Electron Spin Resonance Studies of γ-Irradiated Potassium Hexacyanoferrate(II) in Various Host Lattices

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Four major Fe^I species were detected, one exhibiting hyperfine coupling to one ^{14}N nucleus (N_1), one with coupling to two equivalent ^{14}N nuclei (N_2), one with coupling to one ^{14}N nucleus and one halide nucleus (N_1Hal_1) and one with coupling to two equivalent halide nuclei (Hal_2). The N_1 species is thought to be $Fe(CN)_4CN'H_2O^{4-}$, formed from $Fe(CN)_4H_2O^{3-}$ impurity ions, in which the CN′ ligand is slightly bent off the Fe–CN axis. The N_2 species has two *trans*-cyanide ligands comparably bent off the axis. The halide complexes are then $Fe(CN)_4CN'Hal^{5-}$ and $Fe(CN)_4(Hal)_2^{5-}$ ions respectively, with the halide ligands or halide and bent cyanide ligands in a *trans*-configuration.

In one case, a species exhibited hyperfine coupling to one ^{14}N nucleus and one proton. This is thought to be an Fe^I complex containing the Fe–CNH unit.

ROOT and SYMONS reported[1] an unusual irradiation product from hexacyanoferrate(II) ions, for which hyperfine interaction to only one nitrogen atom was observed. Results from the irradiation of other transition-metal complex cyanides led Danon and his co-workers to postulate the formation of $Co(CN)_4(NC)_2^{4-}$ [2,3] and $Rh(CN)_4(NC)_2^{4-}$ [4] from $K_3Co(CN)_6$ and $K_3Rh(CN)_6$ respectively. We discussed[5] the nature of the 'di-isocyanide' $Co(CN)_4(NC)_2^{4-}$ in the light of more extensive data. The object of the present work was to extend the previous study[1] to obtain more information about the structure and mechanisms for the formation of the Fe^I complexes.

EXPERIMENTAL

Doped samples were obtained by crystallisation of the alkali-metal halide from aqueous solutions containing $K_4Fe(CN)_6$ in concentrations varying from 0·005 to 0·1 mol %. AnalaR reagents were used when possible. Finely powdered samples were exposed to ^{60}Co γ-rays from a Vickrad source at a dose rate of *ca.* 4 Mrad h^{-1} for periods up to *ca.* 4 h. Experiments (A)—(D) were performed on each sample: (A) irradiation at 77 K; (B) annealing (A) to room temperature; (C) irradiation at room temperature; and (D) annealing (C) to 400—500 K for several hours. Other variations on (A)—(D) gave the expected results.[5]

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[1] K. D. J. Root and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 2366.

[2] J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, *J. Mol. Structure*, 1967, **1**, 127.

[3] A. O. Caride, J. Danon, and S. I. Zanette, *J. Chem. Phys.*, 1970, **52**, 4911.

[4] R. P. A. Muniz, N. V. Vugman, and J. Danon, *J. Chem. Phys.*, 1971, **54**, 1284.

[5] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Dalton*, 1972, 1086.

E.s.r. spectra were recorded at 77 K on an *X*-band Varian E3 spectrometer.

RESULTS AND DISCUSSION

Incorporation of Ions into the Lattices.—The hexacyanoferrate(II) ion was successfully doped into NaCl, KCl, NaBr, and KBr but only weakly in LiBr and LiCl. No e.s.r. signal characteristic of iron complexes was obtained even after prolonged irradiation from the cyanide in fluoride or iodide hosts. The results are in the Table.

E.s.r. data for species formed by γ-irradiation of hexacyanoferrate(II) ions doped into various host lattices

