

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 suggested¹ that the d orbital ordering $xz, yz < xy < x^2 - y^2 < z^2$ we suggested^{2,3} for $\text{Fe}(\text{CN})_5\text{NO}^{2-}$, 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 $\text{Fe}(\text{CN})_5\text{NO}^{2-}$; these results strongly suggest that it is not z^2 , but the level derived from $\pi^*\text{NO}$, that lies much lower than previously suspected.^{2,3}

A quantitative molecular orbital calculation of $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ gives our d level ordering^{2,3} but with the e symmetry level derived from $\pi^*\text{NO}$ between xy and $x^2 - y^2$, as shown in the Figure.

$a_1(z^2)$
$b_1(x^2 - y^2)$
$e(\pi^*\text{NO})$
$b_2(xy)$
$e(xz, yz)$

Detailed analysis of the optical absorption spectra of $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ in liquid (300° K) and solid (77° K) solutions and in a single $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ 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 $b_2(xy) \rightarrow e(\pi^*\text{NO})$ and $e(xz, yz) \rightarrow e(\pi^*\text{NO})$, 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 $\text{Fe}(\text{CN})_6^{4-}$ ion.⁵ We expect the $xy \leftrightarrow x^2 - y^2$ separation to be about the same in $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_5\text{NO}^{2-}$, because the ligand interactions in the x, y plane are the same.

The derived levels for $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ suggest the ground-state electronic structures given in the Table for some representative metal nitrosyl complexes. After d^8 , additional electrons are accommodated by molecular orbitals derived from $\pi^*\text{NO}$. Thus $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ is formally $\text{Fe}(\text{II})$ and co-ordinated $\cdot\text{NO}$, 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 $\pi^*\text{NO}$ 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, NO complexes will be presented by Bernal.⁷

MO structure	$(e)^4(b_2)^1$	$(e)^4(b_2)^2$	$(e)^4(b_2)^2(\pi_1^*\text{NO})^1$	$(e)^4(b_2)^2(\pi_1^*\text{NO})^2$
Formal structure	d^5, NO^+	d^6, NO^+	d^6, NO	d^6, NO^-
Examples	$\text{Cr}(\text{CN})_5\text{NO}^{3-}$ $\text{Cr}(\text{H}_2\text{O})_5\text{NO}^{2+}$ $\text{Cr}(\text{NH}_3)_5\text{NO}^{2+}$ $\text{Mn}(\text{CN})_5\text{NO}^{2-}$	$\text{V}(\text{CN})_5\text{NO}^{5-}$ $\text{Mn}(\text{CN})_5\text{NO}^{3-}$ $\text{Fe}(\text{CN})_5\text{NO}^{2-}$	$\text{Fe}(\text{CN})_5\text{NO}^{3-}$	$\text{Co}(\text{CN})_5\text{NO}^{3-}$

⁷ I. Bernal, to be published.

(Received, January 18th, 1965.)