separation varies with spin state. This may be due to exchange striction. The measured dipole–dipole interaction is noticeably smaller than that predicted by a point-dipole calculation which suggests that the unpaired electrons are partially delocalized from the metal to the chloride ligands.

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Registry No. $CsCdCl_3$, 13845-08-4; Mn, 7439-96-5; $Mn_2Cl_9^{5-}$, 58396-13-7.

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Effect of High-Energy Radiation on a Range of Metal Pentacyanonitrosylferrate(II) and Pentacyanonitroferrate(II) Salts

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Exposure of a range of alkali and alkaline earth pentacyanonitrosylferrate(II) salts to ^{60}Co γ rays at 77 K gave electron-capture centers having the unpaired electron largely confined to the nitrosyl ligand, as judged by their ESR spectra. These ESR spectra were almost independent of the salt except that for the hydrated sodium salt which changed reversibly to that exhibited by the other salts on cooling to 4.2 K. In all cases, ESR spectra assignable to normal d^7 iron(I) salts are also obtained, and these were enhanced at the expense of the nitrosyl center on annealing above 77 K. At least two d^7 centers were obtained in most cases. One, having axial symmetry, is assigned the structure $Fe(CN)_4NO^{2-}$, formed by loss of the axial cyanide ligand, and the other, having nonaxial symmetry, is assigned the structure $Fe(CN)_5NO^{3-}$, with both the axial cyanide and the NO group present but bent slightly off the original axis. The nitroferrate(II) salts gave an electron-excess species having the unpaired electron largely confined to the NO_2 group, whose ESR spectra closely resembled that of the nitrosyl center. However, these were not converted into d^7 ferrate(I) salts under any circumstances. The Ag(I) salts also gave Ag(II) centers, whose ESR spectra exhibited hyperfine coupling to four equivalent ^{14}N nuclei in addition to that to ^{107}Ag and ^{109}Ag. These d^9 ions have their unpaired electrons in a $d_{x^2-y^2}$ orbital on silver with considerable delocalization onto four in-plane nitrogen atoms.

There has been considerable speculation about the nature of paramagnetic electron-excess species formed from sodium pentacyanonitrosylferrate(II). Three different types of ESR spectra have been reported. The first spectrum has $g_\perp \simeq 2.3$ and $g_\parallel \simeq 2.0$ with $A_\perp(N) \simeq 14.0$ G and $A_\parallel(N) \simeq 17.0$ G. We have assigned this spectrum to a d^7 iron complex (species I) having an unpaired electron in an a (d_{z^2}) orbital and a strongly coupled NO group which is bent about 10° from the *z* axis of the complex.[1] Van Voorst and Hemmerich[2] have assigned this spectrum to $Fe(CN)_5NOH^{2-}$ when studying the reduction products in DMF. A tetraethylammonium salt having similar ESR parameters has been isolated and shown by x-ray diffraction to be the pentacoordinated $Fe(CN)_4NO^{2-}$ d^7 species.[3] In addition, we have generated this spectrum by the thermal reduction of anhydrous pentacyanonitrosylferrates.[4] Most recently,[5] this same spectrum has been assigned to $[Fe(CN)_5NOH]^{2-}$ in DMF, $Cd[Fe(CN)_5NOH]\cdot 2DMF$ solid, and $Cd_3[Fe(CN)_5NO]_2\cdot$(formamide).

A second ESR spectrum has two *g* values near free spin with the third $g \simeq 1.93$ and *A* values of approximately 30 and 10 G, respectively. Less controversy seems to exist for this spectrum with general agreement that it represents a d^6 complex (species II), $Fe(CN)_5NO^{3-}$, with the unpaired electron largely in a π^* MO on the NO ligand.[2] However, a very similar ESR spectrum has been assigned to $Fe(CN)_5NO_2^{5-}$ (species IV)[6] and this has recently been substantiated.[5] Also, a similar ESR spectrum has been observed upon heating the potassium, rubidium, and cesium pentacyanonitrosylferrates(II) to temperatures of 240 °C.[7]

