$Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$: A New Type of Partially Oxidised Tetracyanoplatinate Salt †

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The preparation and properties of a new type of partially oxidised tetracyanoplatinate salt, $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$, are reported. The electrical conduction properties are compared with those of previously known one-dimensional metallic complexes of platinum.

One-dimensional metal-atom chain compounds based on partially oxidised tetracyanoplatinate (potcp) salts have been extensively studied in recent years since their rediscovery by Krogmann in the 1960s.[1] Until recently the compounds have been confined to the salts of univalent metal cations, although studies of the partially oxidised bis(oxalato)platinates have shown that bivalent metal cation salts can exhibit quite different solid-state properties compared with those of univalent metal cations.[2]

A lead(II) tetracyanoplatinate complex having a metallic appearance was reported in 1861, suggesting the existence of a potcp salt of lead.[3] The preparative method described in the literature involved the treatment of an equimolar mixture of an aqueous solution containing $Pb(NO_3)_2$ [or $Pb(CH_3COO)_2$] and $K_2[Pt(CN)_4]\cdot 3H_2O$ with nitric acid. We have repeated the method and obtained a mass of small copper coloured crystals indicative of a potcp salt. Chemical analysis of the crystals showed them to be a potcp salt containing both potassium and lead cations and having the formula $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$. Fifteen repeat preparations always yielded the same product. The molar concentration ratio in the reaction solution was also varied from 3 : 1 to 1 : 3 but the composition of the product remained unaltered. The fixed composition irrespective of the mole ratio of Pb : K in the crystallising solution indicates that the degree of partial oxidation (d.p.o.) is also fixed for this compound. This result is similar to that involving the preparation of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, in which crystals of the same composition are always obtained regardless of the Pt^{II} : Pt^{IV} ratios initially used in the crystallising solutions.[4]

The d.p.o. of the Pt atom in the salt can be calculated either from the chemical formula or by determining the ratio of Pt^{IV} to total Pt in a solution of the salt. Both of these methods yield an oxidation state for Pt of 2.23 corresponding to a d.p.o. of 0.23.

The crystallographic lattice parameters of $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$ were determined using a Syntex $P2_1$ diffractometer: orthorhombic, $a = 15.790(7)$, $b = 9.568(5)$, $c = 5.799(4)$ Å, space group *Pmmn* or *Pmn*2. These crystallographic parameters indicate that the crystal structure is different from that of any previously observed potcp compound.[1] From the stoicheiometry it is apparent that the ratio of the sum of the potassium and lead cation to platinum is 1 : 1. Thus is appears likely that these cations randomly occupy identical crystallographic sites and this has prevented a detailed analysis of the crystal structure. However, the intrachain platinum–platinum distance, *d*(Pt–Pt) is 2.90 Å, *i.e.* $c/2$ which is within the range previously found for one-dimensional potcp complexes.[1]

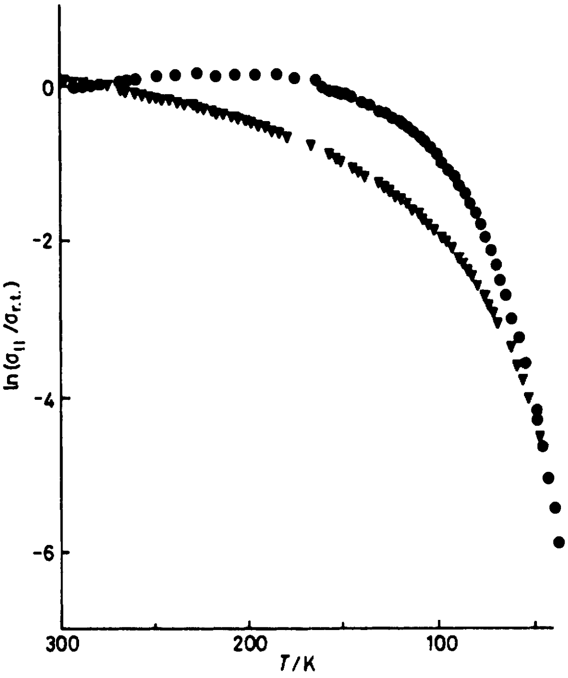

Figure 1. Variation of $\ln(\sigma_{\parallel}/\sigma_{r.t.})$ (r.t. = room temperature) with temperature for a single crystal (●) and compressed disc (▼) of $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$

