62. *Structure and Reactivity of Transition-metal Complexes with Polyatomic Ligands. Part I. Electron Spin Resonance Spectra of* $[Mn(CN)_5NO]^{2-}$ *and* $[Fe(CN)_5NO]^{3-}$.

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Electron spin resonance spectra of dilute fluid and rigid solutions of $K_2[Mn(CN)_5NO]$ and $Na_3[Fe(CN)_5NO]$ have been measured and the principal values for the g-tensors derived therefrom. Both are axially symmetric with $g_\perp$ considerably greater than the free-spin value, and greater than $g_\parallel$. Principal values for the ^{14}N hyperfine coupling tensor for the iron compound have been used to derive approximate values for the contribution of nitrogen $2s$ and $2p(\sigma)$ atomic orbitals to the wavefunction of the unpaired electron, and it is concluded that the orbital is largely d_{z^2} on iron, the z-axis being the Fe–N–O direction. In contrast, no ^{14}N hyperfine structure could be detected for the manganese complex, but the anisotropic hyperfine coupling to ^{55}Mn, considered together with the g-tensor, leads to the conclusion that the unpaired electron is primarily in the manganese d_{xy} level.

Recent studies of the electron spin resonance spectra of simple inorganic radicals have yielded detailed information regarding the form of the molecular orbital of the unpaired electron.[1] Furthermore, it has been amply demonstrated that the pertinent parameters can often be derived from the envelope spectra of powders or rigid glasses, thus bypassing the more difficult, and sometimes impossible, task of obtaining dilute single crystals of the paramagnetic species.[2,3]

One general aim of the present studies is to use these methods to probe the electronic structure of transition-metal complexes having at least one simple inorganic ligand of the type under consideration.

A start has been made with complexes containing the nitrosyl ligand, since others have already shown that these often give well-resolved spin-resonance spectra at room temperature. Thus, Bernal and Hockings [4] reported a triplet spectrum for solutions thought to contain $[Fe(CN)_5NO]^{3-}$, which they assigned to hyperfine interaction with the ^{14}N of the nitrosyl group. Bernal and Harrison [5] studied the spectrum of $K_3[Cr(CN)_5NO]$ in aqueous solution, but they made an error in interpreting the spectrum, which has since been corrected.[6,7] Very recently, Spencer and Myers [8] have reported isotropic hyperfine coupling constants for ^{13}C in both equatorial and axial cyanide ligands. Gibson [9] obtained the g-tensor for $Fe[S_2CN(CH_3)_2]_2NO$ from a study of single crystals, but was unable to detect any hyperfine structure because of the great line-width. His results are very different from those reported by Gray *et al.*[10] for the compound in Styrofoam; the latter workers report a value for the isotropic hyperfine coupling to ^{14}N obtained from solutions in acetone.

A molecular-orbital-level scheme proposed by Gray *et al.*,[10] based on a scheme for molecules having C_{4v} symmetry,[11] seems to have met with general approval.[5-8] For reasons given below, this scheme seems to us to require revision, and it was hoped that, by studying the solid-state spectra of some of these complexes, a choice between this

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[1] Symons, " Advances in Chemistry Series," No. 36, American Chemical Society, 1962, p. 76.
[2] Atkins, Brivati, Keen, Symons, and Trevalion, *J.*, 1962, 4785.
[3] Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.
[4] Bernal and Hockings, *Proc. Chem. Soc.*, 1962, 361.
[5] Bernal and Harrison, *J. Chem. Phys.*, 1961, **34**, 102.
[6] Bernal and Harrison, *J. Chem. Phys.*, 1963, **38**, 2581.
[7] Hayes, *J. Chem. Phys.*, 1963, **38**, 2580.
[8] Spencer and Myers, *J. Amer. Chem. Soc.*, 1964, **86**, 522.
[9] Gibson, *Nature*, 1962, **196**, 64.
[10] Gray, Bernal, and Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3404.
[11] Ballhausen and Gray, *Inorg. Chem.*, 1962, **1**, 111.

scheme[10] and that now proposed (Fig. 4) could be made. Results for $[Mn(CN)_5NO]^{2-}$ and $[Fe(CN)_5NO]^{3-}$ now reported[12] appear to support the present scheme; our results for the chromium compound are more complicated and will be the subject of a forthcoming Paper.

