Evidence for an Orbitally Degenerate Ground State in Hexa-amminecobalt(III) Hexacyanoferrate(III) from Mössbauer Spectroscopy

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The compound $[Co(NH_3)_6][Fe(CN)_6]$ has been found to have trigonal symmetry at the iron site. Mössbauer-spectroscopic measurements show that the ground state of the low-spin iron(III) is an orbitally degenerate ^2E_g state. The effective spin–orbit coupling parameter is $\lambda \simeq -100$ cm^{-1}, and it is shown that non-bonding 3*d* orbitals of t_{2g} symmetry are expanded relative to the free ion under the influence of a cubic ligand field.

POTASSIUM HEXACYANOFERRATE(III), $K_3[Fe(CN)_6]$, has been extensively studied by Mössbauer spectroscopy. The $^2T_{2g}$ (t_{2g}^5) configuration of low-spin iron(III) is perturbed by the low symmetry of the ligand field, but the various attempts to correlate e.s.r., magnetic-susceptibility, and Mössbauer measurements on this material have revealed many problems.[1-10] The analysis is complicated by the low symmetry of the ligand field (the point symmetry at the iron is only C_i). Furthermore, the crystals tend to show extensive polytypism [3]

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with a very close relation of the monoclinic and orthorhombic lattices, and with the exception of one recent work [10] this aspect has been largely ignored.

Very few other stoicheiometric salts of this anion have been characterized by a full *X*-ray analysis: $Cs_2Li[Fe(CN)_6]$ has a cubic lattice and therefore shows no quadrupole splitting,[11] $Cs_2Na[Fe(CN)_6]$ and $Cs_2K[Fe(CN)_6]$ have distorted lattices of monoclinic symmetry,[12] and $La[Fe(CN)_6]\cdot 5H_2O$ has a hexagonal lattice [13] but contains two unco-ordinated water molecules with disorder of the hydrogen positions. The many insoluble derivatives of the Prussian Blue type are not satisfactory for ligand-field studies because their lattices are normally less regular than the stoicheiometry or *X*-ray analysis would suggest.

This paper presents data for the compound hexaamminecobalt(III) hexacyanoferrate(III), $[Co(NH_3)_6][Fe(CN)_6]$, which is found to have trigonal symmetry at the iron site with an orbitally degenerate ground state for the perturbed t_{2g}^5 configuration. In other low-spin iron(III) compounds [14] where the site symmetry is dictated mainly by the geometry of chelating ligands the ground state has been found to be orbitally non-degenerate: $[Fe(phen)_3]^{3+}$, $[Fe(bipy)_3]^{3+}$, $[Fe(phen)_2(CN)_2]^+$, and $[Fe(bipy)_2(CN)_2]^+$ have a non-degenerate ^2A ground term [15,16] (phen = 1,10-phenanthroline, bipy = 2,2′-bipyridyl); $[Fe(terpy)_2]^{3+}$ has a ^2B ground term (terpy = 2,2′:6′,2″-terpyridyl); [14] and several compounds with sulphur ligands [17,18] as in $[Fe(pdt)_3]$ (pdt = pentane-2,4-dithionate) and $[Fe\{S_2C_2(CN)_2\}_3]^{3-}$, and persulphides [19] such as $[Fe(p\text{-}Me\cdot C_6H_4\cdot CS_3)_2(p\text{-}Me\cdot C_6H_4\cdot CS_2)]$ are similar. The orbitally degenerate (^2E_g) ground state in $[Co(NH_3)_6][Fe(CN)_6]$ is therefore particularly interesting.

EXPERIMENTAL

The compound $[Co(NH_3)_6][Fe(CN)_6]$ was prepared as yellow needle-like crystals from mixed aqueous solutions of $[Co(NH_3)_6]Cl_3$ and $K_3[Fe(CN)_6]$. The composition was verified by chemical analysis {Found: C, 19.3; H, 4.65; N, 44.8. Calc. for $[Co(NH_3)_6][Fe(CN)_6]$: C, 19.3; H, 4.8; N, 45.0%}.

