Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis, Structure, and Properties of One-Dimensional Partially Oxidized Tetracyanoplatinate Complexes

Arthur J. Schultz[a]; Jack M. Williams[a]; Richard K. Brown[a]
[a] Chemistry Division Argonne National Laboratory, Illinois

To cite this Article Schultz, Arthur J. , Williams, Jack M. and Brown, Richard K.(1981) 'Synthesis, Structure, and Properties of One-Dimensional Partially Oxidized Tetracyanoplatinate Complexes', Journal of Macromolecular Science, Part A, 16: 1, 313 — 319
To link to this Article: DOI: 10.1080/00222338108082054
URL: http://dx.doi.org/10.1080/00222338108082054

J. MACROMOL. SCI.-CHEM., A16(1), pp. 313-319 (1981)

Synthesis, Structure, and Properties of One-Dimensional Partially Oxidized Tetracyanoplatinate Complexes

Arthur J. Schultz, Jack M. Williams and Richard K. Brown
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

ABSTRACT

The crystal structure of anion-deficient partially oxidized tetracyanoplatinate complexes generally can be classified into one of two categories. The electrical properties of compounds in the two categories are also observed to be different. We have prepared a new complex which does not fall into either of the previous categories. Its synthesis, structure and properties are described.

As recently as 1968, Krogmann [1] reported the preparation, x-ray crystal structure and chemical bonding analysis of the unusual anion-deficient complex $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, KCP(Br). Although partially oxidized tetracyanoplatinate (POTCP) complexes had been reported over 100 years ago [2], the "rediscovery" of these metallic appearing materials by Krogmann came at a time when interest in one-dimensional (1-D) conductivity was rapidly increasing. This was due, in part, to a theory of 1-D high-temperature superconductivity proposed by Little [3]

*Work performed under the auspices of the Office of Basic Energy Sciences of the U. S. Department of Energy

in 1964. In the intervening years, an expanding number of POTCP complexes have been synthesized and studied [4]. In this article, we describe some recent findings and new conclusions concerning 1-D metallic properties in Pt-chain forming complexes.

A common property of all POTCP materials studied to date is that they contain linear, or nearly linear, Pt-atom chains, as depicted schematically in Figure 1. Typical intrachain Pt-Pt separations are in the range of 2.80-2.95 Å, which may be compared with 2.78 Å in Pt metal, with interchain separations of ∿10 Å. The removal of a fractional portion of the electrons from the 1-D band formed by the overlapping Pt d_{z^2} orbitals is responsible for the unusual 1-D metallic or semiconducting properties exhibited by these compounds. The partial oxidation is stabilized in the solid state by anion deficiency, as in KCP(Br), or by cation deficiency, as in $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$, K(def)TCP.

An important finding relevant to the structure-property phenomena in these salts is that the crystal structures of the anion deficient materials generally can now be classified into

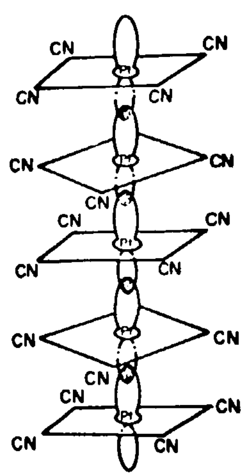

FIG. 1. Schematic diagram of overlapping Pt d_z2 orbitals which form the metallic "chain".

one of two categories. The hydrated compounds crystallize in the noncentrosymmetric primitive tetragonal space group P4mm, which contains cations between the $Pt(CN)_4$ groups in the "upper-half" of the unit cell while the water molecules reside in the "lower-half", as depicted in Figure 2 for KCP(Br)[5-7]. Thus the Pt-Pt intrachain distance can be alternatively compressed or expanded in a pairwise fashion due to the asymmetric packing of cations and water molecules in the unit cell. This is clearly evident in $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ [Pt-Pt = 2.924(8) and 2.877(8) Å] [8] and $(NH_4)_2[Pt(CN)_4]Cl_{0.3}\cdot H_2O$ [Pt-Pt = 2.910(5) and 2.930(5) Å] [9].

