density changes produced by the substituents are reflected in the ligand field strength of the substituted macrocycles. The spectral and electrochemical correlations are both strikingly good, and it is significant that both the functional property ($E_{1/2}$) and the diagnostic property (ν) are sensitive to substituent effects. Correlation between the spectral and electrochemical parameters is evident in Figure 3 (correlation coefficient, 0.98).

The compounds reported here are well suited to continuing studies in which substituents having appropriate electronic effects are used to append additional components to the structure as required by the other major structural consideration stated in the introductory paragraph above, the associated proximate structure. This and the incorporation of biologically important metal ions will be the subjects of subsequent reports.

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A Novel Partially Oxidized Distorted One-Dimensional Platinum Chain in $K_{1.6}Pt(C_2O_4)_2{\cdot}1.2H_2O$[1]

Sir:

Partially oxidized one-dimensional anion-deficient complexes, $K_2Pt(CN)_4{\cdot}Cl_{0.32}{\cdot}3H_2O$[2] and $K_2Pt(CN)_4{\cdot}Br_{0.30}{\cdot}3H_2O$,[3] and cation-deficient complexes, $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$[4] and $Mg_{0.82}Pt(C_2O_4)_2{\cdot}5.3H_2O$,[5] have been recently structurally characterized by x-ray and neutron diffraction techniques. These materials show metallic properties including high conductivity along the crystalline needle axis.[6] $K_{1.6}Pt(C_2O_4)_2{\cdot}xH_2O$ was first synthesized by Söderbaum[7] in 1888 and has been shown only recently to have one-dimensional properties.[8] However, the structure of this material has been rather elusive. The first Pt–Pt distance reported for a material with stoichiometry $K_{1.6}Pt(C_2O_4)_2{\cdot}2.5H_2O$ was 2.75 Å,[9] somewhat shorter than that in Pt metal.[10] Later it was claimed,[11] based on x-ray powder evidence, that at least five different crystalline phases exist and a stoichiometry $K_{1.64}Pt(C_2O_4)_2{\cdot}4H_2O$ was reported for one of them. This latter phase (called phase A) was found to exist in three different forms, which gave different single-crystal diffraction patterns but identical powder patterns. Pt–Pt spacings of 2.84 Å, deduced from the substructure periods, were reported[11] for the three forms of phase A material. Except for these approximate metal spacings, no other structural results have been reported for the partially oxidized potassium bisoxalate complexes. We wish, therefore, to report the synthesis and the molecular and crystal structure of $K_{1.6}Pt(C_2O_4)_2{\cdot}1.2H_2O$ (KDOX), as deduced from single-crystal x-ray diffraction data.

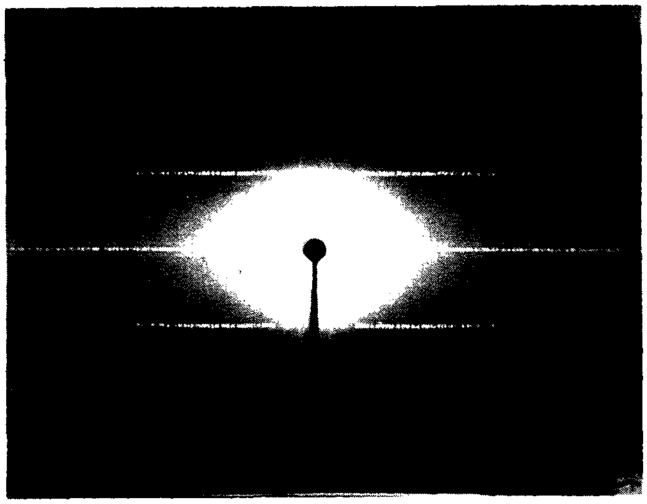

Figure 1. A rotation photograph of a crystal of $K_{1.6}Pt(C_2O_4)_2{\cdot}1.2H_2O$ mounted along the c axis showing the metal lattice (c_m), the intermediate cell (4 × c_m), and the incommensurate metal superlattice (10.25 × c_m).

KDOX was prepared first by the method of Krogmann and Dodel,[11] yielding small copper-colored triclinic needles. Later, somewhat larger coppery needle and lath shaped crystals were obtained by air oxidation of $K_2Pt(C_2O_4)_2{\cdot}2H_2O$ in aqueous oxalic acid solution (pH ~ 2) at 40 °C. Both methods yielded crystals which gave identical diffraction patterns and were triclinic, space group $P\bar{1}$ ($C_i{}^1$, no. 2) with cell dimensions a = 9.744 (12), b = 10.700 (13), c = 11.377 (14) Å, α = 80.23 (6), β = 77.97 (7), γ = 115.87 (3)°, and Z = 4. The molecular weight (455.18 g/equiv) and unit cell volume (997.02 Å^3) give a calculated density of 3.031 g/cm^3, which is in good agreement with an observed density of 3.00 (1) g/cm^3.

