1148. *Charge-transfer Phenomena in Some Inorganic Complexes. Part II.*[1] *The Physical Properties of Trithallium*(I) *Hexacyanoferrate*(III)

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The physical properties of $Tl_3Fe(CN)_6$ have been studied in an attempt to elucidate the mechanism of the electrical conduction of the solid. Infrared spectra show that the $[Fe(CN)_6]^{3-}$ units are not greatly different in $Tl_3Fe(CN)_6$ and $K_3Fe(CN)_6$. However, the quadrupole splitting of the Mössbauer spectrum of $Tl_3Fe(CN)_6$ is much greater than that of $K_3Fe(CN)_6$, which is indicative of a considerable Tl(I)—$[Fe(CN)_6]^{3-}$ interaction. The thallium nuclear magnetic resonance spectrum shows that there is approximately a 0·2% delocalisation of the unpaired electron of $[Fe(CN)_6]^{3-}$ on to the Tl atoms. The visible and ultraviolet spectra are interpreted in terms of a moderately low-lying charge-transfer absorption band. All the properties are consistent with a "hopping" model for conduction.

IN Part I[1] we showed that $Tl_3Fe(CN)_6$ is a good semiconductor with a moderately low activation energy for conduction. This result can be fully interpreted only if the physical properties of $Tl_3Fe(CN)_6$ are examined in detail. The compound is isomorphous with $K_3Co(CN)_6$ and $K_3Fe(CN)_6$ (see below), and the properties of $Tl_3Fe(CN)_6$ will therefore be discussed from a knowledge of the structures of $K_3Co(CN)_6$ and $K_3Fe(CN)_6$.

Structures.[2]—The unit cell of potassium hexacyanocobaltate(III) is monoclinic, space group $P2_1c$. The unit cell contains two molecules of $K_3Co(CN)_6$ with two Co at (000), $(0\frac{1}{2}\frac{1}{2})$; two K′ at $(00\frac{1}{2})$, $(0\frac{1}{2}0)$; and four K″ at approximately $(\frac{1}{2}\frac{1}{4}\frac{1}{8})$, $(\frac{1}{2}\frac{1}{4}\frac{7}{8})$. A two-fold symmetry axis of the octahedral $Co(CN)_6$ groups lies along the *c*-axis. Those octahedra at (000) have the plane containing the four cyanides at approximately 30° to the *ac*-plane, and those at $(0\frac{1}{2}\frac{1}{2})$ are at approximately —30° to this plane. Potassium hexacyanoferrate(III) has a very similar structure. Magnetic measurements have revealed a small rhombohedral distortion in the $[Fe(CN)_6]^{3-}$ octahedra,[3] and a weak antiferromagnetic interaction (0·07 cm.$^{-1}$) between pairs of these ions. The environment of the potassium is such that, although both K′ and K″ have six near-nitrogen atoms, the distances to these atoms are different: K′ two N at 2·87, two N at 3·02, and two N at 3·14; K″ two N at 2·57 and four N at 2·77 Å.

Thallium(I) and potassium hexacyanocobaltates(III) gave almost identical powder diffraction patterns. They have the same space group ($P2_1c$) and only slightly different unit-cell dimensions (Table 1). Since thallium can be substituted in either $K_3Co(CN)_6$ or $K_3Fe(CN)_6$ in all proportions, we shall assume that thallium ions occupy the same sites as potassium ions.

TABLE 1

Unit-cell dimensions of $[M(I)]_3[M(III)(CN)_6]$

Compound	Space group	*a* (Å)	*b* (Å)	*c* (Å)	Angle	Reference
$K_3Fe(CN)_6$	$P2_1c$	7·1	10·4	8·4	107°	1
$K_3Co(CN)_6$	,,	7·00	10·38	8·37	107° 19′	1
$Tl_3Co(CN)_6$	,,	6·9	10·5	8·67	108°	Present work

Infrared Spectra.—The main bands in the infrared are given in Table 2. The absorptions at ~2100 and 580 cm.$^{-1}$ are assigned to the CN antisymmetric stretch and the M–C stretch modes, respectively, on the basis of previous assignments.[4,5] The replacement

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[1] Part I, P. S. Braterman, P. B. P. Phipps, and R. J. P. Williams, preceding Paper.

