The Nitrogen-15 N.M.R. Criterion of Bond Angle in Nitrosyl Complexes

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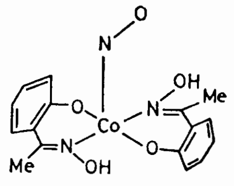
Deshielding of 350—700 p.p.m. is reported for nitrogen in strongly bent nitrosyl groups (∠MNO *ca.* 120°) in complexes of Rh or Co, compared with linear nitrosyl groups in complexes of Fe, Co, Ru, and other transition metals.

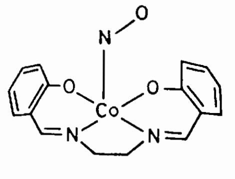
The nitrosyl ligand is unusually versatile, co-ordinating (formally) as NO^+ to give a linear MNO group, as NO^- with ∠MNO *ca.* 120°, or with intermediate structures. The notation $\{M(NO)_m\}^n$ allows for ambiguities,[1] n being the sum of electrons in the d(M) and π^*(NO) orbitals. As well as being structurally important the bond angle affects the reactivity of the NO ligand and the metal,[2] since nitrogen is susceptible to electrophilic attack in the bent nitrosyl form, and transfer of a d electron pair from the metal to nitrogen may facilitate co-ordination by a base.

So far *X*-ray crystallography has been the final arbiter of the MNO structure, but this is limited to solids. In vibrational spectroscopy, the correlation of the bond angle with the NO stretching frequency is unreliable, as the values in Table 1 illustrate. However, the potential of nitrogen n.m.r. spectroscopy as a criterion of geometry, particularly in solution, was revealed by the patterns of nitrogen shifts in organic functional groups: nitrogen carrying a lone pair in a delocalized system is strongly deshielded by low energy $n(N) \rightarrow \pi^*$ circulations in the magnetic field,[3] *C*-nitroso-compounds resonating at very low field. Deshielding by up to 350 p.p.m. was then observed for ligating nitrogen in rhodium diazenido-complexes in which the Rh–N=N–Ar group is doubly bent, with ∠RhNN *ca.* 125°, compared with diazenido-complexes of Mo, W, Re, or Ru where MNN is linear.[4]

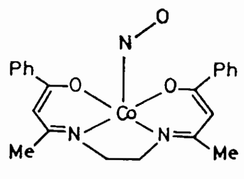
We have now observed deshieldings up to 700 p.p.m. for nitrogen in strongly bent apical nitrosyl groups in square pyramidal $\{M(NO)\}^8$ complexes of cobalt or rhodium, compared with linear nitrosyls in a range of complexes, as shown in Table 1. Some linear nitrosyls have been measured in ^{14}N resonance,[3] and some in ^{15}N resonance in natural abundance in a (180 MHz) widebore spectrometer,[5] which we also achieved for $[Na_2Fe(CN)_5(NO)]$. However, in general the bent nitrosyl groups and rhodium complexes needed high ^{15}N enrichment (99%) owing to solubility and relaxation problems, and were run on a 400 MHz spectrometer.



(1) [Co(NO)(ketox)$_2$]



(2) [Co(NO)(salen)]



(3) [Co(NO)(benacen)]

Table 1. ^{15}N N.m.r. measurements of nitrosyl complexes.

	n^a	Co-ordination geometry	Solvent	$\delta(^{15}NO)^b$/p.p.m.	$\nu(^{14}NO)^c$/cm^{-1}
Linear nitrosyls					
trans-$[RuCl_3(^{15}NO)(PPh_3)_2]$	6	Octahedral	CH_2Cl_2	−36.7	1876
trans-$[RuCl_3(^{15}NO)(PMePh_2)_2]$	6	Octahedral	CH_2Cl_2	−30.9	1845
$Na_2[Fe(CN)_5(^{15}NO)]^d$	6	Octahedral	H_2O	−13.5	1944
$[Co(CO)_3(NO)]^e$	10	Tetrahedral	$CHCl_3$	14	1805
$[W(\eta^5\text{-}C_5H_5)(CO)_2(NO)]^{d,f}$	6	Piano-stool	$CHCl_3$	16.5	1655
trans-$[RhCl(^{15}NO)(PPr^i_3)_2]$ (ClO_4)	8	Square planar	$CHCl_3$	24.0	1842
$[Mo(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(NO)]^{d,f}$	6	Piano-stool	$CHCl_3$	35.4	1607
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)]^{d,f}$	6	Piano-stool	$CHCl_3$	37.6	1663
$[Cr(\eta^5\text{-}C_5H_5)(CO)_2(NO)]^{d,f}$	6	Piano-stool	$CHCl_3$	49.0	1680
Bent nitrosyls					
trans-$[RhCl(CO)(^{15}NO)(PPr^i_3)_2]$ (ClO_4)	8	Square pyramidal	CH_2Cl_2	368.2^g	1712
trans-$[RhCl(^{15}NO)(^{15}NO_2)(PR_3)_2]$					
R = cyclohexyl	8	Square pyramidal	CH_2Cl_2	466.1	1684, 1657
R = Pr^i	8	Square pyramidal	CH_2Cl_2	467.6	1684, 1657
R = Ph	8	Square pyramidal	CH_2Cl_2	481.5	1657, 1629
(3)	8	Square pyramidal	Me_2SO	723.0	1635
(2)	8	Square pyramidal	Me_2SO	736.9	1624
(1)	8.	Square pyramidal	Me_2SO	740.3^h	1675
			$CHCl_3$	717.3^d	

[a] In $\{(MNO)\}^n$ (see the text). [b] Relative to neat liquid nitromethane, positive downfield, measured at 25 °C. [c] Nujol mull, unless otherwise specified. [d] ^{15}N N.m.r. measurement in natural abundance, 180 MHz spectrometer. [e] ^{14}N N.m.r. measurement by R. Bramley, B. N. Figgis, and R. S. Nyholm, *J. Chem. Soc. A*, 1967, 861. [f] Ref. 5, i.r. spectra measured in CH_2Cl_2. [g] $^1J(Rh^{15}N)$ 4.5 Hz. [h] $^1J(Co^{15}N)$ 9 Hz.

The bent nitrosyl groups in Table 1 have been characterised as such in the solid state by *X*-ray single crystal analysis; ∠RhNO is *ca.* 120° for the rhodium nitrosyl groups, which are disordered, as also are the non-phosphine ligands in the basal plane.[6] The cobalt nitrosyl groups are not disordered: ∠CoNO is 126° for (**1**),[7] 128° for (**2**),[8,9] and 123° for (**3**).[10]

The nitrogen shielding in the cobalt complexes is the lowest yet observed for compounds without unpaired electrons.[3] The cobalt complexes are black, and it is likely that the strong deshielding correlates with very low energy magnetic-dipole-allowed excitations in the electronic spectrum, which we are investigating. (Of the bent nitrosyl complexes of rhodium, the one with chloro- and carbonyl-coligands is orange, and those with chloro- and nitro-coligands are green.) Interestingly, the cobalt salen complex (**2**) is known[8] to show temperature-independent paramagnetism, which is found in compounds without unpaired electrons if the positive term in Van Vleck's expression for the magnetic susceptibility[11] outweighs the negative (diamagnetic) term, as for compounds such as MnO_4^-. This therefore correlates with a very small ligand-field splitting, and strong nuclear magnetic deshielding.

The small metal–nitrogen coupling constants reflect the presence of a lone pair on nitrogen, since this makes a contribution to the Fermi contact term which is opposite in sign to the contribution from the bonding electrons and so tends to cancel this.[12]

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