rationalized by known simplified π-MO schemes [81].

In these systems a direct reduction of the N_2 ligand is observed without the addition of a reducing agent.

However, the activation of N_2 ligating group IVB or VB metal centres may not be enough to induce further protonation which often requires the help of an external reducing agent (such as a Grignard reagent or sodium naphthalene $NaC_{10}H_8$); this species may promote the reduction of the N_2 ligand by the transition metal centres through the direct reduction of the latter and/or by direct interaction with ligating N_2 thus enhancing the π-electron release from the transition metal centres.

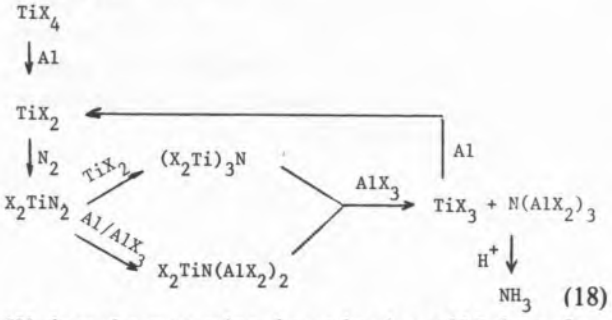
Interesting examples are provided by the following systems where the reduction of N_2 to hydrazine, ammonia or organonitrogenated compounds may occur:

$[\{TiCl(\eta^5\text{-}C_5H_5)_2\}_2] + Pr^iMgCl$ in ether where $[Ti(\eta^5\text{-}C_5H_5)_2(NNMgCl)]$ [$\nu(N_2) = 1255\ cm^{-1}$] was isolated and which on reaction with HCl gives hydrazine (*ca.* 80% yield) [95]; $[MCl_3(thf)_3]$ (M = Ti or V) + Mg with possible formation of [(thf)ClM(NNMgCl)] [96]. These M-N=N-MgCl species are probable intermediates to transition metal-nitride-magnesium adducts, *e.g.*, $[MN(MgCl)_2(thf)]$ (M = Ti or V) which were isolated in the latter system and may lead to NH_3 (upon hydrolysis), to isocyanate ligand NCO (upon reac-

* This type of reaction is followed by organoimido ligands at group VB metal centres, M=N-R, which, by treatment with benzaldehyde, PhCHO, lead to Ph(H)C=N-R + M=O.

tion with CO) or to methylisocyanate MeNCO (upon alkylation by MeI) [96].

These systems are non-catalytic (they are at best stoichiometric) but a catalytic activity was developed since 1968 by VOL'PIN [97,98] through the addition of a Lewis acid (such as $AlBr_3$ or $AlCl_3$) to the abovementioned systems composed of a titanium compound (TiX_4) in the presence of a high excess of reducing agent (such as Al or $LiAlH_4$); as in the latter systems, N_2 binds a reduced Ti centre. The catalytic species appears to be TiX_2 (the Lewis acid adduct $C_6H_6.TiCl_2$. $2AlCl_3$ was isolated in benzene in the absence of N_2 and it exhibits catalytic activity); the reduction of N_2 to nitride(3-) proceeds stepwise (as evidenced by the formation of hydrazine, on hydrolysis, when the reaction is carried out at lower temperatures) and conceivably involves polynuclear systems with N_2 and its reduced derivatives bridging Ti and Al centres such as AlX_3 or AlX_2^+ (reactions 18). The Lewis acid cleaves the Ti-nitride bond thus allowing the regeneration of the Ti(II) active species. Hydrolysis of the aluminum nitride leads to NH_3 with a yield of *ca.* 290 mol NH_3/Ti for the system $TiCl_4 + Al + AlBr_3$ (1:600:1000) at 130°C and $p(N_2) = 100$ atm.



(18)

We have been treating the activation of N_2 by polynuclear systems with low transition group metals which display a high π-backbonding ability although presenting a low number of available *d* valence electrons. The other known examples of N_2 activation towards protonation by polynuclear systems involve the other extreme transition group metals (VIII) which have a high number of *d* electrons but present a low π-electron release capacity. The dinuclear iron complexes $[(PPh_3)_2H(Pr^i)FeN_2Fe(Pr^i)(PPh_3)_2]$ [99] (prepared by reduction of $[FeCl_3(PPh_3)_2]$ with Pr^iMgBr in ether at -50°C under N_2) and $[\{FeMgCl_3(thf)_{1.5}\}_2(N_2)]$ [100] (isolated in the system $FeCl_3 + Mg$ in thf under N_2) give hydrazine (*ca.* 10% based on complex in the former case, whereas the yield was not specified in the latter complex) on treatment with HCl.

The square planar $Li_4[FePh_4].(Et_2O)_4$ complex was isolated in the system $FeCl_3 + LiPh$ in Et_2O under argon and it reacts with N_2 giving an unidentified species which, on treatment with acid, produces ammonia and/or hydrazine. The distances between the Li^+ ions and the Fe(0) centre suggest the possible interaction of the former with ligating N_2 at vacant axial coordination position [101].

The formation of hydrazine (20% based on the metal) has also been reported from treatment of $[Co(N_2)(PPh_3)_3Mg(thf)_2]$ (produced in the reaction of $[CoH(N_2)(PPh_3)_3]$ with Et_2Mg in thf at 0°C) with sulphuric acid [102]. It is, however, unknown if the Mg centre binds to N_2 or to the Co site; a related complex with N_2 bridging cobalt and magnesium is known, $[\{Co(PMe_3)_3(N_2)\}_2Mg(thf)_4]$ [35], but it was not reported if N_2 is reduced in this species.

In the dinuclear nickel(0) complex, $[\{(LiPh)_3Ni\}_2(\mu,\eta^2\text{-}N_2)(OEt_2)_2]$, the side-on bonded N_2 is also activated towards protonation and NH_3 (*ca.* 30 ~ 40% yield) is produced on hydrolysis in thf. Biphenyl and nickel(0) metal are the other products of the reaction, the phenyl anions behaving as the reducing agent; hence, in contrast to the abovementioned examples, the transition metal is not the source of electrons to the N_2 ligand [103].

(ii) *Mononuclear complexes*

The most active mononuclear systems in the activation of N_2 towards protonation involve *electron-rich group VIB* transition metal (Mo and W) centres.

(ii.1) *Reduction of N_2 to NH_3*

When bound to $\{ML_4\}$ (M = Mo or W; L = tertiary monophosphine) in complexes $[M(N_2)_2L_4]$, N_2 undergoes ready protonation by protic acid (HX) to afford NH_3 (and hydrazine) in MeOH at ambient temperature and pressure [104,105]. The reaction also proceeds without HX, under W-filament light, in MeOH which behaves as the protonating agent [104]*.

* Acidic transition metal hydrides, such as $[H_2Fe(CO)_4]$, $[HFeCo_3(CO)_{12}]$ or $[HCo(CO)_4]$, may also be a proton source in these reactions, and NH_3 is obtained (although at lower yield than that obtained by using a mineral acid such as H_2SO_4) on treatment by aqueous KOH (basic distillation) [106].

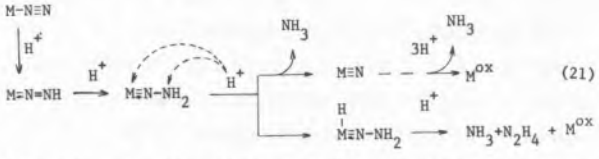
The metal site behaves as the reducing agent, the maximum yield (2 mol NH_3/mol W) corresponding to the consumption of the six valence electrons of W(0) (equation 19); for the Mo(0) system, the maximum yield is *ca.* 1 mol NH_3/mol Mo, the molybdenum(0) being oxidized to the Mo(III) oxidation level (equation 20) [104].

$$N_2 + 6H^+ + 6e^-[W(0)] \longrightarrow 2NH_3 \qquad (19)$$

$$\frac{1}{2}N_2 + 3H^+ + 3e^-[Mo(0)] \longrightarrow NH_3 \qquad (20)$$

The N_2 reduction/protonation proceeds stepwise with gradual weakening of the N-N bond until cleavage (reaction 21).

Hydrazido(2-) intermediate complexes, $[MX_2(NNH_2)L_3]$, have been isolated [107]. They were also detected in solution by ^{15}N n.m.r. [108] and they can undergo further protonation at the *exo* N atom to give NH_3 and a nitride complex which is protonated to NH_3; the metal of the hydrazido(2-) species is also susceptible to protonation to afford an hydrido-hydrazido(2-) complex, *e.g.*, $[WHX_2(NNH_2)L_3]X$ [109], which, on protonation yields ammonia and hydrazine.



(21)

Complexes with other possible dinitrogen derived intermediate moieties have also been isolated, although with a more stable diphosphinic metal centre: the diazenido species of the type $[MX(NNH)(dppe)_2]$ (from deprotonation of the hydrazido(2-) complex by base) [110] and complex $[MoBr(NH)(dppe)_2]^+$ with an imido ligand (representing an intermediate stage of protonation of nitride to NH_3) which was derived from an organohydrazido(2-) precursor through an electrochemical $2e/2H^+$ process [111] (see also reactions 26).

These systems, without an external reducing agent, are not catalytic, but the possibility to regenerate at the metal centre its N_2 binding capacity was demonstrated for Mo complexes. Hence, *e.g.*, protonation of the hydrazido(2-) complex $[MoBr_2(NNH_2)(PMe_2Ph)_3]$, which was formed by reaction of $[Mo(N_2)_2(PMe_2Ph)_4]$ with HBr, leads, as usually, to NH_3 and the Mo(III) complex $[MoBr_3(thf)(PMe_2Ph)_2]$ was isolated; reduction of the latter by sodium amalgam in the presence of phosphine and under N_2 regenerates the parent bis-dinitrogen complex [112], thus completing the N_2 reduction cycle although in a discontinuous way.

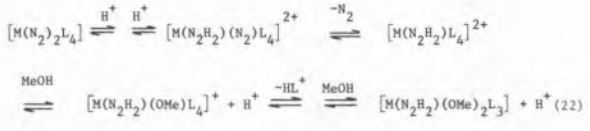
(ii.2) *Mechanisms of the protonation reactions*

Based on stopped-flow spectrophotometric and electronic spectroscopic studies and on product analysis the following mechanisms have been proposed for the initial steps of N_2 protonation. They are mentioned since they present important information on the properties of the involved transition metal centres.

— *Direct electrophilic attack at ligating N_2*

The protonation of the monophosphinic complexes *cis*-$[M(N_2)_2L_4]$ (M = Mo or W; L = PMe_2Ph) by strong acids (HCl, HBr, H_2SO_4) in methanol occurs by two successive direct proton attacks at the *exo* N atom of a ligand N_2 which is activated by the electron rich metal centre [113].

Dinitrogen evolution results from the oxidation of the metal and the vacant coordination position allows the strong net electron donor methoxide anion to bind, giving the cationic complex $[M(N_2H_2)(OMe)L_4]^+$. The neutral $[M(N_2H_2)(OMe)_2L_3]$ complex results from the coordination of a second MeO^- anion by replacement of a phosphine ligand which is removed as a phosphonium species HL^+ (equation 22).



