Electron Spin Resonance Studies of Some Chromium(I) Nitrosyl Complexes

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GRAY and co-workers have recently presented a molecular-orbital energy level scheme for the class of metal nitrosyls ML_5NO, where (L) is any ligand, which contain one strong M–NO bond dominating the overall ligand field.[1] The other five ligands (L) act as perturbations, modifying the spacing of the energy levels by differing degrees depending on the specific complex. This scheme

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[1] H. B. Gray, P. T. Manoharan, J. Pearlman, and R. F. Riley, *Chem. Comm.*, 1965, 62, and references therein.

has been successfully applied to several pentacyanonitrosyl complexes,[2,3] but has not previously been applied to a series of complexes ML_5NO with a common central metal-ion (M) and differing ligands (L). We now report e.s.r. data (Table) obtained in fluid and rigid aqueous solution, for the species $[Cr(CN)_5NO]^{3-}$, $[Cr(NO)(NH_3)_5]^{2+}$ and $[Cr(NO)(H_2O)_5]^{2+}$ and discuss our results in terms of this scheme.

TABLE

Electron Spin Resonance Results for Chromium(I) Nitrosyl Complexes in Aqueous Solution: A values in gauss

Species	g_{av}	$g_{\perp}$	$g_{\parallel}$	$A_{iso}(^{53}Cr)$	$A_{iso}(^{14}N)$	$\bar{\nu}$(N–O)cm^{-1}*
$[Cr(CN)_5NO]^{3-}$	1·994	2·0052†	1·9745†	18·46	5·26	1645vs
$[CrNO(NH_3)_5]^{2+}$	1·980	—	—	21·7	—	1670vs
$[CrNO(H_2O)_5]^{2+}$	1·966	1·991‡	1·916‡	25·3	6·45	1747vs

* Infrared data, taken in mulls, Ref. 5.
† Dilute single crystal study, Ref. 7.
‡ Rigid solution 113°K, all other data from fluid solution.

The compounds were prepared and purified as described in the literature.[4,5,6] E.s.r. spectra were taken using freshly prepared solutions to minimise the possibility of hydrolysis.

The e.s.r. spectrum of $[Cr(NO)(NH_3)_5]^{2+}$ in aqueous solutions consists of one broad main resonance with two weak side-bands, the latter comprising the outer pair of the four resonances resulting from interaction with the ^{53}Cr nucleus. Hyperfine splitting due to ^{14}N of the nitrosyl group is not observed because of further hyperfine interaction with the five NH_3 ligands. However partially resolved hyperfine structure observed in the spectrum of a dimethylformamide solution of the complex shows that such interactions are present. Although it is not possible at this stage to make a clear assignment of such a spectrum, it is interesting to note that this is the first example of NH_3 ligand (^{14}N) hyperfine splitting ever recorded. In the case of $[Cr(NO)(H_5O)_5]^{2+}$ where the H_2O ligands contain ^{16}O ($I = 0$) the triplet due to the nitrosyl ligand is easily resolved. Rigid solution spectra of $[CrNO(H_2O)_5]^{2+}$ give $g_{\parallel}$ and $g_{\perp}$ and show the complex to have axial symmetry indicating a linear M–N–O group as predicted by Gray *et al.* for a d^5NO^+ structure.[1] Values obtained for g_{av}, A_{iso} (^{53}Cr) and A_{iso} (^{14}N) for the three complexes are of the same order thus supporting the suggestion of Gray *et al.* that all possess similar d^5NO^+ structure and $e^4b_2^1 = {}^2B_2$ ground states[1]. We find however, that all three e.s.r. parameters show significant variation with change of ligand (L), indicating considerable perturbation of the molecular orbital energy levels by these ligands.

In each case mixing of the ground state and low excited state $e^3b_2^2 = {}^2E$ *via* spin–orbit coupling places unpaired spin density on the NO ligand since the $e(xz,yz)$ molecular orbital includes a contribution from π^*NO. The unpaired spin density on the NO and hence the value of A_{iso} (^{14}N) will also increase with increasing π^*NO character in the filled $e(xz,yz)$ molecular orbital, Furthermore the value of $\bar{\nu}$(N–O) should decrease with increasing $M \rightarrow \pi^*NO$ interaction as previously confirmed[3] for $[Mn(CN)_5NO]^{2-}$ and $[Cr(CN)_5NO]^{3-}$. In the complexes being studied $A_{iso}(^{14}N)$ and $\bar{\nu}$(N–O) increase simultaneously suggesting that variation of π^*NO character in the $e(xz,yz)$ molecular orbital is not the dominant factor in deciding the magnitude of A_{iso} (^{14}N). We consider that increased π-bonding strength of the ligands (L) gives increased separation of the levels $e(xz,yz)$ and $b_2(xy)$ thus reducing the degree of spin–orbit coupling and hence decreasing the unpaired electron density on the NO ligand with a corresponding reduction of $A_{iso}(^{14}N)$.

Increasing π-bonding ability of the ligands (L) will increase π(L) character in the $b_2(xy)$ orbital at the expense of metal d-orbital character and hence lead to a decrease in $A_{iso}(^{53}Cr)$ as observed. This is confirmed by the departure of g_{av} from a value close to the spin-only value, and a corresponding increase in the difference $(g_{\perp} - g_{\parallel})$ as the π-bonding ability of the ligands (L) decreases and the unpaired electron is increasingly localised in the metal—nitrosyl bond.

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[2] E. F. Hockings and I. Bernal, *J. Chem. Soc.*, 1964, 5029.
[3] P. T. Manoharan and H. B. Gray, *Chem. Comm.*, 1965, 324.
[4] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1959, 872.
[5] W. P. Griffith, *J. Chem. Soc.*, 1963, 3286.
[6] M. Ardon and J. L. Herman, *J. Chem. Soc.*, 1962, 507.
[7] J. J. Fortman and R. G. Hayes, *J. Chem. Phys.*, 1965, **43**, 15.

It is interesting to note that the optical band of $[CrNO(NH_3)_5]^{2+}$ at 4600 Å shows structure even in solution. A room-temperature examination of the aqueous solution shows eleven components separated by about 500 cm^{-1}. Since the *E*-vibration of the $Cr–NH_3$ bonds has a frequency of 500 $cm.^{-1}$, it is interesting to speculate that this is vibrational structure. Should further work demonstrate that this is the case, the results would be in accordance with the postulated bonding scheme of Gray *et al.*,[1] where it was predicted that the second optical band should couple to *E*-vibrations.

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