Studies † on Partially Oxidised Ammonium and Methyl-substituted Ammonium Bis(oxalato)platinates

Masagi Mizuno and Allan E. Underhill *
School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd, LL57 2UW
Kim Carneiro
Physics Laboratory 1, H.C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

The preparation and properties of a series of partially oxidised bis(oxalato)platinate salts of ammonium and methyl-substituted ammonium cations are described. Their electrical conduction properties are related to the value of the Fermi wave-vector determined from *X*-ray diffuse scattering experiments and the presence of three-dimensional superstructures at room temperature.

Over the past few years a series of partially oxidised bis(oxalato)platinate salts containing many different bivalent cations has been prepared and extensively studied.[1-4] It has been observed that there are large differences in the solid-state properties of these compounds depending on the cation. On the other hand, studies of the partially oxidised bis(oxalato)platinate salts of monovalent cations have been restricted to those of potassium and rubidium although there are several modifications of each of these salts.[4] We have now extended the range of salts of monovalent cations to include ammonium and methyl-substituted ammonium salts. This series of salts is particularly important to the study of one-dimensional metallic complexes since it has been shown that in the series of compounds $M_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (M = K, Rb, or NH_4) the ammonium salt has markedly different properties from the other salts.[5] In particular the temperature of the phase transition (T_{3D}), which involves partial three-dimensional ordering of the one-dimensional distorted platinum atom chains, and the electronic band width anisotropy $\eta = (W_\perp / W_\parallel)$ are much greater than for the potassium or rubidium salts. This is due to the additional hydrogen bonding between the chains involving the ammonium cations. Thus the ammonium and methyl-substituted ammonium bis(oxalato)platinate salts have been studied to determine if similar effects are present in the bis(oxalato)platinate series of compounds and to study any systematic change in properties as hydrogen atoms are progressively replaced by methyl groups. Preliminary results on two of the compounds discussed here have appeared elsewhere.[6]

Experimental

Preparation of Platinum(II) *Salts*.—$[NH_4]_2[Pt(C_2O_4)_2]\cdot xH_2O$. The complex $Ag_2[Pt(C_2O_4)_2]$ (4 g) was suspended in water (10 cm^3) and heated to boiling. A solution of NH_4Cl (0.73 g in 10 cm^3 water) was slowly added with continuous stirring until the white precipitate of AgCl coagulated. Filtration through a no. 4 sinta crucible yielded a clear yellow solution. If the solution turned pale green-yellow due to aerial oxidation then SO_2 gas was passed through the solution until it turned dark yellow due to the formation of colloidal platinum. Activated charcoal was then added to remove the platinum metal and the mixture filtered to give a clear yellow solution. The resulting yellow solution was evaporated to dryness on a rotary evaporator to yield the yellow product $[NH_4]_2[Pt(C_2O_4)_2]\cdot xH_2O$.

The complexes $[NH_3Me]_2[Pt(C_2O_4)_2]\cdot xH_2O$, $[NH_2Me_2]_2[Pt(C_2O_4)_2]\cdot xH_2O$, $[NHMe_3]_2[Pt(C_2O_4)_2]\cdot xH_2O$, and $[NMe_4]_2[Pt(C_2O_4)_2]\cdot xH_2O$ were obtained by similar procedures.

Preparation of Partially Oxidised Salts.—$[NH_4]_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$ (1). Ammonium oxalate (0.82 g) was dissolved in a saturated solution (26 cm^3) of $[NH_4]_2[Pt(C_2O_4)_2]\cdot xH_2O$. The solution was filtered through a 0.22-μm Millipore filter and placed in an H-shaped electrolytic cell fitted with 0.4-mm diameter platinum wire electrodes. The cell was designed to separate the crystals of the product which formed on the anode from the precipitate which formed around the cathode. The cell was fitted with air-tight caps to prevent aerial oxidation. The solution was electrolysed at 0.4—0.5 V. After a few days copper coloured needle-shaped crystals of the product were obtained at the anode which were filtered off, washed with ice-cold water, and air-dried {Found: C, 11.75; H, 2.10; N, 5.75; Pt, 46.7. Calc. for $[NH_4]_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$: C, 11.45; H, 2.10; N, 5.65; Pt, 46.5%}.

