Temperature Dependence of Conductivity of Some Partly-Oxidised Platinum Complexes

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The conductivity of single crystals of $K_2Pt(CN)_4Cl_{0\cdot3}2\cdot6H_2O$, $K_{1\cdot6}Pt(C_2O_4)xH_2O$, $Mg_{0\cdot82}Pt(C_2O_4)5\cdot3H_2O$ and $K_{1\cdot74}Pt(CN)_41\cdot8H_2O$ has been determined. The temperature dependence of the conductivity follows a log $\sigma \propto -(1/T)^{\frac{1}{2}}$ relationship consistent with a phonon-assisted hopping model recently proposed. In the last complex a metal-like temperature dependence of conductivity is observed at $T > 243$ K, which resembles the metal–insulator transition observed in a one-dimensional organic solid.

CONSIDERABLE interest has recently been displayed in some square-planar transition metal complexes in which electronic carrier transport is effectively confined to one dimension for structural reasons.[1-6] The 'partly oxidised' or 'mixed-valence' complexes of platinum described by Krogmann[7] have been studied by a number of investigators and the possibility of one-dimensional metallic conduction at low temperatures discussed. In this study, a series of these complexes have been examined which bear similarities to previously published data on the complex $K_2Pt(CN)_4Br_{0\cdot3}2\cdot3H_2O$,[4,5] and in one complex, $K_{1\cdot74}Pt(CN)_41\cdot8H_2O$, a metal-like temperature dependence of conductivity has been observed at $T > 243$ K. The measurements have been aided by the development of a technique of encapsulating the tiny crystals in a non-conducting resin which stabilizes them to temperature cycling.

Single crystals of certain Pt salts (*e.g.* Magnus Green Salt: $[Pt(NH_3)_4][PtCl_4]$) have been previously shown to behave as anisotropic semiconductors[2] with conduction several orders of magnitude higher in the direction of the Pt atom chain than perpendicular to those chains. Miller[8] proposed that in complexes of this type, in which the metal atoms possess a d^8 configuration in a square-planar environment, overlap of the d_{z^2} orbitals on adjacent metal atoms may result in the formation of filled d_{z^2} bands extending throughout the structure in the direction of the metal atom chain. Krogmann[7] has shown that it is possible to produce compounds containing chains of partly oxidised platinum atoms in which electrons are removed from the uppermost (antibonding) part of the d_{z^2} band, leading to greater interaction between adjacent Pt atoms, and shorter intermetallic distances within the chains. Complexes containing this partly-filled band structure would be expected to exhibit very different electronic properties from those possessing filled bands, and might even be expected to be metallic in nature.

In the complexes considered in this work, the Pt atoms are co-ordinated to a square-planar array of either four cyanide ligands or two oxalate ligands, but in each case the crystal structure is similar. The square-planar monomers $[Pt(CN)_4{}^{2-}$ or $Pt(C_2O_4)^{2-}]$ are stacked one above the other in the line of the needle axis of the single crystals. A typical structure is that of $K_2Pt(CN)_4Cl_{0\cdot3}2\cdot3H_2O$ in which the Cl^- and K^+ ions occupy sites located between the chains of Pt atoms. In this complex only 64% of the unit cells contain Cl^- ions, resulting in an oxidation number of +2·30 for the platinum atoms in the chains. All the Pt atoms are crystallographically identical, indicating that the structure does not contain discrete Pt^{2+} and Pt^{4+} sites, but that the excess charge is delocalised along the metal atom chains. In the other complexes studied not all the available cation sites are occupied, and the non-stoicheometry and oxidation state of +2·3 for the platinum atoms results again in the delocalisation of excess charge along the Pt atom chains.

EXPERIMENTAL

Preparation of Compounds.—(1) $K_{1\cdot74}Pt(CN)_41\cdot8H_2O$.[9] Attempts to prepare this compound by oxidation of

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commercial $K_2Pt(CN)_4 2H_2O$ gave a product contaminated with $K_2Pt(CN)_4Cl_{0\cdot3}2\cdot6H_2O$ because of the presence of chloride in the starting material. The chloride impurity was therefore removed from the $K_2Pt(CN)_4 2H_2O$ by conversion to the acid using an ion-exchange column (Dowex 50W-X8) and evaporating the acid to dryness. HCl Was evolved and the resulting acid, free of chloride, was neutralised with 1M-KOH. All the purification procedure was carried out under nitrogen.