EXPERIMENTAL AND RESULTS

Potassium pentacyanonitrosylmanganate(II), $K_2[Mn(CN)_5NO]$, was prepared by the method described by Cotton *et al.*[13] The diamagnetic solid intermediate $K_3[Mn(CN)_5NO]$ was oxidised to $K_2[Mn(CN)_5NO]$ by either dissolving it in concentrated nitric acid or by addition of bromine in ether.

Sodium pentacyanonitrosylferrate(I), $Na_3[Fe(CN)_5NO]$, was prepared by polarographic reduction of sodium nitroprusside in *NN*-dimethylformamide, with tetra-n-butylammonium iodide as supporting electrolyte; the blue solution is readily oxidised by air, and was kept under an atmosphere of nitrogen.

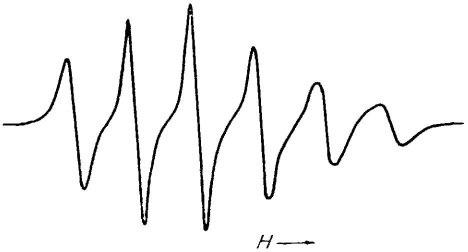

FIG. 1. Electron spin resonance spectrum of a solution containing $[Mn(CN)_5NO]^{2-}$ at 9498·1 Mc./sec. (room temperature).

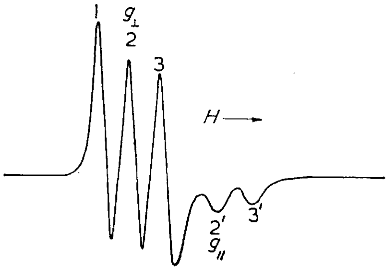

FIG. 3. Electron spin resonance spectrum of a rigid solution containing $[Fe(CN)_5NO]^{3-}$ at 9405 Mc./sec. (77°K).

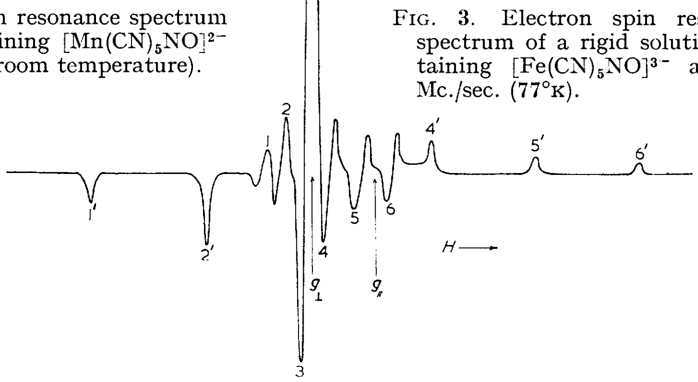

FIG. 2. Electron spin resonance spectrum of a rigid solution containing $[Mn(CN)_5NO]^{2-}$ at 9475·4 Mc./sec. (77°K).

Electron spin resonance spectra were obtained at *X*-band frequencies with a spectrometer described previously[14] and with a Varian V4502 spectrometer.

Interpretation of the Spectra.—Fluid-solution spectra. Fig. 1 shows the spectrum of $[Mn(CN)_5NO]^{2-}$. The six lines arise from interaction between the unpaired electron and the manganese nucleus. The line-width was found to decrease very slightly with increase in temperature and to be virtually independent of the method of oxidation. The use of 98% deuterated water did not alter the line-width. The narrowest line had a width of 11·7 gauss (measured between points of maximum slope), and showed no hyperfine structure due to interaction of the unpaired electron with the nitrogen of the nitrosyl ligand. Assuming that any interaction is hidden within the widths of the various features depicted in Fig. 1, the maximum value of the hyperfine coupling constant $\mathbf{A}_{iso}(^{14}N)$ was calculated (see Table 1).

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[12] Raynor, *Nature*, 1964, **201**, 1216.
[13] Cotton, Monchamp, Henry, and Young, *J. Inorg. Nuclear Chem.*, 1959, **10**, 28.
[14] Brivati, Keen, and Symons, *J.*, 1962, 237.

The spectrum of $[Fe(CN)_5NO]^{3-}$ in solution [12] consisted of three lines similar to that observed by Bernal and Hockings.[4] These lines arise from interaction between the unpaired electron and the nitrogen of the nitrosyl ligand. The line spacing is the hyperfine coupling constant $\mathbf{A}_{iso}(^{14}N)$ (see Table 1). No resonance was observed due to ^{13}C in natural abundance.*

TABLE 1.

Electron spin resonance data for pentacyanonitrosyl complexes at room temperature.