The complex $[NH_3Me]_{1.71}[Pt(C_2O_4)_2]\cdot H_2O$ (2) was prepared by a similar procedure {Found: C, 15.4; H, 2.80; N, 5.35; Pt, 43.0. Calc. for $[NH_3Me]_{1.71}[Pt(C_2O_4)_2]\cdot H_2O$: C, 15.45; H, 2.80; N, 5.40; Pt, 43.9%}.

$[NH_2Me_2]_{1.61}[Pt(C_2O_4)_2]$ (3). This complex was prepared in a similar way to the ammonium salt after adjusting the pH of the electrolytic solution to 5—6 by the addition of either $[NH_2Me_2]OH$ or oxalic acid {Found: C, 19.40; H, 2.00; N, 5.05; Pt, 42.3. Calc. for $[NH_2Me_2]_{1.61}[Pt(C_2O_4)_2]$: C, 19.45; H, 2.90; N, 5.05; Pt, 43.8%}.

$[NMe_4]_{1.65}[Pt(C_2O_4)_2]$ (4). A saturated solution of $[NMe_4]_2[Pt(C_2O_4)_2]$ in water was filtered through a 0.22-μm Millipore filter. The pH was adjusted to *ca*. 1 by the addition of H_2SO_4 or HNO_3. Lath-shaped copper-coloured crystals slowly grew as the solution evaporated on exposure to air. The crystals were filtered off, washed with ice-cold water and air dried. The analysis of the compound will be discussed in the Results section. The complex $[NHMe_3]_{1.59}[Pt(C_2O_4)_2]$ (5) was prepared by an analogous procedure {Found: C, 20.9; H, 2.9; N, 4.5; Pt, 39.9. Calc. for $[NHMe_3]_{1.59}[Pt(C_2O_4)_2]$: C, 22.55; H, 3.45; N, 4.75; Pt, 41.80%}.

Analysis.—Platinum analyses were carried out by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. Carbon, hydrogen, and nitrogen were determined microanalytically.

Physical Measurements.—Electrical conductivity studies were carried out using a 4-probe d.c. technique with aquadag as the contact material between the crystal and the gold wire leads. Details of the apparatus have been published elsewhere.[3] All crystals gave ohmic behaviour under the conditions of measurement.

Single-crystal *X*-ray diffraction measurements were made using a Stoe Weissenberg camera and Cu-K_α radiation (λ =

---

† *Non-S.I. unit employed:* 1 eV ≈ 1.60×10^{-19} J.

Table 1. Structural data

Compound	Crystal system [a]	Unit-cell dimensions (Å)			D/g cm^{-3}		$2k_F/\pi d_{\parallel}^{-1}$
		a	b	c	Obs.	Calc.	
(1) $[NH_4]_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$	O	11.12(1)	16.72(3)	11.31(3)	2.68	2.65	1.69 [b]
(2) $[NH_3Me]_{1.71}[Pt(C_2O_4)_2]\cdot H_2O$	M	9.01(2)	11.04(2)	11.57(4)	2.61	2.56	1.71 [c]
(3) $[NH_2Me_2]_{1.61}[Pt(C_2O_4)_2]$	O	9.71(5)	21.18(3)	5.62(2)	2.55	2.56	1.61 [b]
(5) $[NHMe_3]_{1.59}[Pt(C_2O_4)_2]$	O	13.62(1)	18.36(5)	14.01(4)	2.26	2.24	1.59 [c]
(4) $[NMe_4]_{1.65}[Pt(C_2O_4)_2]$	O	15.75	15.83	11.24	2.37	2.40	1.65 [d]

[a] O = Orthorhombic; M = monoclinic (γ = 83.6°). [b] Ref. 10. [c] Ref. 11. [d] Ref. 13.

1.542 42 Å) to determine lattice parameters. A special fixed-film apparatus was used to measure diffuse scattering.

