Stereospecific Exchange Reactions of the Nitrosyl Cations *cis*-$[M(NO)_2(MeCN)_4]^{2+}$ (M=Mo or W)

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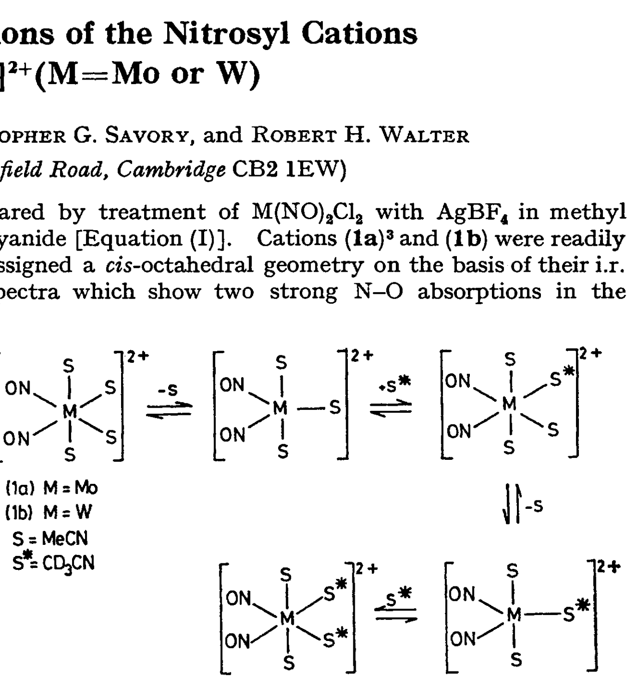
Summary The cations *cis*-$[M(NO)_2(MeCN)_4)]^{2+}$ (M = Mo or W) undergo stereospecific exchange of the MeCN ligands *via* a dissociative pathway.

In recent communications Graham and his co-workers[1] described the stereospecific exchange of carbon monoxide in the complexes *cis*-$Ru(CO)_4(SiCl_3)_2$ and *cis*-$Os(CO)_4(SiCl_3)_2$. This exchange occurs *via* a dissociative pathway and its stereospecificity was attributed to the unusual rigidity of the five-co-ordinate intermediate complex. However, because of the lack of knowledge of axial *vs* equatorial preferences of the $SiCl_3$ ligand in trigonal bipyramidal complexes Graham was unable to comment further on this unusual rigidity. We now report studies on the dinitrosyl cations *cis*-$[M(NO)_2(MeCN)_4]^{2+}$ (M = Mo or W) which undergo ligand (MeCN) exchange of the same type observed for *cis*-$Ru(CO)_4(SiCl_3)_2$ and *cis*-$Os(CO)_4(SiCl_3)_2$. In this case, however, and in contrast to $SiCl_3$, the stereochemical preference and π-bonding requirements of the NO ligand in five-co-ordinate complexes are better understood.[2]

The cation *cis*-$[Mo(NO)_2(MeCN)_4]^{2+}$ (**1a**) has been previously reported,[3] but the tungsten analogue, *cis*-$[W(NO)_2(MeCN)_4]^{2+}$ is new. In this work both cations were prepared by treatment of $M(NO)_2Cl_2$ with $AgBF_4$ in methyl cyanide [Equation (I)]. Cations (**1a**)[3] and (**1b**) were readily assigned a *cis*-octahedral geometry on the basis of their i.r. spectra which show two strong N–O absorptions in the region 1600—1800 cm^{-1} and their ^1H n.m.r. spectra in $MeNO_2$ or $PhNO_2$ which exhibit two resonances of equal intensity in the region of τ 7·4. On addition of CD_3CN to a solution of (**1b**) in $MeNO_2$ one signal (at τ 7·44) diminishes in intensity until eventually after *ca.* 1h at 25° it disappears completely. The second signal at τ 7·36 remains virtually unchanged throughout this process and significantly the half-life for MeCN exchange is essentially independent of CD_3CN concentration indicating that the rate of exchange is first order with respect to acetonitrile. Therefore

$$M(NO)_2Cl_2 \xrightarrow[MeCN]{AgBF_4} \underset{(\mathbf{1})}{[M(NO)_2(MeCN)_4]^{2+}} \qquad (I)$$

a; M = Mo
b; M = W

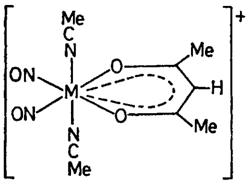


Scheme

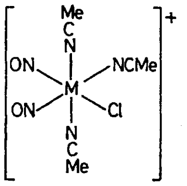
exchange must take place *via* a rate determining dissociative step (Scheme).