Pure $K_2Pt(CN)_4 2H_2O$ (0·2 g) was dissolved in water (0·5 ml) and conc. HNO_3 (0·1 ml) allowed to diffuse into the solution through a No. 4 sinter disc. The product formed as a crystalline mass with thin needle shaped crystals on the outside. The mother liquor was removed, and the product washed with water and methanol and then air-dried at room temperature.

The product was identified as $K_{1\cdot74}Pt(CN)_4 1\cdot8H_2O$ by measuring the *X*-ray diffraction patterns of a powdered sample and comparing it with the published patterns.[9] Electron-probe analysis showed the absence of any chloride impurity in the crystals.

(2) $Mg_{0\cdot82}Pt(C_2O_4)_2 5\cdot3H_2O$. $K_2Pt(C_2O_4)_2$ Was converted to $(H_3O)_{1\cdot6}Pt(C_2O_4)_2$ *via* the silver salt using published methods.[10] A solution (90 ml) containing $(H_3O)_{1\cdot6}Pt(C_2O_4)_2$ (2·5 g) per 100 ml of solution was saturated with $MgCO_3$, warmed at 40 °C and filtered to remove the excess of $MgCO_3$. The $(H_3O)_{1\cdot6}Pt(C_2O_4)_2$ (10 ml) solution was added and the solution allowed to stand undisturbed at room temperature for 14 days.[11] The large (approx. size 0·15 × 0·03 × 0·03 cm) copper-red crystals were filtered off and washed with methanol and ether and air-dried at room temperature.

The *X*-ray diffraction pattern of a powdered sample showed the crystals to be phase A of $Mg_{0\cdot82}Pt(C_2O_4)5\cdot3H_2O$.[11]

(3) $K_{1\cdot6}Pt(C_2O_4)_2xH_2O$.[12] $K_2Pt(C_2O_4)_2xH_2O$ (1·5 g) Was dissolved in water (110 ml) at 50° and a mixture of 0·94 ml of 1M-H_2SO_4 and H_2O_2 (20 vol., 2·5 ml) added. The solution turned blue-black and was stirred vigorously for 2 min until the solution became lighter and a gas was evolved. The solution was allowed to stand for 2—3 days and the thin copper-coloured crystals (approx. size 0·1 × 0·01 × 0·01 cm) obtained by removing the mother liquor, and washing the crystals with water, methanol, and then ether. The crystals were air-dried at room temperature.

Electron-probe analyses were obtained as previously described.[13] *X*-Ray diffraction photographs were obtained with a Philips Debye–Scherrer powder camera type PW 1024 (diameter 114·83 mm) using Cu-K_α radiation (1542 Å).

Conductivity Measurements.—Measurements were made using a cell which could be lowered into a Dewar flask of liquid helium. The cell used was constructed from a thin walled (0·01 in) stainless steel tube fitted with B.N.C. connectors, and closed at the lower end by a removable cover to allow access to the crystal mounting area. This tube was lowered slowly into a Dewar flask of liquid helium, and measurements of the conductivity were taken at different temperatures. The crystal mounting area consisted of a copper block to which was attached a temperature sensing device (Cryogenic Linear Temperature Sensor, Micro-measurements, Michigan); and the crystal to be measured was electrically insulated from this block by mounting it on a thin glass slide using non-conductive glue. Both two-probe and four-probe measurements (where possible) were in agreement and several different electrode materials were used (Au, Ag paste, Aquadag) to establish the absence of electrode effects. All the crystals except $Mg_{0\cdot82}Pt(C_2O_4)5\cdot3H_2O$ exhibited a current–time dependence above a threshold voltage which differed in each case and which at higher fields led to a chemical reaction similar to that described by Gomm and Underhill.[14] Consequently in all measurements of the temperature dependence of conductivities, the electrical field strength was kept at about 1V cm^{-1} which was within the region of ohmic behaviour for all crystals studied.