(22)

The overall stoichiometry of the reaction is shown by equation [23], one mole-equivalent of acid being consumed per mole-equivalent of complex as shown by spectrophotometric titration.

$$[M(N_2)_2L_4] + H^+ + 2MeOH \longrightarrow [M(NNH_2)(OMe)_2L_3] + N_2 + HL^+ \qquad (23)$$

The kinetics exhibit a first-order dependence on complex concentration and a second-order dependence on acid concentration, but they are independent of the anion of the acid (which is strong in MeOH). The observed isotopic effect ($k_H/k_D = 0.3$) is consistent with a mechanism which involves protolytic equilibria before the rate limiting step [113].

The reaction is faster for W than for Mo on account of the higher basic character of the former which is then more effective in the activation of N_2 and derived ligands to protonation.

The strong electron donor ability of the methoxide ligands and the non-cationic character of the complexes $[M(N_2H_2)(OMe)_2L_3]$ favour the metal π-electron release to the hydrazido(2-) ligand which may undergo further protonation to NH_3.* In agreement with these observations, complexes with chelating diphosphine ligands $[M(N_2)_2(LL)_2]$ [$LL = Ph_2PC_2H_4PPh_2$ (dppe), $Et_2PC_2H_4PEt_2$ (depe)], although undergoing ready protonation to $[M(N_2H_2)(OMe)(LL)_2]^+$, do not give NH_3 under mild conditions. The chelating effect of the diphosphine prevents its replacement by a stronger net electron donor anionic ligand, and the hydrazido(2-) species is not protonated.

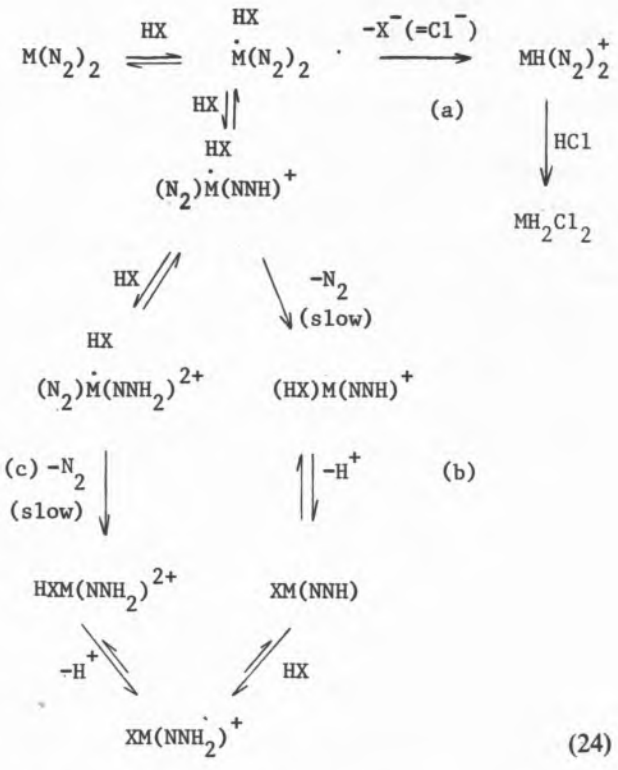
Hence, the *formation of ammonia requires the presence of a labile co-ligand* (monophosphine), besides the other N_2 ligand, *to allow the binding of a strong electron donor anionic species with a promoting effect on protonation.*

— *Direct electrophilic attack at the metal centre*

A distinct mechanism was proposed [114] for the protonation reactions of the diphosphinic complexes *trans*-$[M(N_2)_2(LL)_2]$ (LL = dppe, depe) by mineral acids (HX = HCl, HBr, H_2SO_4). However, solubility reasons precluded the use of MeOH and the studies were performed in thf, a solvent where the acids HX are *not* strong.

The kinetics of the reactions showed a first-order dependence on the concentration of complex whereas the dependence on the concentration of acid was a function of the nature of the acid: zero or first order on [HCl]; second or third order on [HBr] and third order on $[H_2SO_4]$.

The data were interpreted by proposing the initial rapid formation of an adduct between HX and the complex followed by protonation of a ligating N_2 by another molecule of acid prior to the rate-limiting dissociation of N_2 (equations (24) where $M = M(LL)_2$).



(24)

The postulated adduct may correspond to an outer-sphere association of the undissociated form of the acid electrophile (HX) with the electron-rich metal centre (the metal itself or a phosphorus atom); van der Waals interactions may also play an important role.

Although a direct spectroscopic evidence for the adduct formation is lacking, it corresponds to the best rationale of the available kinetic data.

Hence, *e.g.*, the adduct is most extensively formed with HCl which is the weakest acid of this study and the hydride complex $[WH(N_2)_2(dppe)_2]^+$ is formed by fast intramolecular electrophilic attack of HX on the metal within the edduct, following a zero order dependence on [HCl] (route *a* of equations 24, observed for low [HCl], not greater than twice the complex concentration).

However, for higher [HCl] (greater than sixfold the complex concentration), the N_2 deactivating pathway (a) is replaced by the N_2 activating route (b), where ligating dinitrogen undergoes protonation to give the hydrazido(2-) complex, the kinetics following a first-order dependence on [HCl].

The other acids studied (HBr and H_2SO_4) are stronger than HCl, the adduct is formed less extensively at a slower rate, and protonation proceeds through

* Another example of the strong methoxide activating power of a N_2 derived ligand towards protonation will be mentioned in section 3.2.2.

a 2nd-order dependence on [HX] according to pathway (b) or a 3rd-order dependence on [HX] through route (c).

Hence, following an initial electrophilic attack of the protic acid at the metal centre, these reactions proceed through a further electrophilic attack at the metal (N_2 deactivating pathway *a*, for a weak acid) or further electrophilic attacks at a ligating dinitrogen (N_2 activating pathways *b* and *c*, for less undissociated acids).

These protonation reactions are faster for W than for Mo and for the depe ligand than for the dppe analogues as a consequence of the greater basicity of W and depe relative to Mo and dppe, respectively.

3.2.2. FORMATION OF ORGANONITROGENATED SPECIES

The formation of organonitrogenated species from a dinitrogen ligand has already been documented for the transition metal groups IV to VIIB.

However, group IVB transition metal systems involve reactions whose mechanisms are not yet known in detail and the metal centres have not been characterized.

Hence, *e.g.*, amines are formed in some Vol'pin type systems and the reactions are suggested [98] to proceed through an insertion of N_2 into a Ti-C(aryl) bond in mononuclear or dinuclear centres or through a nucleophilic attack of carbanion at the *endo* N of a N_2 ligand — *e.g.*, in the $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$ (or $[Ti(\eta^5\text{-}C_5H_5)_2Ph_2]$) + PhLi system — or through an insertion of N_2 into a Ti-benzyne bond of an intermediate [115] — in the thermolysis of diphenyltitanocene.

Other examples, with possible involvement of intermediate species with the M-N=N-MgCl (M = Ti or V) moiety were already referred to (section 3.2.1.i).

An interesting reaction involving the dinuclear group VB Ta and Nb dinitrogen complexes (where the bridging N_2 ligand is strongly activated by the two high π electron release ability of the two metal centres) and acetone to give dimethylketazine was already mentioned (section 3.2.1.i) but the generality of this type of reaction has yet to be demonstrated.

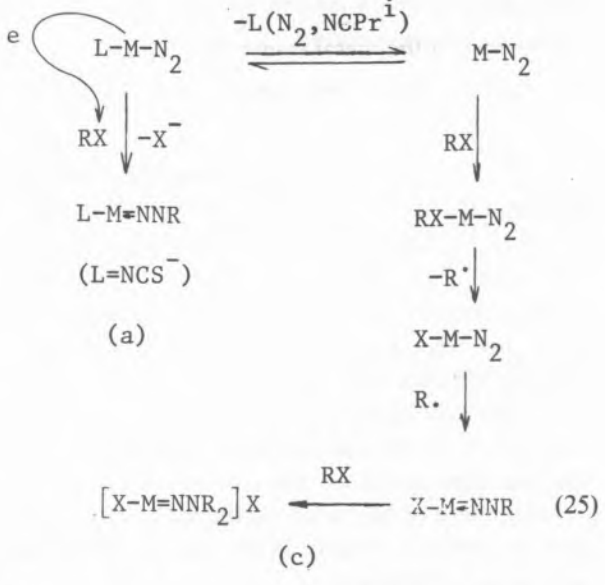
The behaviour of systems with transition metal VIB and VIIB groups is known in more detail and they may reflect opposing dinitrogen activating ways.

(i) *Formation of* exo *nitrogen-carbon bonds*

When N_2 binds an electron rich Mo(0) or W(0) metal centre $\{ML(LL)_2\}$ ($L = N_2$, $NCPr^i$, NCS^-; LL = dppe, depe or phenyl substituted dppe), of the type already mentioned, it may undergo attack by an organo (alkyl, aryl or aroyl) halide (RX).

However, this reaction does not occur *via* a direct electrophilic attack at the N_2 ligand, but it involves the previous oxidation of the metal centre.

If this centre presents a high electron donor co-ligand such as thiocyanate ($P_L = -0.88$ V), its resulting high reducing power leads to the reduction of the organohalide through an outer-sphere electron transfer reaction to afford a radical (R.) which attacks the *exo* N atom of the dinitrogen ligand (reaction 25*a*) leading to an organodiazenido species; the kinetics are first order on both complex and RX concentrations, and the reaction with MeI is *ca.* 38 times faster than with EtI in agreement with a S_N2 type mechanism [116].



(25)

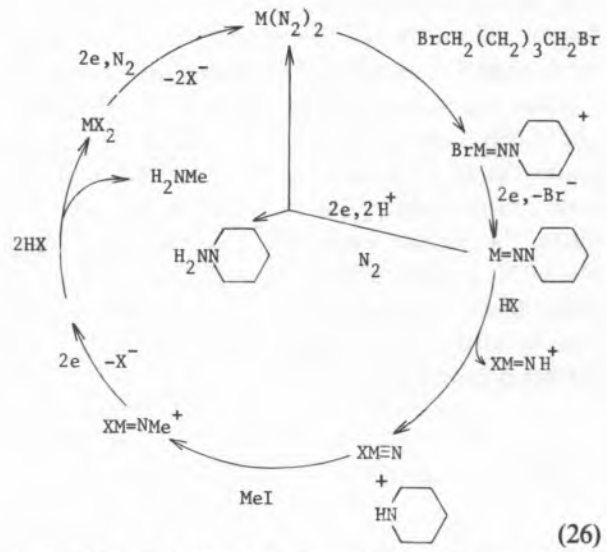
However, the mechanism of the reaction is different if the metal centre presents a lower reducing power and a labile co-ligand such as N_2 ($P_L = -0.1$ V) or $NCPr^i$ ($P_L = -0.6$ V). Addition of the organohalide to the unsaturated species (formed upon loss of the labile ligand) is followed by homolytic cleavage of the halogen-carbon bond to afford, through an inner-sphere electron transfer process, a free radical (R.) which attacks the *exo* N atom of the ligating dinitrogen (reactions 25*b*) [116].

