One-Dimensional Metals Based on Platinum Complexes

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One-dimensional metals based on platinum complexes

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The solid state properties of one-dimensional metals of the type $M_x[Pt(C_2O_4)_2]\cdot 6H_2O$ (where $0.8 < x < 0.84$ and M = Mg, Fe, Co, Ni, Cu, Zn) are reviewed and compared with those of $K_2[Pt(CN)_4]Br_{0.30}\cdot 3H_2O$. The structures and properties of bis(dithiolene)platinates of Group One cations are compared and related to the charge on the anion.

The Krogmann salt $K_2[Pt(CN)_4]Br_{0.30}\cdot 3H_2O$ (KCP(Br)) was the first platinum complex to be shown to possess the properties of a one-dimensional metal (Zeller 1974). Since that initial work in the early 1970s a variety of one-dimensional metals based on platinum complexes have been synthesized and studied in detail. From these studies two basic requirements for the formation of a one-dimensional metal have emerged.

(*a*) The compounds must possess a columnar stack structure based on square coplanar complexes which will allow the overlap of suitable orbitals in the intra-stack direction to form a conduction pathway. The ligands and other anions, cations or water molecules in the lattice will separate the columnar stacks from one another and thus aid the development of one-dimensional properties. However, recent studies have shown the importance of inter-stack interactions on the properties of many compounds of this type.

(*b*) For metallic properties there must be a non-integral number of electrons per platinum atom in the conduction band. In practice, this is generally achieved by 'partial oxidation' of the complex either by the incorporation of a non-stoichiometric number of anions into the structure (anion deficient or a.d. salts, for example KCP(Br)) or by a non-stoichiometric number of cations (cation deficient or c.d. salts, for example, $K_{1.75}[Pt(CN)_4]1.5H_2O$).

Apart from distinguishing between c.d. and a.d. salts it is also important to distinguish between compounds in which the metallic properties arise from the overlap of orbitals that are essentially metal centred and those whose metallic properties arise from the overlap of molecular orbitals involving both metal and ligand orbitals. For the latter, the metal may play only a minor role and the conduction pathway be predominantly through the overlap of the ligand centred orbitals. The partly oxidized tetracyanoplatinates and bis(oxalato)platinates belong to the first category of compound, while the metal porphyrins and phthalocyanines belong to the latter. Recently, a one-dimensional metal containing bis(dithiolene)platinate anions has been shown to belong to the latter group of compounds.

The platinum complexes exhibit metallic properties at room temperature with electrical conductivities in the platinum atom chain direction of up to 2×10^3 S cm^{-1} and with a negative temperature dependence. However, at lower temperature a metal to semiconductor transition occurs as a consequence of the Peierls instability. This transition is associated with the development of correlations between the adjacent distorted platinum atom chains. KCP(Br) is a very anisotropic one-dimensional metallic complex, as shown by the anisotropy of conductivity ($\sigma_{\parallel}/\sigma_{\perp}$) of about 10^5 at room temperature. Because of the very one-dimensional nature of this compound the metal to semiconductor transition is smeared out over a range of 200 K.

PARTLY OXIDIZED BIS(OXALATO)PLATINATES OF DIVALENT CATIONS

A series of compounds of general formulae $M_x[Pt(C_2O_4)_2]\cdot 6H_2O$ (where $0.8 < x < 0.84$ and M = Mg, Fe, Co, Ni, Cu, Zn) has been prepared and studied in single crystal form (A. Braude, K. Carnéiro, C. S. Jacobsen, K. Mortensen, D. J. Turner and A. E. Underhill, unpublished work (1984)). All the salts apart from the Cu^{II} compound exhibit the same structure over a characteristic temperature range. This structure (space group Cccm) was first reported for the Mg^{II} compound (Krogmann 1968) and consists of a columnar stack of $[Pt(C_2O_4)_2]^{n-}$ anions with an intra-stack separation of about 2.84 Å†. The divalent metal ions are located in planes in between the anions and are surrounded by an octahedral arrangement of water molecules. The water molecules form a hydrogen-bonded network involving the oxalate ligands on the adjacent anion columns. Only about 40% of the cation sites are occupied.

Optical reflectivity measurements of many of these salts has revealed a plasma edge for light polarized parallel to the metal atom chain direction and the absence of a plasma edge orthogonal to this direction. The bandwidth deduced from these measurements is about 3.9 eV, slightly smaller than that observed for KCP(Br), although the intra-chain Pt–Pt separation is less. Although the inter- and intra-stack separations in these compounds are comparable to KCP(Br), the electrical conduction properties at room temperature show the compounds to be considerably less anisotropic ($\sigma_{\parallel}/\sigma_{\perp} \approx 3\times 10^2$) than KCP(Br). This is probably in part a reflection of the greater amount of inter-stack hydrogen bonding present in these compounds.