Many of the smaller crystals, especially $K_2Pt(CN)_4Cl_{0\cdot3}$-H_2O consistently broke on cooling, and so a method of encapsulating these in a non-conducting resin (Quickmount, Fulton Metallurgical Corp., Pittsburgh, Pa.) was developed which allowed measurements to be made down to the limits of the apparatus. In all crystals studied in this manner the conduction in the temperature region measurable for the unsupported crystals was identical to that of the same complex when encapsulated. Several attempts were made to measure the room temperature conductivities in an atmosphere of dry nitrogen, but this led to dehydration of the crystals, and the appearance of cracks. Electrode areas were measured by photomicroscopic techniques but still represented the largest source of error, possibly up to 50% in extreme cases.

RESULTS AND DISCUSSION

Table 1 shows the specific conductivities (σ) at 25° of the complexes studied, both in the direction of the Pt atom chains ($\sigma_{\parallel}$) and where measurable perpendicular ($\sigma_{\perp}$) to those chains. Each measurement was repeated using several different crystals, and except for occasional anomalously low conductivities which were ascribed to cracks in the crystal, agreed within experimental error. The conductivity of $K_{1\cdot6}Pt(C_2O_4)_2xH_2O$ is similar to that published by Lecrone and Perlstein;[15] the small difference may be due to the difference between different hydrates. Both compounds for which $\sigma_{\parallel}$ and $\sigma_{\perp}$ have been measured show an anisotropy of conduction with the highest conduction in the direction of the Pt atom chains, indicating the existence of a conduction pathway in the direction of these chains.

The temperature variation of the electrical conductivity of $K_2Pt(CN)_4Cl_{0\cdot3}2\cdot6H_2O$ (A), $K_{1\cdot74}Pt(CN)_4$-$1\cdot8H_2O$ (B), $K_{1\cdot6}Pt(C_2O_4)xH_2O$ (C), and $Mg_{0\cdot82}Pt$-$(C_2O_4)_2 5\cdot3H_2O$ (D), are shown in Figure 1 and show great similarity to each other and to the conductivity dependence of $K_2Pt(CN)_4Br_{0\cdot3}2\cdot3H_2O$ published by Kuse and Zeller.[4] It is clear, however, that except for the upper portion of the curve for (B), the conductivity is not metallic. We feel that the forms of the log σ *vs.* $(1/T)^{\frac{1}{4}}$ plots shown in Figure 1 suggest that only the onset of thermal decomposition in complexes (A),

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TABLE 1

Anisotropies and field dependence of the room temperature conductivities of some partly-oxidised platinum complexes

		D.C.				A.C. (1600 Hz)	
		$\sigma_\parallel$ Ω^{-1} cm^{-1}		$\sigma\perp$ Ω^{-1} cm^{-1}			
		Initial	Final	Field[a] V cm^{-1}	Field V cm^{-1}	$\sigma_\parallel$ Ω^{-1} cm^{-1}	$\sigma\perp$ Ω^{-1} cm^{-1}
$K_2Pt(CN)_4Cl_{0.3}2{\cdot}6H_2O$ Pt–Pt, 2·88 Å	Ag paste	1×10^{-2}	1×10^{-2}	0·01—0·09			
$K_{1.74}Pt(CN)_4 1{\cdot}8H_2O$	Ag paste	1—3 $\times 10^{-4}$ [b]	1×10^{-6}— 9×10^{-7}	100	*c*	1×10^{-5}— 4×10^{-4}	*c*
Pt–Pt, 2·96 Å		4×10^{-6}— 1×10^{-4}	2×10^{-5}— 1×10^{-7}	50			
$K_{1.6}Pt(C_2O_4)_2xH_2O$	Ag paste	2×10^{-2}	1×10^{-2}— 6×10^{-4}	45		1×10^{-2}— 1×10^{-1}	2×10^{-5}— 1×10^{-3}
Pt–Pt, 2·81—2·85 Å		10^{-2}	4×10^{-3}	20			
	Aquadag					8×10^{-2}— 7×10^{-1}	
$Mg_{0.82}Pt(C_2O_4)_2 5{\cdot}3H_2O$	Ag paste	1—2 $\times 10^{-3}$ [b]	1—2 $\times 10^{-3}$	0·04—100	1×10^{-5} 80—320	2×10^{-3} (air)	6×10^{-6}— 1×10^{-4} (air)
Pt–Pt, 2·85 Å						2×10^{-3}— 1×10^{-4} (N_2)	
	Aquadag	2×10^{-2}	2×10^{-2}	85		4×10^{-2}— 1×10^{-3} (air)	

