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PREPARATION AND PROPERTIES OF ONE-DIMENSIONAL BIS-(OXALATO)PLATINATES *

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The preparation of the new 1-D conductors $(NH_4)_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$ (Am-OP) and $[(CH_3)_2NH_2]_{1.61}[Pt(C_2O_4)_2]$ (DMA-OP) is described. The average intra-chain Pt-Pt separation is 2.82 Å in Am-OP and 2.80 Å in DMA-OP. The specific conductivity in the platinum atom chain direction is $\sim 50\ \Omega^{-1}\ cm^{-1}$ and $\sim 20\ \Omega^{-1}\ cm^{-1}$ for Am-OP and DMA-OP respectively. The variation of specific conductivity with temperature in the platinum atom chain direction is compared with that of other 1-D metallic complexes.

INTRODUCTION

Studies on the partially oxidised tetracyanoplatinate salts have shown that the presence of a hydrogen bonded network crosslinking the conducting chains of $[Pt(CN)_4]^{x-}$ ions has an important effect on the solid state properties of these compounds.[1] In particular it was noted that the replacement of a metal cation by NH_4^+ dramatically increased T_{3D}, the three-dimensional ordering temperature, presumably due to the additional hydrogen bonds formed by the ammonium cation compared with a metal cation.[2] We are now carrying out a related study of partially oxidised ammonium and substituted ammonium bis(oxalato)platinates. The properties

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of the ammonium and dimethylammonium salts are described below.

RESULTS AND DISCUSSION

(a) $(NH_4)_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$ (Am-OP)

This salt was prepared by the electrolytic oxidation of a saturated aqueous solution of $(NH_4)_2[Pt(C_2O_4)_2]\cdot xH_2O$ containing $(NH_4)_2C_2O_4$.

(i) X-ray Studies

The unit cell dimensions are given in the Table. The platinum atom chain lies along the c-axis of the unit cell which contains four platinum atoms. The average intra-chain Pt-Pt separation (d_{Pt-Pt}) is 2.82 Å and this is the same as that observed in $K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$.[3]

Diffuse x-ray scattering experiments at room temperature show the presence of diffuse lines around the Bragg reflection layer lines of non-zero order indicating the existence of the Peierls instability in this compound at room temperature. From the position of the diffuse lines the Fermi wavevector is 1.69. This is in good agreement with the degree of partial oxidation calculated from the chemical analysis of Am-OP. In addition to the diffuse lines due to the Peierls instability weak spots are also observed both on the diffuse lines and mid-way between the diffuse lines and the Bragg reflection layer lines. Additional spots of this type have been shown to be indicative of a Non-Peierls (NP) superstructure in related compounds.[4] The presence of spots on the diffuse lines indicates that the Peierls and Non-Peierls superstructures

Table Unit Cell Dimensions (Å)

	Am-OP	DMA-OP
a	11.16 ± 0.01	21.34 ± 0.03
b	16.77 ± 0.03	9.79 ± 0.05
c *	11.27 ± 0.03	5.60 ± 0.02
d_{Pt-Pt}	2.82	2.80

*platinum atom chain direction

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are commensurate and the presence of spots midway between the diffuse line and the Bragg reflection layer lines shows that $2k_F \neq 2q^{NP}$.

(ii) Electrical Conduction Studies

The electrical conduction properties of Am-OP were determined by a 4-probe dc technique. The crystals measured were typically of dimensions 3 x 0.1 x 0.1 mm^3 and measurements were confined to the needle axis direction which is the platinum atom chain direction. An examination of ten high quality crystals gave values in the platinum atom chain direction ($\sigma_{//}$) of between 9 and 50 Ω^{-1} cm^{-1}. These values are very similar to those found for other partially oxidised bis(oxalato)platinates of monovalent cations and with incommensurate Peierls distortions (e.g. $K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$, d_{Pt-Pt} = 2.82 Å; $\sigma_{//}(RT) = 10^2\ \Omega^{-1}cm^{-1}$).[3] The variation of $\sigma_{//}$ with temperature is shown in Figure 1. It can be seen that below room temperature the conductivity is almost temperature independent down to 260 K. Below

