206. *The Electronic Structure of the Iron Atoms in Complex Iron Cyanides.*

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Several complex iron cyanides have been prepared by precipitation from solutions of iron(II) or iron(III) sulphate by addition of potassium cyanoferrate(II) or potassium cyanoferrate(III). Determination of the Mössbauer spectra with these compounds as absorbers shows that the iron atoms in several preparations are very similar in chemical nature, and often quite different from those in the compounds from which they were prepared. There is an observable difference between the two types of iron atom in any particular compound. The cation is invariably spin-free, and the anion spin-paired. In the oxidation of $K_2Fe[Fe^{II}(CN)_6]$, only the cation changes its valency state.

THE structures of Prussian blue, Turnbull's blue, Berlin green, and related compounds were shown in 1936, by *X*-ray methods,[1] to involve cubic lattices with the iron atoms in equivalent positions, the difference between the various compounds arising because alkali-metal atoms may be incorporated in the structures and the iron atoms may be in different oxidation states. We discuss here the evidence provided by nuclear radiation resonance methods, using the ^{57}Fe nucleus,[2] on the electronic structures of the iron atoms in these compounds.

Method.—Approximately 0·1M-solutions of iron(II) and iron(III) sulphate and potassium cyanoferrate-(II) and -(III) were made up. Equivalent quantities (50 ml.) of the first pair were added in turn to each of the second pair, so that four precipitates were obtained. The iron atoms in these complex cyanides are here distinguished by use of arabic symbols (Fe^{2+}, Fe^{3+}) to indicate the valency state of the cationic iron atoms used in the preparation, and with roman numerals (Fe^{II}, Fe^{III}) to indicate the anionic iron atoms, but no structural significance is implied; *e.g.*, Fe^{2+}/Fe^{III} merely indicates that the precipitate was formed by mixing iron(II) sulphate and potassium cyanoferrate(III). After formation, the precipitates were centrifuged off, washed with water (10 ml.), dried on a filter paper, and mounted in aluminium holders with thin mica windows, so that pellets $\frac{3}{4}$ in. in diameter and $\frac{1}{8}$ in. thick could be placed axially

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[1] Keggin and Miles, *Nature*, 1936, **137**, 577.

[2] Mössbauer, *Z. Phys.*, 1959, **151**, 125.

in a Mössbauer assembly described elsewhere.[3] The absorption spectrum was then determined by using a ½-mc source of $^{57}Fe/^{57}Co$ mounted on a copper backing, which gave monochromatic emission with nearly natural line-width.[3] The source was moved axially at velocities up to about ±0·3 cm./sec. A positive sign indicates that the source is moving towards the absorber. For ^{57}Fe, 1 cm./sec. = $4{\cdot}8 \times 10^{-7}$ ev or 0·011 cal./mole.

RESULTS AND DISCUSSION

General Features.—Typical spectra for both the simple and the complex cyanides have been reported elsewhere,[3] but are reproduced for comparison in the Figure. All complex cyanides gave very similar spectra, although there were minor differences that are discussed in detail below. The close similarity of the spectra of the Figure C–G to each other immediately confirms the conclusion from *X*-ray work[1] that all the complex cyanides are structurally related. Further, the positions of the main resonance peaks are different from many of those in the compounds from which the complex cyanides were prepared (see Tables 1 and 2). There must, therefore, be some interaction between the two types of iron atom during the preparation, for it is known that a free ion separated from an iron atom by more than about 4 Å has very little effect on the peak resonance values[3] although it may somewhat affect the shape of the resonance line.[4] Thus the peak resonances for $K_4[Fe(CN)_6],3H_2O$ and $Na_4[Fe(CN)_6],10H_2O$ are very close to each other in spite of the different cations and the different numbers of water molecules in the structure (see Table 1). Simple electrostatic interaction cannot therefore be the only means by which the two types of iron atom in the complex cyanides affect each other. Indeed the electron densities of the nuclei of the two types of iron atom appear to be very similar. This general conclusion may, however, be modified in any particular compound as described below.

TABLE 1.

Assignments of resonances for iron cyanides.

(All figures are in cm./sec.; δ-values are corrected relative to a natural iron absorber by addition of 0·013 to the results for our copper-mounted source.)