[a] In all cases at less than 1 V cm^{-1}, no dependence was observed. [b] Four-probe and two-probe measurements were performed on these crystals. [c] Crystals too small.

(C), and (D) prevents them from undergoing a similar transition to this metal-like state.

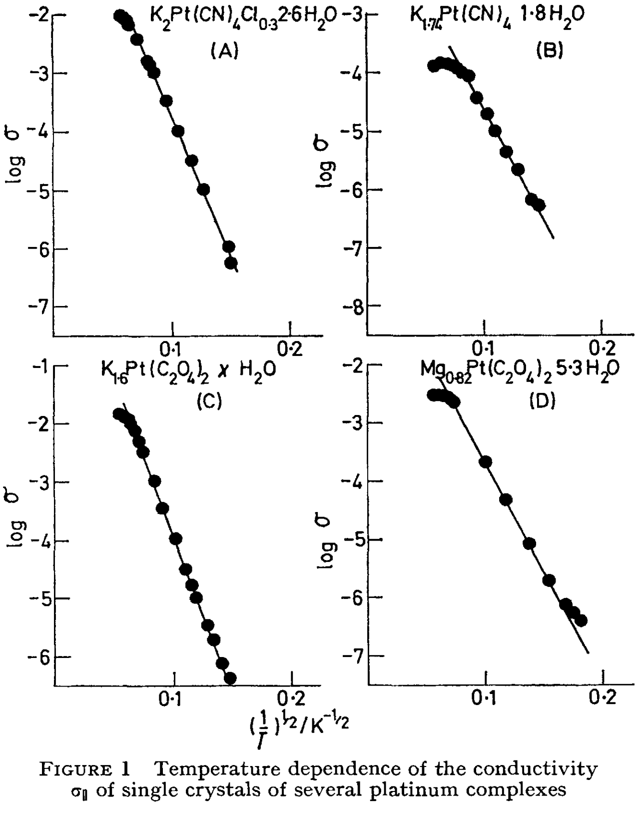

FIGURE 1 Temperature dependence of the conductivity $\sigma_\parallel$ of single crystals of several platinum complexes

The temperature dependence of the conductivity of (B) shows a peak at about 248 K and a negative temperature dependence above this point, indicating the possible existence of a metal–insulator transition in this complex. This is the first time such a transition has been observed in this type of complex, though it has been predicted by Bloch, Weisman, and Varma.[16] A similar transition has been observed by Epstein *et al.*[17] in crystals of the *N*-methylphenazinium salt of tetracyanoquinodimethane (NMP–TCNQ), a one-dimensional organic conductor, and was interpreted by these workers in terms of the one-dimensional Mott–Hubbard model. This interpretation has since been disputed,[16] but further evidence is necessary to establish the exact nature of the conduction in this region.

The absence of the predicted metallic conductivity in these partly oxidised complexes in the lower temperature range can be explained in two ways, both leading to qualitatively similar dependence of electrical conductivity upon temperature. We pointed out previously [18] that the electrical conduction in essentially one-dimensional systems will be extremely sensitive to crystal faults which lead to the production of broken chains. In such a system the conduction behaviour might be expected to depend critically on the mechanism for transport between strands of the broken chains and thus a modified theory of conduction in amorphous systems might be applicable: modified since the conduction is predominantly one-dimensional. This view is supported by recent studies of the optical properties of (A) by Geserich *et al.*[19] Theories of conduction in amorphous semiconductors were proposed by Ambe-

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goaker, Halperin, and Langer[20] and can be adapted to show that the relationship

$$\ln \sigma \propto -(1/T)^{\frac{1}{2}}$$

should be applicable in one-dimensional systems in which small energy gaps exist between adjacent states.