Host	Symbol	Postulated species	Treatment [a]	*g*-Tensor		^{14}N Hyperfine tensor		Halogen hyperfine tensor	
				$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$
Pure	N_1	$Fe^I(CN)_4(CN')H_2O^{5-}$	B, C [b]	1·998	2·093	*c*	2·0		
	N_2	$Fe^I(CN)_4(CN')_2{}^{5-}$	A[b], B	*d*	2·095	*c*	2·5		
	A	Fe^I species [e]	A	*d*	2·084				
	B	Free radical	A, C	2·002					
	C	Fe^I species [e]	A	*d*	2·135 [e,]				
	D	Fe^I species [e]	A[b], B	*d*	2·089				
	E	Fe^I species [e]	A[b], B	*d*	2·083				
	F	Fe^I species [e]	C	1·916	2·128 [g]				
	G	Fe^I species [e]	C [b]	*d*	2·077				
KCl	N_1(a)	$Fe^I(CN)_4(CN')(H_2O)^{5-}$	A, B, C	1·999	2·093	3·5 [h]	2·0		
	N_1(b)	$Fe^I(CN)_4(CN')(H_2O)^{5-}$	A	*d*	2·100		1·8		
	N_2(a)	$Fe^I(CN)_4(CN')_2{}^{5-}$	A	*d*	2·092		2·0		
	N_2(b)	$Fe^I(CN)_4(CN')_2{}^{5-}$	A	*d*	2·089		2·0		
	N_1Cl_1	$Fe^I(CN)_4(CN')(Cl)^{5-}$	C, D	2·002	2·090	3·5 [h]	2·0	8·0 [h]	4·3
	Cl_2	$Fe^I(CN)_4Cl_2{}^{5-}$	C, D		2·197			*g*	4·7
	N_1H_1 [i]	$Fe^I(CN)_4(CNH)H_2O^{5-}$	C, D	*d*	2·110	*c*	2·0		
	H	Fe^I species [e]	B	*d*	2·104				
	I	Fe^I species [e]	C	*d*	2·100				
NaCl	N_1	$Fe^I(CN)_4(CN')(H_2O)^{5-}$	A, B, C	2·002	2·092	*c*	1·95		
	Cl_1	$Fe^I(CN)_4(CN')Cl_1{}^{5-}$	C	2·001	2·073	*c*	*c*	16	10
	Cl_2	$Fe^I(CN)_4(Cl)_2{}^{5-}$	C	2·017	2·148			14	8·5
	J	Fe^I species [e]	A, B, C	*d*	2·076				
	K	Fe^I species [e]	C	*d*	2·083				
	L	Fe^I species [e]	C	*d*	2·097				
KBr	N_1	$Fe^I(CN)_4(CN')(H_2O)^{5-}$	A, B, C	1·998	2·101	*c*	2·0		
	N_1Br_1	$Fe^I(CN)_4(CN')(Br)^{5-}$	C, D	2·002	2·093	3·5	2·0	38	21·7($^{79-79}$Br) 23·4($^{81-81}$Br)
	Br_2	$Fe\text{-}(CN)_4(Br)_2{}^{5-}$	C, D	*g*	2·186			*g*	22·7($^{79-79}$Br) 24·1($^{79-81}$Br) 26·1($^{81-81}$Br)
	M	Fe^I species [e]	A	*d*	2·111				
	N	Fe^I species [e]	A	*d*	2·083				
	O	Fe^I species [e]	A, B, C	*d*	2·077				
NaBr	N_1	$Fe^I(CN)_4(CN')(H_2O)^{5-}$	A, B, C	*d*	2·089	*c*	*c*		
	Br_1	$Fe^I(CN)_4(CN')(Br)^{5-}$	C	2·002	2·075	*c*	*c*	75	45
	P	Fe^I species [e]	A	*d*	2·077				
	Q	Fe^I species [e]	A	*d*	2·072				

[a] See Experimental section. [b] Sample pre-annealed at *ca.* 400 K before irradiation. [c] Unresolved. [d] Fe^I parallel features superimposed to give a broad free-spin line. [e] See text. [f] Three features flanking this *g*-value. [g] Poorly resolved. [h] Estimated from linewidths. [i] $A_\perp(^1H) = 5{\cdot}7$ G.

(Species E). The three broad lines of Species C were better resolved, as was the quintet of Species N_2. Two weak shoulders around $g = 2{\cdot}038$ were also seen. Warming to ambient temperatures resulted in almost complete loss of these signals.

Irradiation at room temperature for several hours produced a low-intensity spectrum with poorly resolved features; a broad line at $g = 2{\cdot}128$ (Species F) with a broad parallel-like feature at $g = 2{\cdot}196$, a free-spin line, and a triplet of lines at $g = 2{\cdot}093$ (Species N_1). When the sample was annealed to 400 K before irradiation, two perpendicular features were observed, one at $g = 2{\cdot}093$ (Species N_1) and the other at $g = 2{\cdot}077$ (Species G), together with a broad parallel feature at $g = ca.\ 2{\cdot}002$.

