Electrical Conduction Properties of the Platinum Chain Complexes $(NH_4)_2Pt(CN)_4Cl_{0\cdot3}\cdot3\cdot2H_2O$ and $(NH_4)_{2\cdot2}Pt(CN)_4Cl_{0\cdot5}\cdot3H_2O$

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Summary The d.c. conduction properties of $(NH_4)_2Pt(CN)_4Cl_{0\cdot3}\cdot3\cdot2H_2O$ and $(NH_4)_{2\cdot2}Pt(CN)_4Cl_{0\cdot5}\cdot3\cdot0H_2O$ are compared with those of $K_2Pt(CN)_4Br_{0\cdot3}\cdot3\cdot2H_2O$ and the unique role of NH_4^+ ions in this type of compound is described.

RECENT work on the platinum complexes which exhibit pseudo-one-dimensional metallic properties at room temperature has concentrated almost exclusively on $K_2Pt(CN)_4Br_{0\cdot3}\cdot3\cdot2H_2O$ (KCP).[1,2] It has been suggested that the ions and water molecules between the one-dimensional metallic strands may play an important role in determining the electrical conduction properties of this class of compounds.[1,3,4,5] The results described here for $(NH_4)_2Pt(CN)_4Cl_{0\cdot3}\cdot3\cdot2H_2O$ (I)[†] and $(NH_4)_{2\cdot2}Pt(CN)_4Cl_{0\cdot5}\cdot3H_2O$ (II)[†] show that these effects can be very dramatic.

Crystals of (I)[†] were obtained by allowing a concentrated aqueous solution of $(NH_4)_2Pt(CN)_4$ and $(NH_4)_2Pt(CN)_4Cl_2$ (5:1 mole ratio) to cool to 4 °C.

Large well formed crystals of (II)[†] were produced by

[†] Satisfactory analytical data were obtained for these compounds.

allowing an aqueous solution of 1·0 M (I) and 3·7 M NH_4Cl to crystallise at room temperature. This compound contains an additional 0·2 mol of NH_4^+ and Cl^- ions per mol of Pt compared with (I). The crystals do not have NH_4Cl on their surfaces and no evidence of lines attributable to NH_4Cl could be found in *X*-ray powder photographs. Therefore, the excess NH_4^+ and Cl^- ions must be present in the lattice.

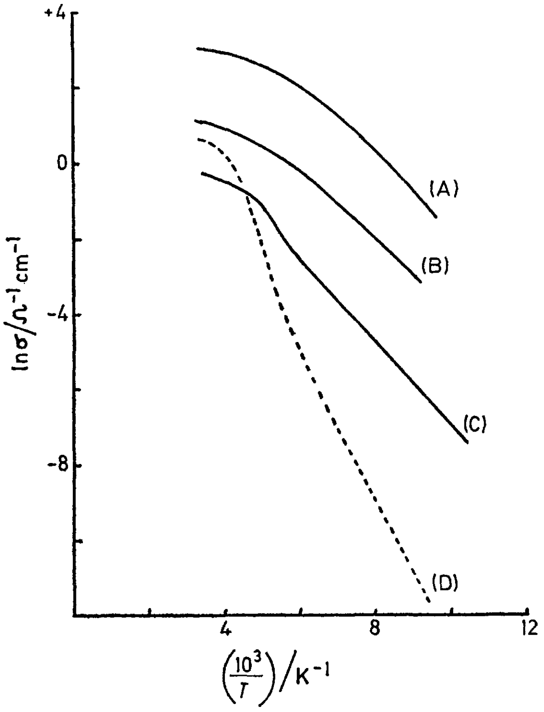

FIGURE. D.c. conductivity as a function of temperature, parallel to the platinum atom chain for: (A), (III); (B), (IV); (C), (I); and (D), (II).

Preliminary *X*-ray studies suggest that the two ammonium complexes are isomorphous and that they have a similar structure to KCP, $K_2Pt(CN)_4Cl_{0\cdot3}\cdot3\cdot2H_2O$ (III), and $Rb_2Pt(CN)_4Cl_{0\cdot3}\cdot3\cdot2H_2O$ (IV),[6] with unit cell dimensions slightly larger than those reported for KCP.[7] In KCP only 60% of the available Br^- sites at the centre of the unit cell are occupied by Br^- ions, the remainder contain water molecules corresponding to $0\cdot2H_2O$ per Pt atom.[7] The presence of 0·5 Cl^- per Pt atom in (II) is just sufficient to occupy completely the halide sites in the KCP structure with Cl^- ions.

Four-probe d.c. conductivity measurements have been made over the temperature range 108—320 K. A comparison of the conductivity parallel to the platinum atom chain direction for (I), (II), (III), and (IV) as determined under the same conditions is shown in the Figure.

The temperature behaviours of the specific conductivities found for (III) and (IV)[6] are very similar to one another and to that reported for KCP over the same temperature range.[8] The general profiles of the temperature dependence of the conductivities of (I) and (II) shown in the Figure are different from one another and from those for the potassium and rubidium compounds but are qualitatively similar to that reported for KCP over the much wider temperature range 26—320 K.[8] In KCP a correlated static Peierls distortion has been shown to exist at low temperatures (< 77 K) whereas above 120 K the distortion is dynamic and uncorrelated.[9] The conductivity results described above suggest that in the ammonium compounds the static Peierls distorted state exists to a much higher temperature (*ca.* 150 K). This difference cannot be due to the different size of the cation since NH_4^+ is very similar in size to Rb^+. We believe that these differences are due to the unique possibility of hydrogen bonding between the NH_4^+ ions and the water molecules in the lattice. This would result in stronger inter-chain coupling and, therefore, make thermal breakdown of the correlated static Peierls distortion more difficult.

The low temperature activation energy (0·18 eV) found for (II) is considerably greater than that found for the ammonium compound with only partial occupancy of the halide sites (0·09 eV). This supports the suggestion[2] that the random potential resulting from partial occupancy of the halide sites in KCP affects the conductivity along the platinum atom chains by reducing the effective band gap.

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