Unfortunately, the crystals of $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$ are very small and this has prevented a detailed study of their electrical conduction properties. The two single crystals that have been examined at room temperature exhibited a four-probe d.c. conductivity in the platinum-atom chain direction, $\sigma_{\parallel}$, of 10 Ω^{-1} cm^{-1}. This may be compared with a value of 0.4 Ω^{-1} cm^{-1} observed previously for $[NH_4]_2[H_3O]_{0.14}[Pt(CN)_4]Cl_{0.42}\cdot 3H_2O$ which has a slightly larger average *d*(Pt–Pt) (2.92 Å).[5] The conductivity of a compressed disc of the present compound was found to be *ca.* 0.2 Ω^{-1} cm^{-1}. Figure 1 shows the variation of $\ln\sigma_{\parallel}$ with temperature for a single crystal: the conductivity slowly rises with decreasing temperature, passes through a maximum at 215 K, and falls rapidly below 150 K indicating a metal to semiconductor transition. Figure 2 shows

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

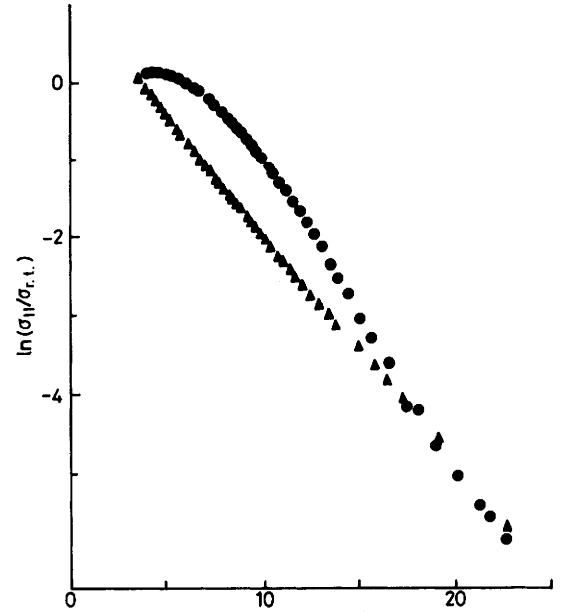

Figure 2. Variation of $\ln(\sigma_{\parallel}/\sigma_{r.t.})$ with inverse temperature for a single crystal (●) and compressed disc (▼) of $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$

the variation of $\ln\sigma_{\parallel}$ with inverse temperature. The temperature dependence of the conductivity of $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$ is similar to that found previously for the anion-deficient tetracyanoplatinates {*e.g.* $K_2[Pt(CN)_4]Cl_{0.3}\cdot H_2O$} except that the activation energy (ΔE) in the semiconductor region (0.23 meV) is much less than that found for potcp compounds of similar d(Pt−Pt).[6] Recent studies have shown that ΔE for $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$, which is isostructural with $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, is also very low due to the influence of the bivalent Pb^{2+} ions on the stiffness of the lattice.[7]

Previously studied potcp compounds were either of the anion-deficient, *e.g.* $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, or cation-deficient type, *e.g.* $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$. The compound $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$ is a new type of potcp since partial oxidation arises solely from the presence of a non-stoicheiometric amount of uni- *and* bi-valent cations. It appears that its solid-state properties resemble those of the anion-deficient potcp compounds but additional examples must be studied before the relationship between structure and properties of this new type of compound can be fully understood.

Experimental

Preparation of $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$.—The compound $K_2[Pt(CN)_4]\cdot 1.3H_2O$ (1 g) was mixed with $Pb(NO_3)_2$ (0.875 g) and dissolved in distilled water (20 cm³) giving a cloudy solution. Then concentrated HNO_3 (0.5 cm³) was added and the resulting clear solution heated to boiling. The solution was cooled, filtered using a 0.22-μm Millipore filter, placed in a siliconised crystallising dish, and allowed to evaporate slowly at room temperature. After a few days copper coloured crystals appeared, and were filtered off, washed with ice-cold water, and air dried {Found: C, 9.85; H, 0.60; K, 1.85; N, 11.6; Pb, 32.7; Pt, 39.0. Calc. for $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$: C, 9.70; H, 0.60; K, 1.80; N, 11.35; Pb, 32.25; Pt, 39.4%}.

Acknowledgements

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