Results and Discussion

It was found that two different methods of preparation had to be used for these compounds to obtain single crystals of suitable size for solid-state measurements. The complexes $[NH_4]_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$ (1), $[NH_3Me]_{1.71}[Pt(C_2O_4)_2]\cdot H_2O$ (2), and $[NH_2Me_2]_{1.61}[Pt(C_2O_4)_2]$ (3) have a relatively low solubility in water and preparations involving aerial oxidation resulted in a matt of very fine crystals. These compounds were therefore prepared by the electrolytic method. Conversely, because of the high solubility of $[NMe_4]_{1.65}[Pt(C_2O_4)_2]$ (4) and $[NHMe_3]_{1.59}[Pt(C_2O_4)_2]$ (5) a combination of aerial oxidation and slow evaporation of the solution proved a better method for the preparation of single crystals of these compounds. Recently (1) and (3) have been prepared using H_2O_2 oxidation of acidified aqueous solutions of the platinum(II) salts at 47 °C in connection with experiments to be carried out in the European Space Agency Spacelab.[7]

It can be seen that whereas (1) and (2) are obtained with one molecule of water of crystallisation the remaining compounds are all anhydrous. These are the first anhydrous partially oxidised bis(oxalato)platinate salts to be obtained although a number of anhydrous anion-deficient tetracyanoplatinate salts have been obtained previously.[8]

Although all the cations in this series of compounds are chemically closely related the compounds themselves show marked differences in both their chemical compositions and in their solid-state properties. Thus first each compound will be discussed individually and then they will be compared with each other and with other related compounds.

$[NH_4]_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$ (1).—The single-crystal X-ray studies on this compound indicate that the platinum atom chain lies along the c axis of the unit cell which contains four platinum atoms (see Table 1). The average intra-chain planar anion separation ($d_{\parallel}$) is 2.83 Å. Ammonium and rubidium cations have very similar ionic radii and it is interesting to note that a modification of the partially oxidised rubidium bis(oxalato)platinum has been reported with very similar unit-cell dimensions.[9] X-Ray diffuse scattering (x.d.s.) studies carried out at room temperature revealed the presence of diffuse lines around the Bragg reflection-layer lines of non-zero order.[10] This indicates the existence of the Peierls instability in this compound and from the position of the diffuse lines the value of $2k_F$ (where k_F is the Fermi wave-vector) is 1.69 (in units of $\pi/d_{\parallel}$). Weak spots are observed both on the diffuse lines and midway between the diffuse lines and the Bragg reflection-layer lines indicating the presence of a three-dimensional superstructure in this compound. These superstructures have been termed ' non-Peierls superstructures (nP) ' because they give rise to distinct spots in X-ray scattering experiments and not to diffuse lines or modulated streaks characteristic of the Peierls distortion.[1,2,4] The nP superstructure may, in part, be associated with cation ordering. The presence of spots on the diffuse lines indicates that the Peierls and non-Peierls superstructures are commensurate along this conducting axis and the presence of spots midway between the diffuse lines and the Bragg reflection-layer line indicates that the nP distortion has a wavelength along c twice that of the Peierls distortion.

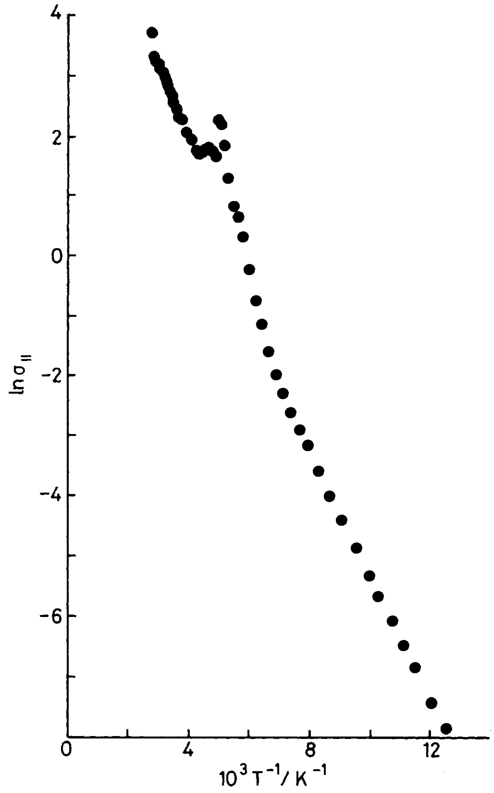

Figure 1. Variation of ln $\sigma_{\parallel}$ with inverse temperature for a crystal of $[NH_4]_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$ (1)

The room-temperature electrical conductivity of 11 crystals of (1) was measured in the platinum-atom chain direction ($\sigma_{\parallel}$). The spread of the values obtained, 5—54 Ω^{-1} cm^{-1}, is not unusual for compounds of this type.[4] The average value of $\sigma_{\parallel}$ was 14 Ω^{-1} cm^{-1}.

