1147. *Charge-transfer Phenomena in Some Inorganic Complexes. Part I. Electronic Conduction in Some Complex Cyanides*

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Conduction in a number of complex cyanides has been examined over a range of temperature, using both single crystals and compressed pellets. Tetrapotassium hexacyanoferrate(II) and tripotassium hexacyanocobaltate(III) show activation energies of about 15 kcal./mole, while that of tripotassium hexacyanoferrate(III) is decidedly lower. Trithallium(I) hexacyanoferrate(III) shows a much lower activation energy of 6 kcal./mole. The activation energies in a series of bivalent-transition-metal hexacyanocobaltate(III) compounds are in the order Fe $<$ Mn $<$ Co $\approx$ Ni $\approx$ Cu $<$ Zn. The nature of the conductivity is discussed.

This Paper, the first in a Series, illustrates the way in which the electronic conduction of inorganic solids containing complex ions casts light on electron-transfer processes in general. Electronic conduction in some inorganic solids, *e.g.*, NiO and $\mathrm{La}_x\mathrm{Sr}_{1-x}\mathrm{Mn(III)}_x\mathrm{Mn(IV)}_{1-x}\mathrm{O}_3$, can usefully be regarded as a form of charge-transfer between ions.[1] This description will be likely to be valid when some analogy between conduction in a solid and charge-transfer reaction between its constituent ions in solution is expected. Such solution reactions have been found to be fastest when they involve complexes of unsaturated ligands. We have therefore selected a series of complex cyanides for our first studies of the conductivity of solids. Since the detailed interpretation of conduction in a single solid is likely to be difficult, we have examined two series of isostructural compounds, the thallium(I) and potassium(I) hexacyanoferrate(III) and hexacyanocobaltate(III) compounds and the bivalent-transition-metal hexacyanocobaltate(III) compounds. The first series will be shown to be isostructural in a second Paper. The second series of compounds all have cubic lattices isomorphous with Prussian Blue (see Figure 1).[2]

Results

The Experimental section contains a detailed description of the preparation of the compounds and the measurement of their conductivity. The logarithms of the observed resistances, σ_T, were plotted against the reciprocal of the absolute temperature, T. The results always fitted a good straight line of the form

$$\log \sigma_T = \log \sigma_\infty + 2{\cdot}3E_a/\boldsymbol{RT}$$

where E_a is the activation energy for the conduction. The value of σ_∞ will not be given much weight in the discussion, especially in the case of the pellet measurements. However, all the values of E_a for pellets were constant from sample to sample, independent of applied voltage, and of the electrodes used, and agreed well with E_a obtained from measurements on single crystals (Table 1).

Potassium and Thallium Salts.—Results are given in Table 1. E_a is independent of the method of measurement to a good approximation. The order of the activation energies for the simple compounds is $K_4Fe(CN)_6 \approx K_3Co(CN)_6 \approx Tl_3Co(CN)_6 > K_3Fe(CN)_6 \gg Tl_3Fe(CN)_6$. The differences between the first three compounds are not significant. The potassium-doped trithallium(I) hexacyanoferrate(III) {$Tl_2KFe(III)(CN)_6$ in the Table} has a higher activation energy than $Tl_3Fe(CN)_6$ and than $Tl_3Co(CN)_6$ doped with 3·4% of $[Fe(CN)_6]^{3-}$. The log σ_∞ values do not show significant changes.

Bivalent-transition-metal Hexacyanocobaltate(III) *Compounds.*—Results are given in Table 2. The value of E_a are independent of sample and of the nature of the accompanying cation,

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[1] E. J. W. Verwey in "Semiconducting Materials," ed. H. K. Henisch, Butterworths, London, 1951, p. 151.

[2] A. Vaciago and A. Mugnoli, *Atti Accad. naz. Lincei*, 1958, **25**, 531; 1959, **26**, 517.