Pure Potassium Hexacyanoferrate(II).—Irradiation for short periods (*ca.* 60 s) at 77 K produced two perpendicular sets of lines, one, a quintet at $g = 2{\cdot}095$ (Species N_2), and the other, a singlet at $g = 2{\cdot}084$ (Species A), Species A being the more intense. The corresponding parallel features were obscured by a free-radical signal (Species B). Prolonged irradiation (*ca.* 1 h) increased the concentration of the Fe^I species relative to Species B. Three broad features at low field ($g = 2{\cdot}135$) were also observed (Species C).

When the samples were annealed for two days at 400 K before irradiation at 77 K (*ca.* 1 h), the features for Species N_2 predominated over two other features, one at $g = 2{\cdot}089$ (Species D), and the other at $g = 2{\cdot}083$

Potassium Chloride doped with Hexacyanoferrate(II) *Ions.*—γ-Irradiation at 77 K for a short period (*ca.* 10 s) produced a triplet at $g = 2{\cdot}093$ [Species N_1(a)], together with $Cl_2{}^-$. Prolonged irradiation (*ca.* 1 h) produced a quintet at $g = 2{\cdot}092$ [Species N_2(a)] superimposed upon the triplet of species N_1(a), together with a low-intensity triplet at $g = 2{\cdot}100$ [Species N_1(b)] [Figure 1(a)]. Further irradiation (*ca.* 3·5 h) produced extra lines to higher field, the hyperfine structure being assigned to a quintet [Species N_2(b)].

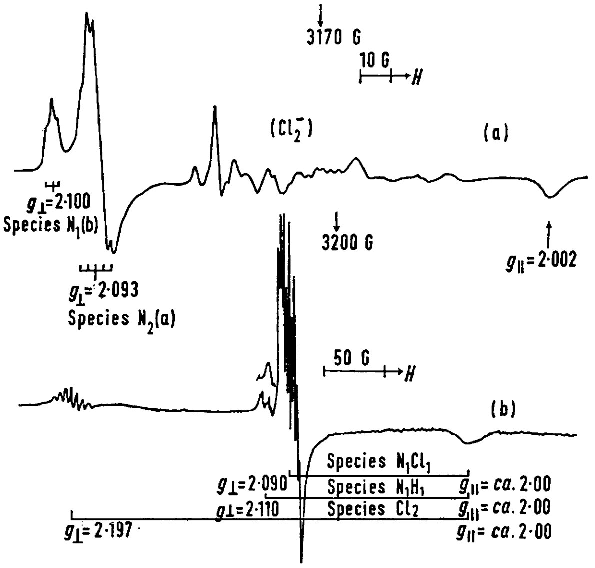

FIGURE 1 *X*-Band e.s.r. spectrum of potassium chloride doped with hexacyanoferrate(II) ions; (*a*) irradiated at 77 K, showing features assigned to Species N_2(a), Species N_1(b), and Cl_2^-, (b) irradiated at R.T. for several hours and annealed at 400 K, showing features assigned to Species Cl_2, Species N_1H_1, and Species N_1Cl_1

On being annealed to ambient temperatures, Species N_2(b) was lost rapidly, and then Species N_1(b) decayed (at about the same rate as Cl_2^- ions). On annealing to room temperature, the e.s.r. signal remaining was that of Species N_1(a), together with a newly formed broad line at $g = 2{\cdot}104$ (Species H).

γ-Irradiation for short periods (*ca.* 60 s) at room temperature produced Species N_1(a), together with three broad low-field features. Prolonging the irradiation up to *ca.* 0·2 h resulted in the appearance of extra low-intensity lines just to high field of Species N_1(a). Irradiation for *ca.* 2 h produced a complex e.s.r. spectrum consisting of a septet at low field (Species Cl_2), together with a well resolved group of lines (Species N_1Cl_1) flanking those for Species N_1(a), and two sets of lines to low field of Species N_1(a). These appeared to be a triplet (or quartet) of triplets superimposed upon a doublet of triplets (Species N_1H_1). The corresponding parallel features were broadened into one line at $g = ca.$ 2·002. Superimposed upon this line were three sharp lines which we assign to the radical HNO_2^-.[6]

Annealing at 400 K for 24 h resulted in complete loss of Species N_1(a). Samples which had been irradiated for short periods only gave Species N_1Cl_1, whereas samples which had undergone irradiation for *ca.* 0·2 h showed e.s.r. spectra of Species N_1Cl_1 and Species Cl_2 [Figure 1(b)]. Irradiation for several hours resulted in halogenation to produce Species N_1Cl_1 and Cl_2. Species N_1H_1 remained on annealing, whereas the other lines disappeared. The possibility that the doublet splitting in Species N_1H_1 was really a result of coupling to a proton was investigated by preparing the doped samples from solutions in D_2O. When an irradiated sample was annealed, a single triplet was found to be centrally superimposed upon the doublet of triplets [Figure 1(b)], thus confirming the assignment.