The similar compound $[Co(NH_3)_6][Co(CN)_6]$ has been shown to crystallize in the rhombohedral space group $R\bar{3}$ [rhombohedral cell, $a = 7.255(3)$ Å, $\alpha = 97.65(2)°$, $U = 370.6$ Å^3, $Z = 1$; hexagonal cell, $a = 10.921(3)$, $c = 10.765(3)$ Å, $Z = 3$] with a point symmetry of $\bar{3} = C_{3i}$ (S_6) at the cobalt site bonded to carbon.[20] The $[Fe(CN)_6]^{3-}$ anion is not isoelectronic with $[Co(CN)_6]^{3-}$, and it is important to confirm that $[Co(NH_3)_6][Fe(CN)_6]$ retains the C_3 axis. Single-crystal *X*-ray measurements showed that the space group is either $R3$ or $R\bar{3}$ [rhombohedral cell, $a = 7.296(1)$ Å, $\alpha = 97.63(1)°$, $U = 377.04(9)$ Å^3, $Z = 1$; hexagonal cell, $a = 10.983(2)$, $c = 10.830(2)$ Å, $Z = 3$] with a point symmetry at the iron site of either $3 = C_3$ or $\bar{3} = C_{3i}$ (S_6). In either case the site has a three-fold axis and the ligand-field description is that of trigonal symmetry. In all probability the two compounds are isostructural, and in the discussion which follows the symbols conveniently used are those of S_6. However, the same arguments are valid if the point symmetry is C_3.

Mössbauer spectra were recorded at 87—292 K using a Ricor MCH-5 variable-temperature cryostat, and calibrated using an enriched iron-metal foil at room temperature. The method of calculating the temperature dependence of the quadrupole splitting from a perturbed t_{2g}^5 configuration has been described in detail elsewhere.[21]

RESULTS AND DISCUSSION

The Mössbauer spectrum of $[Co(NH_3)_6][Fe(CN)_6]$ comprises a simple quadrupole doublet as expected for a distorted t_{2g}^5 configuration. The chemical-isomer shift decreases monotonically from -0.068 mm s^{-1} at 87 K to -0.137 mm s^{-1} at 292 K. The broadening of the linewidth observed in the series $Cs_2M[Fe(CN)_6]$ (M = Li, Na, or K) does not occur even at 87 K in the present instance, showing that the spin–lattice relaxation time is significantly shorter. The temperature dependence of the quadrupole splitting, Δ, is also atypical of $[Fe(CN)_6]^{3-}$ compounds in that it was almost independent of temperature (Figure 1).

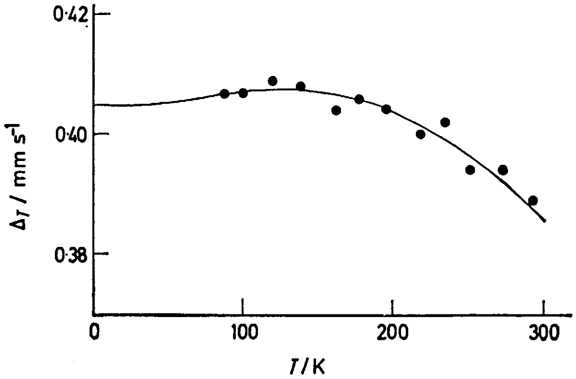

FIGURE 1 Temperature dependence of the quadrupole splitting in $[Co(NH_3)_6][Fe(CN)_6]$. The full line represents the solution $\lambda = -100$ cm^{-1}, $\Delta_{trig.} = -660$ cm^{-1}, $\alpha^2\Delta_0 = -0.853$ mm s^{-1}, and $\Delta_{latt.} = +0.008$ mm s^{-1}

The trigonal field under S_6 causes the $^2T_{2g}$ ground term to split into $^2A_g + {}^2E_g$ with a separation of $\Delta_{trig.}$ (which I define as positive in sign when the ground term is ^2A_g). The spin–orbit coupling causes a further removal of degeneracy to give three Kramers' doublets. The quadrupole splitting at a temperature *T* is usually described for axial asymmetry by an equation of the form (1) where $(1 - R)$ is the Sternheimer shielding