[2] J. A. Kohn and W. D. Townes, *Acta Cryst.*, 1961, **14**, 617; N. A. Curry and W. A. Runciman, *Acta Cryst.*, 1959, **12**, 674; R. Mason, personal communication.

[3] B. Bleaney and D. J. E. Ingram, *Proc. Phys. Soc.*, 1952, *A*, **65**, 953.

[4] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1962, **18**, 89.

[5] L. M. Jones, *J. Chem. Phys.*, 1962, **36**, 1209.

TABLE 2

Infrared absorption bands (cm.$^{-1}$) of $M(CN)_6$ compounds

	Mode no.^{4,5}	K_4Fe^{2+}	$Fe^{3+}Fe^{2+}$	Tl_4Fe^{2+}	K_3Co^{3+}	Tl_3Co^{3+}	K_3Fe^{3+}	Tl_3Fe^{3+}
C–N stretch	6	2045	2090	2020	2130	2108	2120	2100
M–C stretch	7	578	595	573	558	554	505	472 513 590
M–CN bend	8	418 414	507·5 489	417 412·3	413·2	412	390	389

of K^+ by Tl^+ is seen to have little effect on the absorption frequencies although, in the case of thallium(I) hexacyanoferrate(III), the M–CN stretch appears to be split. Force constants for M–CN stretch are estimated on a harmonic-oscillator approximation (Table 3). On the basis of these figures and those for the bond lengths, the Franck–Condon barrier to electron-exchange between hexacyanoferrate-(II) and -(III) must be extremely small, *i.e.*, *ca.* 1·0 kcal.

TABLE 3

Force constants

	Dynes Å^{-1}	Bond length in anion M–CN (Å)
$Tl_4{}^{+}Fe^{+2}$–CN	2·36	1·85 or 1·925
Tl_3Fe^{+3}–CN	1·73	1·90 (ref. 5)
Tl_3Co^{+3}–CN	2·20	1·89 (ref. 4)

Mössbauer Spectrum.—The measurement of the Mössbauer spectrum of a compound will show whether or not there are different ions of an element in more than one valence state. The compound $Tl_3Fe(CN)_6$ could contain a small fraction of Fe(II). In fact no spectrum other than that of $[Fe(CN)_6]^{3-}$ has been detected by us. The interaction of the Fe nucleus with its environment is also revealed by the quadrupole splitting of the Mössbauer spectrum. The splitting in $K_3Fe(CN)_6$ is small (*ca.* 0·2 min. sec.$^{-1}$). The splitting in $Tl_3Fe(CN)_6$ (*ca.* 0·4 min. sec.$^{-1}$) is much larger and is comparable with that in $Ag_3Fe(CN)_6$ (*ca.* 0·5 min. sec.$^{-1}$). $Ag_3Fe(CN)_6$ is a dark solid much as is $Tl_3Fe(CN)_6$; there is charge-transfer interaction in both compounds.

Nuclear Magnetic Resonance.—The n.m.r. spectra of the ^{205}Tl–^{207}Tl compounds were examined at 16 Mc./sec. on a Varian 4200 B wide-line spectrometer using a V 4012 electromagnet system. The compounds were studied as powders. The poor signal-to-noise ratio, field drift rate, scan hysteresis, and overlap of the signals from the two nuclei all limited the accuracy of both shift and width measurements. All uncertainties quoted are estimated 90% confidence limits.

TABLE 4

N.m.r. spectra of some thallium(I) compounds

Compound	Shift, δ (300°K)	Observed line-width (gauss)	Saturation R.F. field (gauss)
$Tl_3Co(CN)_6$	4 ± 1	$1·0 \pm 0·3$	$0·004 \pm 0·002$
$Tl_3Fe(CN)_6$	-140 ± 7	30 ± 10	0·2
$Tl_3Co_{0·934}Fe_{0·066}(CN)_6$	4 ± 1	$1·0 \pm 0·4$	$0·05 \pm 0·02$
	4 ± 2	5 ± 2	0·2
	-60 ± 3	18 ± 5	0·2
$TlFe(SO_4)_2,12H_2O$	4 ± 1	$1·0 \pm 0·5$	$0·04 \pm 0·02$

The chemical shifts, δ (Table 4), were measured relative to a saturated aqueous $TlNO_3$ standard, and are expressed as parts in 10^4 at constant frequency:

$$\delta = \{[H(\text{unknown}) - H(\text{standard})]/H(\text{standard})\} \times 10^4$$

Experimental line-widths are the maximum-slope full widths in gauss of the absorption mode signal. No measurements were made above room temperature because of the chance of decomposition. The width of the resonance in all compounds increased below 300°K.