The second class of anion deficient POTCP complexes are usually anhydrous and crystallize in the centrosymmetric body-centered tetragonal space group I4/mcm. With the exception of $Cs_2[Pt(CN)_4]Cl_{0.3}$ [10] and the azide salt $Cs_2[Pt(CN_4](N_3)_{0.25}\cdot 0.5H_2O$ [11], these materials contain the linear (assumed) triatomic bifluoride anion $(FHF)^-$ [12]. An illustration of this structure type for $Rb_2[Pt(CN)_4]\ (FHF)_{0.40}$ [13] is given in Figure 3. The

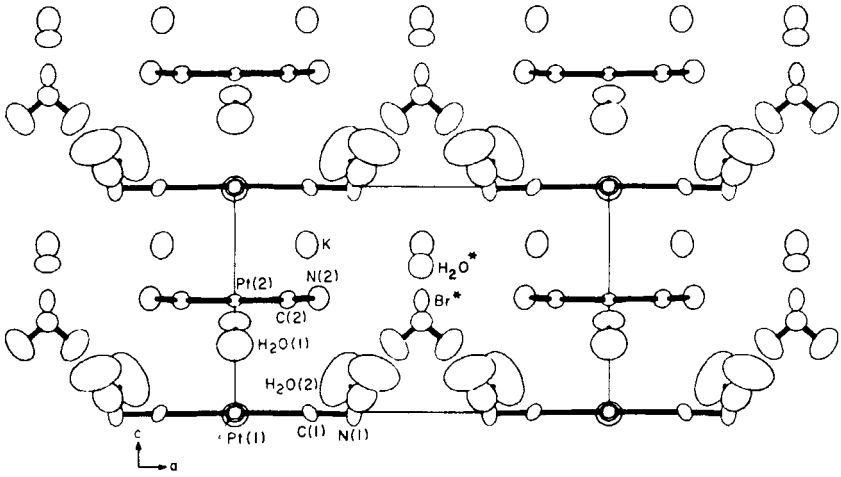

FIG. 2. A b-axis half-cell projection of the structure of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$.

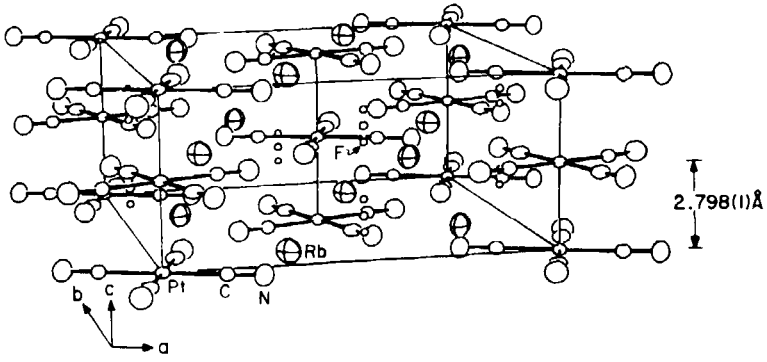

FIG. 3. Perspective view of the unit cell of $Rb_2[Pt(CN)_4](FHF)_{0.40}$. The Pt-Pt spacing is the shortest of any known POTCP salt.

cations reside in the plane of the $Pt(CN)_4$ groups, which serves to tie the $Pt(CN)_4$ groups together directly through CN-M^+-NC interactions, rather than between planes (see Fig. 2). In addition, all Pt-Pt distances are required to be crystallographically equivalent.