Recent unpublished work by Braude *et al.* (1984) has revealed that these salts can be divided into two categories dependent upon the nature of a phase transition near room temperature. The Co^{II}, Ni^{II} and Zn^{II} salts all undergo a Cccm → Pccn transition. This corresponds to a small slippage of the anion stack at the centre of the unit cell relative to the plane formed by the anions at the corners of the unit. Cell. For the Ni^{II} salt the movement is about 0.1 Å. In the Mg^{II} and Fe^{II} compounds the change of space group is from orthorhombic Cccm to twinned monoclinic with an angle of about 1°. Although the distortions involved in these phase transitions are small the compounds belonging to the two classes exhibit quite different temperature-dependent conduction properties.

The three salts that undergo the Cccm → Pccm transition all exhibit a similar type of temperature-dependent conductivity. At some temperature above 300 K they exhibit a metallic-type temperature dependence. Below this temperature, however, the conductivity decreases rapidly with decreasing temperature and below about 250 K they exhibit semiconductor-type temperature dependence. Figure 1 compares the temperature dependence of the conductivity of Co–OP with that of KCP(Br). It can be seen that the metal to semiconductor transition in Co–OP occurs over a much smaller temperature range than in KCP(Br), partly as a result of the decreased anisotropy of this compound.

These bis(oxalato)platinate salts also differ from KCP(Br) in the nature of the three-dimensional ordering that accompanies the metal to semiconductor transitions. In KCP(Br)

† $1\ \text{Å} = 10^{-10}\ \text{m} = 0.1\ \text{nm}$.

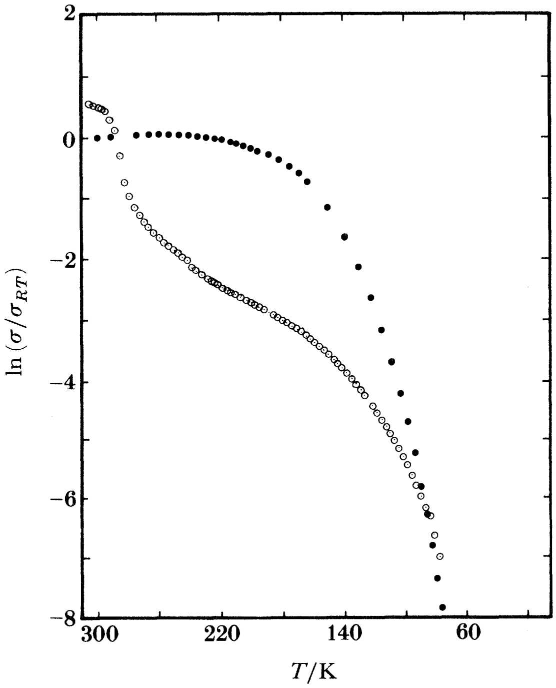

FIGURE 1. Comparison of the variation of electrical conductivity with temperature for (⊙) $Co_{0.82}[Pt(C_2O_4)_2]\cdot 6H_2O$ and $K_2[Pt(CN)_4]\cdot Br_{0.30}\cdot 3H_2O$ (●).

extensive studies showed that the only limited three-dimensional ordering accompanied the metal to semiconductor transition and that inter-chain correlations extended over only about five platinum atom chains. The bis(oxalato) platinate salts are characterized by the appearance of sharp satellite reflections indicative of a highly correlated superstructure. The appearance of these satellite reflections above 300 K corresponds to the onset of the transition as revealed by the conductivity studies. As the temperature is decreased, the intensity of the satellite spots increases. At the temperature of the Cccm → Pccn phase transition the pattern of satellite reflection changes and they continue to increase in intensity until saturation is observed at approximately 250 K. Figure 2 shows the increase of intensity of the satellite reflections for the cobalt salt, Co–OP (Braude 1979) and the variation of electrical conductivity over this temperature range. A small positive temperature-independent thermopower characteristic of a metal is observed for Co–OP above 300 K and this changes to a temperature-dependent thermopower below 300 K (Watkins 1982). The completion of the superstructure formation at 250 K corresponds to a change in the slope of the thermopower with temperature. There is no evidence for the Cccm → Pccn transition in the electrical conduction or thermopower measurements.