Figure 1 shows an x-ray rotation photograph of a crystal of KDOX mounted along the c axis. The KDOX lattice may be described in terms of three cells which differ in their c axis length. The smallest cell (most intense reflection spacing on the photograph) represents a metal–metal spacing along the c axis of 2.844 Å (c_m), the intermediate cell (weak commensurate levels on the photograph) a spacing of exactly 4 × c_m, which is indicative of the ligand repeat and transverse chain distortion; and the largest cell (weak *incommensurate* levels bracketing the most intense lattice reflections) a spacing of 10.25 × c_m, which may be indicative of longitudinal displacements of the metal–ligand groups along the chain axis. Three-dimensional x-ray data were collected on automated Picker-FACS-1 (small cell data) and G.E. XRD-490 (small and intermediate cell data) diffractometers using Mo$K\alpha$ radiation in the θ–2θ scan mode to a 55° 2θ limit. The data were corrected for absorption and the structure solved by a combination of Patterson, Fourier, and least-squares refinement techniques. At the present stage of refinement, with all Pt and K^+ atoms refined anisotropically and all C and O atoms refined isotropically, the R factor is 0.057 for the 1772 observed reflections.

The structural properties which relate to the one-dimensional character are quite similar to those observed in $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$.[4] They include: (1) The formation of parallel zigzag Pt atom chains aligned along the c axis. (2) A transverse Pt atom displacement of 0.056 (5) Å (somewhat smaller than in $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$),[4] and a Pt(1)–Pt(2)–Pt(3) bond angle of 177.8 (2)°. (3) There are three non-

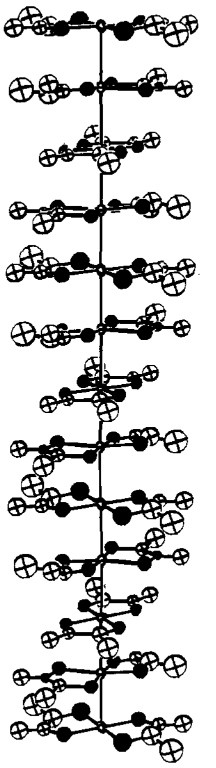

Figure 2. Three wavelengths of the Pt chain along the *c* axis of the unit cell showing the staircase staggering network of oxalate ligands each 45° to the ligand above and below it in the chain. The chelated oxygen atoms are in black.

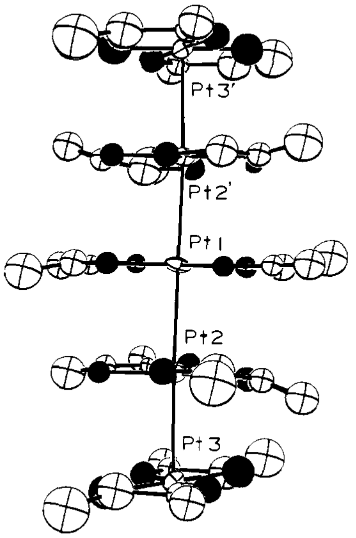

Figure 3. A single wavelength of the Pt chain shows the chain distortion and the ligand nonplanarity. The chelated oxygen atoms are in black.

equivalent Pt atoms in the chain and two Pt-Pt distances, 2.857 (2) and 2.833 (2) Å, the latter distance being the shortest Pt-Pt distance characterized in a 1-D salt. (4) The Pt coordinates are (0, 0, 0), ±(−0.0053, 0.0021, 0.2516), and (0, 0, ½). (5) The oxalate ligands are bidentate and are staggered (~45°) with respect to the ligands directly above and below it in the chain. However, all Pt(2) oxalate ligands are eclipsed (~5°), while Pt(1) and Pt(3) oxalate ligands are staggered (~90°), giving a staircase effect to the ligands (see Figure 2). This staggering of oxalate ligands allows a nominal amount of $p\pi$ overlap between orbitals of the same symmetry and may account for the stabilization of the higher oxidation state and the decreased Pt-Pt separation. (6) Except for a single K^+ ion, all other K^+ ions and water molecules are positionally disordered. There are five K^+ ion sites and five H_2O sites in the asymmetric unit. (7) As is shown in Figure 3, the K^+ ion and water molecule interactions cause the exterior oxygens of the oxalate ligands to be bent from planarity. (8) An oxidation state of 2.4 for Pt is indicated by the crystallographic stoichiometry and is in good agreement with that found by chemical analysis.[11]

The true superlattice reflections persist to very high 2θ angles (160°, Cu$K\alpha$), giving evidence of their origin in scattering from Pt atoms. The supercell becomes commensurate with the intermediate cell at 116.19 Å, which delineates a 41 Pt atom repeat. It seems probable that errors in stacking of the bisoxalatoplatinum groups are responsible for the extended repeat. Since the two independent Pt-Pt distances are substantially unequal, stacking errors occurring at regular intervals will produce a modulated pattern of longitudinal Pt displacements. The modulated cell would become commensurate with the normal cell in a relation determined by the stacking defect frequency. An alternative view is that the two unequal Pt-Pt separations are but an artifact due to lack of inclusion of the superlattice intensities in the analysis. This view is difficult to reconcile with the persistence of superlattice intensity to large scattering angle. Clearly a complete structure analysis utilizing the superlattice intensities is required to establish a detailed model.

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Energy Upconversion and the Minimum Quantum Requirement in Photosynthesis[1]

Sir:

It was proposed in 1974 that the primary light reaction in photosynthesis is activated by a singlet-triplet annihilation mechanism whereby the initial photoexcitation in the far-red