	Anion (*a*)		Cation (*b*)			Quality of
	ΔE_Q	δ	ΔE_Q	δ	$\delta_b - \delta_a$	spectrum
Absorber						
$K_4[Fe(CN)_6],3H_2O$...	0 ± 0·01	0 ± 0·005	—	—		Excellent
$Na_4[Fe(CN)_6],10H_2O$	0 ± 0·02	+0·01 ± 0·005	—	—		Excellent
$K_3[Fe(CN)_6]$	0·026 ± 0·005	−0·01 ± 0·005	—	—		Excellent
Complex cyanides						
Fe^{3+}/Fe^{III}	0 ± 0·01	+0·003 ± 0·01	0 ± 0·01	0·053 ± 0·01	0·05	Excellent
Fe^{3+}/Fe^{II}	0 ± 0·01	+0·003 ± 0·01	0·04 ± 0·01	0·043 ± 0·01	0·04	Good
Fe^{2+}/Fe^{III}	0 ± 0·005	+0·003 ± 0·005	0·04 ± 0·005	0·053 ± 0·005	0·05	Excellent
Fe^{2+}/Fe^{II} (freshly prepared)	0·18 ± 0·02	+0·093 ± 0·02	0·06 ± 0·02	0·033 ± 0·02	0·04	Fair *
Fe^{2+}/Fe^{II} (fully oxidised)	0 ± 0·01	+0·005 ± 0·01	0·035 ± 0·01	0·049 ± 0·01	0·05	Good

* Calc. by using the 0·173 cm./sec. resonance peak as one of the quadrupole arms of the Fe^{2+} spectrum.

TABLE 2.

Typical values of ΔE_Q and σ for iron compounds (relative to a natural iron source).

Absorber	ΔE_Q (cm./sec.)	δ (cm./sec.)
Spin-free Fe^{2+}	0·15 to 0·35	+0·10 to +0·15
Spin-free Fe^{3+}	0 to 0·06	+0·03 to +0·10
Spin-paired Fe^{II}	0 to 0·17	−0·02 to +0·03
Spin-paired Fe^{III}	0 to 0·04	−0·04 to +0·05

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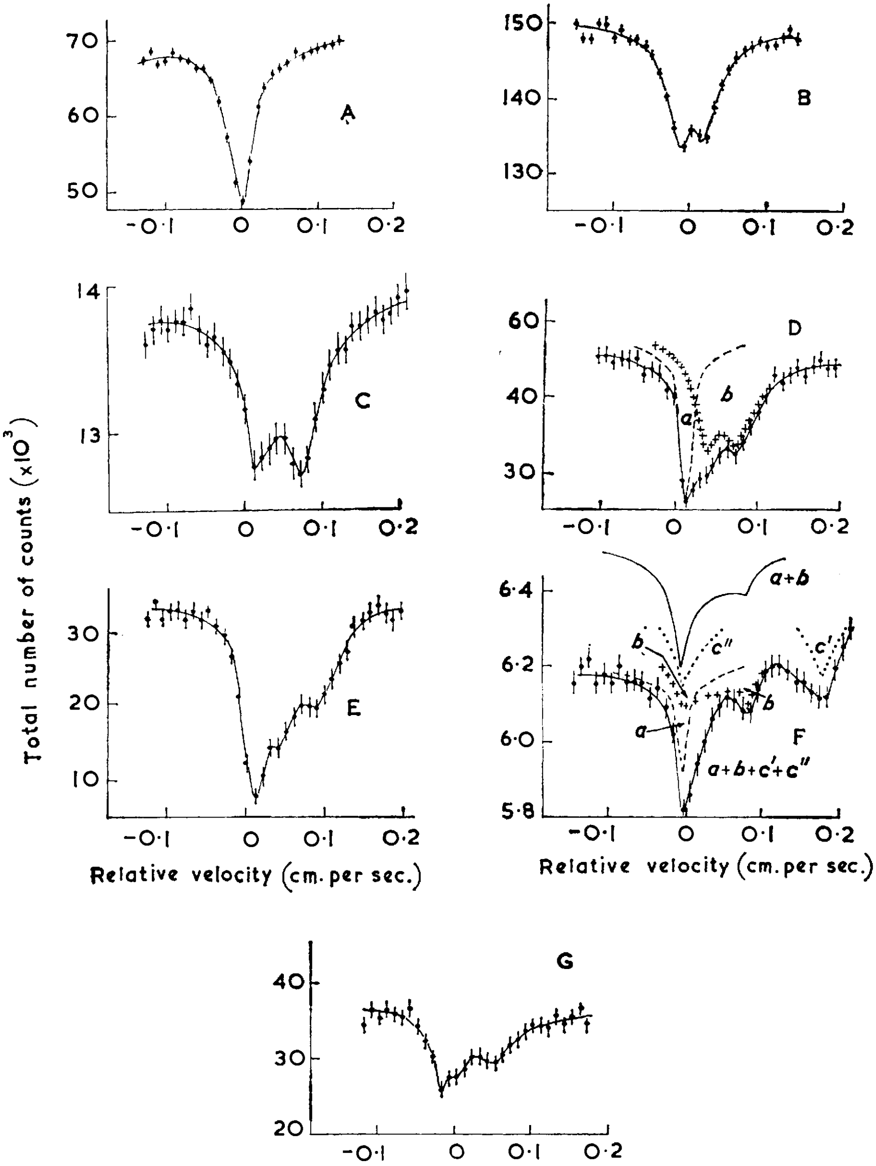
[3] Brady, Wigley, and Duncan, *Rev. Pure Appl. Chem. Australia*, 1962, **12**, in the press; Duncan and Mok, forthcoming publication.