K^+ or Ba^{2+}. The order of the values of E_a is Zn(II) > Cu(II), Ni(II), Co(II) > Mn(II) > Fe(II). The log σ_∞ values do not show significant trends.

TABLE 1

Conductivity data on salts of univalent metals

Compound	Contacts	$E_a \pm 0{\cdot}5$ (kcal.)	$\mathrm{Log}_{10}\ \sigma_{293}$	$\mathrm{Log}_{10}\ \sigma_\infty$
$K_3Fe(III)(CN)_6$	4 Ag	12·5	−9·3	−0·0
	2Ag	12·6	−8·0	−1·3
	2C	12·5	−9·0	−0·3
	Pellet Ni	12·5		
$Tl_3Fe(III)(CN)_6$	4 Ag	6·4	−6·2	−1·5
	4 Ag	6·4	−6·8	2·0
	Pellet Ni	6·2	−2·7	−2·0
$Tl_3Co(III)(CN)_6$ + 3·4% $Fe(III)(CN)_6$	2 Ag	5·8	−9·6	−5·2
	4 Ag	5·8		
$Tl_2KFe(III)(CN)_6$	2 Ag	8·0	−5·9	−2·6
$Tl_3Co(III)(CN)_6$	4 Ag	14·0	−11·0	−0·6
$K_3Co(III)(CN)_6$	2 Ag	14·0	−12·5	−2·1
	2 Ag	13·7	−9·4	−0·8
	Pellet Ni	14·4	−10·0	−0·7
$K_4Fe(II)(CN)_6$	2 Ag	15·5	−9·8	−1·7
	Pellet Ni	14·7	−11·7	−0·7
$Tl_4Fe(II)(CN)_6$	2 Ag		−12·9	

TABLE 2

Conductivity data on divalent-metal hexacyanocobalt(III) compounds

Metal	Preparation	E_a (± 1·0) (kcal.)	Log σ_∞	Notes
Mn(II)	Ba(1)	20·7	3·9 ± 0·3	
	Ba(2)	22·6	5·7 ± 1·0	
	K	20·1	0·8 ± 0·5	500v, one run
Fe(II)	Ba(1)	15·5	2·6 ± 0·4	
	Ba(2)	13·2	1·7 ± 0·4	
	K(1)	15·3	1·4 ± 0·4	1v, 85v
	K(2)	14·9	1·2 ± 0·5	500v
Co(II)	Ba(1)	28·3	4·0 ± 0·6	
	Ba(2)	31·5	5·9 ± 0·2	
	K	27·1	4·0 ± 0·7	
Ni(II)	Ba(1)	27·6	3·9 ± 0·6	
	Ba(2)	27·6	4·3 ± 0·6	
	K(1)	31·1	8·8 ± 0·5	500v
	K(2)	32·6	9·7 ± 0·5	
Cu(II)	Ba(1)	25·9	2·9 ± 0·4	
	Ba(2)	28·1	4·5 ± 0·6	
	K	28·7	2·8 ± 0·3	
Zn(II)	Ba	44·0	10·7 ± 0·8	Near instrument limits

Preparation is from barium or potassium hexacyanocobaltate(III). Numbers indicate different pellets. All figures record the results of four runs, at ±45v and ±90v, unless otherwise stated.

DISCUSSION

Univalent-metal Hexacyanocobaltate(III) *and Hexacyanoferrate*(III) *Compounds.*—The compounds of hexacyanoferrate(II) are hydrated and are not directly comparable with the other compounds of Table 1. Their conductivity is unremarkable. The conductivity of $K_3Co(CN)_6$ and $Tl_3Co(CN)_6$ is very low and is probably due to the movement of ions. The noticeably lower activation energy of conduction for $K_3Fe(CN)_6$ as compared with $K_3Co(CN)_6$ may well be due to electron mobility in this compound, as disproportionation of Fe(III) is energetically more probable than that of Co(III). The conductivity of $Tl_3Fe(CN)_6$ is so different from that of the other compounds that conduction cannot be due to ion migration. This was also demonstrated by a Faraday's Law experiment.