The variation of $\sigma_{\parallel}$ with inverse temperature is shown in Figure 1. Above 260 K the conductivity appears almost independent of temperature and without a pronounced maximum, whereas below 260 K the conductivity falls with decreasing temperature. Between 190 and 240 K all the crystals

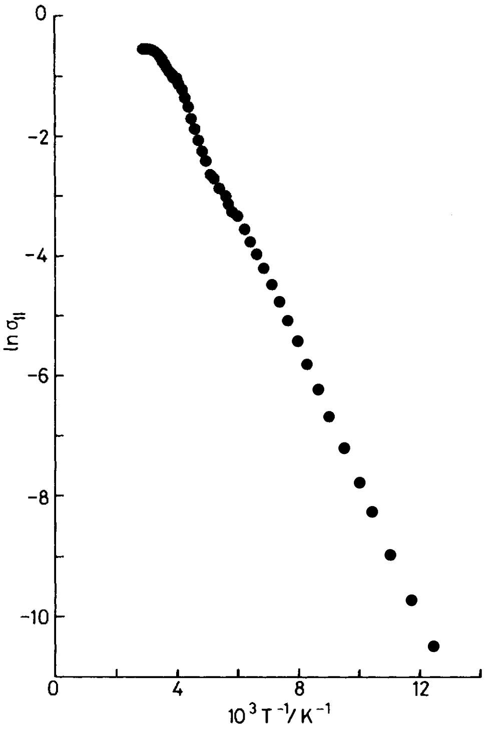

Figure 2. Variation of ln $\sigma_{\parallel}$ with inverse temperature for a crystal of $[NH_3Me]_{1.71}[Pt(C_2O_4)_2]\cdot H_2O$ (2)

show a pronounced anomaly in the temperature dependence of the conductivity. In this region the variation of conductivity with temperature is different from crystal to crystal. This may signify that some form of phase change is taking place. Between 145 and 60 K complex (1) behaves as a semiconductor with an average activation energy of 72 meV.

$[NH_3Me]_{1.71}[Pt(C_2O_4)_2]\cdot H_2O$ (2).—Complex (2) is the only compound in this series not to crystallise in an orthorhombic unit cell. There are again four platinum atoms per chain within the unit cell and the average $d_{\parallel}$ of 2.89 Å is the largest in the series.

X-Ray diffuse scattering studies at room temperature revealed diffuse lines corresponding to $2k_F = 1.71$. There was little indication of superstructure spots between the Bragg reflection-layer lines and the diffuse lines and no indication of superstructure spots on the diffuse lines.[11]

The room temperature values for $\sigma_{\parallel}$ for 12 crystals of (2) lie in the range 0.5—16 Ω^{-1} cm^{-1} with an average value of 5 Ω^{-1} cm^{-1}, only slightly less than that of complex (1) in spite of a large increase in average $d_{\parallel}$. The variation of $\sigma_{\parallel}$ with inverse temperature is shown in Figure 2 and it can be seen that the conductivity is at a maximum at around 310 K. Below 250 K the conductivity falls rapidly with decreasing temperature and over the temperature range 170—80 K it behaves as a semiconductor with an average activation energy of 92 meV.

$[NH_2Me_2]_{1.61}[Pt(C_2O_4)_2]$ (3).—This complex was the first anhydrous partially oxidised bis(oxalato)platinate to be prepared. From the unit-cell dimensions given in Table 1 it can be seen that (3) has an orthorhombic unit cell containing just two platinum atoms. The average intra-chain planar anion separation of 2.81 Å is one of the shortest values so far reported for a partially oxidised bis(oxalato)platinate. *X*-Ray diffuse scattering experiments at room temperature again revealed the presence of diffuse lines indicating the existence of the Peierls instability in this compound.[10] From the position of the diffuse lines, $2k_F$ is calculated to be 1.61. Most unusually for partially oxidised bis(oxalato)platinate compounds there are no weak spots observed in the photograph indicating the absence of a non-Peierls superstructure at room temperature.

