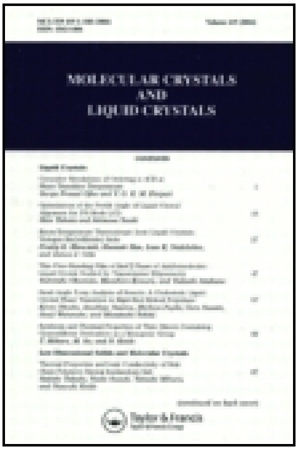

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

$Pb_{0.27}K_{1.73}$ $[Pt(CN)_4]$ $Cl_{0.5}$[mddot]$3H_2O$ - A New Partially Oxidised Tetracyanoplatinate Containing Both Divalent and Monovalent Cations

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Version of record first published: 14 Oct 2011.

To cite this article: A. E. Underhill & G. S. V. Coles (1982): $Pb_{0.27}K_{1.73}$ $[Pt(CN)_4]$ $Cl_{0.5}$[mddot]$3H_2O$ - A New Partially Oxidised Tetracyanoplatinate Containing Both Divalent and Monovalent Cations, Molecular Crystals and Liquid Crystals, 81:1, 183-188

To link to this article: http://dx.doi.org/10.1080/00268948208072564

Mol. Cryst. Liq. Cryst., 1982, Vol. 81, pp. 183–188
0026-8941/82/8101-0183$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

$Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ - A NEW PARTIALLY OXIDISED TETRACYANOPLATINATE CONTAINING BOTH DIVALENT AND MONOVALENT CATIONS *

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Received for publication September 1, 1981

Electrolysis of an aqueous solution of potassium tetracyanoplatinate(II) and lead(II) acetate containing a small quantity of chloride ions yields copper coloured crystals of $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ in low yield. The Pb : K mole-ratio appears to be fixed irrespective of the mole-ratio of the Pb : K in the electrolyte. X-ray studies indicate that the compound has similar unit cell dimensions to $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$. Electrical conduction studies show that the compound is a 1-D metal at room temperature with a specific conductivity in the platinum atom chain direction of $\sim 70\ \Omega^{-1}\ cm^{-1}$.

Partially oxidised tetracyanoplatinate (POTCP) complexes have been the subject of a great deal of intensive research in recent years.[1,2] These compounds fall into two main classes, the cation deficient compounds (e.g. $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$) and the anion deficient compounds (e.g. $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$). Unlike the partially oxidised bis(oxalato)platinate complexes recent studies on the POTCP complexes have been restricted to salts of monovalent cations and until the present work, attempts to pre-

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*We would like to thank the SRC for support and Johnson Matthey & Co Ltd for the loan of platinum salts. One of us (AEU) wishes to acknowledge the support of NATO Grant no 016.81).

pare POTCP salts of divalent cations have not been successful. However, tetracyanoplatinate salts of magnesium and of lead, whose properties suggested that they could be POTCP salts, were reported in the middle of the last century.[3] The magnesium compound has subsequently been shown to be a platinum(II) complex.[4] We now report a study of the preparation and properties of a POTCP containing Pb(II) cations.

All attempts to produce a partially oxidised product by the action of oxidising agents on $Pb[Pt(CN)_4]\cdot H_2O$ were unsuccessful. The original method[3] in which equimolar quantities of lead(II) acetate or nitrate and $K_2[Pt(CN)_4]\cdot 3H_2O$ were treated with nitric acid was repeated. This gave very small copper-coloured crystals which contained both potassium and lead. Electrochemical oxidation (0.8 V, 72 hr) of an equimolar solution of lead(II) acetate and $K_2[Pt(CN)_4]_2\cdot 3H_2O$ in 10% aqueous nitric acid produced small quantities of good quality single crystals of a partially oxidised material which also contained potassium and lead but in different proportions to that obtained by chemical oxidation. This product obtained by electrochemical oxidation is discussed below.