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factor, $\langle r^{-3}\rangle_{3d}$ is the free-ion expectation value of the radial distribution of the $3d$ electrons, λ is the spin–orbit coupling constant, α^2 represents the effect of covalency ($\alpha^2 < 1$), $F(\Delta_{\text{trig.}},\lambda,T)$ represents the effect of a temperature-dependent Boltzmann population of the three Kramers' doublets ($0 < |F| < 1$), and $\Delta_{\text{latt.}}$ is a temperature-independent 'lattice' contribution.[21]

$$\Delta_T = \tfrac{4}{7}(1 - R)\langle r^{-3}\rangle_{3d}\alpha^2 F(\Delta_{\text{trig.}},\lambda,T)(e^2Q/8\pi\varepsilon_0) + \Delta_{\text{latt.}} \quad (1)$$

If we define $\Delta_0 = \tfrac{4}{7}(1 - R)\langle r^{-3}\rangle_{3d}(e^2Q/8\pi\varepsilon_0)$ as a phenomenological parameter which can be equated with the splitting produced by a single t_{2g} electron, then equation (2) may be obtained.

$$\Delta_T = \alpha^2\Delta_0 F(\Delta_{\text{trig.}},\lambda,T) + \Delta_{\text{latt.}} \quad (2)$$

The temperature dependence of the quadrupole splitting can then be expressed in terms of the four phenomenological parameters $\alpha^2\Delta_0$, $\Delta_{\text{trig.}}$, λ, and $\Delta_{\text{latt.}}$ by making use of the 'electron–hole' formalism.[21] The sign of e^2qQ for a ^2A_g ground state is then found to be positive (corresponding to a hole in d_{z^2}), and for a ^2E_g ground state is negative.

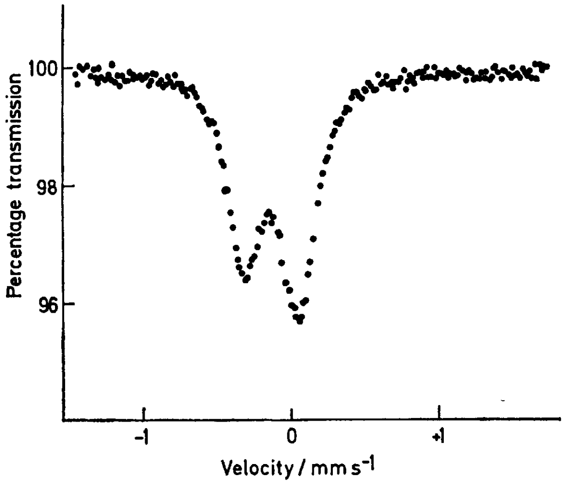

FIGURE 2 Mössbauer spectrum of a matrix of crystals of $[Co(NH_3)_6][Fe(CN)_6]$ orientated with the needle axis (C_3 axis) perpendicular to the direction of observation

A detailed examination of the functional behaviour of Δ_T revealed that the data could not be accounted for in terms of a ^2A_g ground state, but could be consistent with a ^2E_g ground state. This was then confirmed by recording the Mössbauer spectrum (Figure 2) of a matrix of crystals oriented with the needle axis (C_3 axis) perpendicular to the direction of observation. The ratio of the areas of the lines at more negative and positive velocities respectively was found to be 0.71 : 1, compared to the ideal zero-thickness values of 0.60 : 1 when e^2qQ is negative and 1.67 : 1 when e^2qQ is positive.[22] An alternative possibility, that the contribution from $\Delta_{\text{latt.}}$ is negative and dominates the contribution from a ^2A_g state, would not be consistent with the observed temperature dependence.