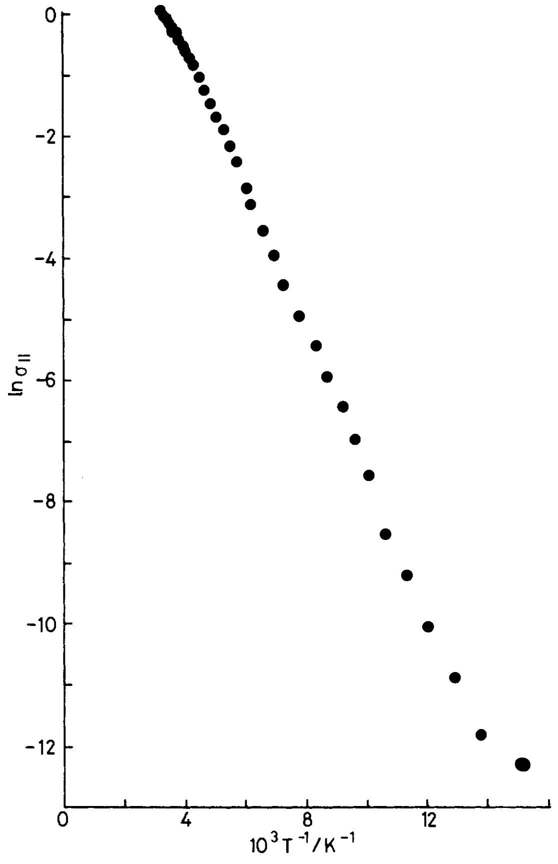

Figure 3. Variation of ln $\sigma_{\parallel}$ with inverse temperature for a crystal of $[NH_2Me_2]_{1.61}[Pt(C_2O_4)_2]$ (3)

The value of $\sigma_{\parallel}$ was determined for 10 crystals and was found to lie in the range 1—20 Ω^{-1} cm^{-1} with an average value of 2.5 Ω^{-1} cm^{-1}. The variation of $\sigma_{\parallel}$ with inverse temperature is shown in Figure 3 and it is apparent that there is a very smooth variation of conductivity with temperature. At low temperatures (3) behaves as a semiconductor with an average activation energy of 84 meV. Above 160 K there is a gradual decrease in the temperature dependence of the conductivity but no maximum is observed below 295 K. From the conductivity study there is no indication of the development of a non-Peierls superstructure above 70 K.

$[NHMe_3]_{1.59}[Pt(C_2O_4)_2]$ (5).—Complex (5) was obtained by aerial oxidation and forms purple-red needle-shaped crystals with a hexagonal cross-section. Preliminary *X*-ray studies indicate an orthorhombic unit cell with five platinum atoms in the chain along the *c* axis of the unit cell. The average $d_{\parallel}$ (2.80 Å) is the shortest so far reported for a bis(oxalato)platinate complex.

X-Ray diffuse scattering studies at room temperature show diffuse lines corresponding to $2k_F = 1.59$.[11] This indicates that, within experimental error, the Peierls distortion is commensurate and complex (5) therefore corresponds to a $\frac{4}{5}$ filled band system. Thus the Peierls distortion should have a wavelength corresponding to five Pt–Pt repeat distances thus ex-

Table 2. Electrical conduction studies

Compd.	$d_{\parallel}$/Å	$\sigma_{\parallel}/\Omega^{-1}$ cm^{-1} Range	$\sigma_{\parallel}/\Omega^{-1}$ cm^{-1} Average	ΔE/meV (average)
(1)	2.83	5—54	14	72
(2)	2.89	0.5—16	5	92
(3)	2.81	1—20	2.5	84
(5)	2.80	5×10^{-3}—7×10^{-2}	2×10^{-2}	85
(4)	2.81	4×10^{-2}—9	0.2	93