RESULTS AND DISCUSSION

Elemental analysis established the empirical formula of the product as $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (K/Pb-CP). Preparations were carried out varying the concentration of lead to potassium in the electrolyte from a mole-ratio of 2:1 to 1:2 but in each case the percentages of lead and potassium in the product were unchanged within experimental error. The presence of chloride ions in the product was unexpected and presumably arises from contamination of the $K_2[Pt(CN)_4]\cdot 3H_2O$ with KCl. The very low concentration of chloride ions in the electrolyte accounts for the very poor yield of material.

The degree of partial oxidation of K/Pb-CP has been determined by three independent methods

(a) from the ratio of cations to platinum obtained by elemental analysis;

(b) from the ratio of Pt(IV) to Pt(II) in a solution of K/Pb-CP as determined from idiometric titration;

(c) from the value of k_F as determined in diffuse x-ray scattering experiments.[5]

The relationship between DPO and k_F is

$$DPO = 2(1 - k_F\, d_{Pt-Pt}/\pi)$$

where $2k_F$ is the wave vector of the Peierls distortion and d_{Pt-Pt} is the intra-chain platinum atom separation.

All these three independent methods indicate an oxidation state of 2.23 for the platinum.

X-ray Studies

The unit cell dimensions for K/Pb-CP have been determined and are given in the Table together with those for $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (KCP(Cl))[6] for comparison. The striking similarity in the two sets of data suggests that the two compounds are isostructural. The crystal structure of KCP(Cl) has been determined from x-ray studies and consists of chains of $[Pt(CN)_4]^{x-}$ groups.[6] The chloride ion sites at the centre of the unit cell have an occupancy of only 60% in KCP(Cl). If K/Pb-CP is isostructural with KCP(Cl) then the unusual stoichiometry and the DPO can readily be understood. In K/Pb-CP presumably all the halide sites at the centre of the unit cell are occupied and Pb(II) ions occupy 13% of the K^+ sites. The similar sizes of Pb^{2+} (1.17Å) and K^+ (1.33Å) is presumably a very important factor in the formation of this mixed cation compound.

Diffuse x-ray scattering experiments at room temperature reveal the existence of diffuse lines around the strong Bragg reflection layer lines of non-zero order. This is indicative of a Peierls instability in this compound and the

TABLE Unit Cell Dimensions (Å)

	K/Pb-CP	KCP(Cl)[6]
c	5.78	5.748
a = b	9.88	9.883
d_{Pt-Pt}	2.90	2.874

diffuse lines correspond to a Fermi wave vector of 1.77.[7] Diffuse streaks were also observed about the strong Bragg reflection layer lines, including the zero level line, corresponding to a weak tetramerisation of the unit cell. This may be due to ordering of the lead cations within the crystal lattice.[7]

Electrical Conductivity Studies

Seven crystals of K/Pb-CP have been studied by a 4-probe dc technique. The room temperature conductivity in the platinum atom chain direction, $\sigma_{\parallel}$, was found to lie in the range 10 - 220 Ω^{-1} cm^{-1} with an average value of 67 Ω^{-1} cm^{-1}. This is similar to the values observed for KCP(Cl) which has a similar intra-chain platinum atom separation.[8]

The variation of $\sigma_{\parallel}$ with decreasing temperature is shown in Figure 1. It can be seen that the conductivity is almost temperature independent with decreasing temperature down to about 200 K. Below 150 K the conductivity falls

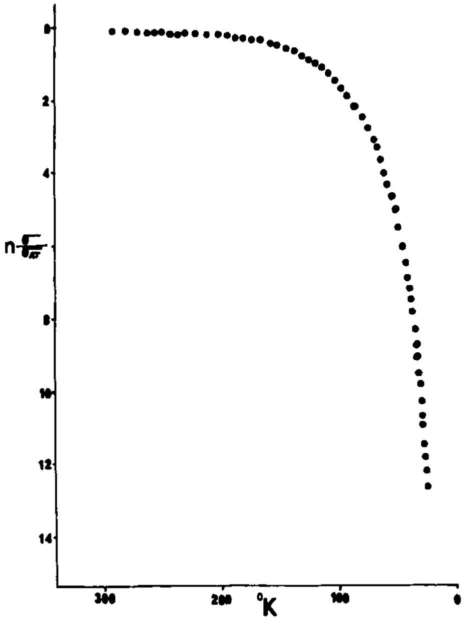

FIGURE 1 Variation of $\mathrm{Ln}(\sigma_{\parallel}/\sigma_{\parallel}(\mathrm{RT}))$ with temperature over the temperature range 300 to 50 K.