Complex	*g*-Tensor g_{av}	Hyperfine coupling (gauss) $\mathbf{A}_{iso}(^{14}N)$	$\mathbf{A}_{iso}(^{55}Mn)$	$\mathbf{A}_{iso}(^{13}C)$	Ref.
$[Fe(CN)_5NO]^{3-}$	2·026	14·8	—	—	Present work
	2·0253	15·3	—	—	4
	2·025	14·7	—	4·60 *	*a*
$[Mn(CN)_5NO]^{2-}$ †	2·0144 ‡	<1·9	77·45 ‡	—	Present work

a Bernal and Hockings, Paper B1—17 presented at 19th International Congress of Pure and Applied Chemistry, London, 1963.

* ^{13}C-Enriched sample, made by exchange with 87% $K^{13}CN$. † Prepared by oxidation of $K_3[Mn(CN)_5NO]$ with concentrated nitric acid. ‡ Corrected by solving Spin Hamiltonian to second order.[15]

Rigid-solution spectra (77°K). The spectrum of $[Mn(CN)_5NO]^{2-}$ is shown in Fig. 2, which also shows the approximate positions of $g_{\perp}$ and $g_{\parallel}$. The separation between the peaks 1, 2, 3, 4, 5, and 6 gives $\mathbf{A}_{\perp}$, and that between the peaks 1′, 2′, 3′, 4′, 5′, and 6′ gives $\mathbf{A}_{\parallel}$. These values have been corrected by solution of the Spin Hamiltonian to second order,[15] and are given in Table 2.

TABLE 2.

Electron spin resonance data for pentacyanonitrosyl complexes at 77°K.

Data	$[Fe(CN)_5NO]^{3-}$	$[Mn(CN)_5NO]^{2-}$	Data	$[Fe(CN)_5NO]^{3-}$	$[Mn(CN)_5NO]^{2-}$
$g_{\perp}$	2·0313	2·0279 *	$A_{iso}(^{14}N)$ (gauss)	15·53	<1·9
$g_{\parallel}$	2·0059	1·9873 *	$A_{\perp}(^{55}Mn)$ (gauss)	—	34·0 *
g_{av}	2·0231	2·0144 *	$A_{\parallel}(^{55}Mn)$ (gauss)	—	164·2 *
$\mathbf{A}_{\perp}(^{14}N)$ (gauss)...	14·75	<1·9	$A_{iso}(^{55}Mn)$ (gauss)	—	77·4 *
$\mathbf{A}_{\parallel}(^{14}N)$ (gauss)	17·10	<1·9			

* Corrected by solving Spin Hamiltonian to second order.[15]

The spectrum of $[Fe(CN)_5NO]^{3-}$ is shown in Fig. 3. The position of $g_{\perp}$ and $g_{\parallel}$ is shown, and the separation between peaks 1, 2, and 3 gives $\mathbf{A}_{\perp}$, and that between peaks 2′ and 3′ gives $\mathbf{A}_{\parallel}$.

Solution Effects.—The character of the rigid-solution spectrum is influenced by the mode of oxidation of $K_3[Mn(CN)_5NO]$. The best spectrum was obtained by dissolving the solid intermediate directly in concentrated nitric acid and then cooling rapidly in liquid nitrogen. When the salt was dissolved in water prior to oxidation with concentrated nitric acid, no spin-resonance signal was observed at 77°K, presumably owing to crystallite formation. Dissolution of $K_3[Mn(CN)_5NO]$ in water, followed by oxidation with bromine in ether, gave only a weak signal.

The fluid-solution spectra showed slight differences depending on the mode of preparation. Direct oxidation of $K_3[Mn(CN)_5NO]$ with concentrated nitric acid gave g_{av} values slightly higher (by 0·002) and $\mathbf{A}_{iso}$ values slightly lower (by 1·1 gauss) than did the other methods of preparation described above. There was evidence of a second species in the aqueous solution prepared by oxidation with bromine in ether, the concentration of which increased with time and with the concentration of bromine used. The second species had $g_{av} = 2{\cdot}002$ and $\mathbf{A}_{iso}(^{55}Mn) = 99{\cdot}5$ gauss, in close agreement with that observed for $[Mn(H_2O)_6]^{2+}$ ($g_{av} = 2{\cdot}0038$, $\mathbf{A}_{iso}(^{55}Mn) = 95{\cdot}2$ gauss), suggesting the formation of $[Mn(H_2O)]^{2+}$ in solution.

TABLE 3.

Derived parameters for $[Fe(CN)_5NO]^{3-}$.