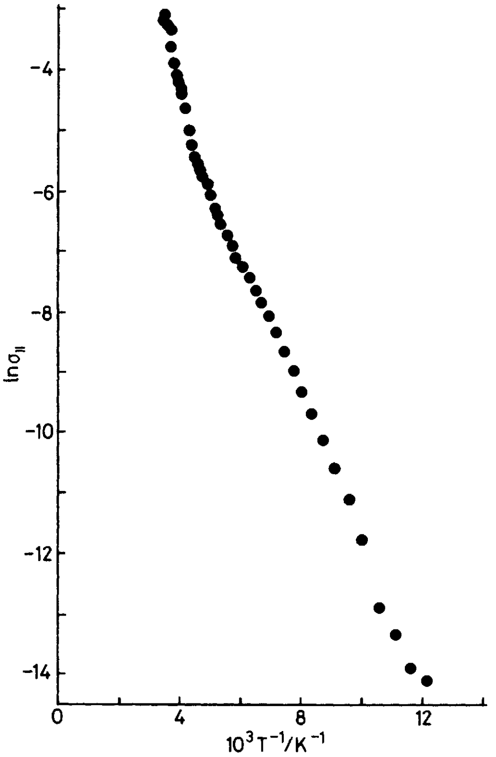

Figure 4. Variation of ln $\sigma_{\parallel}$ with inverse temperature for a crystal of $[NHMe_3]_{1.59}[Pt(C_2O_4)_2]$ (5)

plaining the unusual unit cell containing five platinum atoms. The *X*-ray photographs show the presence of spots on the diffuse lines but none between the diffuse lines and the Bragg reflection-layer lines. This is in agreement with a unit cell with a commensurate Peierls distortion. Complex (5) therefore appears to be analogous to $Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$ but with a five-fold repeat instead of the six-fold repeat platinum chain found for the rubidium salt.[12]

The room temperature $\sigma_{\parallel}$ has been determined for 6 crystals and lies in the range 7×10^{-2}—5×10^{-3} Ω^{-1} cm^{-1} with an average value of 2×10^{-2} Ω^{-1} cm^{-1}. This is the lowest value for any member of the series in spite of (5) having the shortest average $d_{\parallel}$. However, on $Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$ in which the average $d_{\parallel}$ is *ca.* 2.85 Å also exhibits $\sigma_{\parallel}$ of 7×10^{-3} presumably because one of the Pt–Pt intra-chain separations is 3.015 Å.[12] The very low conductivity observed for (5) may indicate that it too possesses very disparate intra-chain Pt–Pt separations.

The variation of $\sigma_{\parallel}$ with inverse temperature is shown in Figure 4. The conductivity of (5) falls steeply with decreasing temperature. Figure 4 shows that (5) behaves as a semiconductor with a change in activation energy from *ca.* 212 to 95 meV at around 250 K. The complex $Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$ has also been shown to behave as a semiconductor below room temperature.[12]

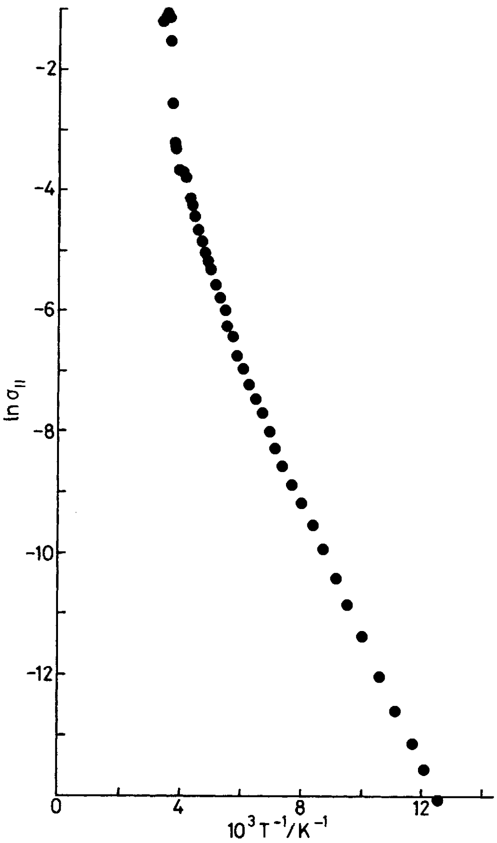

Figure 5. Variation of ln $\sigma_{\parallel}$ with inverse temperature for a crystal of $[NMe_4]_{1.65}[Pt(C_2O_4)_2]$ (4)

$[NMe_4]_{1.65}[Pt(C_2O_4)_2]$ (4).—The characterisation of (4) has presented problems and there are still discrepancies in the various results. Complex (4) is obtained by aerial oxidation of an acidic solution of $[NMe_4]_2[Pt(C_2O_4)_2]$. Some 14 preparations have been carried out and the products analysed. One of the main problems is that the chemical analysis of the products varies from preparation to preparation and it is impossible to reconcile the percentage composition with those expected for the compound based on the well established nature of the other compounds in the series. However the results of the x.d.s. and density measurements lead to a reasonable stoicheiometry for the product.