[4] G. J. Perlow, personal communication.



Measured intensity as a function of absorber velocity for: (A) $K_4[Fe(CN)_6],3H_2O$; (B) $K_3[Fe(CN)_6]$; (C) Fe^{3+}/Fe^{III}; (D) Fe^{2+}/Fe^{III}; (E) Fe^{3+}/Fe^{II}; (F) freshly prepared Fe^{2+}/Fe^{II}; (G) fully oxidised Fe^{2+}/Fe^{II}. The results are corrected relative to a natural iron absorber. The lengths of the lines for the experimental values indicate $\pm\sigma$, where σ is the standard deviation due to statistical variation in counting rate. In (F) the curves c', c'', and $(a + b)$ are displaced vertically.

Simple Iron Compounds.—Before discussing the complex cyanides in detail, we recall [3,5] that, with respect to a natural iron source (to which all our data are corrected), complexes of iron(II) with a $d^6[d^4s^2p^6]$ structure and a symmetrical arrangement of ligands, normally exhibit a very small chemical shift (δ) and no quadrupole interaction (ΔE_Q). But for symmetrical iron(III) spin-paired complexes, δ may have any value, whilst ΔE_Q is usually observable, but small. The quadrupole interactions in the latter case arise because the *d*-electron shell has one vacancy which causes anisotropic screening of the *s*-electrons at the iron nucleus. A similar anisotropy accounts for the very large quadrupole split obtained for most spin-free iron(II) compounds. Thus, for $FeSO_4,7H_2O$, from which some of these compounds were prepared, $\Delta E_Q = 0{\cdot}315$ cm./sec. and $\delta = +0{\cdot}13$ cm./sec. (ref. 3). For spin-free iron(III) compounds, both ΔE_Q and δ are small (see Table 2). These results are important for interpretation of the results for the complex iron cyanides.

Electronic Structure of Complex Iron Cyanides.—The spectra can be interpreted as due either to two single resonance lines, or to the superposition of a quadrupole split level and a single line. Both interpretations accord with the general features discussed above. We prefer the latter interpretation, however, because there is evidence of two shoulders in many of the spectra, which fit accurately with the quantitative aspects of this interpretation.

On this basis, the observed spectrum can be considered to be the sum of two levels, one (*b*) may show quadrupole interactions, the other (*a*) none. The contributions of these two components to the composite spectra were evaluated by assuming that all resonance lines were symmetrical with respect to their peak resonances, and that the quadrupole pair were of equal intensity. The components of some of the spectra are shown by broken lines in the Figure. Values of ΔE_Q and δ obtained from these results are listed in Table 1.