Sodium Chloride doped with Hexacyanoferrate(II) *Ions.*—γ-Irradiation at 77 K for short periods (*ca.* 1 min) produced a single line at $g = 2{\cdot}076$ (Species J) and on longer irradiation (*ca.* 1 h) a shoulder at $g = 2{\cdot}083$ (Species K) appeared. On warming to ambient temperatures, Species J was retained and a broad triplet at $g = 2{\cdot}092$ (Species N_1) appeared.

Pre-annealing the samples at 400 K for several days produced no effect on the e.s.r. spectra of the irradiated samples but on warming to room temperature no triplet (Species N_1) was observed. After irradiation for *ca.* 1 h at room temperature, the e.s.r. spectrum was identical to that of the annealed low-temperature irradiated samples. Irradiation times of greater than 0·1 h produced a broad quartet of lines (Species Cl_1) flanking that for Species J. (With use of Laboratory Grade Reagent in a preliminary experiment, six isotropic lines appeared at free spin with a hyperfine splitting of *ca.* 17 G. These lines have been attributed to Mn^0 impurity ions in interstitial sites in the host lattice.[7]) Irradiation for several hours produced a more complex e.s.r. spectrum. A line at $g = 2{\cdot}097$ appeared and the intensity of Species Cl_1 had increased relative to that of Species J. Also the parallel features of Species Cl_1 were better defined. A septet at $g = 2{\cdot}148$ (Species Cl_2) was also observed, together with its parallel features at $g = ca.$ 2·002. Annealing at 400 K for several days resulted in complete loss of Species J (Figure 2).

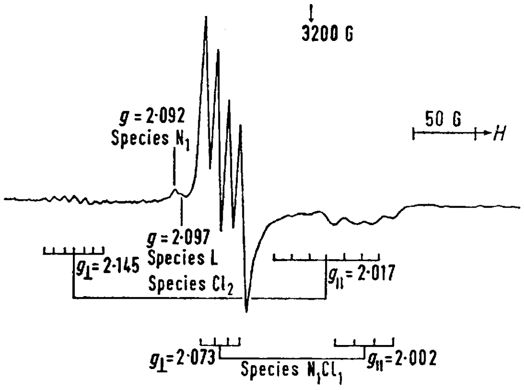

FIGURE 2 *X*-Band e.s.r. spectrum of sodium chloride doped with hexacyanoferrate(II) ions, irradiated for several hours at room temperature and annealed at 400 K for 2 days, showing features assigned to Species N_1, Species L, Species N_1Cl_1, and Species Cl_2

Potassium Bromide doped with Hexacyanoferrate(II) *Ions.*—γ-Irradiation for short periods (*ca.* 1 min) produced Species N_1 at $g = 2{\cdot}011$, together with a low-field line at $g = 2{\cdot}111$ (Species M) and two weak higher-field lines (Species N and Species O), together with the normal broad free-spin parallel feature. Longer irradiation (*ca.* 1 h) increased the intensity of the low- and high-field

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[6] F. J. Adrian, E. L. Cochran, and Vernon A. Bowers, *J. Chem. Phys.*, 1969, **51**, 1018.

[7] N. Itoh and M. Ikeya, *Radiation Effects*, 1970, **4**, 161.

lines relative to that of Species N_1. Hyperfine structure was just resolvable on these shoulders but a satisfactory analysis was not achieved. Warming to ambient temperatures resulted in loss of the high-field lines and reduction of the intensity of the low-field lines, leaving a triplet at $g = 2{\cdot}011$ (Species N_1) and two broad shoulders to lower field.

At room temperature, low irradiation doses (*ca.* 60 s) produced the e.s.r. spectrum of Species N_1, but on prolonging the irradiation a quartet Species N_1Br_1 was observed in low concentration. Irradiation for several hours produced a low-field septet Species Br_2, the e.s.r. spectrum being more intense overall. The spectrum of HNO_2^- was also observed in the free-spin region. On annealing at 400 K, the low-dosed samples gave only the e.s.r. spectrum of Species N_1Br_1; but for those with relatively high doses, the spectra of Species N_1Br_1 and Br_2 were intensified, whilst that of Species N_1 was diminished (Figure 3).