A charge of 5×10^{-5} faradays was passed through a crystal of $KTl_2Fe(III)(CN)_6$ containing 10^{-5} g.molecules. It was observed that (i) the resistance did not change irreversibly due to the passage of current, (ii) there was no thallium deposited at the electrodes, and (iii) there was no colour gradient in the crystal after the passage of current although the intensity of optical absorption of thallous ferricyanide diluted in potassium cobalticyanide increases with increasing concentration of thallous and ferricyanide. Conductivity is clearly electronic.

Hall-effect measurements (Experimental section) show that the current carriers in $Tl_3Fe(CN)_6$ have a very low mobility. Thus, $Tl_3Fe(CN)_6$ is comparable with mixed-valent conductors such as $Li_xNi(III)_xNi(II)_{1-x}O$ or $La_xSr_{1-x}Mn(III)_xMn(IV)_{1-x}O_3$. In these conductors the interaction between neighbouring equivalent atoms is much weaker than in classical semiconductors such as PbS, and a band theory for conduction is not appropriate. As the electron moves, the lattice around it relaxes and the electron becomes trapped in a self-polarisation well.[3] Conduction is best described as a series of " hops " from one localised site to another. Now, $Tl_3Fe(CN)_6$ does not contain one element in two valence states but a reducing ion, Tl(I), of one element and an oxidising ion of another, Fe(III). The activation energy of conduction could relate to the production of Tl(II) ions in the crystal by electron-transfer to Fe(III), or to the subsequent mobility of the carriers between Tl(II) and Tl(I) ions. Comparison between $[Fe(CN)_6]^{3-}$-doped $Tl_3Co(CN)_6$, Tl(I)-doped $K_3Fe(CN)_6$, and $Tl_3Fe(CN)_6$ itself shows that removal of thallium increases the activation energy but removal of $[Fe(CN)_6]^{3-}$ only decreases σ_∞. Thus, the 6·0 kcal. activation energy refers to the hopping of electrons between the thallium atoms. In Part II we shall show that even in the ground state there is strong interaction between Tl(I) and $[Fe(CN)_6]^{3-}$. In the case where electron-conduction proceeds by hopping, no correlation between the photon absorption energy required to produce charge-transfer and the activation energy for semiconduction is expected. As will be shown in Part II, none is found for $Tl_3Fe(CN)_6$.

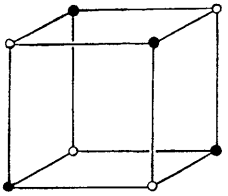

FIGURE 1. The cubic lattice of $M(II)[Co(III)(CN)_6]$. Black circles are M(II) ions and white circles are Co(III) ions at the centre of six CN− ions which stretch along the sides of the cube

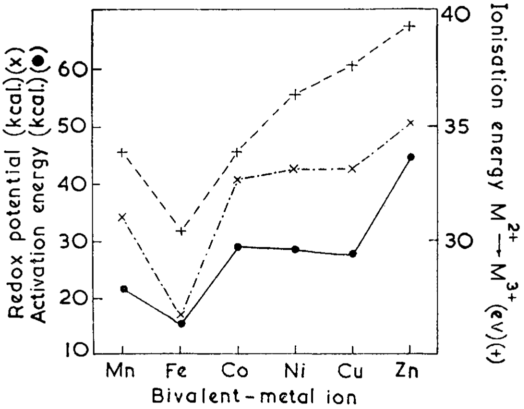

FIGURE 2. A comparison of the activation energies of conduction with the redox energies of the couples M(II)/M(III) in water and with the ionisation energies M(II) ⟶ M(III)

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[3] A. R. Heikes and W. D. Johnston, *J. Chem. Phys.*, 1957, **26**, 582.