The following features are common to all the spectra of the complex cyanides: (i) The quadrupole interactions (*b*) with $\Delta E_Q = 0{\cdot}03$ to $0{\cdot}06$ cm./sec. and $\delta = +0{\cdot}033$ to $+0{\cdot}053$ cm./sec. can arise only from the cationic iron atom, since ΔE_Q is much larger than is obtained with potassium cyanoferrate(III). (ii) The unsplit line (*a*) with $\delta = \sim 0{\cdot}003$ cm./sec. ascribed to the anionic iron atom has characteristics which are very similar to those of the cyanoferrate(II) anion, even in cases where the anionic iron atom is undoubtedly tervalent (see below). (iii) The intensities of the two resonances, although in general not equal, are of the same order of magnitude. The effective Debye temperatures, and the binding energies of the two types of iron atom, are therefore comparable. The (cationic) iron atom, which exhibits quadrupole interactions, usually appears to be slightly more tightly bound than the (anionic) iron atom with no quadrupole effects. (iv) The displacement, $\delta_b - \delta_a$, equal to $0{\cdot}04 - 0{\cdot}05$ cm./sec. indicates a small, but significant, difference between the *s*-electron densities at the nuclei of the two types of iron atom. Except for the fully reduced species, this displacement is almost constant throughout the series, so that the difference in the electron densities (but not the field gradients) at the two iron nuclei are almost the same.

Apart from these common features, the individual complex iron cyanides do display some differences which are discussed in detail below.

Fully oxidised species $[Fe^{3+}/Fe^{III}]$. If we regard the fully oxidised compound (Berlin green) as $Fe^{3+}[Fe^{III}(CN)_6]^{3-}$, then peak (*a*) at $+0{\cdot}003$ cm./sec. is reasonably ascribed to the cyanoferrate(III) ion. However, the small quadrupole interaction ($\Delta E_Q = 0{\cdot}02$ cm./sec.) expected for this anion {as in $K_3[Fe^{III}(CN)_6]$} is not detectable above the statistical variation. If this is not due to experimental difficulties arising from the presence of the two types of iron atom (which we believe unlikely), it suggests that the electronic environment of the anionic iron atom approaches the spherical symmetry of the spin-paired cyanoferrate(II) ion.

The cationic resonance (*b*) is expected from the d^5-structure for Fe^{3+} in a symmetrical environment to be unsplit, as was invariably observed.

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[5] DeBenedetti, Lang, and Ingalls, *Phys. Rev. Letters*, 1961, **6**, 60.

Half-oxidised species [Fe^{2+}/Fe^{III}; Fe^{3+}/Fe^{II}]. There appear to be no essential differences between the spectra of these compounds, irrespective of whether the cation or the anion was the original reduced species. The Fe^{3+}/Fe^{II} compound (soluble Prussian blue) has a magnetic moment [6] corresponding to the composition $KFe[Fe^{II}(CN)_6]$. The Fe^{2+}/Fe^{III} compound has a similar composition, although its magnetic moment has not been reported.

The Mössbauer spectra may be interpreted by first noting that the observed values of the chemical shift for the two types of iron atom (δ_a and δ_b) are very similar to those of the fully oxidised species. This requires that the screening of *s*-electrons by addition of an extra 3*d*-electron be largely compensated by a shift of the screening electrons away from the iron atoms, into the cyanide groups or elsewhere in the structure. The similarity of the anionic iron atom to a spin-paired Fe^{II} state in the fully oxidised species would allow an easy means by which this would occur since the extra electron would have to be provided in the Fe^{3+}/Fe^{III} compound by the six cyanide groups.

The values of δ and ΔE_Q are not typical of spin-free Fe^{2+} in either compound. The anion is, however, quite clearly in a spin-paired iron(II) state, whilst the cation corresponds most closely to a spin-free iron(III) atom. The quadrupole interactions of the cation ($\Delta E_Q = 0{\cdot}04$ cm./sec.) would be high for a regular cubic structure.[1] But the formulation $KFe[Fe(CN)_6]$ requires that every cation should have a tetrahedral arrangement of potassium ions, each of which are about 4·4 Å away, as well as an octahedral arrangement of CN groups which are not co-ordinated to the cationic iron atom. It is known that free cations have little effect on the Mössbauer spectra of spin-paired complexes, which explains why the anion peak is unsplit. But such an arrangement would undoubtedly cause some electron anisotropy in the region of the spin-free iron cation. The magnitude of the quadrupole split seems to be reasonable, for if a free ammonium ion is introduced into spin-free iron(III) chloride a distinct quadrupole split of 0·03 cm./sec. (for $FeCl_3,2NH_4Cl,H_2O$) is observable, although it is undetectable ($<0{\cdot}02$) for both anhydrous (known to be octahedral) and hexahydrated ferric chloride.