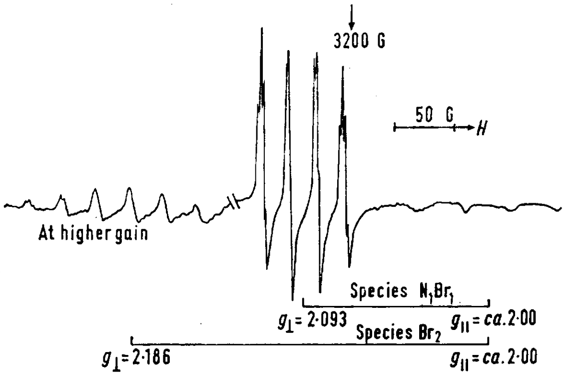

FIGURE 3 *X*-Band e.s.r. spectrum of potassium bromide doped with hexacyanoferrate(II) ions, irradiated for several hours at room temperature and annealed at 400 K for 2 days, showing features assigned to Species N_1Br_1 and Species Br_2

Sodium Bromide doped with Hexacyanoferrate(II) *Ions.*—γ-Irradiation at 77 K (*ca.* 1 h) produced three perpendicular features at $g = 2{\cdot}089$ (Species N_1); $g = 2{\cdot}077$ (Species P); and $g = 2{\cdot}072$ (Species Q), with their corresponding parallel features broadened into one line at $g = 2{\cdot}002$. Hints of hyperfine structure were seen on the perpendicular lines but optimum conditions for its resolution could not be obtained. On warming to ambient temperatures, only Species N_1 remained. γ-Irradiation for short periods (*ca.* 1 min) at room temperature produced Species N_1 and on prolonging the irradiation a broad quartet of lines (Species Br_1) appeared at $g = 2{\cdot}078$.

Identification.—All the species listed above are thought to be Fe^I complexes since the $Fe(CN)_6^{4-}$ unit replaces a $M(Hal)_6^{5-}$ unit in the alkali-metal halide lattice and is, therefore, a good electron-trap. Further, in all cases the form of the *g*-tensor components accords with expectation for an Fe^I (d^7) complex with axial distortion.

The species having no detectable hyperfine coupling to ligand nuclei cannot be identified completely from their e.s.r. spectra. By analogy with our results for alkali-metal halides doped with $Co(CN)_6^{3-}$ ions, one of these species is probably $Fe(CN)_5^{4-}$. For the cobalt series, we found that $g_\perp$ was markedly dependent upon the number of ligands[8] and hence we would expect $Fe(CN)_5^{4-}$ to have $g_\perp$ values considerably greater than those for the N_1 or N_2 complexes. Hence we suggest that the complexes having $g_\perp = ca.\ 2{\cdot}13$ are probably the pentacyanide. The remainder have $g_\perp = ca.\ 2{\cdot}085$. These presumably have six ligands, and are probably $Fe(CN)_5X^{5-}$ or $Fe(CN)_4X_2^{5-}$ species (see below).

In some cases, species in sodium halides which, by analogy with their potassium halide analogues, were expected to show triplet or quintet hyperfine features, showed only broad singlets. These are, nevertheless, tentatively described as N_1 or N_2 Species (Table). The extra broadening probably arises from weak hyperfine interaction with surrounding sodium nuclei, since these have far greater magnetic moments than have potassium nuclei.

The N_1 species have ^{14}N hyperfine parameters comparable with those found for the analogous Co^{II} complexes,[5] and presumably have similar structures. In our previous discussion[5] of this problem, we concluded that the ligand responsible for the ^{14}N coupling was a cyanide ion twisted off the *z*-axis to a relatively small extent, rather than through 180° to give an isocyanide, as suggested by Danon and his co-workers.[2] Our arguments were based partly on analogy with the behaviour of nitrosyl ligands, which are known to move so that the M–N–O angle becomes bent. Also, the small magnitude of the ^{14}N coupling is far more in keeping with a bent M–C–N configuration, rather than a linear or slightly bent M–NC configuration.[5] We therefore write the complex as $Fe(CN)_4(CN')X^{5-}$, CN′ signifying the 'twisted' ligand, and X being the other ligand on the *z*-axis. This could be a normal cyanide, as previously assumed,[1] but, as we indicate below, there are reasons for doubting this.