Of the compounds that exhibit the Cccm → twinned monoclinic transitions only the magnesium salt (Mg–OP) has been studied in detail (Mizuno 1983). The phase transition is again accompanied by the formation of a superstructure, as shown by the appearance of satellite reflections. However, in this case, the superstructure is not commensurate with the Peierls distortion in the platinum atom chain direction. The change in electrical conductivity with temperature in the region of the transition is much less marked than those observed for the first series of compounds. Both hysteresis and a time dependence of the conductivity at a fixed

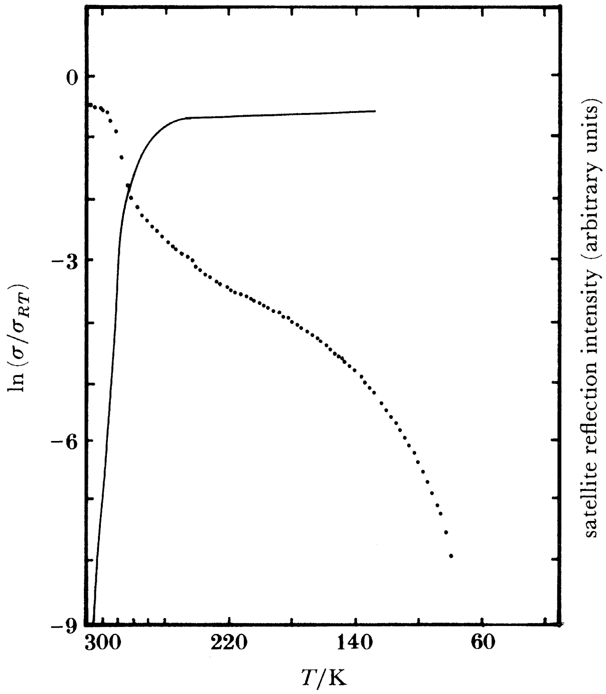

FIGURE 2. Comparison of the variation of (•) electrical conductivity and of (——) the intensity of the satellite reflection with temperature for $Co_{0.82}[Pt(C_2O_4)_2]\cdot 6H_2O$.

temperature have been observed close to the transition, behaviour not observed for the first series of compounds. The existence of chaotic behaviour during this transition due to competition between the different incommensurate instabilities has been proposed (Carneiro 1983) to account for these observations. Recently, detailed studies in this neighbourhood of the transition have revealed evidence of possible metastable states, thus supporting these suggestions.

BIS(DITHIOLENE)PLATINATES OF GROUP 1 CATIONS

The planar bis(dithiolene) metal anions have great potential for the synthesis of highly conducting compounds. In particular, the ability to change the substituent on the ligand confers a flexibility not possible for the Krogmann salts. Up to the present, however, only a limited number of compounds has been obtained as single crystals and this has restricted the development of these compounds.

Aerial oxidation of an acetone/water solution of $H_2[Pt(S_2C_2(CN)_2)_2]$ in the presence of LiCl gives rise to a mixture of black shiny needle-shaped and black plate-shaped crystals over a period of several weeks (Ahmad 1982). The needle-shaped crystals were initially reported to have the composition $Li_{0.8}[Pt(S_2C_2(CN)_2)_2]2H_2O$, suggesting a slightly less than half-filled band. However, a positive value for the thermopower at room temperature was most readily explained by the presence of a more than half-filled band. Recent potentiometric titrations have revealed the presence of 0.33 protons per platinum atom in the needle-shaped crystals, presumably associated with water molecules in the formation of hydroxonium ions. The average charge of the anion has also been determined by iodine titration and this indicates an average charge of about 1.15 on the anions. X-ray studies (Kobayashi *et al.* 1984*a*) are equally consistent with a 0.41 or 0.59 band-filling and therefore the compound is now considered to have the composition $Li_{0.8}(H_3O)_{0.33}[Pt(S_2C_2(CN)_2)_2]$ $1.67H_2O$(Li–Pt(mnt)).

The crystal structure at room temperature contains the anions stacked face to face along the *c*-axis of the crystal with an intra-chain Pt–Pt separation of 3.639 Å (Kobayashi 1982). This distance is very much greater than those found in the Krogmann salts (2.8–2.9 Å) and indicates that in this compound the metallic properties arise from overlap of molecular orbitals of the anion, rather than overlap of the platinum d_z^2 orbitals. The columns of anions in the lattice form sheets along *b* and these are separated from one another along *a* by Li^+ cations and water molecules. Within the sheets there are short S–S contacts between anions in adjacent columns. In this respect, the structures resemble those of the recently studied organic metals and superconductors such as $(TMTSF)_2X$ and $(BEDT\text{-}TTF)_2ReO_4$.