Bivalent-transition-metal Hexacyanocobaltate(III) *Compounds*.—The extremely low conductivity of $ZnK[Co(CN)_6]$ indicates that ions are much less mobile in these compounds than in $[M(I)]_3[Co(CN)_6]$. This may well be due to the polymerised nature of the lattice, as shown in Figure 1. In such circumstances the differences in conductivity of the compounds in Table 2 must be related to electron motion. This motion must involve the charge-transfer of an electron from M(II) to Co(III), for there is no interaction between the M(II) ions. Thus, the activation energy for conduction is expected to contain the energy of the charge-transfer step to the hexacyano-complex. To show that this is the case, we compare the observed activation energies with the ionisation energies M(II) ⟶ M(III) and with the standard oxidation–reduction potentials M(II)/M(III) in water in Figure 2. There is a decided correlation.

Once again in this series of compounds there is no equality between the activation energy for semiconduction and the optical absorption energy of the charge-transfer band. However, as the charge-transfer band moves to lower energy, the activation energy for conduction decreases. The conductivity of Prussian Blue, potassium iron(III) hexacyanoferrate(II), is greater and its activation energy lower ($\approx$10 kcal.) than that of any of the hexacyanocobaltate(III) compounds. It has an absorption band at lower energies too.

EXPERIMENTAL

Materials.—*Barium hexacyanocobaltate*(III). $CoSO_4,7H_2O$ (56 g.) was dissolved in water (500 ml.), and the resulting solution was refluxed over $Ba(CN)_2,2H_2O$ (156 g.) in a Soxhlet extractor. This procedure gave a weakely alkaline supernatant, and a blue-green precipitate of unknown composition. The mixture was neutralised with dilute sulphuric acid, and the supernatant centrifuged from the (now pink) solid, evaporated (to 300 ml.), and filtered. At this stage the solution was neutral. The filtrate was further evaporated until a white solid appeared on the surface and then left to cool overnight. The resultant bulky white solid was heavily hydrated barium hexacyanocobaltate(III) and highly soluble. The hexacyanocobaltate(III) ion was assayed using the absorption at 3110 Å, no other cobalt compound being spectroscopically detectable.

Transition-metal hexacyanocobaltate(III). This was prepared from both potassium and barium salts, a 0·1M-solution of the anion being added to an equal volume of 0·2M-cation chloride, and the excess ion being removed by repeated washing with distilled deionised water. An ion(II) solution for this purpose was prepared by dissolving pure (~99·9%) iron in 2N-hydrochloric acid, under a steady stream of hydrogen gas in the presence of a platinised platinum surface, and barium hexacyanocobaltate(III) solution, swept out with the same stream of hydrogen, was added dropwise when solution was complete.

Thallium(I) *perchlorate*. This was prepared by dissolving 99·999% (spectroscopically pure thallium in AnalaR 2N-perchloric acid in Pyrex vessels; it was twice recrystallised at ~0°.)

Potassium hexacyanoferrate(II). This was AnalaR grade.

Potassium hexacyanoferrate(III). The AnalaR compound was recrystallised from boiled out, deionised water by cooling to ~0° in a Polythene vessel in the dark to avoid photolytic hydrolysis.

Potassium hexacyanocobaltate(III). This was prepared as in *Inorg. Synth.*, Vol. II, 203, and recrystallised as for potassium hexacyanoferrate(III).

Thallium(I) *hexacyanocobaltate*(III). This was prepared by adding 4M-perchloric acid to saturated potassium hexacyanocobaltate(III), centrifuging off the potassium perchlorate at 0°, and adding the hexacyanocobaltate(III) acid solution thus obtained to thallous carbonate. The solution was recrystallised by evaporation in a Polythene vessel in a dark desiccator over fresh silica gel.

Thallium(I) *hexacyanoferrate*(II). This was prepared by precipitation from 5% aqueous alcohol solutions of thallous nitrate and potassium hexacyanoferrate(II).

