

Electron Spin Resonance Study of $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ in a Single Crystal

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McNEIL, RAYNOR, and SYMONS recently reported the e.s.r. spectra of $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ in liquid solutions at room temperature and in frozen glasses at 77°K.^{1,2} In their experiments they did not detect any hyperfine splittings due to ^{14}N of the NO group and estimated that both $A_{\perp}(^{14}\text{N})$ and $A_{\parallel}(^{14}\text{N})$ are smaller than 1.9 gauss. This is a rather surprising result since the ^{14}N hyperfine splittings are easily detected in the isoelectronic $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ complex,^{1,3} with $A_{\perp}(^{14}\text{N}) = 7.10$ and $A_{\parallel}(^{14}\text{N}) = 2.89$ gauss. Since the ^{55}Mn hyperfine lines in $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ are very broad, ^{14}N hyperfine splittings larger than 1.9 gauss could be hidden. Thus, we have examined e.s.r. spectra of $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ in a single crystal.

Analytically pure samples of $\text{K}_2\text{Mn}(\text{CN})_5\text{NO}$ were prepared according to a literature procedure.⁴ Our repeated bulk-susceptibility measurements on a solid sample of $\text{K}_2\text{Mn}(\text{CN})_5\text{NO}$ give $\mu_{\text{eff}} = 1.73$ B.M., indicating $S = \frac{1}{2}$ with no abnormal magnetic behaviour. Thus the magnetic moment of 0.50 B.M. reported earlier⁴ for solid $\text{K}_2\text{Mn}(\text{CN})_5\text{NO}$ at 300°K is apparently in error. All the e.s.r. measurements were made at room temperature on a small crystal of $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ ⁵ containing approximately 0.3% $\text{K}_2\text{Mn}(\text{CN})_5\text{NO}$. The splittings due to ^{14}N from NO are well resolved, particularly for large Θ , where Θ is the angle between the symmetry axis NC-Mn-NO and the applied magnetic field H . Thus the hyperfine splittings due to ^{14}N were obtained for $\text{Mn}(\text{CN})_5\text{NO}^{2-}$. The results of our e.s.r. study of $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ in a single crystal are given in the Table and compared with the corresponding values for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ given by Kuska and Rogers.³

McNeil and his co-workers interpreted their e.s.r. results on the basis of different ground-state electronic structures for the isoelectronic $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ complexes.¹ The results in the Table show that there is no need to resort to different electronic structures for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Mn}(\text{CN})_5\text{NO}^{2-}$. Indeed, the striking similarities in the symmetries of the g and A tensors and the ratios g_{\perp}/g_{\parallel} and A_{\perp}/A_{\parallel} strongly support the assignment^{3,7,8} of the same ground state for both complexes.

The calculated ground state for both $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ is $e^4b_2^1 = {}^2B_2$. Mixing of the ground state and the low excited

TABLE

Electron Spin Resonance Results for $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ and $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ in Single Crystals

		A values in gauss	
		$\text{Mn}(\text{CN})_5\text{NO}^{2-}$ ^a	$\text{Cr}(\text{CN})_5\text{NO}^{3-}$ ^b
g_{\parallel}	1.9922	1.9722
g_{\perp}	2.0311	2.0045
g_{av}	2.0181	1.9937
$A_{\parallel}(^{55}\text{Mn}$ or $^{53}\text{Cr})$	159.98	33.4
$A_{\perp}(^{55}\text{Mn}$ or $^{53}\text{Cr})$	36.6	11.9
A_{av}	77.72	19.1
$A_{\parallel}(^{14}\text{N})$	1.91	2.89
$A_{\perp}(^{14}\text{N})$	4.75	7.10
$A_{\text{av}}(^{14}\text{N})$ ^c	3.80	5.70

^a The g and A values were corrected by solving the spin Hamiltonians to second order; see ref. 6.

^b From ref. 3.

^c Calculated from A_{\parallel} and A_{\perp} ; solution value for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ is 5.32 gauss (ref. 10).

¹ D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *Proc. Chem. Soc.*, 1964, 364.

² D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.*, 1965, 410.

³ H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, 1965, 42, 3034.

⁴ F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nuclear Chem.*, 1959, 10, 28.

⁵ P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, 1963, 2, 1043.

⁶ B. Bleaney, *Phil. Mag.*, 1951, 42, 441.

⁷ P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, 1965, in the press.

⁸ H. B. Gray, P. T. Manoharan, R. J. Pearlman, and R. Riley, *Chem. Comm.*, 1965, 62.

state $e^3b_2^2 = {}^2E$ via spin-orbit coupling places unpaired spin density on the NO, since the $e(xz,yz)$ molecular orbital includes a contribution from π^*NO . The fact that the $A_{av}({}^{14}N)$ for $Cr(CN)_5NO^{3-}$ is larger than $A_{av}({}^{14}N)$ for $Mn(CN)_5NO^{2-}$ indicates that there is more π^*NO character in the filled $e(xz,yz)$ molecular orbital in the $Cr(CN)_5NO^{3-}$ complex. This result is consistent with quantitative calculations similar to the one performed⁷ on $Fe(CN)_5NO^{2-}$ which show that the $e(xz,yz)$ orbital is 60% π^*NO for $Cr(CN)_5NO^{3-}$ and only 42% π^*NO for $Mn(CN)_5NO^{2-}$. Also, comparison of $\bar{\nu}$ (N-O)

values for $Cr(CN)_5NO^{3-}$ (1645 cm^{-1})⁹ and $Mn(CN)_5NO^{2-}$ (1885 cm^{-1})⁴ indicates a higher degree of $M \rightarrow \pi^*NO$ interaction in $Cr(CN)_5NO^{3-}$.

Thus, we conclude that the $e(xz,yz) < b_2(xy) < \pi^*NO < b_1(x^2-y^2) < a_1(z^2)$ ordering of molecular orbitals obtained from the quantitative calculations of $M(CN)_5NO^n-$ systems and supported by extensive optical spectral work^{7,8} on $Fe(CN)_5NO^{2-}$ gives a satisfactory accounting of the ground states of $Mn(CN)_5NO^{2-}$ and $Cr(CN)_5NO^{3-}$.

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⁹ W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1959, 872.

¹⁰ H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, 1964, **40**, 910.