Electronic Structures of Some Transition-metal Nitrosyl Complexes

By H. B. GRAY and P. T. MANOHARAN

(*Department of Chemistry, Columbia University, New York, U.S.A.*)

and J. PEARLMAN and R. F. RILEY

(*Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York, U.S.A.*)

MCNEIL, RAYNOR, and SYMONS recently suggested[1] that the d orbital ordering $xz,yz < xy < x^2 - y^2 < z^2$ we suggested[2,3] for $Fe(CN)_5NO^{2-}$, in which the Fe–N–O is known to be linear,[4] should be modified to $xz,yz < xy < z^2 < x^2 - y^2$ to accommodate certain e.s.r. results. We present here a summary of extensive optical spectral results for $Fe(CN)_5NO^{2-}$; these results strongly suggest that it is not z^2, but the level derived from π^*NO, that lies much lower than previously suspected.[2,3]

A quantitative molecular orbital calculation of $Fe(CN)_5NO^{2-}$ gives our d level ordering [2,3] but with the e symmetry level derived from π^*NO between xy and $x^2 - y^2$, as shown in the Figure.

$a_1(z^2)$

$b_1(x^2 - y^2)$

$e(\pi^*NO)$

$b_2(xy)$

$e(xz,yz)$

Detailed analysis of the optical absorption spectra of $Fe(CN)_5NO^{2-}$ in liquid (300° K) and solid (77° K) solutions and in a single $Na_2Fe(CN)_5NO,2H_2O$ crystal is consistent with the calculated energy levels. Comparison of spectra at 77° and 300° K shows that the first two electronic absorption bands, at 20,080 cm.$^{-1}$ ($\epsilon = 8$) and 25,380 cm.$^{-1}$ ($\epsilon = 24$) are slightly more intense at the lower temperature and thus are orbitally allowed. Further, the 20,080 cm.$^{-1}$ band is x,y polarised and the 25,380 cm.$^{-1}$ band is z polarised. This establishes the assignments $^1A_1 \rightarrow {}^1E$ (20,080 cm.$^{-1}$) and $^1A_1 \rightarrow {}^1A_1$ (25,380 cm.$^{-1}$), consistent with the one-electron transitions $b_2(xy) \rightarrow e(\pi^*NO)$ and $e(xz,yz) \rightarrow e(\pi^*NO)$, respectively. The weak shoulder, indicating a maximum at 30,300 cm.$^{-1}$, is logically assigned $^1A_1 \rightarrow {}^1A_2$ or $b_2(xy) \rightarrow b_1(x^2-y^2)$. Support for this assignment is derived from the fact that a similar d–d band at 31,000 cm.$^{-1}$ is observed in the $Fe(CN)_6^{4-}$ ion.[5] We expect the $xy \longleftrightarrow x^2-y^2$ separation to be about the same in $Fe(CN)_6^{4-}$ and $Fe(CN)_5NO^{2-}$, because the ligand interactions in the x,y plane are the same.

The derived levels for $Fe(CN)_5NO^{2-}$ suggest the ground-state electronic structures given in the Table for some representative metal nitrosyl complexes. After d^6, additional electrons are accommodated by molecular orbitals derived from π^*NO. Thus $Fe(CN)_5NO^{3-}$ is formally Fe(II) and co-ordinated ·NO, as suggested by Griffith.[6] It is probable that all the NO⁺ complexes have a linear M–N–O grouping. However, to be consistent with observed magnetic properties, the NO

[1] D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *Proc. Chem. Soc.*, 1964, 364.
[2] H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.*, 1962, **36**, 1151.
[3] H. B. Gray, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3404.
[4] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, 1963, **2**, 1043.
[5] H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, 1963, **85**, 2922.
[6] W. P. Griffith, *Quart. Rev.*, 1962, **16**, 188.

and especially the NO^- systems are expected to have a bent M–N–O grouping, providing a non-degenerate level derived from π^*NO for the one or two extra electrons. E.s.r. results supporting the ground states suggested here for the d^5,NO^+ and $d^6,\cdot NO$ complexes will be presented by Bernal.[7]

MO structure	$(e)^4(b_2)^1$	$(e)^4(b_2)^2$	$(e)^4(b_2)^2(\pi_1{}^*NO)^1$	$(e)^4(b_2)^2(\pi_1{}^*NO)^2$
Formal structure ..	d^5,NO^+	d^6,NO^+	d^6,NO	d^6,NO^-
Examples	$Cr(CN)_5NO^{3-}$	$V(CN)_5NO^{5-}$	$Fe(CN)_5NO^{3-}$	$Co(CN)_5NO^{3-}$
	$Cr(H_2O)_5NO^{2+}$	$Mn(CN)_5NO^{3-}$		
	$Cr(NH_3)_5NO^{2+}$	$Fe(CN)_5NO^{2-}$		
	$Mn(CN)_5NO^{2-}$			

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[7] I. Bernal, to be published.