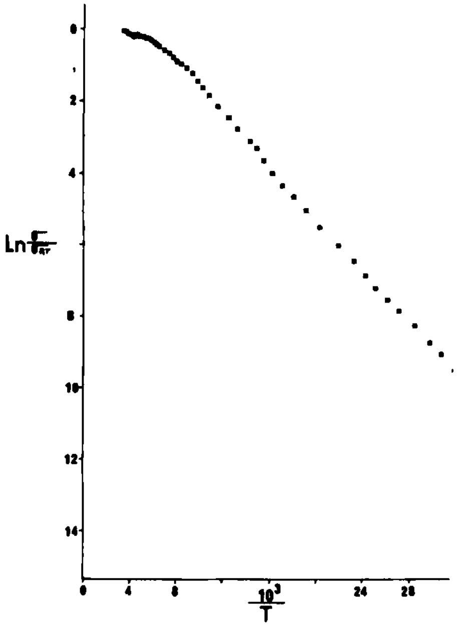

FIGURE 2 Variation of $\mathrm{Ln}(\sigma_{\parallel}/\sigma_{\parallel}(RT))$ with inverse temperature.

rapidly with decreasing temperature. Figure 2 shows the variation of conductivity with inverse temperature. The general shape of the curve is similar to that observed for $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ and related compounds.[9] The activation energy for K/Pb-CP below 60 K (27 meV) is much lower than that observed for KCP(Cl) (70 meV) indicating a much smaller band gap. It has been shown previously that it is possible to obtain T_{3D}, the three-dimensional ordering temperature, from the variation of conductivity with temperature.[10] For K/Pb-CP this is found to be ∿ 85 K which is slightly lower than that found for KCP(Cl).[9]

Further work is in progress on this compound and on the preparation of other POTCP salts containing divalent cations substituted into a monovalent cation host lattice.

REFERENCES

1. J. M. Williams, A. J. Schultz, A. E. Underhill and K. Carneiro, Extended Linear Chain Compounds (Plenum, in press).
2. A. E. Underhill and D. M. Watkins, Chem. Soc. Rev., 9, 429 (1980).
3. Gmelin, Handbuch de Anorg Chemie, Platinum Part C (Springer-Verlag, Berlin, 1940).
4. T. R. Koch, E. Gebert and J. M. Williams, J. Amer. Chem. Soc., 98, 4017 (1976).
5. R. Comes, M. Lambert and H. R. Zeller, Phys. Status Solidi B, 58, 587 (1973); A. Braude, A. Lindegaard-Andersen, K. Carneiro and A. Steen Pedersen, Solid State Commun., 33, 365 (1980).
6. J. M. Williams, M. Iwata, S. W. Peterson, K. A. Leslie and H. J. Guggenheim, Phys. Rev. Lett., 34, 1653 (1975).
7. G. S. V. Coles, A. Lindegaard-Andersen and A. E. Underhill, unpublished results.
8. A. E. Underhill and D. J. Wood, Ann. N. Y. Acad. Sci., 313, 519 (1978).
9. A. E. Underhill, D. J. Wood and K. Carneiro, Synthetic Metals, 1, 395 (1979/80).
10. K. Carneiro, Molecular Metals. NATO Conference Series: VI Materials Science (Plenum Press, New York, 1979), vol. 1, p. 369; M. Thielemans, R. Deltour, D. Jérome and J. R. Cooper, Solid State Commun., 19, 21 (1976).