A third spectrum having a large hyperfine coupling to ^{14}N and two low *g* values (species III) was obtained by irradiating the hydrated sodium salt.[8] It was tentatively suggested that this species is chemically identical with the d^6 complex with the unpaired electron largely in the π^* MO on the NO ligand, differing only in the extent of NO group libration. Trapped radical pairs have also been observed upon prolonged exposure of $Na_2Fe(CN)_5NO\cdot 2H_2O$ to γ radiation at room temperature.[9]

The aim of the present study was threefold: to investigate the relationship between spectra II and III, to distinguish, if possible, between the spectra assigned to $Fe(CN)_5\dot{N}O^{3-}$ and $Fe(CN)_5\dot{N}O_2^{5-}$, and to examine the effects of environment upon the three different spectra. Incidental to this study, we

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Table I. g and A^a Values for Species I and II[b]

	Species I				Species II[c]				
Metal	$g_\perp$ or g_x, g_y	$g_\perp$ or g_z	$A_\perp$ or A_x, A_y	$A_\parallel$ or A_z	g_1	g_2	g_3	A_1	A_2
Li[d]	2.0326	2.0059	14.6	17.0	2.0049	1.9974	1.920	25.5	29.8
	2.0388, 2.0376	2.0059	15.5, 13.8	17.0					
Na	2.0387, 2.0341	2.0050	14.1, 14.6	16.3	Species III formed				
K	2.0377, 2.0338	2.0064	13.5, 14.2	16.0	2.0024[e]		1.9310	33[e]	
Rb	2.0361	2.0057	14.5	16.5	2.0088	1.9995	1.9288	26	34.3
Cs	2.0352	2.0046	14.7	16.3	2.0075	1.9991	1.9327	26.3	29.8
Mg	2.0365	2.0052	13.9	16.7	2.0029	1.9976	1.9321	25.8	29.3
Ca	2.0395, 2.0338	2.0064	13.8, 14.3	16.9	2.0063	1.9975	1.9249	24.3	32.0
Sr	2.0371	2.0057	14.1	17.0	2.0054	1.9974	1.9244	24.8	32.5
Ba	2.0384	2.0071	13.9	17.6	2.0058	1.9969	1.9262	24.2	29.4
Zn	2.0349, 2.0311	2.0050	14.3, 15.3	17.6	2.0062	1.9959	1.9282	27.0	30.0
Cd	2.0360	2.0055	13.9	17.0	2.0066	1.9966	1.9317	26.1	31.7
Hg(II)	2.0367	2.0065	14.4	17.6	2.0058	1.9972	1.9329	25.5	31.2
Ag	2.0364	2.0058	14.4	*f*	2.0037	1.9973	1.9252	27.3	31.3
Hg(I)	2.0345	2.0046	14.7	17.1	2.0061	1.9972	1.9326	25.8	31.9

[a] A values in gauss (1 G = 10^{-4} T). [b] Species I was prepared by radiolysis for 2 h at room temperature and species II by radiolysis at 77 K for 2 h. [c] A_3 = 8–10 G in all cases (see text). [d] Both axial and nonaxial are formed. [e] Appears to be axial. [f] Ag(II) features interfere.

have formed silver(II) cations in the silver(I) pentacyanonitrosyl salt and studied their ESR spectra.

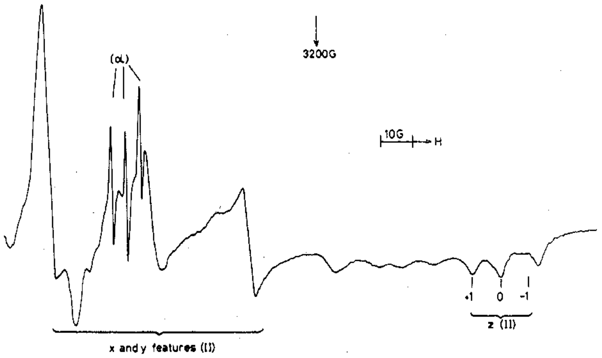


Figure 1. First-derivative X-band ESR spectrum for $ZnFe(CN)_5NO$ after exposure to ^{60}Co γ rays at 77 K for 2 h, showing features assigned to species II. The three narrow features (α) are assigned to ·CN radicals or, possibly, to N atoms.

