A Novel Quasi-One-Dimensional Zig-Zag Platinum Atom Chain in $K_{1.75}Pt(CN)_4·1.5H_2O$. A Neutron Diffraction Study[1]

Sir:

Of the mixed-valence linear-chain Pt compounds formed by partial oxidation of the metal atom, only the prototype Krogmann salt, $K_2Pt(CN)_4Br_{0.3}·3H_2O$, KCP(Br) hereafter, has been extensively studied to date.[2] While KCP(Br) and KCP(Cl) have been well characterized using neutron diffraction,[3] little is known about the closely related *cation* deficient cyanoplatinate compounds.

We wish to report the results of the first single-crystal neutron diffraction study of a potassium deficient cyanoplatinate complex, $K_{1.75}Pt(CN)_4·1.5H_2O$, hereafter K(def)TCP. An entirely new type of zig-zag Pt atom chain is observed and the structure reported here should provide a model for the interpretation of the electronic properties and one-dimensional conductivity of these unusual salts.

The literature regarding K(def)TCP is confusing, as summarized in Table I, but it appears (*vide infra*) that although the compounds are given different formulations they are structurally identical. First, although the cell dimensions reported by Krogmann and Hausen[4] for K(def)TCP are different from the others listed, the powder x-ray diffraction patterns of our crystals and of material prepared by Miller[5] match Krogmann and Hausen's published pattern perfectly. Second, the triclinic cell parameters of K(def)TCP which we have observed from single crystals are identical with those given by Minot, Perlstein, and Kistenmacher[6] who also reported the presence of a slight amount of Br^- in their material.[7]

K(def)TCP was prepared using the method outlined by Levy,[8] and crystals were grown by evaporation from aqueous solution. Triclinic cell parameters are given in Table I. No additional peaks were observed in a careful search for possible "superlattice" reflections. Four octants of intensity data were measured employing a θ-2θ step scan yielding 3969 independent reflections (3276 with $(F_o^2) > 1\sigma\,(F_o^2)$), at 22 ± 2°C to a maximum $\sin\theta/\lambda = 0.72$ at the Argonne National Laboratory CP-5 neutron source (λ 1.142 (1) Å). The data were corrected for absorption ($\mu = 1.00\ \mathrm{cm}^{-1}$) and scaled against a standard NaCl crystal using a method described previously.[9,10] The structure was solved from the neutron Patterson map. Full-matrix least-squares refinement (with anisotropic thermal parameters and an isotropic extinction correction) has led, at this stage, to a value of the reliability index of $R(F_o^2) = 0.059$ using all data and $R(F_o^2) = 0.055$ for all data with $(F_o^2) > 1\sigma(F_o^2)$. The standard deviation of an observation of unit weight, Σ_1, is 1.19 and the ratio of observations to parameters is ca. 14:1.

The most significant and surprising structural finding regarding K(def)TCP, compared to KCP(Br), is the pronounced nonlinearity of the Pt-atom chain as illustrated in Figure 1. Three crystallographically independent Pt atoms comprise the basic repeat unit of the zig-zag metal atom chain which extends along *c*. The Pt(2), at the general position ($z \simeq \frac{1}{4}$),[10] is displaced from the *c* axis (on which the other two Pt atoms reside) by 0.175 (1) Å, the Pt(1)-Pt(2)-Pt(3) bond angle being significantly nonlinear at 173.2 (1)°. The two *independent but equal* Pt-Pt bond lengths (2.961 (1) and 2.965 (1) Å) are 0.069-0.077 Å longer than in KCP(Br) (2.888 (6) and 2.892 (6) Å) at room temperature.[3] In this case the Pt-Pt separation exceeds that in the metal itself by ~0.2 Å, and the difference is almost twice that observed in KCP(Br).[11] The equality of the Pt-Pt separations suggests that this is an important, intrinsic property of metal atom chain formation in these salts. Adjacent $Pt(CN)_4{}^{2-}$ groups extending along the Pt-Pt chain are not precisely parallel and a staggered conformation very similar to that in KCP(Br) is observed. The short Pt-Pt separations and staggered conformations indicate considerable d_{z^2} metal overlap.[12] However, the Pt chain nonlinearity and increased Pt-Pt separation indicates less d_{z^2} overlap than in KCP(Br). These are probably key factors contributing to the reportedly lower electrical conductivity of K(def)TCP vs. KCP(Br).[13]

As in KCP(Br), water molecule hydrogen bonding to cyanide ligands binds the cyanoplatinate chains in K(def)TCP. However, in marked contrast to KCP(Br), all cyanides do not form the same number of hydrogen bonds. Multiple hydrogen bond formation by -CN ligands of Pt(2) may contribute to the Pt-chain deformation (see Figure 1). The H_2O molecules are tightly bound and all lone-pair orbitals appear to be directed toward K^+ ions.