The diazenido product of these reactions, activated by the metal centre, may undergo a secondary alkylation [117] through a direct electrophilic attack at the *exo* N atom in a bimolecular reaction which is promoted by the factors which enhance the electron richness of the metal centre (increase of the electron donor character of the substituents on the phosphorus atoms, and use of W instead of Mo central metal). These factors also affect in the same way the primary alkylation through the outer-sphere electron transfer pathway (reactions 25*a*) but they hinder the inner-sphere pathway (b) since the labile ligand dissociation is hampered by an increase in the π-backbonding ability of the metal centre. From the above considerations one may conclude, however, that these reactions may occur only at a metal centre with, at least, the following features in a delicate balance: strong (route *a*) or considerable (route *b*) electron release power for the organohalide to lead to the C-X bond cleavage with formation of free or bonded X^-, respectively; high π-electron donor capacity to ligating N_2 which should stay coordinated to the metal even after its oxidation by reaction with the organohalide; coordinative unsaturation (for route *b*).

Hence, it is not surprising that these types of reactions are unknown for group VIII transition metals which present a high electronegativity. However, ligating N_2 in the heavy group VIIB metal complex $[ReCl(N_2)(PMe_2Ph)_4]$ (with a considerable electron π-releasing metal centre) may undergo acylation and aroylation leading to $[ReCl_2(NNCOR)(PMe_2Ph)_3]$ (R = alkyl or aryl) [118].

Treatment of the Mo and W organohydrazido(2-) complexes with a reducing agent (such as $NaBH_4$ in methanol) leads to the formation of amines and ammonia [119,120] but with destruction of the N_2 binding ability of the metal centre. However the liberation of ligating organonitrogenated species with regeneration of the nitrogen fixation centre was already achieved by an electrochemical route in the cyclic organohydrazido complex $[MoBr\{NN\text{-}CH_2(CH_2)_3CH_2\}(dppe)_2]^+$ which was derived from double alkylation of N_2 ligand by 1,5-dibromopentane (reactions 26) [121,122].

The electrochemical reduction at a Pt electrode of this complex cation in thf confers on the metal centre such a high electron richness which promotes the protonation of that ligand (to afford an organohydrazine) and the N_2 binding ability with regeneration of the parent bisdinitrogen complex, as shown by the inner cycle of reactions 26.



(26)

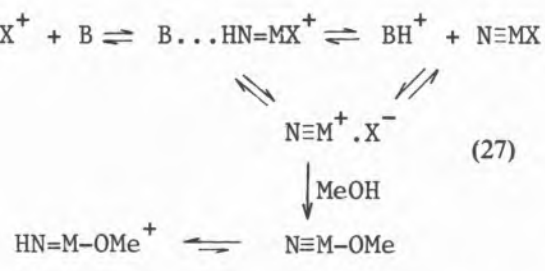
Other amines may be formed according to the outer cycle, *via* protonation of the neutral organohydrazido(2-) complex. Cleavage of the N-N bond occurs in a first step to afford piperidine, an imido and a nitride species; the latter may undergo alkylation and the resulting organoimido species is susceptible to protonation, following a two electron electrochemical reduction, to give methylamine and the dihalide complex which, on reduction under N_2, regenerates the parent dinitrogen complex.

The fundamentals of these cycles, based on the *promotion of the ligand nucleophilic character upon electrochemical reduction of the metal center*, is certainly susceptible to extension to other systems with different types of N_2 derived ligands, and it will be worthwhile to verify the generality of its application to the catalytic synthesis of nitrogenated species from dinitrogen ligand.

In contrast to the monophosphinic Mo and W complexes which activate N_2 towards reduction to NH_3, the metal centres of the present cycles do not present a labile phosphine to be displaced by a stronger net electron donor ligand: *the electron releasing character of the centre is enhanced by electrochemical reduction.* However, *replacement of the halide ligand by a stronger net electron donor species* may also be used for a similar purpose as shown in the following example.

The imido complex *trans*-$[M(NH)X(dppe)_2]^+$ prepared in the sequence of the outer cycle (reactions

26), although unreactive in refluxing acidified methanol, affords NH_3 (70% yield for M = Mo) in basic methanol. The mechanism of this basis catalysed reaction was studied [123] by stopped-flow spectrophotometry and is shown by the sequence (27): the imido ligand is deprotonated by the base (B) to form a nitride which, due to its high *trans* effect, induces the halide evolution and the ionic pair $N\equiv M^+X^-$ is formed; binding of the strong electron donor MeO^- to the unsaturated centre promotes the basicity of the nitride ligand which then undergoes further protonation to NH_3.



(27)

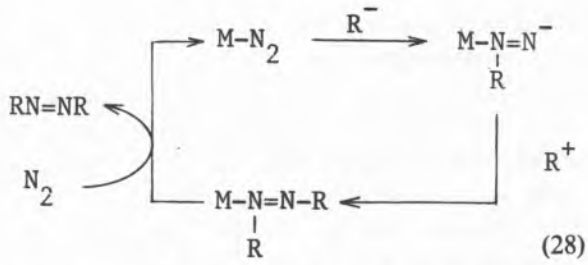
(ii) *Formation of* endo *nitrogen-carbon bond*

When N_2 binds a metal centre with a considerable lower electron-richness than those mentioned in the previous sections, the *endo* nitrogen atom may become susceptible to undergo a nucleophilic attack by a carbanion with formation of a N-C bond.

Although this type of attack has been postulated [98] in the formation of anilines from the reaction of N_2 with PhLi in the presence of some high valent Ti(IV) species such as $[TiCl_2(\eta^5\text{-}C_5H_5)_2]$ or $[Ti(\eta^5\text{-}C_5H_5)_2Ph_2]$, as mentioned in the previous section, the only well documented [124] system involves the dicarbonyl Mn(I) complex $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$.

This complex presents $E^{ox}_{1/2}$ and i.r. $\nu(N_2)$ at high values (+1.2 V *vs.* s.c.e. and 2160 cm^{-1}, respectively) in agreement with a relatively low electron-rich character of the metal centre and a low π-backbond ability to N_2 (the presence of the two strong π electron competitor CO co-ligands may well play a role in this behaviour).

The diazenido ligand (in the unisolated intermediate) derived from nucleophilic attack of carbanion (from MeLi or Ph Li) at the *endo* N atom of ligating N_2 can undergo reaction with an electrophile (carbocation or protic acid) to afford an organodiazene (reactions 28) which may be replaced by N_2 (at 100



(28)

atm pressure) thus regenerating the initial dinitrogen complex although with a low cyclic yield.

$[M = Mn(\eta^5\text{-}C_5H_5)(CO)_2]$

3.2.3. ADDUCT FORMATION

The Lewis basic nature of dinitrogen when ligating an electron-rich Mo(0), W(0) or Re(I) centre accounts for the formation of dinitrogen bridged di-and tri-nuclear complexes on reaction of $[M(N_2)_2L_4]$ (M = Mo, W) with $AlMe_3$ (or $AlEt_3$) or of *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ with a variety of representative or transition metal acceptor species such as $AlMe_3$, $TiCl_4$ or derived from $[CrCl_3(thf)_3]$ and $[MoCl_4L_2]$ (L = thf or PPh_3).

Hence, *e.g.*, the $[Mo(NNAlEt_3)_2(PMe_2Ph)_4]$ [125] and the $[M(NNAlMe_3)(N_2)(dppe)_2]$ (M = Mo or W) [126] adducts are derived from reaction of $AlEt_3$ and $AlMe_3$, respectively, with the parent N_2 complexes, whereas $[\{WX(PMe_2Ph)_3(Py)(\mu_3\text{-}N_2)(AlX_2)\}_2]$ (where Py = pyridine) (see section 2.2.1.) is derived from attack of AlX_3/Py at *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (X = Cl or Br) [41].

Moreover, the following Re(I) complexes [127] are formed by reactions of *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ with the appropriate acceptor species: $[TiCl_4\{(N_2)ReCl(PMe_2Ph)_4\}(thf)]$, $[TiCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2]$, $[MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}]$ and $[MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2]$.

3.3. *ACTIVATION OF ISOCYANIDES AND THEIR APPLICATION AS PROBES IN THE STUDY OF DINITROGEN BINDING METAL CENTRES AND OF DINITROGEN REACTIVITY*

After studying the reactivity of N_2 when activated by a transition metal centre, the difficulties encountered in its activation justify a brief reference to the attempts to apply other more reactive substrates of nitrogenase as probes in the study of N_2 binding centres.

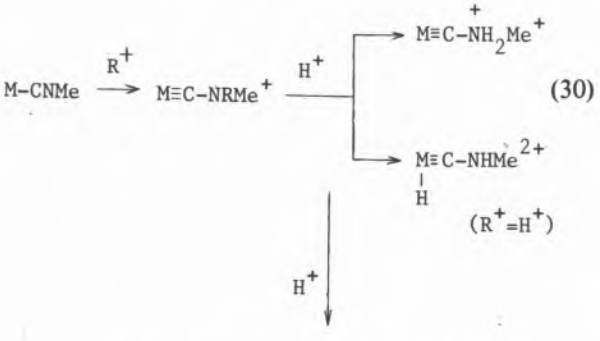
The isocyanides, organic species formulated as $C\equiv NR$, are isoelectronic with N_2; they are also

substrates of nitrogenase being reduced, as N_2, with complete cleavage of the unsaturated bond in an overall process which requires 6 protons and 6 electrons per molecule (reaction 29, although C_2 and C_3 hydrocarbons are also produced in lower yields).

$$C{\equiv}NR \xrightarrow{6e^-,\ 6H^+} CH_4 + H_2NR \qquad (29)$$

When bound to a nitrogen fixation group VIB Mo(0) or W(0) metal centre, with a high electron-richness, *e.g.*, as in *trans*-[M(CNMe)$_2$ (dppe)$_2$], isocyanides present, as a result of the extensive π-backbonding, very low i.r. ν(CN) values (much lower than in the free ligands, by *ca.* 300 ~ 400 cm^{-1}) [64]; a high electron density is then localized at the N atom (it may present a bent geometry) [128] which becomes susceptible to undergo attack by electrophilic agents (a Lewis acid such as $AlEt_3$ [129], protic acids [129,130] or alkylating agents [131]) to give carbyne-type ligands (with a triple metal-carbon bond) as in *trans*-[M(CNRMe) (CNMe) (dppe)$_2$]$^+$ (reactions 30 where $R^+ = H^+$, Me^+ or Et^+); the metal site may also undergo protonation and hydrido-carbyne complexes, [MH(CNHMe) (CNMe) (dppe)$_2$]$^{2+}$, are formed [132] in reactions which are related to those followed by the analogous dinitrogen complexes (equations 21).

If the metal centre presents labile monophosphines, the isocyanide ligand may undergo a more extensive protonation until complete cleavage of the unsaturated bond (as it was observed in the related N_2 complexes with monophosphines) to afford amine, ammonia and hydrocarbon (reactions 31) [133]. The metal is also the reducing agent, the maximum yield corresponding to the consumption of its six valence electrons as observed for [W(CNMe)$_3$(PMe$_2$Ph)$_3$] [133].