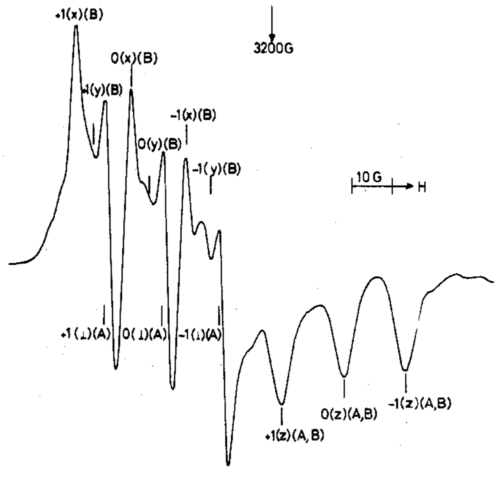


Figure 2. First-derivative X-band ESR spectrum for $Na_2Fe(CN)_5NO\cdot 2H_2O$ after exposure to ^{60}Co γ rays at room temperature for 4 h, showing features assigned to species I. A is for I_{ax} and B for I_{nonax}.

Experimental Section

Sodium pentacyanonitrosylferrate(II) of Analar reagent grade was used in the preparation of all other compounds in this study. The Zn, Cd, Hg(I), Hg(II), and Ag(I) salts of $Fe(CN)_5NO^{2-}$ were prepared by the method of Ayers and Waggoner.[10] The alkali and alkaline earth metal salts were prepared by adding the chlorides to $Ag_2Fe(CN)_5NO$ as previously reported.[11] Samples of these salts were dehydrated at 80 °C in a vacuum oven for a period of 2–3 days with the absence of water confirmed by recording their ir spectra as Nujol mulls. The $Na_4Fe(CN)_5NO_2$ salt was prepared as described in the literature.[12] Other salts of $Fe(CN)_5NO_2{}^{4-}$ were prepared by adding the appropriate metal nitrate to a cooled solution of $Na_4Fe(CN)_5NO_2$ at pH 12 in the absence of light. The resultant precipitate was washed with water, alcohol, and anhydrous ether to apparent dryness.

Samples of the powdered salts were exposed to γ radiation from a ^{60}Co source at 77 K and room temperature for variable periods at a dose rate of ca. 4 Mrad h^{-1}. ESR spectra were recorded on a Varian E3 spectrometer equipped with a conventional insert Dewar. Samples irradiated at 77 K were annealed by allowing them to warm up in the cold Dewar in the absence of liquid nitrogen, with rapid quenching back to 77 K whenever interesting changes were observed. Samples were cooled to 4.2 K using a liquid helium Dewar insert. At no time were distinct color changes observed in the solid samples, although the samples appeared slightly darker on occasion after irradiation.

Results and Discussion

With the exception of the hydrated sodium salt, low-field ESR features for species II dominated, with weak contributions from species I in the free spin region when γ radiated and observed at 77 K (Figure 1). This result was found to be independent of whether the rest of the metal nitrosyl salts were hydrated or anhydrous.

In addition, in all but the silver salts, features from Fe(III) centers were detected at lower fields. These will not be discussed herein. In the unique case of the hydrated sodium salt, species III was obtained in place of II (see Figure 1 of ref 8 for typical ESR spectrum). However, on cooling to ca. 4.2 K these features broadened and then narrowed to a typical spectrum of II. This effect was completely reversible.

The calcium salt and to a less marked extent the strontium and barium salts had ESR spectra at 77 K which exhibited far greater yields of species I, although II was still clearly detectable. In all cases on annealing, features for species II rapidly and reversibly broadened beyond detectability and at higher temperatures were irreversibly lost, with simultaneous gain of features for species I.

Two extreme forms of species I were obtained, as shown in Figure 2, one exhibiting an axially symmetric ESR spectrum and the other exhibiting three distinct g values. Data for all these centers are collected in Table I.