An important and common property displayed by all POTCP complexes is the existence of modulated lattice distortions arising from electron-phonon coupling. At low temperature, a 3-D ordering of the lattice instabilities occurs (at T_{3D}) and leads to an electrically insulating state (Peierls insulator) [4]. Detailed analysis by Wood and Underhill [14] of the conductivity data shown in Figure 4 reveals that T_{3D} occurs at ∿100°K for KCP(Br), and ∿73°K for $CsCP(FHF)_{0.4}$. Thus, we are able to conclude that in relations to the *hydrated* POTCP compounds, the anhydrous complexes generally have higher degrees of partial oxidation (DPO), smaller Pt-Pt repeat distances, higher conductivities at all temperatures, and lower 3-D ordering temperatures. The last property may be due to the absence of interchain hydrogen bonding interactions in the anhydrous crystals, which results in less interchain coupling and higher anisotropy.

Finally, we have recently prepared a new POTCP salt $Rb_3[Pt(CN)_4](O_3SO{\cdot}H{\cdot}OSO_3)_{0.49}{\cdot}H_2O$, RbCP(DSH), which is highly unusual

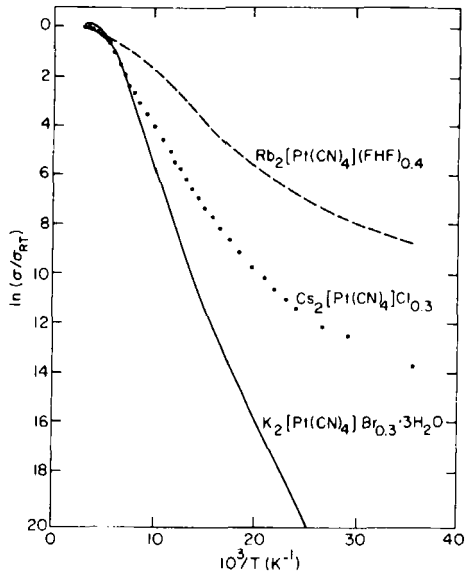

FIG. 4. The temperature dependence of ratio of the conductivity to the room temperature conductivity.

for many reasons. It contains a large polyatomic trianion and a ratio of three alkali metal ions per Pt atom, instead of the usual two. The crystals are triclinic ($P\bar{1}$), have a short Pt-Pt repeat distance (2.826(1) Å), and a relatively high room temperature conductivity parallel to the Pt-atom chain (2000 ohm^{-1} cm^{-1}). This conductivity is approximately triple that of KCP(Br). Although the material is hydrated, the water molecules do not couple the chains of $Pt(CN)_4$ stacks, but hydrogen bond to the disulfatohydrogen anions, linking them together parallel to the Pt chain direction (see Fig. 5). The physical properties of this new material are presently under study.

The DPO for Pt, derived from the least-squares refinement of the sulfate ion occupancy in the x-ray structure, is +0.49. From the stoichiometry derived from elemental analyses, the DPO is ∿0.47. A more reasonable value of ∿0.40, roughly predictable from the

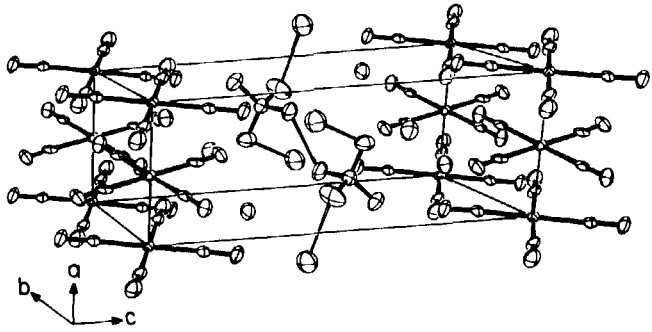

FIG. 5. Perspective view of the unit cell of $Rb_3[Pt(CN)_4](O_3SO{\cdot}H{\cdot}OSO_3)_{0.49}{\cdot}H_2O$. Hydrogen bonding interactions are indicated by unshaded bonds and the O-H-O separation in the disulfatohydrogen ion is 2.52(2) Å. The Rb ions are shown without any bonds drawn to them.