2*s*-Character N(π^*) orbital = $\mathbf{A}_{iso}/550$ = 2·8%
2*p*-Character N(σ^*) orbital = $(\mathbf{A}_{\parallel} - \mathbf{A}_{iso})/34{\cdot}1$ = 4·6%
Total spin-density on nitrogen = 7·4%
p : *s* Ratio = 1·6

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[15] Bleaney, *Phil. Mag.*, 1951, **42**, 441.

Derivation of Parameters for $[Fe(CN)_5NO]^{3-}$.—Table 3 gives the *s*- and *p*-character of the nitrogen σ^* orbital contributing to the molecular orbital of the unpaired electron. This is derived from the following expressions:

$$s\text{-character} = \mathbf{A}_{iso}/\mathbf{A}_s,$$

where $\mathbf{A}_s$ is the isotropic coupling expected for 100% 2*s*-character on ^{14}N (= 550 gauss).[16]

$$p\text{-character} = (\mathbf{A}_{\parallel} - \mathbf{A}_{iso})/\mathbf{A}_p,$$

where $\mathbf{A}_p$ is the hyperfine coupling for fields parallel to the density axis of the 2*p* orbital, expected for 100% 2*p*-character on ^{14}N (= 34·1 gauss).[16]

DISCUSSION

We discuss our results in terms of the simplified qualitative molecular-orbital energy-level scheme given in Fig. 4, suitable for an octahedral complex with C_{4v} symmetry. The *z*-axis is taken as the N–C–M–N–O direction; this grouping, by analogy with the nitroprusside ion,[17] is taken to be linear. The *x*- and *y*-axes then pass through the equatorial cyanide ligands.

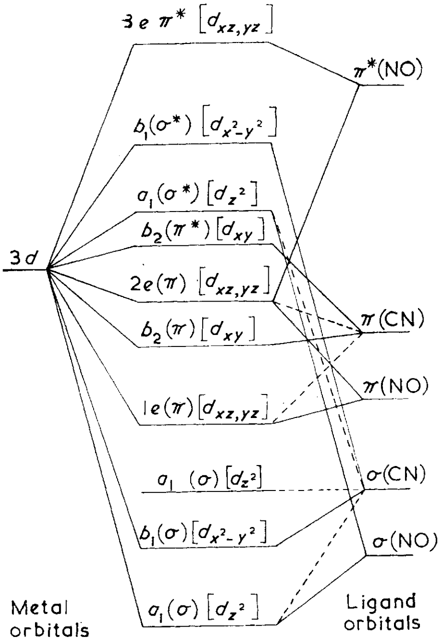

FIG. 4. Simplified molecular-orbital energy-level diagram for Fe′ and Mn″ pentacyanonitrosyl complexes, omitting, for simplicity, the metal 4*s* and 4*p* and the CN (π^*) levels.

The lowest σ level will have considerable lone-pair character on the nitrosyl group, especially since this ligand bears a formal positive charge.[18] Similarly, the first *e* level will have considerable π(NO) character. The second *e* level, which is expected to resemble $d_{xz,yz}$, will be depressed below the b_2 $[d_{xy}]$ level since the π^*(NO) level is relatively deep. Electrons in this level will thus tend to neutralise the formal positive charge on the nitrosyl group. The a_1 (σ^*) level will resemble d_{z^2}, and should be considerably deeper than the b_1 (σ^*) level $[d_{x^2-y^2}]$, in view of the charge on the nitrosyl group and the depth of the σ(NO) level. It is especially in this respect that our scheme differs from that of Gray *et al.*[10] who place the b_1 level below the a_1 level. This arrangement is satisfactory

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[16] Symons, " Advances in Physical Organic Chemistry," ed. Gold, Academic Press, 1962, Vol. 1, p. 332.

[17] Manoharan and Hamilton, *Inorg. Chem.*, 1963, **2**, 1043.

[18] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

for the vanadyl case (C_{4v}),[11,19] where the σ-bonding to oxygen is very strong, but is not expected to apply in this problem where the σ-bonding to NO is expected to be weaker than that to the remaining ligands.

The g-*Tensor for* $[Mn(CN)_5NO]^{2-}$.—The axial symmetry of the g-tensor is in accord with the linear arrangement suggested for the nitrosyl group. In terms of the scheme proposed (Fig. 4), the electron configuration should be . . . $e\ [d_{xz,\,yz}]^4 b_2\ [d_{xy}]^1$. A magnetic field along the z-axis will then mix the b_2 level with the empty $d_{x^2-y^2}$ level slightly, giving rise to a small negative value for Δg. In fact, $\Delta g_{\parallel} \doteqdot -0{\cdot}01$ (Table 2). For fields perpendicular to the z-axis, however, the $b_2\ [d_{xy}]$ level will be mixed with the filled e level, and hence will lead to a positive g-shift. Again in agreement, we find $\Delta g_{\perp} \doteqdot +0{\cdot}03$.