The presence of an orbitally degenerate ^2E_g ground state is clearly established. It has been stated recently [14,23] that such a configuration is Jahn–Teller forbidden, but it should be noted that spin–orbit coupling causes further splitting of the ^2E_g level to give two Kramers' doublets, thereby satisfying the Jahn–Teller theorem without invoking an additional lowering of symmetry.

The weak temperature dependence of Δ_T makes it impossible to determine all the four phenomenological parameters from the one data set. However, in any pair of $[Fe(CN)_6]^{3-}$ compounds the values of $\alpha^2\Delta_0$ and λ should be effectively the same, so that a self-consistent interpretation of several compounds is not only feasible but also desirable. Unfortunately, the choice of data is limited, and in view of the introductory remarks it is better to exclude $K_3[Fe(CN)_6]$ from the analysis if possible. Although the point symmetry of the iron site in $Cs_2Na[Fe(CN)_6]$ is only C_i, the unit cell is pseudo-tetragonal, the $[Fe(CN)_6]^{3-}$ ion is octahedral within experimental error, the overall distortion from cubic symmetry is small, and the quadrupole splitting depends strongly on the temperature. There are therefore good grounds for believing that the ligand field in this compound will approximate closely to tetragonal (*e.g.* D_{4h}). A tetragonal field splits the $^2T_{2g}$ state into $^2B_{2g} + {}^2E_g$ with a separation of $\Delta_{\text{tetr.}}$ (which I define as negative in sign when the ground state is $^2B_{2g}$). The analysis now follows the previous argument except that $F(\Delta_{\text{trig.}},\lambda,T)$ in equations (1) and (2) is replaced by a similar function $F(\Delta_{\text{tetr.}},\lambda,T)$.

A self-consistent interpretation of the data for both compounds can now be attempted in terms of six parameters. Unfortunately these are interactive such that a completely unambiguous interpretation is not possible, although several important points do emerge. It is clear that the effective value of λ is substantially less than -150 cm^{-1} (compared to the free-ion value of $\lambda_{3d} = -420$ cm^{-1}). A larger value of λ results in Δ_T being almost constant at <100 K. For a given value of λ the curvature of the data for $Cs_2Na[Fe(CN)_6]$ shown in Figure 3 can be used to define values for the other three parameters. The full line in Figure 3 represents the solution $\lambda = -100$ cm^{-1}, $\Delta_{\text{tetr.}} = -60$ cm^{-1}, $\alpha^2\Delta_0 = -0.853$ mm s^{-1}, and $\Delta_{\text{latt.}} = -0.054$ mm s^{-1}. The values of $\Delta_{\text{tetr.}}$ and $\Delta_{\text{latt.}}$ are both small, which is consistent with the small distortion in this structure. The value of $|\alpha^2\Delta_0|$ is substantially reduced from the free-ion value [24] of *ca.* 4.8 mm s^{-1}. These same values for λ and $\alpha^2\Delta_0$ were then used to obtain the solution for $[Co(NH_3)_6][Fe(CN)_6]$ of $\Delta_{\text{trig.}} = -660$ cm^{-1} and $\Delta_{\text{latt.}} = +0.008$ mm s^{-1}. This is shown as the full line in Figure 1. It is to be noted that the small temperature dependence of the data is satisfactorily reproduced, adding con-

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[22] T. C. Gibb, 'Principles of Mössbauer Spectroscopy,' Chapman and Hall, London, 1976, p. 41.

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fidence to the ^2E_g assignment. The large value for $\Delta_{\text{trig.}}$ is not unexpected as the *X*-ray data for the $[\mathrm{Co(CN)_6}]^{3-}$ anion show a measurable distortion. The small value of $\Delta_{\text{latt.}}$ is consistent with the nominal charges of the cation and anion being largely distributed over the ligands,[20] but is very sensitive to the choice of the other parameters.