These results demonstrate that Krogmann type cyanopla-

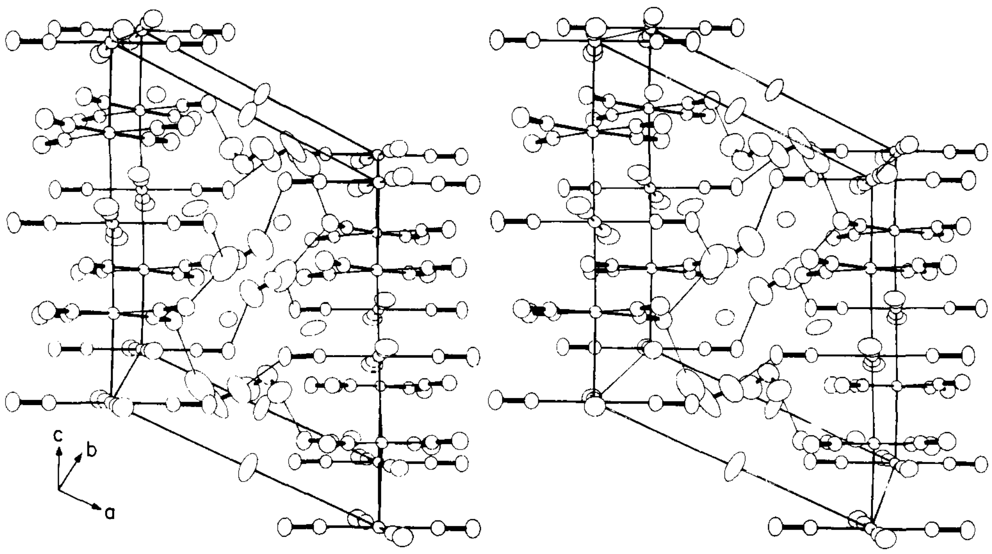

Figure 1. Stereographic view of the structure of $K_{1.75}Pt(CN)_4·1.5H_2O$ showing all atoms in the unit cell (thermal ellipsoids are scaled to enclose 50% probability). Note the zig-zag nature of the Pt atom chain along the *c* axis.[10] The basic repeat unit of the metal chain comprises Pt(1), Pt(2), and Pt(3) at z = 0.0, ~0.25, and 0.50, respectively. The Pt(1)-Pt(2)-Pt(3) bond angle is 173.2 (1)° and inversion centers occur at Pt(1) and Pt(3). Water molecule to cyanide nitrogen atom hydrogen bonds (H···N < 2.6 Å) are indicated with faint lines and K^+ ions are drawn without bonding interactions.

Table I.[a] Published Structural Data on $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$

Compound formulation	Cell data						Pt–Pt separation (Å)	Ref
	Crystal system	a, Å (α, deg)	b, Å (β, deg)	c, Å (γ, deg)	ρ_{obsd}, g/cm^3 (ρ_{calcd})	V_{cell} (Å^3)		
$K_7Pt_4(CN)_{16}\cdot 6H_2O$[b] or $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$	–	– –	– –	– –	– –	–	–	Levy,[8] (1912)
$K_{1.74}[Pt(CN)_4]\cdot 1.8H_2O$	Triclinic[c]	15.59 (92.5)	10.01 (92.5)	2.96 (92.1)	2.79 (2.87)	460.6	2.96 (c length)	Krogmann and Hausen,[4] (1968)
$K_{1.78}[Pt(CN)_4]Br_{0.034}\cdot 2H_2O$	Triclinic[d]	·10.32 (1) (102.6 (1))	11.80 (1) (106.2 (1))	9.29 (1) (114.8 (1))	–	910.4	2.95 (b/4 length)	Minot *et al.*[6] (1973)
$K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$	Triclinic[e] [C_i^1-$P\bar{1}$] [$Z = 4$]	10.36 (2) (102.4 (1))	11.83 (2) (106.4 (1))	9.30 (2) (114.7 (1))	2.82 (1) (2.85)	918.3	2.96 (b/4 length)	This work

[a] The estimated standard deviations are given in parentheses and refer to the least-significant figures. [b] Original formulation by Levy.[8] [c] Powder x-ray diffraction data; faint lines referred to as "superlattice" lines indicate c axis length should be doubled (5.92 Å). [d] Single-crystal x-ray data. Triclinic cell data are those for the primitive Delauney-reduced cell. [e] Single-crystal neutron data. Data for the primitive Delauney-reduced cell are given.[10] X-Ray powder patterns of this material are identical with those reported by Krogmann and Hausen;[4] hence all materials reported in this table appear to have the same molecular structure.

tinate compounds form nonlinear Pt–Pt chains in which equal metal-repeat separations are maintained even though they are not required crystallographically. At this time there is no evidence to indicate that the Pt chain deformation is caused by a charge density wave or Peierls distortion[14] as in $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$. The full structural study will be reported at a later date.

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References and Notes

(1) Research performed under the auspices of the U.S. Energy Research and Development Administration.

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(7) Chemical analysis of our compound for C, H, N, and halogen agrees very well with the formula obtained from the diffraction study, except for a trace of halogen (<1.0%) which apparently originated in our $K_2Pt(CN)_4\cdot 3H_2O$ starting material. A final Fourier difference density map is virtually featureless and, at this stage, gives no indication of any possible halide position. However, this is a matter of continuing study.

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(10) All coordinates given, and Figure 1, refer to the triclinic cell used in data collection (a = 10.360 (17) Å, b = 9.303 (15) Å, c = 11.832 (19) Å, α = 77.57 (9)°, β = 114.74 (5)°, and γ = 73.64 (7)°). Cell parameters were derived from a least-squares refinement of 28 intense neutron reflections ($40° < 2\theta < 60°$). Calibration of the neutron wavelength of 1.142 (1) Å was made with two standard cubic crystals: NaCl (a = 5.6397 Å) and Si (a = 5.4308 Å) at 22 ± 2°. The Delauney-reduced cell parameters presented in Table I were derived using the computer program "TRACER II, A Fortran Lattice Transformation-Cell Reduction Program" written by Dr. S. L. Lawton.

(11) Although the Pt–Pt separations in K(def)TCP are equal the *environments* about individual Pt atoms are not identical. Using photoelectron spectroscopy we are investigating these effects in an attempt to discern if the Pt atoms all have equivalent (fractional) valence states.

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A Partially Oxidized One-Dimensional Complex Containing a Distorted Platinum Chain. The Molecular and Crystal Structure of $K_{1.75}$ $Pt(CN)_4\cdot 1.5H_2O$

Sir:

With the observation of anisotropic metallic properties in $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ and in various organic charge trans-