(30)

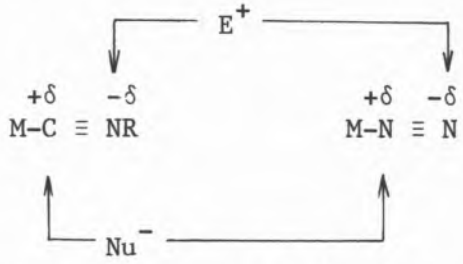
$$NH_2Me, NH_3, CH_4, (C_2H_4, C_2H_6) + M^{ox} \qquad (31)$$

In contrast, if the isocyanide binds a low electron-rich metal centre, such as of the abovementioned Mn(I) type which activates N_2 towards attack by a nucleophile, the i.r. ν(CN) may occur at higher values than those observed for the free ligand, and the ligating isocyanide carbon is susceptible to attack by a nucleophilic agent (see, *e.g.*, reaction 32) [134].

$$[Mn(\eta^5\text{-}C_5H_4Me)(NO)(CO)(CNMe)]^+ + C_6F_5^- \longrightarrow \qquad (32)$$

$$\longrightarrow [Mn(\eta^5\text{-}C_5H_4Me)(NO)(CO)\{C(C_6F_5)=NMe\}]$$

We may then propose that both isocyanide ν(CN) and dinitrogen ν(NN) reflect the electron-richness of the metal centre and the possibility of electrophilic attack (at the β atom) for high electron-rich sites or of attack by a nucleophile (at the α atom) for metal centres with a much lower electron-rich character:



Since isocyanides present a much easier coordination (they are better σ-donors and π-acceptors) than N_2, and a higher reactivity, it would be interesting to extend the comparison between their electronic and chemical properties to a variety of metal centres in order to attempt the development of coordination and reactivity criteria for N_2 on the basis of the known behaviour of the isocyanides bound to the common sites.

4 — INORGANIC CLUSTERS AS STRUCTURAL MODELS FOR THE ENZYMATIC CENTRE

Following the consideration of the isocyanide potential models for the N_2 activating properties of transition metal centres, let us illustrate the attempts to develop structural models of the N_2 binding enzymatic centre, which fall within a general aim of bioinorganic chemistry: the proposal of synthetic models for the metaloenzyme and metaloprotein active centres.

Nitrogenase is formed by two iron-sulphur proteins and the presence of both of them is required for catalytic activity.

The heavier protein, called component 1, has molecular weight of *ca.* 220 000, 1 ~ 2 Mo atoms and 24--34 Fe atoms. whereas the smaller protein (component 2) presents molecular weight of *ca.*60 000 and 4 Fe atoms (without Mo); in both proteins, iron is associated with a similar amount of sulphur, conceivably forming [4Fe-4S] cubane type clusters (the so-called P centres which have not yet been fully characterized) [135].

It was possible the isolation [136], from component 1, of a Mo and Fe co-factor (FeMoco) (the so-called M centre in the intact protein) with the Mo:Fe:S stoichiometry of 1:6 ~ 8:4 ~ 6 (two of these centres may be present in the Mo-Fe protein) and which generates an active Mo-Fe protein when added to a deffective form of nitrogenase (without Mo) produced by a mutant bacterium.

The Mo-Fe protein, in the resting state, presents an EPR resonance [137] which is associated to six iron atoms (as evidenced by Mössbauer studies [138]) in a total electron spin S = 3/2 metal centre present in the FeMoco.

^{95}Mo and ^{1}H ENDOR (Electron Nuclear Double Resonance) spectroscopic studies on the resting state of the Mo-Fe protein evidence (from the observed hyperfine coupling to Mo) the presence of a single Mo atom in the S = 3/2 centre (which is redox active during the N_2 reduction) and suggest (from the magnitude of the ^{95}Mo hyperfine coupling) that this Mo atom presents a pair oxidation state, possibly tetrahedral Mo(II) or Mo(VI) [139].

XAS (X-ray Absorption Spectroscopy) and EXAFS (Extended X-ray Absorption Fine Structure) studies evidence that the numbers of Fe (3-4) and S(2-3) atoms in the vicinity of Mo and their distances to this atom in the co-factor are analogous to those observed in the Mo-Fe protein (the Mo-S distances are 2.35 and 2.36 Å in the co-factor and in the protein, respectively, whereas the Mo-Fe distances are 2.66 and 2.68 Å, respectively) [140].

Based on these properties, a few Mo-Fe-S clusters have been proposed as structural models for the active site, namely these shown in fig. 6: the single cubane $MoFe_3S_4$ with a cubic arrangement of the metal and sulphur atoms, the double cubane (dimer with two single cubane units linked by sulphur or thiolate bridges) and the linear model where the metal atoms follow a straight line [141]; other models have been proposed such as the complex "string bag" [142] arrangements which are composite clusters of hepta (h-type) and nona (n-type) simpler structures (with 7 and 9 atoms, respectively).

However, only recently it was demonstrated the nitrogen fixation ability of one of these clusters: the reduced (5-) form of the double cubane $[Mo\text{-}Fe]^{3-}$ of fig. 6, prepared by controlled potential electrolysis of the latter at a Hg electrode (-1.3 V *vs.* s.c.e.) in a protic solvent, MeOH/thf or an aqueous alkaline suspension [143].

The maximum yield was *ca.* $2NH_3$/complex in an aqueous suspension during 4 days, although with a low current efficiency (lower than 0.1%, defined by the ratio between the charge which reduced N_2 to NH_3 and the total charge which passed through the cell) due to the high consumption in the protic reduction to H_2.

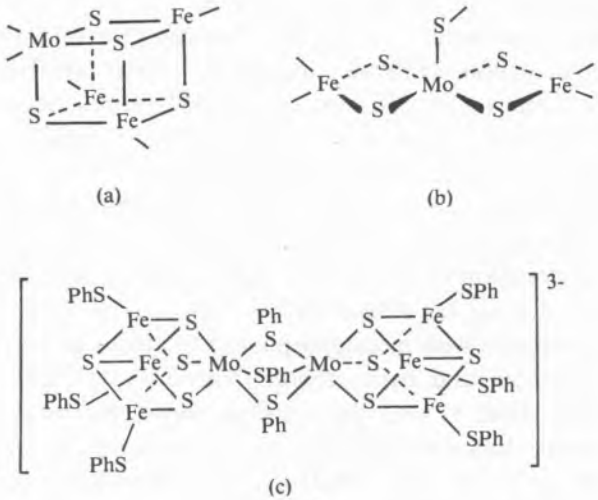


Fig. 6

Structural model clusters for the enzymatic Mo centre of nitrogenase. (a) Single cubane $MoFe_3S_4$. (b) Linear FeS_2MoS_2Fe (c) Double cubane $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ or $[Mo\text{-}Fe]^{3-}$

The same reduced $[Mo\text{-}Fe]^{5-}$ cluster also reduces other substrates of nitrogenase such as methylisocyanide [to CH_4 and other C_2 and C_3 hydrocarbons and $MeNH_2$, CO_2 also being formed probably through oxidation, by an oxidized form of the complex, of HCOOH which is obtained by hydrolysis of the isocyanide] [144], acetonitrile [to $NH_3 + C_2H_6$ and C_2H_4] and acetylene [which is stereoselectively reduced to ethylene: *cis*-$C_2D_2H_2$ is formed from C_2D_2] [145].

In these systems the role of the Mo centre is yet unknown since the 3- and 4- reduced forms of the Fe-S cluster (without Mo) $[Fe_4S_4(SPh)_4]^{2-}$, also exhibit reducing activity.

Moreover, in the double cubane structure the Mo atoms are coordinatively saturated and present thiolate bridges which are resistent to displacement; the substrate activation may then occur from coordination to iron. Hence, structures, *e.g.*, of the single cubane type, with an unsaturated Mo centre, may become more favourable.

This type of structure (fig. 6*a*) has been prepared [146] and authenticated by X-rays [147], the Mo(III) centre presenting a quelating catecholate ligand and an unsaturated character [the sixth coordination position is occupied by a labile solvent (*e.g.*, NCMe) ligand which undergoes ready replacement by a variety of neutral (CO, PEt_3) and anionic (CN^-, OPh^-, SR^-) species]. An electron spin $S = 3/2$ is observed as in the resting FeMoco.

The solvated cluster undergoes a reversible single electron electrochemical reduction, and the reduced form adds CO to give a 1:1 adduct, and the low observed i.r. $\nu(CO)$ value (1810 cm^{-1}) which is comparable to that known for $[Mo(N_2)\ (CO)\ (dppe)_2]$ (1799 cm^{-1}) suggests that the reduced single cubane cluster species presents an electron π releasing power similar to that of $\{Mo(N_2)\ (dppe)_2\}$! The study of the interaction of this cluster with enzymatic substrates is conceivably under progress but has not yet been reported.

5 — FINAL COMMENTS

The topic of this work possibly initiated in 1965 with the accidental preparation of the first dinitrogen complex. Since then, important developments on the search for N_2 activating metal centres have occured: catalytic conversion of the Vol'pin system (Vol'pin 1968); development of aqueous systems (Shilov, Schrauzer, 1970); conversion of N_2 into organonitrogenated species and hydrides of nitrogen in isolated complexes (Chatt, Leigh, Richards, 1972, 1975); the isolation of FeMoco (Shah 1977); the electrochemical quantification of the electronic properties of the metal centres (Pickett 1980); application of Mo-Fe-S clusters as structural models for the enzymatic metal centre; use of isocyanides as coordination and reactivity models and as probes in the study of the activating properties of the metal centres.

The third, fifth and seventh topics, which were covered in this work, are those which have given more information on the electronic properties of the N_2 activating centres: high electron-richness (E_s), high polarisability (β), high π-backbonding capacity and/or high σ-acceptor character. The convenient geometry and the coordinative unsaturation (due to the lability of N_2 and/or other ligands) are also features of the involved metal centres and all these properties, in variable intensity, rationalize the stabilization of unstable π-acceptors (such as organodiazenido and carbyne-type species), as well as the chemical reactivity: ready oxidation, addition and oxidative addition reactions, involvement in catalysis, susceptibility to electrophilic attack and activation of π-acceptor ligands such as N_2 and isocyanides. The half-wave oxidation potential of the complex and the i.r. stretching vibration associated to the triple bond of the unsaturated ligand reflect the type of activation it undergoes which promotes attack by a nucleophile or, more usually, by an electrophile.

The reactions of N_2 ligand with electrophiles involve a fundamental electron density transfer from the metal centre to the electrophile through a direct way [*e.g.*, in alkylation and protonation reactions of dinitrogen at diphosphinic group VIB Mo(0) or W(0) metal centres] or an indirect pathway, *via* dinitrogen [*e.g.*, in the protonation reactions of ligating N_2 at monophosphinic Mo(0) or W(0) complexes by strong acids, and in the attack by Lewis acids].

The activation of N_2 towards electrophilic attack depends concomitantly on the tendency to π-backbonding donation of the metal centre and on its available number of *d* electrons: transition metals of the lower periodic groups have a high π-electron release ability but present a small number of *d* electrons, whereas the metals in high periodic groups, with a high number of *d* electrons, have a weak π-backbonding capacity. Fig. 5 can now be extended to the central groups, typically to Mo and W group VIB transition metals, with a privileged localization which corresponds to a compromise between those two tendencies, presenting the maximum known N_2 activating power in mononuclear complexes (fig. 7).