Although these fits to the data are not unique, it is evident that the effective spin-orbit coupling constant for the t_{2g} orbitals is $\lambda \simeq -100$ cm^{-1}, and that $|\alpha^2\Delta_0| \simeq 0.9$ mm s^{-1}. An analysis [6] of the quadrupole-splitting data for $\mathrm{K_3[Fe(CN)_6]}$, which gave a similar value for the spin–orbit coupling constant of $\lambda = -80$ cm^{-1}, has been recently criticized as being incompatible with the e.s.r. and magnetic-susceptibility data.[25] However, it is possible to explain the low values for λ and $|\alpha^2\Delta_0|$ which have been observed in a way which is compatible with e.s.r. measurements, and it is the value of $\lambda = -270$ cm^{-1} derived from magnetic data [25] which seems unsatisfactory.

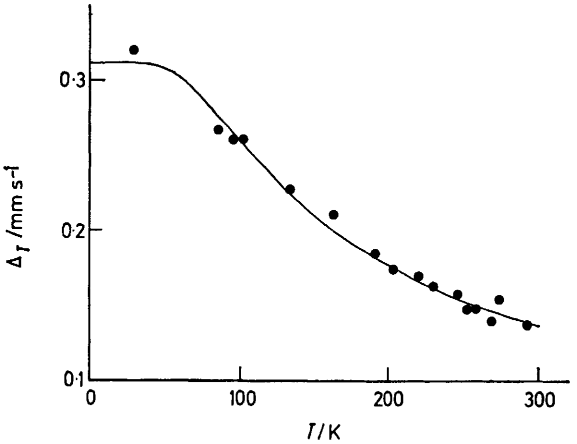

FIGURE 3 Temperature dependence of the quadrupole splitting in $\mathrm{Cs_2Na[Fe(CN)_6]}$. The full line represents the solution $\lambda = -100$ cm^{-1}, $\Delta_{\text{tetr.}} = -60$ cm^{-1}, $\alpha^2\Delta_0 = -0.853$ mm s^{-1}, and $\Delta_{\text{latt.}} = -0.054$ mm s^{-1}

In octahedral symmetry the metal t_{2g} orbitals are not involved in σ bonding, but there may be a degree of covalent bonding due to π overlap with suitable orbitals on the ligands. This π overlap is responsible for an apparent reduction in the orbital angular momentum which finds expression in e.s.r. spectroscopy as the orbital-reduction factor, *k*.[26,27] If the covalent bonding is represented by molecular orbitals of the form (3)

$$\tilde{t}_{2g} = N[t_{2g} + \tfrac{1}{2}\varepsilon(\pi_1 - \pi_2 + \pi_3 - \pi_4)] \qquad (3)$$

such that $N^{-2} = 1 + 4\varepsilon S + \varepsilon^2$ where the overlap S is given by $S = \langle t_{2g}|\pi_1\rangle$, *etc.*, then the orbital-reduction factor for the t_{2g} orbitals can be represented by (4)

$$k = 1 - \tfrac{1}{2}N^2\varepsilon^2 \qquad (4)$$

and is independent of the spin–orbit coupling parameter. The latter can be shown [26] to be given by (5) where λ_{3d}

$$\lambda = N^2(\lambda_{3d} + \tfrac{1}{2}\varepsilon^2\lambda_p) \qquad (5)$$

is the free-ion value for the metal 3*d* orbitals and λ_p is the value for the ligand atom. For light elements the value of λ_p is much smaller than λ_{3d} so that $\lambda \simeq N^2\lambda_{3d}$. One frequently finds that N^2 is equated with the covalency factor α^2 in equation (1). This carries the implicit assumption that as the π overlap tends to zero then $\lambda \longrightarrow \lambda_{3d}$. However, for non-bonding t_{2g} orbitals in a cubic ligand field the radial distribution as manifested in the value of $\langle r^{-3}\rangle_t$ is not necessarily the same as that of a *d* orbital in the spherical free ion, $\langle r^{-3}\rangle_{3d}$. If $\langle r^{-3}\rangle_t$ differs from $\langle r^{-3}\rangle_{3d}$ then the effective value of λ will be given by (6).

$$\lambda \simeq N^2\lambda_{3d}\langle r^{-3}\rangle_t/\langle r^{-3}\rangle_{3d} \simeq \alpha^2\lambda_{3d} \qquad (6)$$

