Electrical Conduction Studies on the Partially Oxidised Metal-atom Chain Compounds $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ and $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$

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The a.c. and d.c. conductivities are reported for single crystals of the partially oxidised metal-atom chain compounds $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ and $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$. For d.c. fields of <120 V cm^{-1} the initial conductivity in the direction of the metal-atom chain is 10^{-4} Ω^{-1} cm^{-1} but this decreases with time to 10^{-6} Ω^{-1} cm^{-1}. The conductivity in the direction perpendicular to the metal-atom chains is 100 times lower. The a.c. conductivity is similar to those measured using d.c. potentials. The application of a d.c. field of >120 V cm^{-1} in the direction of the metal-atom chain induces an oxidation–reduction reaction which commences at the anode and spreads through the crystal to the cathode; the product of the reaction is $K_2Pt(CN)_4,2H_2O$ in a polycrystalline form.

RECENTLY there has been considerable interest in the electrical properties of transition-metal complexes which contain linear chains of interacting metal atoms.[1-4] Complexes of this type may be capable of development to give compounds which behave as one-dimensional metallic conductors or possibly even as high-temperature superconductors.[5] Single crystals of Magnus' green salt; $[Pt(NH_3)_4][PtCl_4]$,[1,3] and $Ir(CO)_2(acac)$ (acac = acetylacetone)[2] have been shown to behave as anisotropic ohmic semiconductors with the specific conductivity in the direction of the metal-atom chains 100 times greater than that measured perpendicular to the metal-atom chains. Miller proposed that, in complexes of this type which contain metal atoms with a d^8 configuration, overlap of the d_{z^2} orbitals on adjacent metal atoms can result in the formation of a completely filled d_{z^2} band. This filled band will be separated from the next (empty) band formed by overlap of adjacent p_z orbitals.[6]

Krogmann[7,8] has shown that it is possible to produce compounds containing chains of partially oxidised platinum atoms in which, it is suggested, electrons have been removed from the uppermost (anti-bonding) part of the d_{z^2} band. This results in a much shorter metal–metal distance [*e.g.* $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$; 2·88 Å] compared with distances of *ca.* 3·2 Å in those complexes containing metal atoms with a d^8 configuration.[8] The existence of a partially occupied band should result in electrical conduction properties quite different from those previously observed for compounds containing a filled d_{z^2} band. We have published a preliminary account of some of our results[9] on $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ and here we report in detail our studies on this and the related chloride complex. During the course of this work Minot and Perlstein published[10] a preliminary result on the bromide complex which is at variance with our work and will be discussed later.

RESULTS AND DISCUSSION

The structure[7] of $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ consists of square-planar $[Pt(CN)_4]^{2-}$ units stacked above one another along the *c* (needle)-axis of the crystal (see Figure 1). The Cl^- ions are in the centre of the unit cell surrounded by a tetrahedral arrangement of K^+ ions. However, only 64% of the unit cells contain Cl^- ions and this corresponds to $0\cdot32Cl^-$ per Pt atom and results in an oxidation number of 2·32 for the platinum. All the platinum atoms are crystallographically identical indicating that the excess charge is delocalised along the metal-atom chain. $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ possesses a similar structure and the platinum–platinum distances in the two compounds (Cl, 2·880; Br, 2·887 Å) are almost identical.[7]

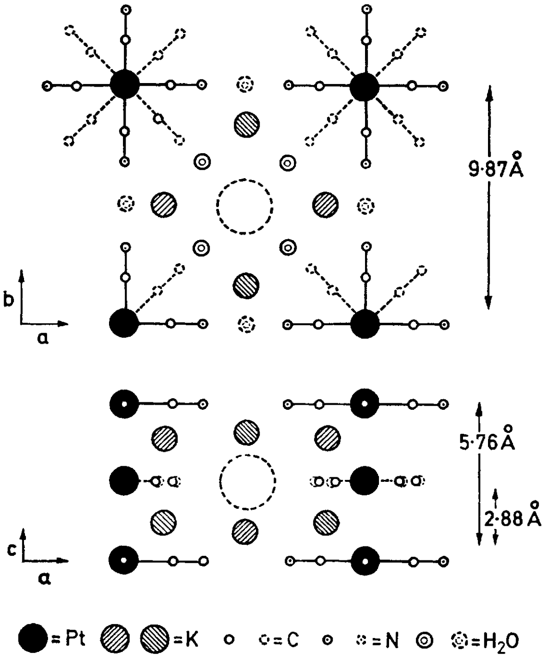

FIGURE 1 The unit cell of $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ projected along the *c* and *b* axes (after Krogmann and Hausen[7])

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[1] J. P. Collman, *Chem. Eng. News*, 1967, **45**, No. 52, 50.