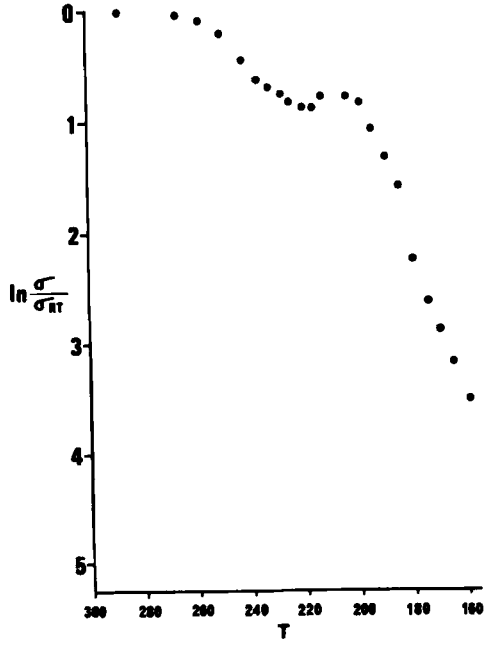

FIGURE 1 Variation of $\ln(\sigma/\sigma_{RT})$ with temperature for $(NH_4)_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$

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200 K the conductivity falls sharply with decreasing temperature and Am-OP behaves as a semiconductor. In between these two regions the variation of conductivity is complex and the reproducible anomaly around 240 K may indicate that a phase change is taking place.

(b) $[(CH_3)_2NH_2]_{1.61}[Pt(C_2O_4)_2]$ (DMA-OP)

This salt is the first anhydrous partially oxidised bis-(oxalato)platinate salt to be prepared. It is obtained as shiny copper coloured needles by electrolysis of a solution of $[(CH_3)_2NH_2]_2[Pt(C_2O_4)_2]$ either in anhydrous dimethylformamide or in aqueous solution.

(i) X-ray Studies

The unit cell dimensions are given in the Table. There are two platinum atoms per unit cell and the average d_{Pt-Pt} is 2.80 Å which is the shortest value reported for a partially oxidised bis(oxalato)platinate salt to date.

Diffuse x-ray scattering experiments at room temperature reveal the existence of a Peierls distortion with a Fermi wavevector of 1.61 in agreement with the value determined by chemical analysis (1.63). No evidence of superstructure spots could be detected either on or between the diffuse lines. The absence of superstructure spots in a partially oxidised bis(oxalato)platinate salt is unusual.

(ii) Electrical Conduction Studies

The electrical conductivity in the platinum atom chain direction ($\sigma_{//}$) was measured for 9 good quality crystals of typical size 3 x 0.07 x 0.06 mm^3. The values for $\sigma_{//}$ at room temperature were in the range 0.6 - 20 Ω^{-1} cm^{-1}.

The variation of conductivity with inverse temperature is shown in Figure 2. Unlike the behaviour of Am-OP there are no abrupt changes in conductivity. The conductivity decreases with decreasing temperature throughout the temperature range studied (293 - 60 K) but the rate of decrease around room temperature is less than that at lower temperatures suggesting that a temperature independent region may exist at some higher temperature.

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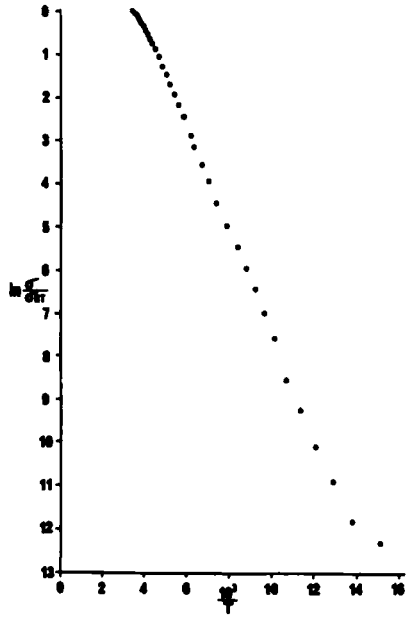

FIGURE 2 Variation of $\ln(\sigma/\sigma_{RT})$ with inverse temperature for $[(CH_3)_2NH_2]_{1.61}[Pt(C_2O_4)_2]$

GENERAL DISCUSSION

Previous studies on partially oxidised bis(oxalato)-platinate salts of monovalent cations have shown them to possess structures with large unit cell dimensions in the platinum atom chain direction with several different intra-chain Pt-Pt separations. The chains themselves often have transverse as well as longitudinal modulation.[5] It seems likely that the hydrated salt Am-OP possesses a similar type of structure and this is supported by the observation of NP-superstructure spots and the similarity of the temperature dependence of the conductivity with that of $K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$.[3]

The anhydrous salt DMA-OP, however, does not fit into this previously observed pattern of behaviour. The short unit cell dimension in the platinum atom chain direction and the absence of NP-superstructure spots is not typical of the partially oxidised bis(oxalato)platinate salts. The temperature dependence of the conductivity is also different to

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that of previously studied monovalent cation salts and in some respects it is similar to that of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$.[6] The absence of water molecules in the lattice may be responsible for the differences between Am-OP and DMA-OP but further structural studies are required before these differences can be understood.

Work is in progress on the study of partially oxidised bis(oxalato)platinate salts of other substituted ammonium cations.

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