Louis rather than some upwind source. On 11 August, the plume again stretched out toward the northeast and was mapped in detail out to 145 km and tracked out to 240 km. Winds on this date were lighter than on 18 July but the plume was as well defined, and concentrations and flow rates were similar.

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4 February 1976; revised 28 June 1976

8 OCTOBER 1976

## **Electrochemical Growth of Highly Conducting Inorganic Complexes**

Abstract. The formation of single crystals of highly conducting inorganic complexes, for example,  $K_2Pt(CN)_4X_{0.3} \cdot 3H_2O(X = Cl, Br), K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$ , or  $K_{1.64}Pt(O_2C_2O_2)_2 \cdot 2H_2O$ , has been effected via electrochemical growth from concentrated aqueous solutions of potassium tetracyanoplatinate(II) and potassium bis(oxalato)platinate(II).

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In recent years there has been a great interest (1) in the chemical and physical properties of highly conducting molecular complexes. This interest has resulted from observation of a number of unusual anisotropic physical phenomena (for example, high conductivity, metallic state, metal-insulator transition, charge density wave, superconductivity) and chemical properties (for example, novel structures containing infinite chains with short interplanar spacings, mixed valency, and homogeneous nonstoichiometric compositions) directly associated with numerous one-dimensional systems (2, 3). In order to measure the intrinsic physical properties of such complexes, it is necessary to have high-quality single crystals suitable for various measurements. Typically, various highly conducting materials containing a transition metal form fibrous needles that are difficult to analyze by single-crystal techniques. Furthermore, because of the pseudo one-dimensionality of such systems, impurities or defects, or both, will strongly influence various physical properties and, in particular, the electrical transport (for example, conductivity) properties of such materials. Thus, because large single crystals of  $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$  (KCP) have been available, this material has been the most extensively studied highly conducting inorganic one-dimensional system to date.

Single crystals of highly conducting inorganic complexes have traditionally been grown by crystallization from solution (2). However, the electrical properties of such materials can be utilized to grow single crystals via electrolysis at an anode. Upon nucleation at the anode, growth proceeds primarily along the conducting axis of the crystal such that the introduction of an impurity or defect will impede the current flow and crystal formation. However, as a result of microscopic reversibility, defects may be eliminated and growth may proceed, thereby making possible the fabrication of a high-quality crystal. Such electrochemical synthesis has been effected with the use of aqueous  $\sim 0.2M$  solutions of  $K_2Pt(CN)_4$  and  $\sim 0.02M$   $K_2Pt(O_2C_2O_2)_2$  in an electrolysis cell comprised of a platinum anode and cathode. Application of a 1.5-volt potential (4) causes nucleation and growth of needle crystals of  $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$  and gas evolution at the cathode. This process is consistent with the following anodic and cathodic half cell reactions:

$$5H_2O + 1.75K^+ + Pt(CN)_4^{2-} \xrightarrow{H_2O}$$
  

$$K_{1.75}Pt(CN)_4 \cdot 1.5H_2O + 0.25e^-$$
  

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

In the presence of halide ions, that is, Cl<sup>-</sup> or Br<sup>-</sup>, KCP nucleates by an alternate anodic reaction:

$$\begin{array}{l} .3X^{-} + 2K^{+} + Pt(CN)_{4}^{2-} + \\ & 3H_{2}O \xrightarrow[X = -l]{, \ Br} \\ KPt(CN)_{4}X_{0.3} \cdot 3H_{2}O + 0.3e^{-} \end{array}$$

In a similar manner, other highly conducting inorganic complexes can be grown. For example, anodic oxidation of potassium bis(oxalato)platinate(II) results in the formation of the cationdeficient species  $K_{1.64}$ Pt( $O_2C_2O_2$ )<sub>2</sub> · 2H<sub>2</sub>O presumably via the anode reaction:

$$.64K^{+} + Pt(O_{2}C_{2}O_{2})_{2}^{2-} \xrightarrow{H_{2}O} \\ 0.36e^{-} + K_{1.64}Pt(O_{2}C_{2}O_{2})_{2} \cdot 2H_{2}O$$

A typical electrochemical growth is shown on the front cover.

Thus, electrochemical growth provides an attractive alternate technique for the synthesis of highly conducting pseudo one-dimensional inorganic complexes. Furthermore, evaluation of the electrochemical parameters makes it possible for us to probe for the first time the stoichiometric, kinetic, and thermodynamic features of these systems.

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22 January 1976