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[4] L. V. Interrante and F. P. Bundy, *Inorg. Chem.*, 1971, **10**, 1169.

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[6] J. R. Miller, *J. Chem. Soc.*, 1965, 713.

[7] K. Krogmann and H. D. Hausen, *Z. anorg. Chem.*, 1968, **358**, 67.

[8] K. Krogmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35.

[9] P. S. Gomm and A. E. Underhill, *Chem. Comm.*, 1971, 511.

[10] M. J. Minot and J. H. Perlstein, *Phys. Rev. Letters*, 1971, **26**, 371.

(a) *D.C. Conductivity* (*Applied D.C. Field* <120 V cm^{-1}).—The application of a d.c. field of less than *ca.* 120 V cm^{-1} along the direction of the metal-atom chain [*i.e.* along the *c* (needle)-axis of the crystal] to a single crystal of either $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ or $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ produces a current which decreases exponentially with time and reaches a steady value after 5—10 min (see Figure 2). This suggests the presence of space-charge effects.[11] This behaviour is observed for silver paste, steel, or colloidal graphite electrodes and for crystals with or without earthed guard-rings.

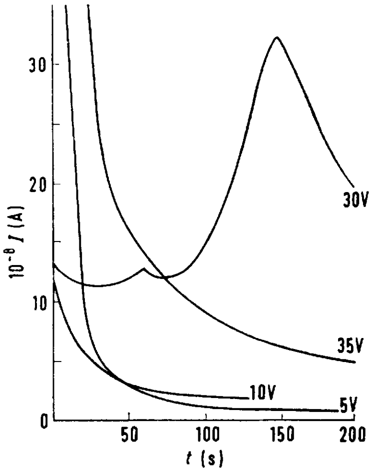

FIGURE 2 Variation of current with time for a series of d.c. voltages applied to a crystal of $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$

In the Table are listed the average initial and final conductivities found for single crystals of the chloride and bromide. The initial conductivity was obtained by extrapolating the current against time curves to zero time and the final conductivity is that corresponding to the steady current observed after 5—10 min. It has been observed that individual crystals may vary from the average value by up to one order of magnitude. Similar values for the conductivity were obtained using both silver paste and graphite electrodes and therefore the conductivity appears to be independent of the electrode materials. Similar values were also obtained on crystals with or without earthed guard rings thus eliminating surface conduction as a major effect.

D.c. and a.c. conductivities (Ω^{-1} cm^{-1})

	D.c.								A.c.	
	$\sigma_\parallel$				$\sigma_\perp$					
	Without guard-ring		With guard-ring		Without guard-ring		Disc			
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	$\sigma_\parallel$	$\sigma_\perp$
$K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$	10^{-4}	10^{-6}(6) *	10^{-4}	10^{-6}(4)	10^{-7}	10^{-8}(7)	10^{-6}	10^{-8}	10^{-5}(3)	10^{-7}(4)
$K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$	10^{-4}	10^{-6}(7)	10^{-4}	10^{-5}(4)	10^{-6}	10^{-8}(7)	10^{-7}	10^{-7}	10^{-5}(8)	10^{-7}(6)

* Figures in parentheses indicate number of crystals measured.

The initial conductivity of 10^{-4} Ω^{-1} cm^{-1} is comparable to that reported briefly by Krogmann and Hausen.[7] Recently however, Minot and Perlstein have reported[10] the much higher conductivity of 4 Ω^{-1} cm^{-1} for the bromide using a 4-probe method. Previous workers have not reported observing the current–time dependence we describe.

A similar dependence of current on time was observed with the electrodes positioned perpendicular to the *c* (needle)-axis of the crystal and the initial conductivity was 10^{-6} Ω^{-1} cm^{-1}. Thus the conductivity in the direction of the metal-atom chain is much higher than that in the direction perpendicular to the chain ($\sigma_\parallel : \sigma_\perp$ = *ca.* 100 : 1) and this can be interpreted as indicating greater electron delocalisation along the metal-atom chain. A similar degree of anisotropy of conduction has been found in Magnus' green salt.[1,3]

Compressed discs of the two compounds show the same current–time behaviour as observed for single crystals. The initial conductivity is lower than $\sigma_\parallel$ observed in single crystals and comparable to $\sigma_\perp$.