Thallium(I) *hexacyanoferrate*(III). This was prepared by adding saturated thallous perchlorate to potassium hexacyanoferrate(III) and centrifuging the potassium perchlorate at 0°. The solution was recrystallised twice, as for thallium(I) hexacyanocobaltate(III).

All materials were stored in the dark, to prevent photolysis.

Analysis of Materials.—Thallium and potassium were estimated by flame photometry, and the hexacyanometallates were estimated spectrophotometrically using a Unicam S.P. 600. The potassium salts were taken as the spectrophotometric standard of the anion absorptions, and thallium(I) perchlorate as the standard for thallium in flame photometry. Thallium(I) hexacyanoferrate(III) then analysed as $Tl_{2.93}K_{0.07}[Fe(CN)_6]$, and the hexacyanocobaltate(III) salt as $Tl_{2.985}K_{0.015}[Co(CN)_6]$. Potassium hexacyanocobaltate(III) was shown to contain less than 1 part in 10^5 of pentacyanoaquocobaltate(III).

Conductivity Measurements.—*Single crystals.* Because of the large size of the resistances to be measured, crystals of a suitable size were mounted on a Teflon insulator with the minimum capacitance between leads. The leads were joined to copper rods which passed through a Teflon block cut into a B40 ground glass cone, this cone fitting the socket of a glass vessel, connected to a vacuum line, which was suspended inside a Dewar flask for temperature control. Current through, or potential across, a crystal was measured by a 33C E.I.L. (Electronic Instruments Ltd.) vibrating-reed electrometer (nominal input resistance 10^{18} ohms), connections outside the vacuum line being of amicrophonic coaxial cable of a type recommended by E.I.L. for this purpose. A screen was built round the vacuum vessel containing the crystal and its leads, and the shields were well earthed. Temperature was measured by a copper–constantan thermocouple mounted on the Teflon insulator which carried the crystal.

Measurements of resistance can be " two-probe " or " four-probe " (Figure 3). Two-probe methods are known to be unsatisfactory for classical semiconductors of high resistance, as the measured current–voltage characteristics may depend on a region near the probe contacts which is not representative of the bulk material. In this situation the two-probe current–voltage characteristic is often non-linear, and the sample is said to be non-ohmic. This difficulty is avoided in the four-probe arrangement, in which the voltage probes are no longer the same as the current probes. The voltage probes themselves draw negligible current, and are well separated in space from the region of possible " barriers " near the current probes. The circuit of Figure 3(c) was used, in which the current (measured by the potential difference across a standard resistance in series with the crystal), and the difference in potential of the voltage probes (P_1, P_2) relative to the same point in the circuit, can be simply determined by three readings of the electrometer.

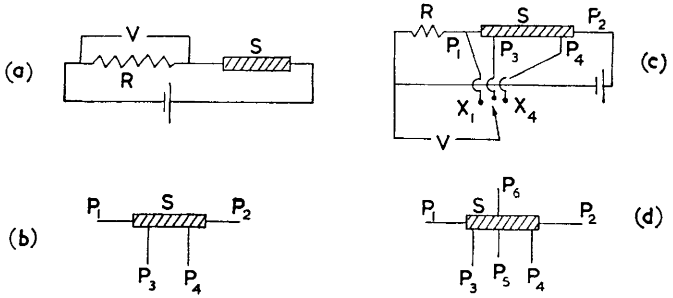

FIGURE 3. Diagrams showing electrical contacts to single crystals for (a) simple two-probe methods, (b) four-probe methods, (c) four-probe methods together with some circuit detail, and (d) Hall-effect measurements