Discussion of Nuclear Magnetic Resonance Spectra.—There are two distinct thallium sites in the lattice of $Tl_3Fe(CN)_6$ and $Tl_3Co(CN)_6$, but only one signal was observed in each compound. We assume that the two sites are sufficiently similar to give indistinguishable signals on the instrument used.

The shift in $Tl_3Fe(CN)_6$ is much greater than in any other thallium salt, *e.g.*, TlI,[6] and cannot be due to the magnetic field of the paramagnetic Fe(III) [see the value for $TlFe(SO_4)_2,12H_2O$ in Table 4). We conclude that the shift is due to unpaired electron-density on the Tl transmitted from Fe(III) through CN^-. Thus, the Tl spends a fraction of its time as Tl(II). On applying a magnetic field, the magnetic moments of the $[Fe(CN)_6]^{3-}$ ions are partially aligned and enhance the magnetic moment at the Tl nucleus. This alignment is proportional to the reciprocal of the absolute temperature (Table 5). The slope of the plot of the Tl resonance shift against $1/T$ gives the coupling constant[6,7] between the Tl and the $[Fe(CN)_6]^{3-}$ (Table 6). Following Shulman and Jaccarino[8] we can interpret these constants as follows.

TABLE 5

N.m.r. shifts at different temperatures

Compound	Temp. (°K)	% shift of ^{207}Tl signal from that in $Tl_3Co(CN)_6$
$Tl_3Fe(CN)_6$	298	-1.34 ± 0.05
	257	-1.60 ± 0.05
	222	-1.70 ± 0.15
	213	-1.94 ± 0.25
$Tl_3Co(CN)_6$	298	-0.44 ± 0.05
$+6.6\%$ $[Fe(CN)_6]^{3-}$	263	-0.48 ± 0.05
	227	-0.58 ± 0.10
	198	-0.62 ± 0.15

TABLE 6

Compound	Coupling constant	Reference
$Tl_3Fe(CN)_6$	$90\ (\pm 20) \times 10^{-4}$ cm.$^{-1}$	Present work
$Tl_3Co_{0.934}Fe_{0.066}(CN)_6$..........................	$27\ (\pm 7) \times 10^{-4}$ cm.$^{-1}$	Present work
Tl(II) gaseous ($6s^1$)	5 cm.$^{-1}$	7
Tl(II) gaseous ($6p^1$)	0·04 cm.$^{-1}$	7

If the ground-state wave function is written

$$\Psi = \frac{1}{\sqrt{1 + \lambda^2}} \left(\Psi_{Tl(6s)} + \lambda \Psi_{Fe(3d)} \right)$$

then the observed n.m.r. shift is proportional to λ^2.

We know the coupling constant for the free Tl^{2+} ion from the spin–orbit coupling constant derived from the ultraviolet spectra, and we take that in the state $Tl^{2+}Fe^{2+}$ to be the same (Table 5). The ratio of the observed coupling constant of $Tl_3Fe(CN)_6$ to that of Tl^{2+} leads to $\lambda = 0.04$ in $Tl_3Fe(CN)_6$. Thus, effectively, an electron is transferred from each Tl to the Fe 0·16% of the time.

The three signals observed in the diluted $Tl_3Fe(CN)_6$ appeared to have intensities roughly proportional to the line-widths, although accurate comparison was hampered by their different relaxation times. No signal was found in the position of undiluted $Tl_3Fe(CN)_6$. Only about 5% of the thallium gives the same signal as in $Tl_3Co(CN)_6$, although 93·4% of the hexacyanometallate anion is $[Co(CN)_6]^{3-}$. The probability that a given Tl has no $[Fe(CN)_6]^{3-}$ amongst its four nearest neighbours is approximately 0·75.