The pentacyanonitro salts all gave species IV, having an ESR spectrum remarkably similar to that for species II, the small differences being insufficient to enable us to make a clear differentiation. However, species II invariably changed thermally into species I, but species IV never exhibited this behavior, simply disappearing upon warming and then recooling. We consider that this difference is the best method

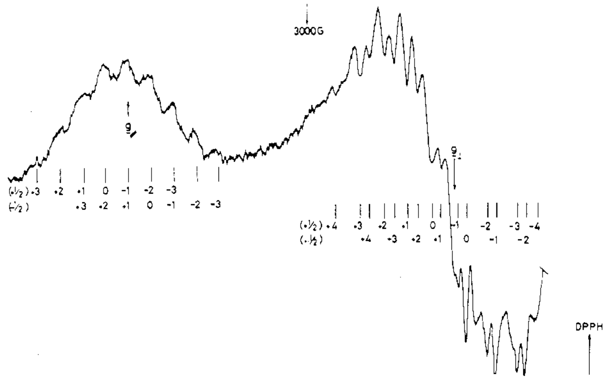


Figure 3. First-derivative X-band ESR spectrum for $Ag_2Fe(CN)_5$-NO after exposure to ^{60}Co γ rays at 77 K, showing features assigned to Ag(II) centers. The features to high field of A were merged with those from the pentacyanonitrosylferrate centers. M_I values for ^{14}N are displayed with those for ^{109}Ag in parentheses.

Table II. ESR Data for the Ag(II) Center Formed in Irradiated $Ag_2Fe(CN)_5NO$ together with Data for the Cu^{2+} Doped into $ZnFe(CN)_5NO$[13]

	$A(^{109}Ag)$, G[a]	$A(^{63}Cu)$, G[a]	$A(^{14}N)$, G[a] b	c	g values
Ag(II)	40	28	24	18	2.275, 2.076
Cu(II)	146	21	17.5	12.5	2.337, 2.060

[a] 1 G = 10^{-4} T. [b] Calculated setting the perpendicular splitting as $(A_{\parallel} + A_{\perp})/2$. [c] Taken from the parallel (low-yield) features.

for distinguishing between these two species.

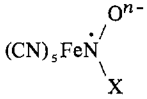
For the zinc salt, and to a small extent for several others, a narrow-line, isotropic triplet (α) having A_{iso} = 4.5 G and g = 2.00 was also detected at 77 K (Figure 1). This species rapidly decayed on annealing.

Only in the case of the silver(I) salt was any evidence obtained for cation involvement. In this case, Ag^0 centers were not detected, but Ag(II) features showing well-defined interaction with four nitrogen ligands were clearly defined (Figure 3 and Table II).

Species II and III. There can be little doubt that species II is formed by electron capture at the NO ligand.[13] Direct capture by the iron atom can also occur, especially in the case of the calcium salt. We interpret this as a competition involving distortions. Given that the electron resides, initially, in the π^* NO orbital, then bending of the Fe–N–O system will tend to trap the electron on the ligand, while stretching of the Fe–(NO) and $Fe–(CN)_{trans}$ bonds will tend to trap the electron on iron. The latter gives the more thermally stable product, but the former is more facile at 77 K.

The initial trapping of the electron in the π^* NO orbital as the main product is consistent with the molecular orbital scheme of Manoharan and Gray.[14] Also considering the charge distribution which they assigned to $Fe(CN)_5NO^{2-}$, it is logical that γ irradiation at 77 K would yield both d^7 Fe and π^* NO capture with the latter being the dominant feature.

The species[2,5] in solution which are stable at room temperature and assigned the same spectrum as II are converted to I by addition of acid. We have found that the higher energy metal π^* NO charge transfer band[14] is shifted to lower energy with decreasing solvent polarity indicating solvent interaction with the NO ligand. Therefore, the species being reduced in solution cannot be considered as a simple $Fe(CN)_5NO^{2-}$, but pentacyanonitrosylferrate ion is solvated in an ion–dipole interaction involving the NO^+ ligand. In a recent report[5] $Cd_3[Fe(CN)_5NO]_2$·(formamide) had an ESR spectrum of species I in the solid state but when dissolved in a formamide solution gave an ESR spectrum assignable to species II. This indicates that the species in solution yielding a spectrum assignable to species II would better be considered as



$$(CN)_5Fe\dot{N}\begin{matrix} O^{n-} \\ X \end{matrix}$$

where X is a solvent molecule or the conjugate base of the solvent. This, of course, would account for the conversion to species I by addition of acid, if this caused removal of X allowing the electron to migrate to the iron atom.