(b) *A.C. Conductivity*.—The a.c. conductivity of single crystals of $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ and $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ have been measured at a fixed frequency (1592 Hz). When the a.c. potential is applied to the crystals the conductivity and capacitance appear to fluctuate in a random fashion but the size of the fluctuations decreases with time and a fairly constant reading is obtained after 5 min. These fluctuations may be due to a property inherent in the crystal or to a contact effect but it is significant that crystals of Magnus' green salt give perfectly constant readings under the same circumstances. A wider range of conductivities was obtained from the a.c. measurement than from the corresponding d.c. determinations but the averages of the two sets of values were the same order of magnitude (see Table). The a.c. conductivities for the chloride and bromide show $\sigma_\parallel : \sigma_\perp$ to be 100 : 1 in agreement with the d.c. results. Attempts to study the variation of a.c. conductivity with temperature were only partially successful because the crystals almost invariably broke on raising or lowering the temperature. The results that were obtained indicated that the conductivity increases with temperature suggesting that the conduction process involves excitation of the electrons and not a metallic conduction mechanism.

The results in the Table show that the conduction properties of the chloride and bromide are the same

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[11] F. Gutmann and L. E. Lyons, 'Organic Semiconductors,' John Wiley, New York, 1967.

indicating that the conduction process is not concerned the with X^- ion but with the platinum-atom chain.

(c) *Application of a D.C. Field of* >120 V cm^{-1}.—If a succession of increasing voltages is applied in the direction of the metal-atom chains to a single crystal of $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ or $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ then at a certain voltage the specific conductivity suddenly increases (see Figure 2). This voltage varies from crystal to crystal but in general corresponds to a field of *ca.* 120 V cm^{-1}. The sudden increase in current is immediately accompanied by a change of colour of the crystal at the anode from the metallic copper colour of the original compound to a much lighter colour with no metallic lustre. This large increase in current is usually observed on increasing the field by a few volts but it has also been observed to occur spontaneously during the normal (low field) decay curve for applied fields close to 120 V cm^{-1}. This type of behaviour is shown in Figure 2 (curve for applied voltage of 30 V). In this case the increase in current lasted for only a short time before the normal (low-field) decay curve was resumed.

The colour change brought about by fields >120 V cm^{-1} commences at the anode end of the crystal and moves through the crystal towards the cathode with a sharp boundary between the two colours. The rate of movement of the colour boundary decreases as the reaction proceeds across the crystal and this is accompanied by a decrease in the current through the crystal. There is a very good correlation between the movement of the colour boundary and the decreasing current (see Figure 3). Most crystals are completely and smoothly changed to the lighter coloured product but occasionally the reaction falters, probably due to lattice imperfections in the crystal, and this is accompanied by a corresponding change in the current–time curve.

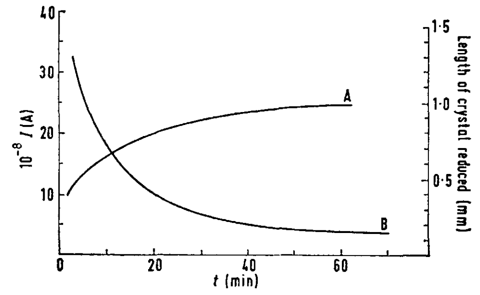

FIGURE 3 Length of crystal reduced (curve A) and decrease in current (curve B), with time for a crystal of $K_2Pt(CN)_4Cl_{0\cdot32},$-$2\cdot6H_2O$ (applied voltage −50 V)

The reaction occurs at high d.c. fields using silver paste, steel, or colloidal graphite electrodes showing the reaction to be independent of the electrode material. The reaction is irreversible and reversal of the potential before the crystal has completely changed causes the reactions to start at the (new) anode.

The speed of the colour boundary moving across the crystal increases markedly with increasing field. For a given crystal the ratio, length of product : length of unchanged crystal, is a linear function of time. The slope of this function is a measure of the rate of the reaction moving across the crystal. Figure 4 shows the variation of the gradient of this function with the applied field for a series of crystals of the bromide and chloride. Figure 4 shows that the rate of the reaction is the same in both the chloride and bromide.

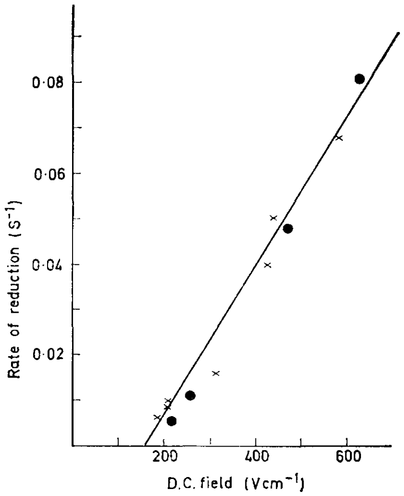

FIGURE 4 Variation of rate of reaction with applied d.c. field (×, $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$; ●, $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$)

It is also clear from Figure 4 that the rate of the reaction is field dependent and that there appears to be a threshold voltage below which the reaction will not proceed. This confirms the indication of a threshold voltage obtained by applying a succession of increasing voltages to a single crystal. We have found, however, that the application of a low field (*e.g.* 100 V cm^{-1}) will produce a light colouration in the vicinity of the anode over a period of several hours. The change in colour of the crystal appears at a much slower rate than the reaction observed above the threshold voltage and may arise from a different mechanism.