Li-Pt(mnt) exhibits a conductivity of about 200 S cm^{-1} along the needle axis of the crystal. Studies (Ahmad 1982) have shown that along the direction of the anion stack the conductivity rises to a maximum at about 250 K and then decreases with decreasing temperature and at low temperature exhibits semiconductor properties with an activation energy of 36 meV. The metal to semiconductor transition is around 200 K.

Studies (Ahmad 1984*a*) of the thermopower confirmed the conductivity studies and showed a small positive (+10 μV K^{-1}) temperature-independent thermopower above a transition temperature of around 215 K. Below the transition temperature, S increased to 35 μV K^{-1} at 155 K before going to negative values at low temperatures. Optical reflectivity measurements have revealed the presence of a Drude-type plasma edge indicative of a metal with $\omega_p = 7000\ cm^{-1}$ and assuming a one-dimensional tight-binding approximation this indicates a bandwidth of about 0.4 eV.

X-ray studies at low temperatures (Kobayashi *et al.* 1984*a*) revealed the existence of strong satellite spots on oscillation photographs around the *c*-axis. The intensity of these satellite reflections decreases above about 110 K and at higher temperatures disappears rapidly towards a transition temperature of 220 K. This transition temperature is in good agreement with those observed by thermopower and magnetic susceptibility measurements.

The room-temperature structure and the average structure of the 153 K superstructure are almost the same. The interplanar distances between the $[Pt(S_2C_2(CN)_2)_2]^{n-}$ anions are 3.592 and 3.537 Å and the Pt–Pt distances are 3.639 and 3.597 Å at room temperature and 153 K respectively. However, the S–S inter-stack contacts between adjacent columns in the *b* direction are considerably shortened at low temperatures. This increasing two dimensionally at low temperature is also observed in many of the $(TMTSF)_2X$ and $(BEDT\text{-}TTF)_2X$ compounds, and the development of a strong transverse network of S or Se interactions could be an important mechanism for suppressing the metal to semiconductor transition.

The pressure dependence of the conductivity has been examined (K. Carneiro, J. Vasquez, R. L. Greene, J. C. Scott, A. E. Underhill and P. J. Clemenson, unpublished results (1984)) up to pressures of 1 GPa. At room temperature, pressure was found to have little effect on the conductivity, but at lower temperature the conductivity does become pressure dependent. In particular, the activation energy in the low-temperature semiconductor region decreased with increasing pressure from 36 meV at atmospheric pressure down to 10 meV at 1 GPa pressure. These results suggest that at higher pressures the transition might be suppressed and metallic properties retained down to very low temperatures.

As discussed earlier, the preparation of LiPt(mnt) is accompanied by the formation of a second product in the form of black platelets. Structural studies have shown (Kobayashi 1984*b*) that this compound $Li_{0.5}[Pt(S_2C_2(CN)_2)_2]\cdot 2H_2O$ (β-LiPt(mnt)) has $[Pt(S_2C_2(CN)_2)_2]^{0.5-}$ anions stacked in a face to face configuration. Unlike LiPt(mnt), where all the anion to anion intra-stack distances are the same, in β-LiPt(mnt) the unit cell contains a fourfold platinum chain with three independent platinum distances, 3.346, 3.987 and 4.298 Å. In this compound the half negative charge on each anion will result in a quarter-filled band and the fourfold structure corresponds to the $2k_F$ Peierls structure.

Short S–S distances between anions in adjacent stacks (3.540–3.589 Å) similar to those observed in LiPt(mnt) are also found in this compound resulting in a two-dimensional sheet structure separated by the cations and water molecules. The conductivity at room temperature in the stack direction is 1 S cm^{-1}, but the conductivity is activated all the way up to room temperature as expected from the Peierls structure.

Studies (Ahmad 1984*b*) have also been made on $Rb[Pt(S_2C_2(CN)_2)_2]\cdot 2H_2O$(Rb–Pt(mnt)). This compound is also obtained as black needle-shaped crystals, but the conductivity along the needle axis is only 2.5×10^{-5} S cm^{-1}. The structure again consists of a columnar stack of anions with close inter-stack S–S contacts forming two-dimensional sheets separated by the cation and water molecules. The arrangment of mono-anions will result in a half-filled band and the structure exhibits the expected dimerization in the stack direction with two intra-stack spacings of 3.356 and 3.512 Å.

The results of these studies show that it is possible by the use of hydrated alkali metal cations to stabilize eclipsed columnar stacks of bis(dithiolene)platinate anions with strong inter-stack interactions. The structures and electrical conduction properties of these compounds are very dependent upon the extent of band filling. In certain respects, they resemble some of the recently discussed organic metals.

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