Exchange may also be conveniently studied in neat CD_3CN or $PhNO_2$ in the presence of at least ten-fold excess of CD_3CN. Half-life times were determined by integration of the resonances due to co-ordinated MeCN *vs* the resonance due to added Me_2SO_4.

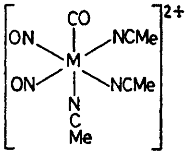
Over much longer periods (*ca.* 24h) and at higher temperatures complete exchange occurs. Cation (**1a**) behaves similarly. In contrast, the chromium cation $[Cr(NO)_2(MeCN)_4]^{2+}$ for which a *trans*-stereochemistry has been established,[4] does not undergo exchange. These observations are obviously closely related to those of Graham and his co-workers.[1]



(2)



(3)

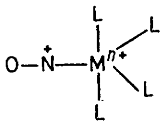


(4)

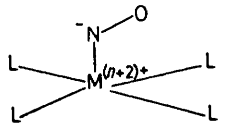
Throughout this discussion we have assumed that the two labile MeCN ligands are those *trans*-disposed to the two NO groups. This is reasonable not only since NO is known to be a strongly *trans*-labilising ligand but also because the cation $[M(NO)_2(acac)(MeCN)_2]^+$ for which structure (**2**) may be unambiguously assigned on the basis of i.r. and ^1H n.m.r. spectroscopic data does not undergo appreciable MeCN exchange at 25° and complexes (**3**) and (**4**)[3] which are thought[5] to possess the structures shown undergo exchange of one and two methyl cyanide ligands respectively.

Although stereochemically rigidity is not a feature exhibited by the great majority of five-co-ordinate complexes or intermediates it is an emerging aspect of five-co-ordinate nitrosyl species[6] and may be reconciled with the valence tautomerism exhibited by the NO group.

In the structures of the majority of five-co-ordinate nitrosyl complexes examined so far the (formally) NO^+ ligand (A) occupies an equatorial site in a trigonal bipyramidal structure with linear M–N–O arrangement[7] whereas the (formally) NO^- ligand (B) prefers the apical site in the square pyramidal geometry with a bent M–N–O system ($\angle$M–N–O *ca.* 120°).[8]



(A)



(B)

Interchange between these two geometries, which has been observed[6] for $Co(NO)X_2(R_3P)_2$ complexes, is slow in comparison with other five-co-ordinate systems and the barrier of interconversion may be reasonably associated with interchange of the type $A \rightleftarrows B$. On the reasonable assumption that the more strongly π-bonding NO ligands would prefer to occupy equatorial positions the rigidity of the five-co-ordinate, 16-electron, intermediate $[M(NO)_2(MeCN)_3]^{2+}$ is, therefore, understood.

These exchange reactions are significant not only for the stereospecificity which they show but also because they occur *via* a dissociative pathway. In general, metal nitrosyl complexes undergo exchange *via* an associative pathway because of the ability of the NO ligand to function as either a (formally) one electron donor or (formally) a three electron donor.[9] It is interesting to note that not all reactions of $M(NO)_2^{2+}$ (M = Mo or W) systems follow a dissociative pathway but in cases where reaction occurs *via* association loss of an NO ligand is observed.[5]

(*Received*, 21*st June* 1974; *Com.* 727.)

[1] R. K. Pomeroy and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **12**, 272, 274.

[2] S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 1974, **13**, 770 and refs. therein.

[3] M. Green and S. H. Taylor, *J.C.S. Dalton*, 1972, 2629.

[4] N. G. Connelly and L. F. Dahl, *Chem. Comm.*, 1970, 880.

[5] B. F. G. Johnson, C. G. Savory, and R. Walter, unpublished observations.

[6] See *e.g.* J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304.

[7] See *e.g.* G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 119.

[8] See *e.g.* D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

[9] F. Basolo, *Chem. Ber.*, 1969, **5**, 505.