Pt-Pt distance, may be accommodated by the addition of ~0.1 H^+ ions per Pt to form HSO_4^- or H_3O^+ ions. Because of the highly acidic medium used in the preparation, this is not entirely unexpected.

EXPERIMENTAL

Electrochemical [15] Synthesis of RbCP(DSH): A 0.8 M solution of Rb_2SO_4 is prepared by adding 1.34 g of Rb_2SO_4 to 6 ml of water. The solution is then saturated with 1.08 g of $Rb_2[Pt(CN)_4]{\cdot}1.5H_2O$) and acidified to a pH of less than 1 with 0.25 ml of 9 M H_2SO_4. The clear solution is transferred to a 50 ml polyethylene beaker with Pt electrodes and electrolyzed at 0.8 volts for 72 hours. The reddish-bronze crystals were isolated by filtration and washed with cold water.

Crystal Structure Analysis of RbCP(DSH): The compound crystallizes in the triclinic space group $P\bar{1}$ with cell constants of a = 5.652(1) Å, b = 9.372(2) Å, c = 13.762(2) Å, α = 71.19(1)°, β = 81.94(2)°, γ = 73.44(1)°, V_c = 660.40 $Å^3$ and z = 2. The

structure was solved with x-ray diffraction data obtained on a syntex $P2_1$ diffractometer using MoKα radiation.

REFERENCES

[1] Krogmann and H. D. Hausen, Z. Anorg. Allg. Chem., 358, 67 (1968); K. Krogmann, Angew. Chem. Internat. Edit., 8, 35 (1969).
[2] W. Knop, Justus Liebig's Ann. Chem., 43, 111 (1842).
[3] W. A. Little, Phys. Rev. A 134, 1416 (1964).
[4] For reviews, see J. S. Miller and A. J. Epstein, Prog. Inorg. Chem., 20, 1 (1976); G. D. Stucky, A. J. Schultz and J. M. Williams, Ann. Rev. Mater. Sci., 7, 301 (1977); J. S. Miller and A. J. Epstein, Eds., Synthesis and Properties of Low-Dimensional Materials, Annals N. Y. Acad. Sci., 313, (1978).
[5] J. M. Williams, J. L. Petersen, H. M. Gerdes and S. W. Peterson, Phys. Rev. Lett., 33, 1079 (1974); J. M. Williams, M. Iwata, S. W. Peterson, K. A. Leslie and H. J. Guggenheim, Phys. Rev. Lett., 34, 1653 (1975).
[6] C. Peters and C. F. Eagen, Inorg. Chem., 15, 782 (1976).
[7] G. Heger, H. J. Deiseroth and H. Schultz, Acta Cryst. B34, 725 (1978).
[8] J. M. Williams, P. L. Johnson, A. J. Schultz and C. C. Coffey, Inorg. Chem. 17, 834 (1978).
[9] P. L. Johnson, A. J. Schultz, A. E. Underhill, D. M. Watkins, D. J. Wood and J. M. Williams, Inorg. Chem., 17, 839 (1978).
[10] R. K. Brown and J. M. Williams, Inorg. Chem., 17, 2607 (1978).
[11] R. K. Brown, D. A. Vidusek and J. M. Williams, Inorg. Chem., 18, 801 (1979). Although there is evidence of a small degree of hydration, and the actual space group is P4b2, the crystal structure of the azide salt is pseudo body centered and is nearly isomorphous with the I4/mcm compounds.
[12] J. M. Williams, A. J. Schultz, K. B. Cornett and R. E. Besinger, J. Am. Chem. Soc., 100, 5572 (1978).
[13] A. J. Schultz, C. C. Coffey, G. C. Lee and J. M. Williams, Inorg. Chem., 16, 2129 (1977).
[14] A. E. Underhill and D. J. Wood, private communication.
[15] R. E. Besinger, D. P. Gerrity and J. M. Williams, Inorg. Synth., in press.