For the central transition metal groups (VIB and VIIB) the activation of ligating N_2 towards electrophiles appears to increase down the group as eviden-

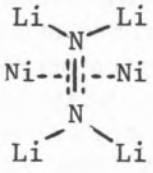
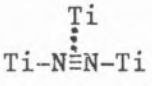
Group		IVB Ti ...	VB V ...	VIB Cr ...	VIIB Mn ...	VIII Fe,Co,Ni ...
π-Backbonding ability		High ←				→ Low
Number of *d* electrons		Low →				High
N_2 activation	Mononuclear centres			High		Low
	Polynuclear centres	M–N=N–M'				M–N≡N–M'  

Fig. 7
Activation of N_2 along the periodic groups. M-Transition metal centre. M'-Transition or representative metal centre

ced by the higher rates of the protonation and alkylation (by an outer-sphere electron transfer mechanism) reactions of N_2 when bound to W rather than to Mo, *e.g.*, in $[M(N_2)_2(dppe)_2]$ (the W centre appears to display a higher basicity than the Mo one). Moreover, when N_2 binds a Re(I) centre, in *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, it undergoes attack by a Lewis acid, an acyl- and aroyl-halide, whereas when bound to a lighter Mn(I) centre, in $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$, it reacts with a nucleophile; however, a direct comparison between the two transition metals is precluded by the different electronic properties of their ligands.

However, N_2 may also be activated towards reduction by transition metals of the extreme periodic group in polynuclear complexes where the N_2 activation results from the combined effect of two or more metal centres with a possible promoting role of cations of less electronegative non-transition metal atoms (fig. 7).

In the reduction of N_2 to NH_3 or to organonitrogenated species by group VIB metal centres, it is also fundamental the enhancement of the electron releasing ability of the binding centre through replacement of a labile co-ligand by a stronger net electron donor ligand or through an electrochemical reductive pathway.

The current knowledge on the rationalization of the N_2 binding metal centres is yet incipient but already promising, namely on attempting to design N_2 activating systems which may reduce, in mild conditions, N_2 to compounds with industrial or agricultural interest.

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REFERENCES

[1] J. Chatt, L.M.C. Pina, R.L. Richards, eds., "New Trends in the Chemistry of Nitrogen Fixation", Academic Press, 1980 (Academia das Ciências de Lisboa; 1982).

[2] J.R. Dilworth, R.L. Richards, "Reactions of Dinitrogen Promoted by Transition Metal Compounds", *in* "Comprehensive Organometallic Chemistry", G. Wilkinson, ed., Pergamon Press, 1982, Ch. 60, p. 1073.

[3] J. CHATT, J.R. DILWORTH, R.L. RICHARDS, "Recent Advances in the Chemistry of Nitrogen Fixation", *Chem. Rev.*, **76**, 589 (1978).
[4] J. CHATT, R.L. RICHARDS, "The Reactions of Dinitrogen in its Metal Complexes", *J. Organometal. Chem.*, **239**, 65 (1982).
[5] R.W.F. HARDY *in* "Nitrogen Fixation", vol. I, W.E. Newton, W.E. Orme-Johnson, eds., University Park Press, 1980, p. 3; V.P. Gutschick, *ibid.*, p. 17.
[6] H. BORTELS, *Archiv. Mikrobiol.*, **1**, 333 (1930).
[7] W.A. BULEN, J.R. LECOMTE, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 979 (1966).
[8] M.E. VOL'PIN, V.B. SHUR, *Dokl. Akad, Nauk SSSR*, **156**, 1102 (1964).
[9] A.D. ALLEN, C.V. SENOFF, *Chem. Comm.*, 621 (1965).
[10] H. HUBER, T.A. FORD, W. KOTZBÜCHER, G.A. OZIN, *J. Amer. Chem. Soc.*, **98**, 3176 (1976).
[11] W.E. KLOTZBÜCHER, G.A. OZIN, *J. Amer. Chem. Soc.*, **95**, 3790 (1973); G.A. OZIN, W.E. KLOTZBÜCHER, *ibid.*, **97**, 3965 (1975).
[12] J.K. BURDETT, M.A. GRAHAM, J.J. TURNER, *J.C.S. Dalton*, 1620 (1972).
[13] J. CHATT, R.H. CRABTREE, J.R. DILWORTH, R.L. RICHARDS, *J.C.S. Dalton*, 2358 (1974).
[14] A.J.L. POMBEIRO, R.L. RICHARDS, unpublished work; A.J.L. POMBEIRO, P.B. HITCHCOK, R.L. RICHARDS, *Inorg. Chim. Acta*, **76**, L22 (1983).
[15] D. CRUZ-GARRITZ, H. TORRENS, J. LEAL, R.L. RICHARDS, *Trasition Met. Chem.*, **8**, 127 (1983).
[16] M. ARESTA, A. SACCO, *Gazzetta Chim. Ital.*, **102**, 155 (1972).
[17] S.M. VINOGRADOVA, A.F. SHESTAKOV, *Bull. Russ. Acad.*, **7**, 474 (1981).
[18] R. SANNER, D. DUGGAN, T.C. MCKENZIE, R. MARSH, J. BERCAW, *J. Amer Chem. Soc.*, **98**, 8358 (1976).
[19] R. SANNER, I. MANRIQUEZ, R. MARSH, J. BERCAW, *J. Amer. Chem. Soc.*, **98**, 8351 (1976).
[20] H.W. TURNER, J.D. FELLMANN, S.M. ROCKLAGE, R.R. SCHROCK, *J. Amer. Chem. Soc.*, **102**, 7808 (1980).
[21] M.R. CHURCHILL, H.J. WASSERMAN, *Inorg. Chem.*, **21**, 218 (1982).
[22] See, *e.g.*, T. UCHIDA, Y. UCHIDA, M. HIDAI, T. KODAMA, *Bull. Chem. Soc. Japan*, **44**, 2883 (1971); *Acta Cryst.*, **B31**, 1197 (1975).
[23] See, *e.g.*, B.R. DAVIS, J.A. IBERS, *Inorg. Chem.*, **10**, 578 (1971).
[24] C.A. GHILARDI, S. MIDOLLINI, C. SACCONI, P. STOPPIONI, *J. Organometal. Chem.*, **205**, 193 (1981).
[25] F. BOTTOMLEY, S.C. NYBURG, *Acta Cryst.*, **24B**, 1289 (1968).
[26] R. FORDER, K. PROUST, *Acta Cryst.*, **B30**, 2778 (1974).
[27] M.L. ZIEGLER, K. WEIDENHAMMER, H. ZIEGLER, R.S. SKELL, W.A. HERRMANN, *Angew. Chem. Int. Ed.*, **15**, 695 (1976).
[28] J. CHATT, G.A. HEATH, R.L. RICHARDS, *J.C.S. Dalton*, 2074 (1974); G.A. HEATH, R. MASON, K.M. THOMAS, unpublished results.
[29] W. LIEBELT, K. DEHNICKE, *Z. Naturforsch*, **34b**, 7 (1979).
[30] B. DAVIS, N. PAYNE, J.A. IBERS, *J. Amer. Chem. Soc.*, **91**, 1240 (1969).
[31] R. HOFFMAN, T. YOSHIDA, T. OKANO, S. OTSUKA, J.A. IBERS, *Inorg. Chem.*, **15**, 2462 (1976).
[32] P.W. JOLLY, K. JONAS, C. KRÜGER, Y.-N. TSAY, *J. Organometal. Chem.*, **33**, 109 (1971).
[33] K. JONAS, D.J. BRAUER, C. KRÜGER, P.J. ROBERTS, Y.-H. TSAY, *J. Amer. Chem. Soc.*, **98**, 74 (1976).
[34] R. HAMMER, H.-F. KLEIN, P. FRIEDRICH, G. HUTTNER, *Angew. Chem. Int. Ed.*, **16**, 485 (1977).
[35] R. HAMMER, H.-F. KLEIN, U. SCHUBERT, A. FRANK, G. HUTTNER, *Angew. Chem. Int. Ed.*, **15**, 612 (1976).
[36] B. CHAUDRET, J. DEVILLERS, R. POILBLANC, *J.C.S. Chem. Comm.*, 641 (1983).
[37] G.A. OZIN, A.V. VOET, *Can. J. Chem.*, **51**, 637 (1973).
[38] M.J.S. GYNANE, J. JEFFERY, M.F. LAPPERT, *J.C.S. Chem. Comm.*, 34 (1978); J. JEFFERY, M.F. LAPPERT, P.I. RILEY, *J. Organometal. Chem.*, **181**, 25 (1979).
[39] C. KRÜGER, Y.-H. TSAY, *Angew. Chem. Int. Ed.*, **12**, 998 (1983).
[40] G.P. PEZ, P. APGAR, R.K. CRISSEY, *J. Amer. Chem. Soc.*, **104**, 482 (1982).
[41] T. TAKAHASHI, T. KODAMA, A. WATAKABE, Y. UCHIDA, M. HIDAI, *J. Amer. Chem. Soc.*, **105**, 1680 (1983).
[42] B.P. STOICHEFF, *Can. J. Phys.*, **82**, 630 (1954).
[43] K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, New York, 1963.
[44] A.J.L. POMBEIRO, P.B. HITCHCOCK, R.L. RICHARDS, *Inorg. Chim. Acta*, **76**, L22 (1983).
[45] R.D. SANNER, D.M. DUGGAN, T.C. MCKENZIE, R.E. MARSH, J.E. BERCAW, *J. Amer. Chem. Soc.*, **98**, 8358 (1976).
[46] J.M. ROBERTSON, *J. Chem. Soc.*, 232 (1939).
[47] H.W. SCHROETTER, *Naturwissenschaften*, **54**, 513 (1967).
[48] "Interatomic Distances", Chemical Society, London, 1958.
[49] J.R. DURIG, S.F. BUSH, E.E. MERCER, *J. Chem. Phys.*, **44**, 4238 (1966).
[50] E.P. KÜNDIG, M. MOSKOVITS, G.A. OZIN, *Can. J. Chem.*, **51**, 2710 (1973); J.K. BURDETT, J.J. TURNER, *J.C.S. Chem. Comm.*, 885 (1971); M. MOSKOVITS, G.A. OZIN, *J. Chem. Phys.*, **58**, 1251 (1973); H. HUBER, E.P. KÜNDIG, M. MOSKOVITS, G.A. OZIN, *J. Amer. Chem. Soc.*, **95**, 332 (1973); G.A. OZIN, M. MOSKOVITS, P. KÜNDIG, H. HUBER, *Can. J. Chem.*, **50**, 2385 (1972); D.W. GREEN, J. THOMAS, D.M. GRUEN, *J. Chem. Phys.*, **58**, 5453 (1973).
[51] G.M. BANCROFT, M.J. MAYS, B.E. PRATER, F.P. STEFANINI, *J. Chem. Soc. (A)*, 2146 (1970).
[52] B. BELL, J. CHATT, G.J. LEIGH, *Chem. Comm.*, 576 (1970).
[53] D.F. SHRIVER, *Accounts Chem. Res.*, **3**, 231 (1970).
[54] R.C. SPIKER, JR., L. ANDREWS, C. TRINDLE, *J. Amer. Chem. Soc.*, **94**, 2401 (1972); V.E. AVDEEV, I.I. ZAKHAROV, YU. A. BORISOV, N.N. BULGAKOV, *Izvest. Akad, Nauk SSSR, Ser. Khim.*, 239 (English translation, p. 227) (1976).
[55] K.C. PATIL, C. NESAMANI, V.R. PAI VERNEKER, *Polyhedron*, **1**, 421 (1982).
[56] K.H. LINKE, R. TAUBERT, *Z. Anorg. Allgem. Chem.*, **74**, 383 (1971); K.H. LINKE, R. TAUBERT, T.H. KRUCK, *ibid.*, **1**, 396 (1973).