Reduced species [Fe^{2+}/Fe^{II}]. Since, in this case, aerial oxidation readily occurs, it was very difficult to obtain a Mössbauer spectrum characteristic of the pure compound. However, with care during the preparation, so that only superficial oxidation occurred, the results shown in the Figure F could be obtained two hours after preparation. Apart from the main anionic resonance, there is a distinct peak at $+0{\cdot}173$ cm./sec. This we assign to one arm (c') of the spin-free iron(II) cation, suffering quadrupole interactions, characteristic of such atoms. Since there are no extra shoulders on the main resonance (apart from that which might be due to oxidation), the other arm (c'') coincides with that for the cyanoferrate(II) anion. This leads to typical spin-free iron(II) values of $\delta = 0{\cdot}093$ cm./sec. and $\Delta E_Q = 0{\cdot}18$ cm./sec.

When this compound is allowed to oxidise completely (after more than 14 days in the atmosphere) the spectrum shown in the Figure G is obtained (unaltered by time). The resonance at $+0{\cdot}173$ cm./sec. has now disappeared, and the shape of the main resonance is somewhat altered, so that it now appears to be very similar to those obtained for the half-reduced compounds. This confirms the view that the compound initially contained Fe^{2+}, which was oxidised to Fe^{3+} by air, whilst the spin-paired cyanoferrate(II) was substantially unaltered. Confirmation is afforded by the following observations:

(i) Since the stoicheiometry of the major constituents cannot change during the oxidation, we expect the primary species $K_2Fe[Fe(CN)_6]$ to contain another anion, O^{2-}, of OH^- after oxidation. Analysis showed the oxidation product to have a composition close to that corresponding to $KFe[Fe(CN)_6],KOH$ (Found: C, 17·75; H, 2·1; N, 23·6. Calc.: C, 19·6; H, 0·3; N, 23·1%). Although other formulæ, such as $KFe[Fe(CN)_6],KOH,H_2O$, $KFe[Fe(CN)_6],\frac{1}{2}K_2CO_3$, etc., would give as good agreement, the

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[6] Davidson and Welo, *J. Phys. Chem.*, 1928, **32**, 1191.

results suggest that the unoxidised compound is not far from the expected composition designated above.

(ii) After oxidation, the magnetic moment, on the assumption of one magnetic iron atom, was 5·09 B.M., compared with a theoretical value of the effective magnetic moment for $KFe[Fe^{II}(CN)_6]$ of 5·9 B.M. This is as expected, but unfortunately the magnetic evidence is not as clear-cut as the Mössbauer evidence, for if we assume two magnetic iron atoms the effective magnetic moment is 3·59 B.M., compared with a spin-only theoretical value of 3·67 B.M. for $KFe[Fe^{III}(CN)_6]$.

Conclusions.—From this work we conclude that all the complex cyanides have spin-free cations and spin-paired anions. The former are those expected from currently accepted formulæ, but the anions appear preferentially to form spin-paired cyanoferrate(II). In both the Fe^{2+}/Fe^{III} and the Fe^{3+}/Fe^{II} compound, the cation has a spin-free iron(III) electronic structure which is modified to some extent by interactions with the cyanide group and free potassium ions. Oxidation of the Fe^{2+}/Fe^{II} compound occurs exclusively at the cation. The very fast oxidation compared with that of most other spin-free iron(II) compounds, combined with the relatively small values of ΔE_Q and δ for the cation in the fully reduced compound, is in accordance with a small interaction[7] between the spin-free cation and the cyanide groups.

The spectra on which this paper is based were determined by Dr. M. A. Clarke, Mr. W. F. Mills, and Mr. G. C. Dixon on absorbers prepared by one of us (J. F. D.) in 1961 whilst a visitor to the Atomic Energy of Canada, Ltd., Chalk River, Canada. Thanks are offered to A.E.C.L. for providing facilities to do the experimental work, which has already been reported elsewhere.[3] The analysis and magnetic measurements on the oxidised Fe^{II}/Fe^{2+} compound were done, respectively, by Dr. W. Zimmerman of C.S.I.R.O., Melbourne, and Dr. C. R. Kanekar, Senior Fellow in the Chemistry Department, University of Melbourne, Australia. The results were evaluated, and the spectra normalised, and corrected for instrumental variations in Melbourne.

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[*Received, July 2nd,* 1962.]

[7] Thompson, *J. Amer. Chem. Soc.*, 1948, **70**, 1045.