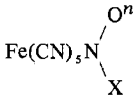
Species III has proved to be unique in that it is only obtained from the sodium hydrate. This strongly supports the concept that this is just a physical modification of species II, and our results at 4.2 K confirm this. As tentatively postulated in our earlier work,[8] the data for III at 77 K can be explained in terms of NO group librations, and it must be purely fortuitous that such librations are only facile in this particular solid. However, the extensive line broadening observed for II at temperatures above 77 K strongly suggests the onset of libratory movement prior to chemical change.

One characteristic of species II is the uneven distribution of the +1, 0, and −1 (^{14}N) features in the high-field ("z") component (see Figure 1). This cannot arise for any fundamental reason and must mean that those features experience different turning points, none of which represent true limiting values (i.e., the turning points seen in the powder spectra do not correspond to the true z components of the **g** and **A** tensors). This situation is often found when the **g** and **A** tensors have different axes,[15] and hence the estimated g_z and A_z values are not the true tensor components. Nevertheless, they are likely to be close to the true values, and since our main purpose is one of identification, we have not endeavored to derive the true components from single crystals.

Species I. There now seems no doubt that I is formed from II by electron transfer from ligand to metal in the case of the solids. This will occur when the z-axis ligands move outward, stabilizing the σ^* orbital involved, one extreme being complete loss of the trans cyanide ligand.[3] However, as we have shown in our studies of cobalt(II) cyanides,[16] another method is to bend the N–C–metal group. This usually results in a small hyperfine coupling to the cyanide nitrogen,[17] but no clear evidence of such secondary structure has been detected in our work. However, the features for I_{nonax} are considerably broader than those for I_{ax}, which could well be indication of unresolved hyperfine coupling.

We stress that formation of I is irreversible in the solids studied here. Addition of cyanide ion to I_{ax} would simply give I_{nonax} and not II as implied by Schmidt et al.[3] unless a solvent molecule is present to aid the NO group in attracting the electron.

Species IV. This is undoubtedly the d^6 Fe(II) complex $Fe(CN)_5NO_2^{5-}$, formed by electron capture at the NO_2 ligand. The same species was prepared by Raynor and Symons by chemical reduction in solution[6] and has recently been isolated as the sodium salt.[5] Although confusion has arisen because the ESR parameters for this anion are indistinguishable from those of II, this is supportive of



$$Fe(CN)_5N\begin{matrix} O^{n-} \\ X \end{matrix}$$

being the species observed in solution. That is, X is, in this case O^{2-}, and it is not too surprising that similar ESR spectra are obtained in view of the structural similarities of the two species. [Thus, RNO^- and RNO_2^- (R is alkyl) have quite similar magnetic properties.] Since no d^7 species is formed on annealing species IV, we must conclude that this complex is unstable.

Radical Pairs. We have previously shown that a range of radical-pair "triplet-state" species are formed during room-temperature irradiation of $Na_2Fe(CN)_5NO{\cdot}2H_2O$.[9] We have searched for similar pair trapping during radiolysis of all of the new salts studied, but only in the case of the sodium hydrate have the characteristic features been obtained. We therefore tentatively postulate that these pairs arise as a consequence of initial damage to the hydrate water

$$H_2O \rightarrow H_2O^+ + e^-$$

$$e^- + Fe(CN)_5NO^{2-} \rightarrow I$$

$$H_2O^+ \rightarrow (H^+) + {\cdot}OH$$

$${\cdot}OH + Fe(CN)_5NO^{2-} \rightarrow ONC\text{–}Fe\text{–}NO^{3-}\ (V)$$

Species V would be expected to have properties very similar to those for I_{nonax}. Provided electron capture is efficient, this could lead to pair trapping of species I as observed.

The Ag(II) Center. Our results demonstrate that electron loss from Ag^+ competes favorably with loss from the nitrosylferrate ion. The spectra are clearly caused by d^9 Ag(II) centers having four strongly coupled nitrogen ligands. Just this situation was observed for metal(II) pentacyanonitrosylferrate salts doped with Cu^{2+} ions.[18] In both cases the unpaired electron occupies a b_{2g} level which is σ antibonding with respect to four isocyanide ligands in the x–y plane and mainly $d_{x^2-y^2}$ on the metal.