[57] D. TEVAULT, K. NAKAMOTO, *Inorg. Chem.*, **15**, 1282 (1976); D. TEVAULT, D.P. STROMMEN, K. NAKAMOTO, *J. Amer. Chem. Soc.* , 2997 (1977).

[58] M.W. ANKER, J. CHATT, G.J. LEIGH, A.G. WEDD, *J.C.S. Dalton*, 2639 (1975); L.J. ARCHER, T.A. GEORGE, M.E. NOBLE, *J. Chem. Ed.*, **58**, 727 (1981).

[59] J. CHATT, C.T. KAN, G.J. LEIGH, C.J. PICKETT, D.R. STANLEY, *J.C.S. Dalton*, 2032 (1980).

[60] A.J.L. POMBEIRO, C.J. PICKETT, R.L. RICHARDS, *J. Organometal. Chem.*, **224**, 285 (1982).

[61] M.F.N.N. CARVALHO, A.J.L. POMBEIRO, O. ORAMA, U. SCHUBERT, C.J. PICKETT, R.L. RICHARDS, *J. Organometal. Chem.*, **240**, C18 (1982).

[62] A.J.L. POMBEIRO, *Rev. Port. Quím.*, **21**, 90 (1979).

[63] M. SATO, T. TATSUMI, T. KODAMA, M. HIDAI, T. UCHIDA, Y. UCHIDA, *J. Amer. Chem. Soc.*, **100**, 4447 (1978).

[64] J. CHATT, C.M. ELSON, A.J.L. POMBEIRO, R.L. RICHARDS, G.H.D. ROYSTON, *J.C.S. Dalton*, 165 (1978).

[65] J. CHATT, A.J.L. POMBEIRO, R.L. RICHARDS, *J. Organometal. Chem.*, **190**, 297 (1980).

[66] M. HIDAI, K. TOMINARI, Y. UCHIDA, *J. Amer. Chem. Soc.*, **94**, 110 (1972).

[67] A.J.L. POMBEIRO, C.J. PICKETT, R.L. RICHARDS, S.A. SANGOKOYA, *J. Organometal. Chem.*, **202**, C15 (1980).

[68] A.D. ALLEN, E. BOTTOMLEY, R.O. HARRIS, V.P. REINSALU, C.V. SENOFF, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

[69] T. TATSUMI, H. TOMINAGA, M. HIDAI, Y. UCHIDA, *J. Organometal. Chem.*, **199**, 63 (1980).

[70] D.L. HUGHES, A.J.L. POMBEIRO, C.J. PICKETT, R.L. RICHARDS, *J. Organometal. Chem.*, **248**, C26 (1983).

[71] C.T. KAN, P.B. HITCHCOCK, R.L. RICHARDS, *J.C.S. Dalton*, 79 (1982).

[72] G.W. PARSHALL, *J. Amer. Chem. Soc.*, **90**, 1669 (1968).

[73] F.G.N. CLOKE, K.P. COX, M.L.H. GREEN, J. BASHKIN, K. PROUT, *J.C.S. Chem. Comm.*, 393 (1982).

[71] C.T. KAN, P.B. HITCHCOCK, R.L. RICHARDS, *J.C.S. Dalton*, 79 (1982).

[72] G.W. PARSHALL, *J. Amer. Chem. Soc.*, **90**, 1669 (1968).

[73] F.G.N. CLOKE, K.P. COX, M.L.H. GREEN, J. BASHKIN, K. PROUT, *J.C.S. Chem. Comm.*, 393 (1982).

[74] M.G. BRADLEY, D.A. ROBERTS, G.L. GEOFFROY, *J. Amer. Chem. Soc.*, **103**, 379 (1981); D.R. ROBERTS, G.L. GEOFFROY, M.G. BRADLEY, *J. Organometal. Chem.*, **198**, C75 (1980).

[75] T. TATSUMI, H. TOMINAGA, M. HIDAI, Y. UCHIDA, *J. Organometal. Chem.*, **215**, 67 (1981).

[76] M.G. BRADLEY, B.R. HOFMANN, *J.C.S. Chem. Comm.*, 1180 (1982).

[77] L.J. ARCHER, T.A. GEORGE, *J. Organometal. Chem.*, **54**, C25 (1973).

[78] J. CHATT, R.L. RICHARDS, J.R. SANDERS, J.E. FERGUSSON, *Nature (London)*, **221**, 551 (1969).

[79] J. CHATT, G.A. HEATH, R.L. RICHARDS, *J.C.S. Dalton*, 2079 (1974).

[80] J. CHATT, G.J. LEIGH, H. NEUKOMM. C.J. PICKETT, D.R. STANLEY, *J.C.S. Dalton*, 121 (1980).

[81] A.J.L. POMBEIRO, "Preparation, Structure, Bonding and Reactivity of Dinitrogen Complexes", Ch. 6 *in* "New Trends in the Chemistry of Nitrogen Fixation", J. Chatt, R.L. Richards, L.L.C. Pina, eds., Academic Press, 1980 (Academy of Sciences of Lisbon, 1982).

[82] F. PENNELLA, R.L. BANKS, *J. Catalysis*, **35**, 73 (1974); F. PENNELLA, *Coordination Chem. Rev.*, **16**, 51 (1975).

[83] F. PENNELLA, *J. Organometal. Chem.*, **78**, C10 (1974); S. TYRLIK, *ibid.*, **39**, 371 (1972); A. YAMAMOTO, S. KITAZUME, L.S. PU, S. IKEDA, *J. Amer. Chem. Soc.*, **93**, 371 (1971).

[84] C.-P. LAU, B.-H. CHANG, R.H. GRUBBS, C.H. BRUBAKER, *J. Organometal. Chem.*, **214**, 325 (1981).

[85] T. YOSHIDA, T. OKANO, K. SAITO, S. OTSUKA, *Inorg. Chim. Acta*, **44**, L135 (1980).

[86] V.S. LENENKO, A.G. KNIZHNIK, E.I. MYSOV, V.B. SHUR, M.E. VOL'PIN, *Dokl. Akad. Nauk SSSR*, **255**, 1131 (1980).

[87] (a) H.L.M. VAN GALL, F.G. MOERS, J.J. STEGGERDA, *J. Organometal. Chem.*, **65**, C43 (1974); (b) See, *e.g.*, C. Masters, "Homogeneous Transition Metal Catalysis", Chapman and Hall, 1981, p. 40.

[88] G. J. LEIGH, J.N. MURREL, W. BREMSER, W.G. PROCTOR, *Chem. Comm.*, 1616 (1970); P. FINN, W.L. JOLLY, *Inorg. Chem.*, **11**, 1434 (1972).

[89] G.J. LEIGH, R.H. MORRIS, C.J. PICKETT, D.R. STANLEY, J. CHATT, *J.C.S. Dalton*, 800 (1981).

[90] A.E. SHILOV, "Comparison of Biological Nitrogen Fixation with its Chemical Analogues", Ch. 5 *in* "New Trends in the Chemistry of Nitrogen Fixation", J. Chatt, R.L. Richards, L.M.C. Pina, eds., Academic Press, 1980 (Academy of Sciences of Lisbon, 1982); G.N. SCHRAUZER, "Studies of the Mechanism of Biological Nitrogen Fixation with Functional Model Systems", Ch. 4, *ibid.*

[91] B.J. WEATHERS, J.M. GRATE, N.A. STRAMPACH, G.N. SCHRAUZER, *J. Amer. Chem. Soc.*, **101**, 925 (1979).

[92] A.E. SHILOV, 5th Intern. Symp. Nitrogen Fixation, Noordwijkerhout, Holland, 1983.

[93] J.M. MANRIQUEZ, D.M. MCALLISTER, E. ROSENBERG, A.M. SHILLER, K.L. WILLIAMSON, S.I. CHAN, J.E. BERCAW, *J. Amer. Chem. Soc.*, **100**, 3078 (1978).

[94] S.M. ROCKLAGE, R.R. SCHROCK, *J. Amer. Chem. Soc.*, **104**, 3077 (1982).

[95] YU. G. BORODKO, I.N. IVLEVA, L.M. KACHAPINA, S.I. SALIENKO, A.K. SHILOVA, A.E. SHILOV, *J.C.S. Chem. Comm.*, 1178 (1972); YU. G. BORODKO, I.M. IVLEVA, L.M. KACHAPINA, E.F. KVASHINA, A.K. SHILOVA, A.E. SHILOV, *J.C.S. Chem. Comm.*, 169 (1973); I.N. IVLEVA, A.K. SHILOVA, S.I. SALIENKO, YU. G. BORODKO, *Dokl. Akad. Nauk SSSR*, **213**, 116 (1973).

[96] P. SOBOTA, B.J.-TRZEBIATOWSKA, *Coord, Chem. Rev.*, **26**, 71 (1978); P. SOBOTA, B.J.-TRZEBIATOWSKA, Z. JANAS, *J. Organometal. Chem.*, **118**, 253 (1976).

[97] M.E. VOL'PIN, M.A. ILATOVSKAYA, L.V. KOSYAKOVA, V.B. SHUR, *Dokl. Akad. Nauk SSSR*, **180**, 103 (1968); *Chem. Comm.*, 1074 (1968).

[98] M.E. VOL'PIN, V.B. SHUR, "Fixation of Molecular Nitrogen in Aprotic Media", Ch. 3 *in* "New Trends in the Chemistry of Nitrogen Fixation", J. Chatt, R.L. Richards, L.M.C. Pina, eds., Academic Press, 1980 (Academy of Sciences of Lisbon, 1982).

[99] YU. G. BORODKO, M.O. BROITMAN, L.M. KACHAPINA, A.E. SHILOV, L. YU UKHIN, *J.C.S. Chem. Comm.*, 1185 (1971).

[100] B.J.-TRZEBIATOWSKA, P. SOBOTA, *J. Organometal. Chem.*, **46**, 339 (1972).

[101] T.A. BAZHENOVA, R.M. LOBKOVSKAYA, R.P. SHIBAEVA, A.K. SHILOVA, A.E. SHILOV, M. GRYUZEL, ZH. LENI, B. CHUBAR, *Kinetika i Kataliz*, **23**, 246 (1982) (English translation, p. 210).

[102] Y. MIURA, A. YAMAMOTO, *Chem. Letters*, 937 (1978).

[103] K. JONAS, C. KRÜGER, *Angew. Chem. Int. Ed. Engl.*, **19**, 520 (1980).

[104] J. CHATT, A.J. PEARMAN, R.L. RICHARDS, *J.C.S. Dalton*, 1852 (1977).

[105] T. TAKAHASHI, Y. MIZOBE, M. SATO, Y. UCHIDA, M. HIDAI, *J. Amer. Chem. Soc.*, **101**, 3405 (1979).

[106] H. NISHIHARA, T. MORI, F. SAITO, Y. SASAKI, *Chem. Letters*, 667 (1980).

[107] J. CHATT, A.J. PEARMAN, R.L. RICHARDS, *J.C.S. Dalton*, 1766 (1978); J.CHATT, M.E. FAKLEY, I.R. HANSON, D.L. HUGHES, R.L. RICHARDS, *J. Organometal. Chem,*, **170**, C6 (1979).

[108] S.N. ANDERSON, M.E. FAKLEY, R.L. RICHARDS, J. CHATT, *J.C.S. Dalton*, 1973 (1981).