X-Ray diffuse scattering experiments indicate the presence of the Peierls instability with a value of $2k_F$ of 1.65 suggesting a formula of $[NMe_4]_{1.65}[Pt(C_2O_4)_2]$.[13] The molecular weight can also be deduced from the unit-cell dimensions determined from *X*-ray studies and density measurement. The molecular weight calculated in this way is 482, in reasonable agreement with that based on the formula proposed from the x.d.s. experiment ($M = 505$).

The unit cell of (4) contains 4 platinum atoms in the chain with an average $d_{\parallel}$ of 2.81 Å. The value of $\sigma_{\parallel}$ at room temperature was found to vary from 4×10^{-2} to 9 Ω^{-1} cm^{-1}. This is a greater variation than that observed for any other compound in the series again suggesting that there is a variation in the product from preparation to preparation. The variation of conductivity with inverse temperature is shown in Figure 5.

General Discussion.—The series of compounds described in this paper represents one in which there is a regular and progressive change in the cation. The change from $[NH_4]^+$ to $[NMe_4]^+$ is one of increasing size and a decreasing capacity for hydrogen bonding to water or oxalate ions. However, the observation of simple trends in the properties of the compounds in this series cannot be expected because the *X*-ray studies have shown that the compounds do not possess a common structure. Whereas complexes (1), (2), and (4) possess structures with four platinum atoms per chain, (3) contains two and (5) five platinum atoms per chain within the unit cell. Structures consisting of four $[Pt(C_2O_4)_2]$ anions stacked along one axis of the unit cell are quite common for partially oxidised bis(oxalato)platinate salts of monovalent cations. This arrangement is found in both $K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$ and $K_{1.81}[Pt(C_2O_4)_2]\cdot 2H_2O$ where detailed structural studies have revealed the presence of zigzag chains of platinum atoms.[14] In $K_{1.81}[Pt(C_2O_4)_2]\cdot 2H_2O$ two intra-chain Pt–Pt distances of 2.837 and 2.868 Å were observed.[14] It seems likely that more detailed structural studies of the present series of compounds will reveal the existence of similar non-linear chains of platinum atoms. In addition (1) and (2) are obtained with one molecule of water of crystallisation whereas complexes (3)—(5) are anhydrous. In the anion-deficient tetracyanoplatinates it was also observed that the salts of small cations were hydrated whereas the salts of large cations were anhydrous.[8] Thus a correlation between cation size and $d_{\parallel}$ for the whole series should not be expected. There is an increase in $d_{\parallel}$ with cation size for the hydrated compounds but for the anhydrous compounds, $d_{\parallel}$ is approximately constant and represents a very short intra-chain anion separation.

The range of degree of partial oxidation (d.p.o.) found in this series of compounds [0.41—0.29 for (5)—(2)] lies within the range reported previously for partially oxidised bis(oxalato)platinates.[4] Within this series of compounds, and unlike the partially oxidised anion-deficient tetracyanoplatinates, there is not a good correlation between the d.p.o. and $d_{\parallel}$. This is probably a consequence of the much larger unit cells and hence more complicated and diverse structures found for the present series of compounds. This does however make a general understanding of the series of compounds difficult.

It might be expected, and has been observed for the anion-deficient partially oxidised tetracyanoplatinates, that there will be a correlation between the average $d_{\parallel}$ and the room-temperature electrical conductivity.[5,15] No such correlation is evident in the series of compounds under discussion. Again this is presumably because of the possible presence of zigzag chains of platinum atoms and unequal intra-chain Pt–Pt distances both of which will adversely affect the electrical conduction properties of the chain. The presence of a non-Peierls superstructure has also been detected at room temperature in some of these compounds and this too may depress the conductivity.

All the compounds exhibit semiconductor behaviour at low temperatures with activation energies, ΔE, in the range 70—100 meV. These are similar to those observed for $Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$ (77 meV) and $K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$ (100 meV).[12,16] However, the temperature dependence of the conductivity between the semiconducting region and room temperature varies from compound to compound. These differences are probably due to differences in the structural changes taking place in the individual compounds over the temperature range. A detailed understanding of this behaviour must await variable-temperature structural studies.