Plots of log σ *vs.* $(1/T)^{\frac{1}{2}}$ are given in Figure 1 and show this relationship to be applicable to our systems at low temperatures. However those parts of the curves at high temperatures show considerable deviation from linearity. Figure 2 is a plot of σ *vs.* T K for complex (B), which shows clearly the negative temperature dependence of conductivity above 248 K.

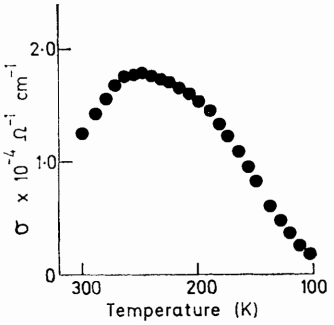

FIGURE 2 Variation of $\sigma_{\parallel}$ in the region 100—300 K for $K_{1\cdot74}Pt(CN)_4 1\cdot8H_2O$

Very recently Bloch, Weisman, and Varma[16] have proposed a theory to account for the conductivity behaviour in pseudo-one-dimensional conductors in which they propose a phonon-assisted hopping model. It is proposed that the random array of ions located between the chains of Pt atoms in these partly-oxidised structures leads to destruction of the over-all band structure and to localisation of the charges. Subsequent conduction is then thought to be by thermally assisted hopping of electrons between localised states along the chain. Under these conditions it has been calculated that

$$\ln \sigma \propto -(T_0/T)^{\frac{1}{2}}$$

where T_0 is a constant for each complex studied. Clearly the curves of Figure 1 are in agreement with this relationship and allow the calculation of T_0 for each system. Bloch *et al.*[16] also define two further parameters T_H and T_D for each system, these being the temperatures at which each curve begins to deviate from linearity, and at which it reaches a peak respectively, and demonstrate that the relationship

$$\nu_c^2 = T_0 T_H / T_D^2$$

where ν_c is a constant which depends only on the dimensionality, should hold true for all such one-dimensional complexes. The values for T_0, T_H, and T_D for each of the complexes studied are given in Table 2.

TABLE 2

Variation of parameters defined by Bloch *et al.*[a] for partly-oxidised platinum complexes

Material	T_0	T_H	T_D	ν_c
$K_2Pt(CN)_4Cl_{0\cdot3}2\cdot6H_2O$	$1\cdot06 \times 10^4$	156	331	3·9
$K_{1\cdot74}Pt(CN)_4 1\cdot8H_2O$	$7\cdot72 \times 10^3$	140	248	4·2
$K_{1\cdot6}Pt(C_2O_4)_2 xH_2O$	$1\cdot69 \times 10^4$	226	400[b]	4·9
$Mg_{0\cdot82}Pt(C_2O_4)_2 5\cdot3H_2O$	$7\cdot20 \times 10^3$	188	278	4·2
$K_2Pt(CN)_4Br_{0\cdot3}2\cdot3H_2O$	$5\cdot79 \times 10^4$	120	580	4·5[a]
NMP–TCNQ	$1\cdot72 \times 10^4$	50	200	4·6[a]

[a] Ref. 16. [b] Estimated value.

The agreement between values of ν_c is considered excellent, and they also agree very well with similar values calculated for $K_2Pt(CN)_4Br_{0\cdot3}$ and several 'one-dimensional' organic systems. Using this theory it can be predicted that at low temperatures the tunnelling will become insensitive to the anisotropy of the crystal and a three-dimensional law ($T^{-\frac{1}{4}}$) of amorphous conduction should hold. This is supported by the results for (D) and is shown in Figure 1 (D). Furthermore, Bloch *et al.*[16] have pointed out that the reversal of the temperature dependence at higher temperatures might be expected in a disordered one-dimensional system at temperatures at which kT is of the order of the activation energy of conduction.* Further experiments to determine the mobility and the sign of the majority charge carriers are in progress and should aid in determining the exact nature of the conduction in these unusual complexes.

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