[109] J. CHATT, M.E. FAKLEY, P.B. HITCHCOCK, R.L. RICHARDS, N.T. LUONG-THI, D.L. HUGHES, *J. Organometal. Chem.*, **172**, C55 (1979); T. TAKAHASHI, Y. MIZOBE, M. SATO, Y. UCHIDA, M. HIDAI, *J. Amer. Chem. Soc.*, **102**, 7461 (1980).

[110] J. CHATT, A.J. PEARMAN, R.L. RICHARDS, *J.C.S. Dalton*, 1520 (1976).

[111] W. HUSSAIN, G.J. LEIGH, C.J. PICKETT, *J.C.S. Chem. Comm.*, 747 (1982).

[112] R. DILWORTH, R.A. HENDERSON, G.J. LEIGH, C.J. PICKETT, R.L. RICHARDS, *in* "Current Perspectives in Nitrogen Fixation", A.H. Gibson, W.E. Newton, eds., Australian Academy of Sciences, 1981, p. 349.

[113] R.A. HENDERSON, *J. Organometal. Chem.*, **208**, C15 (1981).

[114] R.A. HENDERSON, *J.C.S. Dalton*, 917 (1982).

[115] E.G. BERKOVICH, V.B. SHUR, M.E. VOL'PIN, B. LORENZ, S. RUMMEL, M. WAHREN, *Chem. Ber.*, **113**, 70 (1980).

[116] J. CHATT, R.A. HEAD, G.J. LEIGH, C.J. PICKETT, *J.C.S. Dalton*, 1638 (1979); *J.C.S. Chem. Comm.*, 299 (1977).

[117] J. CHATT, W. HUSSAIN, G.J. LEIGH, H. NEUKOMM, C.J. PICKETT, D.A. RANKIN, *J.C.S. Chem. Comm.*, 1024 (1980).

[118] J. CHATT, G.A. HEATH, N.E. HOOPER, G.J. LEIGH, *J. Organometal. Chem.*, **57**, C67 (1973).

[119] P.C. BEVAN, J. CHATT, G.J. LEIGH, E.G. LEELAMANI, *J. Organometal. Chem.*, **139**, C59 (1977).

[120] D.C. BUSBY, T.A. GEORGE, *Inorg. Chim. Acta*, **29**, L273 (1978); G.E. BOSSARD, D.C. BUSBY, M. CHANG, T.A. GEORGE, S.D.A. ISKE, *J. Amer. Chem. Soc.*, **102**, 1001 (1980).

[121] C.J. PICKETT, G.J. LEIGH, *J.C.S. Chem. Comm.*, 1033 (1981).

[122] W. HUSSAIN, G.J. LEIGH, C.J. PICKETT, EUCHEM Conf. Intermediates and Mechanisms in Nitrogen Fixation Processes, Brigton, 12 (1983).

[123] R.A. HENDERSON, *J.C.S. Dalton*, 51 (1983).

[124] D. SELLMANN, W.WEISS, *Angew. Chem. Int. Ed.*, **16**, 880 (1977); **17**, 269 (1978).

[125] M. ARESTA, *Gazz. Chim. Ital.*, **102**, 781 (1972).

[126] J. CHATT, R.H. CRABTREE, E.A. JEFFERY, R.L. RICHARDS, *J.C.S. Dalton*, 1167 (1973).

[127] J. CHATT, R.C. FAY, R.L. RICHARDS, *J. Chem. Soc. (A)*, 702 (1971); M. MERCER, R.H. CRABTREE, R.L. RICHARDS, *J.C.S. Chem. Comm.*, 808 (1973); R. ROBSON, *Inorg. Chem.*, **13**, 475 (1974); M. MERCER, *J.C.S. Dalton*, 1637 (1974); P.D. CRADWICK, J. CHATT, R.H. CRABTREE, R.L. RICHARDS, *J.C.S. Chem. Comm.*, 351 (1975).

[128] J. CHATT, A.J.L. POMBEIRO, R.L. RICHARDS, G. ROYSTON, K. MUIR, R. WALKER, *J.C.S. Chem. Comm.*, 708 (1975).

[129] J. CHATT, A.J.L. POMBEIRO, R.L. RICHARDS, *J.C.S. Dalton*, 492 (1980).

[130] A.J.L. POMBEIRO, R.L. RICHARDS, *Transition Met. Chem.*, **5**, 55 (1980).

[131] J. CHATT, A.J.L. POMBEIRO, R.L. RICHARDS, *J. Organometal. Chem.*, **184**, 357 (1980).

[132] J. CHATT, A.J.L. POMBEIRO, R.L. RICHARDS, *J.C.S. Dalton*, 1585 (1979).

[133] A.J.L. POMBEIRO, R.L. RICHARDS, *Transition Met. Chem.*, **5**, 281 (1980).

[134] P.M. TREICHEL, *Adv. Organometal. Chem.*, **11**, 21 (1973); P.M. TREICHEL, J.J. BENEDICT, R.W. HESS, J.P. STENSON, *Chem. Comm.*, 1627 (1970).

[135] See, *e.g.*, A.J. THOMSON, R.N.F. THORNELEY, *Chem. Britain*, 176 (1982).

[136] U.K. SHAH, W.J. BRILL, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 3249 (1977).

[137] J. Rawlings, V.K. SHAH, J.R. CHISNELL, W.J. BRILL, R. ZIMMERMAN, E. MUNCK, W.H. ORME-JOHNSON, *J. Biol. Chem.*, **253**, 1001 (1978).

[138] E. MUNCK, H. RHODES, W.H. ORME-JOHNSON, L.C. DAVIS, W.J. BRILL, U.K. SHAH, *Biochim. Biophys. Acta*, **400**, 32 (1975).

[139] B.M. HOFFMAN, J.H. ROBERTS, W.H. ORME-JOHNSON, *J. Amer. Chem. Soc.*, **104**, 860 (1982).

[140] W.E. NEXTON, *et al.*, eds., "Current Perspectives in Nitrogen Fixation", Australian Academy of Sciences, Camberra, 1981, p. 30, p. 71.

[141] S.P. CRAMER, W.O. GILLUM, K.O. HODGSON, L.E. MORTENSON, E.I. STIEFEL, J.R. CHISNELL, W.J. BRILL, U.K. SHAH, *J. Amer. Chem. Soc.*, **100**, 3814 (1978); S.P. CRAMER, K.O. HODGSON, W.O. GILLUM, L.E. MORTENSON, *ibid.*, **100**, 3398 (1978).

[142] LU JIAXI, "Composite String Bag Cluster Model for the Active Centre of Nitrogenase", *in* "Nitrogen Fixation", Vol. I, W.H. Newton, W.H. Orme-Johnson, eds., University Park Press, 1980, p. 343.

[143] K. TANAKA, Y. HOZUMI, T. TANAKA, *Chem. Letters*, 1203 (1982).

[144] K. TANAKA, Y. IMASAKA, M. TANAKA, T. TANAKA, M. HONJO, T. TANAKA, *J. Amer. Chem. Soc.*, **104**, 4258 (1982).

[145] K. TANAKA, M. TANAKA, T. TANAKA, *Chem. Letters*, 895 (1981).

[146] W.H. ARMSTRONG, P.K. MASCHARAK, R.H. HOLM, *Inorg. Chem.*, **21**, 1700 (1982).

[147] P.K. MASCHARAK, W.H. ARMSTRONG, Y. MIZOBE, R.H. HOLM, *J. Amer. Chem. Soc.*, **105**, 475 (1983).

RESUMO

O presente trabalho constitui uma tentativa de caracterização dos centros de metais de transição com capacidade coordenadora de diazoto e uma reflexão sobre o modo como se manifestam as suas propriedades na activação desta espécie. Embora existam publicados vários artigos recentes de revisão sobre complexos de diazoto [1-4] não foi ainda nenhum elaborado sob esta perspectiva, pelo que o trabalho complementa, deste modo, assuntos tratados, necessariamente com mais pormenor, nesses artigos. Após um breve introdução à importância e actualidade da fixação de azoto, descreve-se a constituição dos centros de metais de transição coordenadores de diazoto, procede-se à sua caracterização estrutural e são apresentadas as suas propriedades electrónicas (riqueza electrónica, capacidade aceitadora σ e retrodoadora π, polarizabilidade) fundamentais àquela coordenação e é discutida a sua dependência em relação ao grupo periódico do metal central e ao efeito de co-ligandos.

Descreve-se em seguida o comportamento químico destes centros, em geral determinado por factores electrónicos e estruturais (nomeadamente o carácter insaturado derivado da labilidade do ligando diazoto), após o que são tratadas as formas de activação de N_2 por coordenação, em complexos poli-ou mono-nucleares. É analisada a dependência desta activação em relação ao grupo periódico do metal de transição e à presença de iões de metais representativos de baixa electronegatividade.

É ainda proposto o uso de isonitrilos como modelos potenciais de coordenação e reactividade do diazoto e apresentados modelos estruturais e de reactividade do centro enzimático fixador de azoto.

NOTA DO EDITOR

Este artigo de revisão foi submetido à Revista Portuguesa de Química a convite do Editor e é baseado na lição de síntese proferida pelo Prof. Doutor Armando J.L. Pombeiro no âmbito das provas de agregação realizadas em 21-22 de Dezembro de 1984 no Instituto Superior Técnico.

THE GENERALIZATION OF THE HILDEBRAND RELATIONSHIP BETWEEN THE ENTHALPY OF VAPORIZATION AND THE SURFACE TENSION OF LIQUIDS

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INTRODUCTION

The physical properties of liquids such as surface tension, the heat of vaporization, internal pressure, cohesive energy density and static permittivity are macroscopic properties, all of which reflect intermolecular interactions.

The existence of relationships between some of these quantities is the direct consequence of the fact that all these quantities depend on the same interactions at molecular level. Research into such relationships is therefore a way of obtaining a better insight into the knowledge of the liquid structure as far as these relations can be explained on the basis of theoretical models. Many of the known relationships were discovered empirically and explained *a posteriori* on a theoretical basis. This is the case 1°) for COOMBER'S relationship [1,2] between the static permittivity and the internal pressure of non-polar liquids, 2°) for PAPAZIAN'S relationship [3,4] between surface tension and static permittivity, also relative to non-polar liquids and 3°) the relationship (equality) between the internal pressure and the cohesive energy density of several liquids described by HILDEBRAND [5-7].

Previously, Hildebrand pointed out the existence of a linear relationship between the free energy associated with the molar surface expansion of a liquid, $\gamma_0 S$, and the energy of vaporization [8], ΔE_V (γ_0: surface tension, $S = 4\pi r^2 N_{Av}$: molar area of an ensemble of spherical molecules or radius r). For spherical molecules, S is proportional to $V^{2/3}$ ($V = \frac{4\pi}{3} r^3 N_{Av}$: molar volume) and therefore, a proportionality can also be predicted between ΔE_V and $\gamma_0 . V^{2/3}$.

Such a relationship is in fact observed for non polar liquids [5] and a justification of this relationship has been derived by SCHONHORN [9] DAVIS and SCRIVEN [10] and VAVRUCH [11] on the basis of statistical thermodynamics. This theoretical approach leads to a linear relation between the cohesive energy density $\frac{\Delta E_V}{V}$ (where V is the molar volume) and $\gamma_0 . V^{-1/3}$ but the theoretical model does not explain the deviations to the Hildebrand's empirical relationship observed for polar and associated liquids. LEE [12] has tried to modify Hildebrand's empirical relationship in order to make it applicable, even in the case of polar and associated solvents.