Hall-effect measurements. The apparatus was constructed by Drs. Russel and Rollin (Clarendon Laboratory, Oxford) to whom we are greatly indebted. A crystal of thallium(I) hexacyanoferrate(III) (being the best conductor investigated) was mounted with six electrodes as in Figure 3(d) for Hall-effect measurements. Spring electrodes of copper or tungsten of 0·001 in. diameter proving electrically noisy, contacts of 0·001 in. diam. platinum wire were mounted on the crystal with silver paste. The limit of sensitivity was set by fluctuations in potentials of the contact. To lower this limit, the optimum applied e.m.f. (~10 v/cm.) was found, the crystal inspected under constant current conditions, the Hall e.m.f. displayed on a pen recorder, and a parallel resistance capacitance assembly used to damp out noise on the signal fed from the Vibron electrometer to the pen. No Hall effect was observed. Net carrier mobility was thus not greater than 3 $cm.^2 sec.^{-1} v^{-1}$. No magnetoresistance effect was observed to within 0·02% with a field of 4000 gauss, confirming that the mobility of the carriers is low.

A number of measurements were also taken by a two-probe method. If the resistance so measured was ohmic and reversible (*i.e.*, non-rectifying), then the series current is a measure of the bulk conductivity. All measurements on crystals satisfied these conditions at both room temperature and lowered temperature except where otherwise stated. All measurements satisfy the requirements of reproducibility. All measurements of resistance as a function of temperature were shown to be independent of the rate of change of temperature, thus showing that the crystal was in equilibrium with the temperature probe at all times under the conditions of the experiments.

The whole circuit was well shielded, and a feed-back terminal used to maintain insulation across the selector switch on the meter. All the insulators were of Teflon. To reduce resistance/capacitance time, sample capacitance was minimised by enclosing the sample in a wide bore (4 cm. diameter) glass jacket, and placing the electrical shield round the outside of the cooling Dewar flask. A McLeod gauge showed a pressure lower than 10^{-4} mm. during the electrical measurements.

Pellet measurements. Direct-current electrical conductivity was measured as a function of temperature for the bivalent-transition-metal hexacyanocobaltate(III) compounds (of which it is not possible to grow crystals) and of potassium hexacyanocobaltate(III), hexacyanoferrate(III) and of hexacyanoferrate(II) (thus giving a comparison between pellet and single-crystal measurements). Pellet discs of 13 mm. diameter and thickness 1—3 mm. were prepared in an evacuated KBr press at pressures of 2·5—6 tons/sq. in., and mounted between nickel discs in a holder basically similar to that described by Jacobs[4] but using Teflon instead of quartz insulators. This holder was suspended in a glass jacket surrounded by a Dewar flask for temperature control and screened with aluminium foil which also helped to stabilise the sample temperature. The glass jacket, which was connected to a vacuum line, could be broken into through a B50 flange.

The pellet measurements were carried out by a two-probe method, using either the Vibron electrometer, or, when possible, an E.I.L. "20 Million Megohmeter," which requires larger currents but has a more rapid response and is less sensitive to stray fields. Voltage was supplied either by the internal source of the Megohmeter, or by high-tension radio batteries, which were periodically checked. When the Vibron electrometer was used, the voltage was maintained across the sample throughout the run, while, if the Megohmeter was used, readings could be taken in both directions at each of two different voltages. As pellets occasionally proved to be non-ohmic and rectifying, the conduction was in all cases studied at two or more voltages and in both directions, so that pellet runs on the Vibron were of necessity repeated four times.

In all cases, measurements were shown to be reproducible with time, and independent of the rate of temperature change. Temperature was controlled by a suitable bath liquid in a Dewar flask surrounding the glass of the vacuum jacket, and measured by an individually calibrated copper–constantan thermocouple. All runs sere carried out at pressures below 10^{-3} mm., using a continuously operated mercury-diffusion pump. We therefore ignore the effect of of adsorbed gases, though it might be wrong to do so if they are very strongly held.

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[4] P. W. M. Jacobs, *J. Sci. Instr.*, 1953, **30**, 204.