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[6] S. Hafner and N. H. Nachtrieb, *J. Chem. Phys.*, 1964, **40**, 2891.

[7] J. C. McClennan, A. B. McLay, and M. F. Crawford, *Proc. Roy. Soc.*, 1931, *A*, **133**, 652.

[8] R. Shulman and V. Jaccarino, *Phys. Rev.*, 1957, **108**, 1219.

Thus, it appears that in order that a Tl should give the signal of Tl in $Tl_3Co(CN)_6$ it must have no near-neighbour hexacyanoferrate(III) and its nearest anions (12) must also have no near-neighbour $[Fe(CN)_6]^{3-}$. The probability of this occurring is approximately 0·03. The magnitude of the shift, the broadness of the lines, and areas under the absorption maxima do not lend themselves to any further obvious interpretation.

Absorption Spectra.—Solid thallium(I) hexacyanoferrate(III) absorbs in a region of the spectrum in which neither of the component ions in aqueous or solid solution nor the ion-pair absorbs. We observe quantitatively the following differences from potassium hexacyanoferrate(III): (*a*) a moderately intense absorption ε_{molar} 1000, $\lambda_{max.}$ 21,200 cm.$^{-1}$; (*b*) an increase in intensity and band-width of absorption at 24,000 cm.$^{-1}$, Tl^+ ε_{molar} 1300, K^+ ε_{molar} 600. The absorption at 21,000 cm.$^{-1}$ is considered to be due to charge-transfer $Tl^+ \curvearrowright [Fe(CN)_6]^{3-}$, as similar absorption bands occur only in those compounds containing both a reducible and an oxidisable ion, *e.g.*, in $Tl_3{}^+Fe^{3+}(CN)_6$, $Ag_3{}^+Fe^{3+}(CN)_6$ but not in $Tl_4Fe^{2+}(CN)_6$, $Ag_4Fe^{2+}(CN)_6$, $Tl_3Co(CN)_6$, TlCN, $K_3Fe(CN)_6$, etc.

The Tl^+–$[Fe(CN)_6]^{3-}$ charge-transfer band is polarised perpendicular to the *c*-axis, showing that interaction is strongest in the plane perpendicular to this axis. This could account for the observed splitting in the infrared and Mössbauer spectra and for the relative intensities of the n.m.r. signals.

Conduction in $Tl_3Fe(CN)_6$.—In Part I [1] conduction in $Tl_3Fe(CN)_6$ was shown to be due to carriers which had a very low mobility. Consequently, a " hopping " model was proposed for the conduction mechanism. The present Paper helps to substantiate the mechanism, for we have shown that (i) the $[Fe(CN)_6]^{3-}$ units are essentially the same in $Tl_3Fe(CN)_6$ and $K_3Fe(CN)_6$ (infrared and Mössbauer spectra), (ii) there is at least 25% of Tl(I) in $Tl_3Co(CN)_6$ doped with 6·3% of $[Fe(CN)_6]^{3-}$, which shows no chemical shift from Tl(I) in pure $Tl_3Co(CN)_6$, implying that all thalliums are not equivalent, (iii) the energy of the charge-transfer band $Tl(I) \curvearrowright [Fe(CN)_6]^{3-}$ does not greatly alter from Tl(I) doped into $K_3Fe(CN)_6$ to $Tl_3Fe(CN)_6$. All these properties suggest that interactions between the Tl(I) and $[Fe(CN)_6]^{3-}$ units are strongly localised, as is required by the " hopping " model.

EXPERIMENTAL

Compounds.—The preparations of all the compounds are described in Part I.[1]

Spectra.—Aqueous solution spectra were measured using a Unicam S.P. 600 spectrophotometer. The spectra of single crystals were taken on an instrument to be described shortly.[9] Powder reflection spectra were measured using the reflection attachment of the Unicam S.P. 600 by the method described by Kortum.[10] Infrared spectra were taken from 4000 to 400 cm.$^{-1}$ using a Perkin-Elmer 221 spectrometer and Nujol mulls. Mössbauer spectra were obtained for us by Mr. P. Edwards, using facilities at A.E.R.E., Harwell. We are grateful to Professor R. E. Richards for the use of the n.m.r. spectrometer.

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