The large value for $g_\parallel$ indicates strong coupling between the $d_{x^2-y^2}$ and d_{xy} orbitals on silver and is quite normal for Ag(II) complexes. The far smaller shift for $g_\perp$ is again quite normal and arises because of the larger separation between the $d_{x^2-y^2}$ and filled $d_{xz,yz}$ orbitals on silver. The factors controlling the g values and $A(^{109}Ag, ^{107}Ag)$ coupling constants are discussed in depth for the copper complexes.[18]

There is an appreciable increase in the $A_\parallel$ and $A_\perp$ (^{14}N) coupling constants relative to the Cu^{2+} complexes. These are compared in Table II. We stress that the "parallel" features for the silver A- and g-tensor components display the "perpendicular" coupling to ^{14}N. The "perpendicular" g and A features then display a nitrogen coupling equal to $[A_\parallel(^{14}N) + A_\perp(^{14}N)]/2$.[19] This increase corresponds to an increase in both 2s and 2p character on nitrogen, relative to the copper complex. This can be understood in terms of the greater polarizability of silver. Thus, the σ-bonding level gains more silver character, and the σ^*-orbital gains more ligand character.

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Registry No. $Li_2Fe(CN)_5NO$, 33751-92-7; $Na_2Fe(CN)_5NO$, 14402-89-2; $Na_2Fe(CN)_5NO{\cdot}2H_2O$, 13755-38-9; $K_2Fe(CN)_5NO$, 14709-57-0; $Rb_2Fe(CN)_5NO$, 33751-93-8; $Cs_2Fe(CN)_5NO$, 33751-94-9; $MgFe(CN)_5NO$, 58512-43-9; $CaFe(CN)_5NO$, 58512-44-0; $SrFe(CN)_5NO$, 58512-45-1; $BaFe(CN)_5NO$, 24378-32-3; $ZnFe(CN)_5NO$, 14709-62-7; $CdFe(CN)_5NO$, 17569-97-0; $HgFe(CN)_5NO$, 15393-68-7; $Hg_2Fe(CN)_5NO$, 58512-46-2; $Ag_2Fe(CN)_5NO$, 13755-36-7; $Na_4Fe(CN)_5NO_2$, 14099-03-7; $Fe(CN)_4NO^{2-}$, 55188-49-3; $Fe(CN)_5NO^{3-}$, 14636-58-9; $Fe(CN)_5NO_2^{5-}$, 27709-47-3; Ag^{2+}, 15046-91-0.

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Competition between Ammonia and the Nitrite Ion as Leaving Groups in Cobalt(III) Complexes. I. Hydrolysis of the Nitropentaamminecobalt(III) Ion in Ammonia Buffers

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Kinetic measurements are reported on the base hydrolysis and the spontaneous aquation of the nitropentaamminecobalt(III) cation in weakly alkaline ammoniacal solutions, at a constant ionic strength. The results are at variance with the generally accepted picture of the inert $Co^{III}(NH_3)_n$ frame. On the basis of kinetic evidence for the occurrence of the *trans*-hydroxonitrotetraamminecobalt(III) ion as an intermediate in the aquation of nitropentaammine, a novel mechanism is presented for the hydrolysis reaction: in the aquation the first step is loss of the trans NH_3 group, whereas in base hydrolysis NO_2^- is the first group to leave. Numerical values of activation parameters agree with published results.

Introduction

The hydrolysis of the nitropentaamminecobalt(III) ion has been widely investigated. Roughly there are three independent reaction paths: base hydrolysis, acid-catalyzed hydrolysis, and a spontaneous reaction of the complex. Of these, especially the acid-catalyzed reaction has been thoroughly studied.[1-4] Much less is known about the base hydrolysis reaction of the complex.[5,6] The mechanism of the spontaneous reaction seems to present some difficulties. There are indications[2] that a direct aquation is not involved.

An additional disturbing aspect appears to be that extrapolation of hydrolysis rates measured in acid solutions under