The Hyperfine Tensor for $[Mn(CN)_5NO]^{2-}$.—No hyperfine interaction with ^{14}N could be detected under any conditions. The maximum value calculated is far smaller than the interactions found for the iron complex, and is in accord with the level-scheme proposed, since there is no direct interaction between the b_2 level and the NO ligand. (These results also differ markedly from those for the isoelectronic chromium complex;[5-7] reasons for this difference will be suggested in a later Paper.)

The isotropic coupling to ^{55}Mn is similar in magnitude to that generally found for electrons in $3d$ levels on manganese. Since this arises from complex spin-polarisation effects, it does not seem safe to make any inference regarding electron-delocalisation from the slight reduction found compared with the value (95 gauss) for Mn^{2+} in water.

The anisotropic coupling is then of the form expected for an electron largely in the d_{xy} orbital, provided the isotropic coupling is taken to be negative. The results can then be used to calculate $\langle r^{-3}\rangle$ for the d_{xy} level or, alternatively, where this parameter is known with sufficient accuracy, an estimate of the delocalisation on to the cyanide ligands can be obtained. The estimated value of 4·44 a.u., assuming 100% occupany of the atomic d_{xy} orbital, may be compared with the value of 4·16 a.u. calculated for the neutral atom. The slight increase is that expected for a small positive charge on manganese, and hence we conclude that delocalisation onto the ligands is small.

The g-*Tensor for* $[Fe(CN)_5NO]^{3-}$.—Again, the observed axial symmetry is in accord with the assumption that the NO axis lies along z, as for the d^6 ion.[17]† The electron configuration is now expected to be . . . . . . $e^4 b_2^{\,2} a_1\ [d_{z^2}]^1$. Field along z should have no direct effect, and in fact $g_{\parallel}$ is very close to the free-spin value. In contrast, for fields perpendicular to the z-axis, coupling with the filled $e\ [d_{xz,\,yz}]$ level is expected to give rise to a relatively large positive increment, as is in fact found ($\Delta g_{\perp} \doteqdot 0{\cdot}029$). These results are thus in good accord with the model, and would have been quite contrary to expectation had the unpaired electron been in the $b_1\ [d_{x^2-y^2}]$ level.[10]

The Hyperfine Tensor for $[Fe(CN)_5NO]^{3-}$.—The $p:s$ ratio for the nitrogen σ orbital contributing to the molecular orbital of the unpaired electron is about 1·6, and the total spin-density on nitrogen is 7·4%. This result confirms that the unpaired electron is in the d_{z^2} level, since π-interaction would not give rise to such a low $p:s$ ratio, unless an angular nitrosyl group were rotating about z sufficiently rapidly to average a great deal of the anisotropic coupling to zero. This seems unlikely, since the lines were not broadened on cooling. We conclude that the nitrogen σ level is markedly hybridised, and recall that similar results have been obtained for the σ* levels of metal fluorides.[20] The unpaired electron will have some density on oxygen, but, in view of the greater electron affinity of oxygen, this is expected to be less than that on nitrogen.

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† [*Note Added in Proof*.—Our studies of γ-irradiated sodium nitroprusside single crystals (D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *Proc. Chem. Soc.*, 1964, 364 show that the direction of the ^{14}N hyperfine and g-tensors for $[Fe(CN)_5NO]^{3-}$ are not in fact the same, but are separated by about 10°. Also, hyperfine components for ions containing ^{13}C in natural abundance have been observed.]

[19] Mishra and Symons, *J.*, 1963, 4490.

[20] Shulman and Sugano, *Phys. Rev.*, 1963, **130**, 506.

Had the electron been in the b_1 [$d_{x^2-y^2}$] level,[10] it is hard to see how this large coupling to ^{14}N could have arisen, especially since the result for the manganese complex indicates very minor interaction for an electron in the similar b_2 [d_{xy}] level.

It is hoped that single-crystal studies of this complex, currently underway, will shed further light on the problem, in particular, by providing information about the relative directions of the hyperfine and the *g*-tensor. We stress that, at this stage, interpretation of powder spectra, although often successful,[1] is nevertheless fraught with pitfalls.

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