The lighter coloured product of the reaction will not oxidise potassium iodide to iodine and therefore contains platinum in the oxidation state II. The C, N, and K content is similar to that expected for $K_2Pt(CN)_4,2H_2O$. *X*-Ray powder and single-crystal rotation photographs of the product obtained from the bromide are similar to those obtained for $K_2Pt(CN)_4,2H_2O$ and quite different from those found for the original bromide. The rotation photographs show the reaction product to be polycrystalline although the overall shape of the original single crystal is retained. Electron-probe analysis shows the absence of halogen from the reaction products.

If the electrodes are applied perpendicular to the metal-atom chains a much higher d.c. field is required before the reaction starts. The colour boundary does not move directly between the electrodes but spreads out from the anode along the needle-axis of the crystal. Fields in excess of 10,000 V cm^{-1} are needed to convert all the crystal between the electrodes into the lighter coloured product.

GENERAL DISCUSSION

The electrical conduction properties of the two compounds at low d.c. fields are quite different from those observed for Magnus' green salt and related complexes in which the metal atom possesses a d^8 configuration. The decrease in current with time is consistent with a trap-filling process which removes the charge carriers before they can traverse the full width of the crystal. Trap-filling continues until an equilibrium state is reached in which the number of carriers entering traps is equal to the number leaving and this corresponds to the steady-state conditions observed after 10 min. Different applied voltages produce different steady currents. The initial current recorded for a 'fresh' crystal should correspond to the current before trap-filling occurs but this could only be obtained by an extrapolation procedure. The anisotropy of conduction ($\sigma_{\parallel} : \sigma_{\perp} = 100 : 1$) and the similar conduction properties of the chloride and bromide indicate that the conduction path is associated with the metal-atom chain.

The oxidation–reduction reaction observed at d.c. fields >120 V cm^{-1} is unusual since it takes place away from the electrodes. It is also significant that it starts at the anode even though the effect of the reaction is to reduce the oxidation state of the platinum. The loss of X^- in the reaction as shown by electron-probe analysis is clearly very important. This suggests that X^- is discharged at the anode to form X_2, *e.g.* $2Br^- \longrightarrow Br_2 + 2e$. The electrons released by this reaction are then available to reduce the platinum atoms from the partially oxidised state to Pt^{II}. This is a very localised reaction occurring initially only at the anode. The interface of the reaction then passes down the needle axis of the crystal. The absence of bromine or chlorine from the light-coloured reaction product shows that the halogen is released to the atmosphere at the interface and that the halide ions do not move through the crystal to the external anode. The observation that the reaction interface moves down the crystal at the same speed for both chloride and bromide (see Figure 4) at a given field strength confirms that the movement of the halide ions is not a rate-determining step. This suggests that as the reaction moves through the crystal the newly formed $K_2Pt(CN)_4,2H_2O$ acts as the electrode for the reaction.

The observation of a threshold field for the rapid spread of the reaction may indicate that a certain extent of trap-filling is required in order that electron transfer from the bromide ion to the platinum atom can proceed.

The value of *ca.* $5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ found for both the d.c. and a.c. conductivities together with the evidence of increasing conductivity with temperature indicates that the conduction mechanism is not metallic but requires promotion of electrons. It has been suggested [3] that lattice imperfection will hinder the movement of the carriers in a one-dimensional conductor more than in a two- or three-dimensional conductor. It is possible that the conduction along the metal-atom chains is metallic in nature but that in a single crystal the path from one electrode to the other is broken by faults and that the carrier requires an activation energy to jump across the fault from one metal-atom chain to the next. The difference in the value of $\sigma_{\parallel}$ reported by Minot and Perlstein and those reported here could be a reflection of the number of faults occurring in the crystals.

EXPERIMENTAL

$K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ and $K_2Pt(CN)_4Br_{0\cdot30}2\cdot3H_2O$ were prepared as previously described [7] and recrystallised from water. The more perfectly formed crystals were selected for the conduction measurements. The a.c. and d.c. conductivities were determined as previously described.[3] The movement of the colour boundary across the crystal was recorded by photomicrography. Electron probe analyses were determined on a JEOL JXA-3A micro-analyser and the *X*-ray rotation photographs were determined using a Unicam S25 camera.

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