This important point is often overlooked despite there being good experimental evidence to support it. For example, neutron-scattering data for magnetic compounds containing $\mathrm{Mn^{2+}}$ or $\mathrm{Ni^{2+}}$ have shown that the spin density in $\mathrm{Mn^{2+}}$ is expanded relative to the free-ion Hartree–Fock value, but is contracted in $\mathrm{Ni^{2+}}$. An interpretation [28,29] on the basis of fully variational unrestricted Hartree–Fock calculations has shown that the two unpaired e_g electrons in both $[\mathrm{MnF_6}]^{4-}$ and $[\mathrm{NiF_6}]^{4-}$ are contracted; however, the three unpaired t_{2g} electrons in $[\mathrm{MnF_6}]^{4-}$ are expanded, resulting in this case in a net overall expansion relative to the free ion. Even in these compounds with a weak ligand field, the value of $\langle r^{-3}\rangle_t$ is significantly smaller than the value of $\langle r^{-3}\rangle_{3d}$. The same argument has been applied to quadrupole-splitting data for high-spin iron(II) compounds.[24,30,31] Although a similar opinion has been expressed [7] for $\mathrm{K_3[Fe(CN)_6]}$, the analysis has been severely criticized on other grounds,[8] and in any case the ligand-field description is clearly incorrect.

It was recently pointed out [32] that the observed orbital-reduction factor *k* for a nominal $t_{2g}{}^5$ configuration is strongly influenced by configuration interaction with excited $t_{2g}{}^4e_g$ states. Consequently the observed value has to be substantially corrected to obtain a 'true' value for the t_{2g} orbitals, *k*′. Thus in $\mathrm{K_3[Fe(CN)_6]}$ the observed value of $k = 0.87$ can be corrected to give $k' = 0.72$.[9,33] In principle the admixture of excited states into the ground state will affect the observed quadrupole splitting. Using published parameters,[32] the mixing coefficients and electric-field-gradient behaviour have been considered in detail for the $^2T_{2g}$-$[t_{2g}{}^4(^3T_{1g})e_g]$ and $^2T_{2g}[t_{2g}{}^4(^1T_{2g})e_g]$ excited states under a tetragonal perturbation. As a result it is estimated

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that they will have only a small effect on Δ_T which is expected to be reduced by <2%. Thus in the present case the Mössbauer spectrum can be treated quite accurately in terms of a pure $t_{2g}{}^5$ configuration (although this may not be true in compounds closer to the ${}^6A_1$-${}^2T_2$ crossover).

With these observations in mind it is possible to give a sensible interpretation of the present data. If the value of $k' = 0.72$ in $K_3[Fe(CN)_6]$ is meaningful, then by neglecting overlap the normalization coefficient for the orbital $\tilde{t}_{2g}$ becomes $N^2 = 0.44$. The covalency parameter in the expression for Δ_T is given by (7). If $|\Delta_0|$ is taken [24] to be $\simeq 4.8$ mm s^{-1}, then from $|\alpha^2\Delta_0| \simeq 0.9$ mm s^{-1} one obtains $\alpha^2 \simeq 0.19$. From $\lambda \simeq -100$ cm^{-1} and $\lambda_{3d} = -420$ cm^{-1} one obtains $\alpha^2 \simeq 0.24$. The two

$$\alpha^2 = N^2\langle r^{-3}\rangle_t/\langle r^{-3}\rangle_{3d} \qquad (7)$$

values are reasonably self-consistent. Thus an approximate value of $\langle r^{-3}\rangle_t/\langle r^{-3}\rangle_{3d} \simeq 0.5$ emerges. This represents the expansion of non-bonding $3d$ orbitals under the influence of the cubic ligand field and thereby parallels experience in octahedral high-spin compounds.

The *X*-ray data for $[Co(NH_3)_6][Fe(CN)_6]$ were kindly provided by Dr. W. S. McDonald of this Department.

[7/599 *Received, 5th April,* 1977]