The N_2 species, previously described as 'di-isocyanides', are now thought to have two cyanides bent off the *z*-axis equivalently, and possibly displaced laterally also. The ^{14}N hyperfine parameters are close to those found for the cobalt complexes,[5] as also are the $g_\perp$ values. For the latter, $g_\parallel$-values were generally in the region of 2·013, and it was suggested that the positive shift might arise from spin on the twisted cyanide ligands. Since, in the present work, no such *g*-shift was observed, we must conclude that this is not the case. Possibly the unusual shift in $g_\parallel$ for the cobalt complexes resulted from a small libration about the *z*-axis.

The monohalogeno-species again have halogen hyperfine tensor components and $g_\perp$-values comparable with those for the cobalt analogues.[5] Some show clear triplet splitting on each line indicative of coupling to ^{14}N, so the species are clearly $Fe(CN)_4(CN')Cl^{5-}$ ions. However, the Cl_1 species in sodium halide lattices which do not have resolved triplets have broad features which could well conceal unresolved triplet components. We

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[8] M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 2069.

therefore class all the monohalogeno-complexes as $Fe(CN)_4(CN')Hal^{5-}$ species.

The dihalogeno-complexes, like their cobalt analogues, have much greater $g_\perp$-values. This is indicative of more ionic bonding and accords with a *trans*-arrangement for the two halide ions, as does their equivalence in both parallel and perpendicular directions.

Electronic Structure.—All these complexes have a single unpaired electron primarily in the iron d_{z^2} atomic orbital which is well separated from the other *d*-orbitals. Only the ligands on the *z*-axis show any hyperfine interaction, the couplings being normal for σ-delocalisation.[5] The levels closest to that of the unpaired electrons which can couple magnetically are probably the filled d_{xz},d_{yz} pair. This coupling is responsible for the positive deviations from the free-spin value for $g_\perp$.

Damage Mechanisms.—The most striking aspect of the present results is the marked product dependence upon dose. This is unusual, and cannot readily be interpreted in terms of competing processes or secondary reactions, since no ' thermal ' changes were detected at 77 K. Quite the most probable explanation is that very low concentrations of impurity ions were incorporated together with the $Fe(CN)_6^{4-}$ ions, which act as more efficient electron traps. At very low doses these impurities react preferentially until their concentration is so low that the less favoured interaction with $Fe(CN)_6^{4-}$ ions dominates. This interpretation adequately accommodates all the results so far obtained.

The most likely impurity ions in crystals grown from aqueous solution are $Fe(CN)_5H_2O^{3-}$ or $Fe(CN)_4(H_2O)_2^{2-}$, or possibly their conjugate bases. The effect of high-temperature annealing is then probably to displace water by halide ions.

If this is correct, the N_1 species is probably $Fe(CN)_4$-$CN'H_2O^{4-}$ rather than $Fe(CN)_5CN'^{5-}$ as previously supposed. This offers a ready explanation for the fact that both mono- and di-' isocyanide ' complexes can be formed. This differentiation cannot be purely electronic, because it is highly improbable that a distortion would sometimes involve the movement of one axial cyanide, and sometimes that of two cyanides. Danon and his co-workers [3] suggested previously that the choice depended upon the presence of one or two compensating cation vacancies. This agreed well with our earlier results for $Fe(CN)_6^{4-}$, when only the N_1 species was observed,[1] since there is only one induced cation vacancy. However, it offers no explanation for the fact that the favoured product after prolonged exposure is the N_2 species. We therefore suggest that the normal mode of distortion for $Fe(CN)_6^{5-}$ ions is for both axial cyanide ions to twist and move away slightly so as to reduce the antibonding effect of the added electron.

It is noteworthy that we have been able to detect a complex exhibiting weak hyperfine coupling to a proton. We originally postulated protonation as a possible cause of the asymmetry of the N_1 species,[1] and it now seems that this can indeed occur. The proton is probably bonded to nitrogen to give a complex containing the Fe–CNH unit. This resembles the organic isocyanide complexes containing M–CNR units, studied by Kimball and his co-workers.[9] These structurally similar complexes also exhibited hyperfine coupling to ^{14}N of the same magnitude (*ca.* 5 G).

We thank the S.R.C. for a grant (to J. G. W.).

[2/1311 *Received, 9th June*, 1972]

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[9] M. E. Kimball, D. W. Pratt, and W. C. Kaska, *Inorg. Chem.*, 1968, **7**, 2006.