Unfortunately, as BEERBOWER [13] observes, this modification breaks down the dimensional coherence of the relationship.

BEERBOWER [13] has also studied this problem by using a multiparametric empirical relationship. This approach does not bring any new fundamental results but the behaviour of approximately a hundred liquids can be described by the empirical equation.

In the present work we would like to attempt a theoretical relation between surface tension, γ_0, and vaporization enthalpy, ΔH_V, by focusing out attention on a single molecule situated in a cavity which, itself, is surrounded by a liquid which is considered to be a continuum.

THEORETICAL TREATMENT

From the pioneering work of STEFAN [14], followed by that of EYRING [15], it is easy to show that the energy required to create a spherical cavity in a liquid (with a volume equal to the molecular volume: V/N_{Av}) is equal to the molecular energy of vaporization ($\Delta E_V/N_{Av}$) in the same conditions of temperature and pressure.

This conclusion is confirmed by calculations of the interactions of a single molecule with its all surroundings [16] and appears valid for all kinds of liquids (apolar, polar and associated). Strictly speaking, the treatment which leads to this result neglects the difference between the kinetic energy of the molecules in the bulk of the liquid, at its surface or in its gas phase. As far as different liquids can be compared with each other, the error associated with this omission seems negligible, however.

The work $\tau(r)$ associated with the formation of a spherical macroscopic cavity of radius r in a liquid can be described as the sum of two terms (see for example [17])

$$\tau(r) = \frac{4}{3}\pi r^3 p + 4\pi r^2 \gamma_0 \qquad (1)$$

where p is the external pressure. Under atmospheric pressure, the first term is nebligible compared with the second one for $r < 10^3$ Å. We therefore have

$$\tau(r) = 4\pi r^2 \gamma_0 \qquad (2)$$

If the cavity is formed at constant pressure, $\tau(r)$ is a Gibbs free energy.

We can assume that equation (2) also holds for a cavity of microscopical size if the macroscopic surface tension is corrected in order to take into account the curvature of the surface. On the basis of the work of TOLMAN [17], KIRKWOOD and BUFF [18], KOENIG [19], WAKESHIMA [20], EYRING [21] and SINANOGLU [22], it appears possible to apply to γ_0 a multiplicative corrective factor K(r) to obtain the correlaction due to the curvature of the surface. In these conditions, the Gibbs energy associated with the formation of a mole of cavities with volumes equal to the molecular volume is expressed by

$$\bar{G}_{cav} = 4\pi r^2 N_{Av} \gamma_0 K \qquad (3)$$

From the identity $H = G - T(\frac{\partial G}{\partial T})_P$ it is easy to derive the corresponding relationship giving $\bar{H}_{cav}$ i.e.

$$\bar{H}_{cav} = K^H N_{Av} 4\pi r^2 \gamma_0 \{1 - T(\frac{1}{\gamma_0}\frac{\partial \gamma_0}{\partial T} + \frac{2}{3}\alpha)\} \qquad (4)$$

where K^H itself is expressed by

$$K^H = K - \frac{T}{1 - T(\frac{1}{\gamma_0}\frac{\partial \gamma_0}{\partial T} + \frac{2}{3}\alpha)}\frac{\partial K}{\partial T} \qquad (5)$$

α is the coefficient of the thermal expansion of the liquid.

On the basis of the equality stated above between $\bar{H}_{cav}$ and ΔH_V, it therefore appears that equation (4) must be looked upon as a theoretically well-founded generalized from of Hildebrand's relationship.

If the product $K^H.A$, i.e.

$$K^H.\,A = K^H.\,\{1 - T(\frac{1}{\gamma_0}\frac{\partial \gamma_0}{\partial T} + \frac{2}{3}\alpha)\}$$

remains constant for a series of liquids, a proportionality must exist between ΔH_V and $4\pi r^2 \gamma_0$. On the other hand, if $K^H.A$ varies from one particular solvent to another, the proportionality between ΔH_V and $4\pi r^2 \gamma_0$ disappears.

The analysis we made for more than fifty pure liquids shows different kinds of behaviour. Apolar solvents are characterized by K^H and A values which are more or less constant leading to constant $K^H.A$ values and, therefore, to a excellent proportionality between ΔH_V and $4\pi r^2 \gamma_0$ (see Table 1). K^H and A values for the other liquids can be compared with those determined for apolar liquids.

Such a comparison makes it possible to analyse the origin of the deviations with respect to Hildebrand's relationship. In the case of dimethylsulfoxyde and formamide, the high values of K^H are partially compensated for by the small values of A, but a discrepancy still exists with regards to Hidebrand's relationship. Alcohols are characterized by very high K^H values whereas nitromethane and dimethylformamide are characterized by high A values. Low A values are observed for aniline and formic acid.

Table 1
K^H and A parameters for organic liquids at 25°C

Solvent	K^H	A	$K^H.A$
n-hexane	0.687	2.428	1.668
cyclohexane	0.654	2.229	1.457
n-heptane	0.718	2.260	1.622
methylcyclohexane	0.690	2.129	1.469
n-octane	0.738	2.177	1.608
carbon tetrachloride	0.655	2.194	1.437
methylene chloride	0.649	2.441	1.584
chloroform	0.693	2.211	1.532
t-butyl chloride	0.653	2.525	1.649
chlorobenzene	0.778	1.872	1.456
carbon disulphide	0.647	2.143	1.387
benzene	0.660	2.227	1.470
toluene	0.711	2.080	1.479
mesitylene	0.800	1.908	1.526
dioxane	0.678	2.175	1.475
diethyl ether	0.677	2.688	1.820
cyclohexanone	0.871	1.680	1.463
acetone	0.826	2.298	1.898
acetonitrile	0.973	2.086	2.030
nitromethane	0.750	2.401	1.800
dimethylformamide	0.726	2.505	1.819
dimethylsulphoxide	0.999	1.758	1.756
formamide	1.826	1.289	2.354
methanol	1.819	1.919	3.489
ethanol	1.625	1.931	3.139
n-propanol	1.513	1.845	2.792
t-butyl alcohol	1.227	2.232	2.738
n-octanol	1.290	1.819	2.347
aniline	1.015	1.549	1.572
formic acid	0.692	1.683	1.164
acetic acid	0.710	1.985	1.409
water	1.359	1.598	2.172

K^H values were obtained from eq. (4) taking into account the equality between H_{cav} and ΔH_v

CONCLUSIONS

Our theoretical treatment leads to a generalization of Hidebrand's relationship. Equation (4) has the great advantage of permitting the determination of K^H from easily obtainable experimental parameters. Such a procedure has been used with success in a previous work [23]. The importance of this K^H factor has been ignored by ABDULNUR [24] in his attempt to obtain a linear relationship between H_V and $V^{2/3}\gamma_0 A$. Our treatment also allows us to classify solvents according to the origin of the deviation with respect to the linear relationship ("abnormal" values fo K^H and/or A).

Our present aim is to give interpretation at molecular level of the high (or low) K^H and A values which characterize non-apolar solvents.

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REFERENCES

[1] D.I. COOMBER, *Trans. Faraday Soc.*, **35**, 304 (1939).
[2] G.H. MEETEN, *Nature*, **223**, 827 (1969).
[3] H.A. PAPAZIAN, *J. Am. Chem. Soc.*, **93**, 5634 (1971).
[4] C.F. HOLMES, *J. Am. Chem. Soc.*, **95**, 1014 (1973).
[5] J.H. HILDEBRAND, R.L. SCOTT, The solubility of non-electrolytes (Dover, New York, 1964).
[6] E.B. BAGLEY, T.P. NELSON, S.A. CHEN, J.W. BARLOW, *Ind. Eng. Chem., Fundamentals*, **10**, 27 (1971).
[7] E.B. BAGLEY, T.P. NELSON, J.W. BARLOW, S.A. CHEN, *Ind. Eng. Chem., Fundamentals*, **9**, 93 (1970).
[8] J.H. HILDEBRAND, *J. Chem. Soc.*, **41**, 1067 (1949).
[9] H. SCHONHORN, *J. Phys. Chem.*, **71**, 4578 (1967).
[10] H.T. DAVIS, L.E. SCRIVEN, *J. Phys. Chem.*, **80**, 2805 (1976).
[11] I. VAVRUCH, *J. Colloid Interface Sci.*, **63**, 600 (1978).
[12] L.H. LEE, *J. Paint Technology*, **42**, 365 (1970).
[13] A. BEEBOWER, *J. Colloid Interface Sci.*, **35**, 126 (1971).
[14] J. STEFAN, *Wied. ann.*, **29**, 655 (1886).
[15] H. EYRING, *J. Chem. Phys.*, **4**, 283 (1936).
[16] M.J. HURON, P. CLAVERIE, *J. Phys. Chem.*, **76**, 2123 (1972); *ibid.*, **78**, 1862 (1974).
[17] R.C. TOLMAN, *J. Chem. Phys.*, **16**, 758 (1948); *ibid.*, **17**, 118 (1949); *ibid.*, **17**, 333 (1949).
[18] J.G. KIRKWOOD, F.P. BUFF, *J. Chem. Phys.*, **17**, 338 (1949); *ibid.*, **18**, 991 (1950).
[19] F.O. KOENIG, *J. Chem. Phys.*, **18**, 449 (1950).
[20] M. WAKESHIMA, *J. Phys. Soc. Japan*, **16**, 6 (1961).
[21] D.S. CHOI, M.S. JOHN, H. EYRING, *J. Chem. Phys.*, **53**, 2608 (1970).
[22] O. SINANOGLU, in "Molecular Associations in Biology", ed. B. Pullman (Academic Press, New York, 1969), p. 427.
[23] J.J. MOURA RAMOS, M. LEMMERS, M.L. STIEN, R. OTTINGER, R. REISSE, *J. Chem. Research (M)*, 0658 (1977).
[24] S.F. ABDULNUR, *J. Am. Chem. Soc.*, **98**, 4039 (1976).

ABSTRACT

The Hidebrand relationship which relates the enthalpy of vaporization to the surface tension of a liquid is derived on the basis of a theoretical model. Moreover, a generalized expression is obtained which makes it possible to explain deviations from the linear Hildebrand relationship. The theoretical model itself takes into account the work which is associated with the formation of cativities in liquids. A correct estimation both of this work and of the corresponding enthalpy contribution is important in the description of the dissolution process of a solute in a solvent.

RESUMO

Generalização da relação de Hildebrand entre a entalpia de vaporização e a tensão superficial de Líquidos.

A expressão de Hildebrand que relaciona a entalpia de vaporização com a tensão superficial de um líquido é deduzida neste trabalho a partir de um modelo teórico. Obtém-se assim uma expressão generalizada que permite dar uma explicação dos desvios à relação linear de Hildebrand. O modelo utilizado baseia-se no cálculo do trabalho associado à formação de cavidades em líquidos. O cálculo correcto deste trabalho, assim como o da contribuição entálpica correspondente, é importante para a descrição do processo de dissolução de um soluto num solvente.

NATO ADVANCED STUDY INSTITUTE

SOLID STATE BATTERIES

SOLID-STATE ELECTROCHEMICAL FUNDAMENTALS AND THEIR APPLICATION TO BATTERIES AND RELATED DEVICES

SEPTEMBER 2 - 14, 1984 ALCABIDECHE - CASCAIS, PORTUGAL

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