The contrast in the properties of (3) and (5) is most interesting. For both compounds x.d.s. studies indicate that $2k_F = 1.60\ \pi/d_{\parallel}$, within experimental error, and therefore that both should possess a $\frac{4}{5}$ filled band leading to a commensurate Peierls distortion with a repeat unit containing five platinum atoms. This is observed for (5) and the value of $\sigma_{\parallel}$ at room temperature is correspondingly low. Complex (3) however, has a relatively simple unit cell with only a two-platinum-atom chain repeat unit. The smooth temperature dependence of the conductivity of this compound is reminiscent of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ and quite different from that of most of the other partially oxidised bis(oxalato)platinates studied so far.[4,5] The differences observed between (5) and (3) could be due to random occupation and/or orientation of the $[NH_2Me_2]^+$ ions in the cation sites of the lattice of (3) as opposed to an ordered arrangement of $[NHMe_3]^+$ ions in (5). However, a further discussion must await the results of more detailed structural studies which are in progress.

In the series of anion-deficient tetracyanoplatinates the substitution of ammonium cations for potassium produced a large change in ΔE.[5] However, the results discussed above show that the substitution of ammonium or methyl-substituted ammonium ions in the bis(oxalato)platinate series of salts produces only a relatively small change in ΔE. There is however some indication of the expected effect on the dimensionality of these compounds when T_{3D} (as determined from the steepest slope in Figures 1—5) is compared with ΔE since the ratio $T_{3D}/\Delta E$ varies within a factor of 2. This indicates a significant change in the inter-chain parameter η.

Acknowledgements

We wish to acknowledge the support of the S.E.R.C. and N.A.T.O. (to A. E. U. and K. C.) and Johnson Matthey for the loan of platinum salts.

References

1 A. Braude, A. Lindegaard-Andersen, K. Carneiro, and A. E. Underhill, *Synth. Metals*, 1979/80, **1**, 35.

2 D. M. Watkins, A. E. Underhill, and C. S. Jacobsen, *J. Phys. Chem. Solids*, 1982, **43**, 183.

3 M. Mizuno, A. E. Underhill, and K. Carneiro, *J. Phys. C*, 1983, **16**, 2105.

4 A. E. Underhill, D. M. Watkins, J. M. Williams, and K. Carneiro, in ' Extended Linear Chain Compounds,' ed. J. Miller, Plenum Press, New York, 1982, vol. 1, p. 119 and refs. therein.

5 A. E. Underhill, D. J. Wood, and K. Carneiro, *Synth. Metals*, 1979/80, **1**, 395; K. Carneiro, A. Steen Petersen, A. E. Underhill, D. J. Wood, D. M. Watkins, and G. A. Mackenzie, *Phys. Rev. B*, 1979, **19**, 6279.

6 A. E. Underhill, M. Mizuno, and D. M. Watkins, *Mol. Cryst. Liq. Cryst.*, 1982, **81**, 217.

7 L. Groth Andersen and I. Johannsen, personal communication.

8 J. M. Williams and A. J. Schultz, in ' Molecular Metals,' ed. W. E. Hatfield, Plenum Press, New York, 1979, vol. 6, p. 343.

9 R. J. Collins, A. H. Reis, jun., E. Sherry, and S. W. Peterson, personal communication, ref. 31 in ref. 4.

10 G. S. V. Coles, A. Lindegaard-Andersen, J. M. Williams, A. J. Schultz, R. K. Brown, R. E. Besinger, J. R. Ferraro, A. E. Underhill, and D. M. Watkins, *Phys. Scr.*, 1982, **25**, 873.

11 K. Mortensen, A. Lindegaard-Andersen, and K. Carneiro, unpublished work.

12 A. Kobayashi, Y. Sasaki, and H. Kobayashi, *Chem. Lett.*, 1978, 1167; *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3682.

13 G. S. V. Coles, A. Lindegaard-Andersen, K. Carneiro, and A. E. Underhill, unpublished work.

14 H. Kobayashi, I. Shirotani, A. Kobayashi, and Y. Sasaki, *Solid State Commun.*, 1977, **23**, 409.

15 J. M. Williams, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 651.

16 F. N. Lecrone, M. J. Minot, and J. N. Perlstein, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 173.

Received 29*th November* 1982; *Paper* 2/2001