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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 19. Synthesis and Crystal Structure of Cs₂[Pt(CN)₄]Cl_{0.30}, the First Anhydrous One-Dimensional Tetracyanoplatinate Chloride Complex¹

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The preparation and single-crystal x-ray structural characterization of a new, partially oxidized tetracyanoplatinate (POTCP), Cs₂[Pt(CN)₄]Cl_{0.30}, CsCP(Cl), has been carried out. This one-dimensional conducting salt crystallizes with four formula units in the tetragonal unit cell *I4/mcm*, with cell constants *a* = 13.176 (2) Å, *c* = 5.718 (1) Å, and *V* = 992.7 Å³. A total of 3112 observed data were averaged to yield 427 independent reflections. The structure was solved by standard heavy-atom methods and was refined by full-matrix least squares to a final *R*(*F*_o²) = 0.045 and *R*_w(*F*_o²) = 0.059. Pertinent structural features include perfectly linear chains of Pt atoms with Pt-Pt separations crystallographically constrained to a value of (*c*/2) = 2.859 (2) Å and interchain Pt-Pt distances of 9.317 Å. Separations between the Cs⁺ and Cl⁻ ions are significantly shorter than the sum of the ionic radii. A discussion of these unusually short interionic distances and the absence of hydration as determined from the structural study and thermogravimetric analyses is given.

Introduction

The one-dimensional tetracyanoplatinate (TCP) conductors have received a great deal of attention in recent years.² The interest in these systems has been generated in no small measure by the search for high-temperature excitonic superconductors. The one-dimensional properties of partially oxidized tetracyanoplatinates are presently under extensive study in our laboratory.³ These polynuclear systems with infinitely long metal atom arrays offer a suitable series on which to test further details and applicability of one-dimensional band theory⁴ in a comprehensive manner. Structural studies of these systems are a necessary prerequisite for the development of meaningful interpretive models. By incrementally varying such parameters as cation and anion site occupancy, size, and charge ratios, theoretical predictions may be tested in minute detail. With this in mind we have undertaken the synthesis and structural characterization of a new one-dimensional conducting salt, cesium tetracyanoplatinate chloride, Cs₂[Pt(CN)₄]Cl_{0.30}.

Experimental Section

Crystal Preparation. The preparation of Cs₂[Pt(CN)₄]Cl_{0.30}, CsCP(Cl) hereafter, was carried out by the direct interaction of Cs₂[Pt(CN)₄], Cl₂(g), and CsCl in aqueous solution. A 15-mL aqueous solution containing 0.5 g of Cs₂[Pt(CN)₄] was saturated with Cl₂(g) at 1 atm. After driving off excess Cl₂ at 100 °C, an additional 2.5 g of Cs₂[Pt(CN)₄] was added. The resulting solution was concentrated to a volume of 5 mL and cooled to 0 °C. A mass of microcrystalline brown product was collected and redissolved in 50 mL of a 2.0 M CsCl solution. This step was found to be necessary in the preparation of Rb₂[Pt(CN)₄]Cl_{0.3}·3H₂O in order to avoid formation of the cation-deficient material.⁵ After 24 h at room temperature, bronze colored crystals of CsCP(Cl), suitable for a detailed x-ray structural analysis, were collected. Anal. Calcd for Cs₂[Pt(CN)₄]Cl_{0.30}: C, 8.35; N, 9.73; Cl, 1.85. Found (Midwest Microlab Inc., Indianapolis, Ind.): C, 8.34; N, 9.49; Cl, 1.87, 1.90, 2.05 (average = 1.94). The presence of Cs and Pt was confirmed by emission spectrographic analyses.¹⁶

Collection of X-Ray Diffraction Data. A well-formed crystal of approximate dimensions 0.06 × 0.10 × 0.22 mm was sealed in a glass capillary and mounted on a Syntex P2₁ diffractometer equipped with

a molybdenum x-ray tube and a graphite monochromator. From the observed Laue symmetry (*4/mmm*) and the systematic absences (*hkl* for *h + k + l = 2n + 1* and *h0l* (*0kl*) for *l = 2n + 1*) a body-centered tetragonal cell was indicated. The same results were obtained for three different crystals. The centrosymmetric space group *I4/mcm* [*D*_{4h}¹⁸, No. 140] was chosen initially and confirmed by the satisfactory least-squares refinement. The refined cell parameters, determined from 25 diffractometer-centered reflections with 2θ ≥ 22.5°, are *a* = 13.176 (2) Å, *c* = 5.718 (1) Å, and *V* = 992.7 Å³ with *Z* = 4 and a calculated density of 3.88 g cm⁻³. Intensity data were collected using a coupled ω-2θ scan for 3112 reflections in the region +*h*, ±*k*, ±*l* with 5° ≤ 2θ ≤ 60°. The reflection scan ranges were from [2θ(Kα₁) - 1.0]° to [2θ(Kα₂) + 1.0]° with scan rates from 2.0°(2θ)/min to 29.3°(2θ)/min. The actual scan rate was determined from a preliminary peak intensity measurement for each reflection. Stationary background counts were taken at each extremity of the scan such that the total background counting time was equal to half of the total scan time. Three standard reference reflections (600, 060, 004) were measured after every 50 reflections and showed an average decrease in intensity of 9% during the course of data collection. An isotropic correction was applied to the intensity data to account for this effect. Net intensities (*I*) were calculated as

$$I = \left(P - \frac{t_P}{t_B}(B_1 + B_2) \right) SR$$

where *P* is the total scan count, *B*₁ and *B*₂ are the background counts, SR is the scan rate, and *t*_P and *t*_B are the counting times for the peak and background, respectively. The value of σ(*I*) was evaluated as

$$\sigma(I) = \left[I + \left(\frac{t_P}{t_B} \right)^2 (B_1 + B_2) + (cI)^2 \right]^{1/2} SR$$

where *c*, a factor to account for errors other than those arising from counting statistics, was assigned a value of 0.05.

The 3112 reflections were averaged to yield 427 symmetry-independent data. The "agreement index"

$$R(F_o^2) = \sum (F_{av}^2 - F_o^2) / \sum F_o^2$$

between averaged reflections was 0.121 before application of absorption corrections and 0.048 after the data were corrected for absorption (*μ*_c = 185.4 cm⁻¹).

Table I. Positional and Thermal Parameters for $\text{Cs}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.30}$ ^a

Positional Parameters			
atom	x	y	z
Pt	0.0000	0.0000	0.0000
Cs	0.3368 (1)	0.1632	0.0000
C	0.0547 (6)	0.1437 (6)	0.0000
N	0.0868 (6)	0.2234 (6)	0.0000
Cl	0.5000	0.0000	0.099 (7)

Anisotropic Thermal Parameters ^b						
atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.0270 (4)	0.0270	0.0110 (2)	0.0000	0.0000	0.0000
Cs	0.0591 (8)	0.0591	0.0593 (6)	-0.0124 (5)	0.0000	0.0000
C	0.039 (4)	0.037 (4)	0.015 (3)	-0.000 (3)	0.0000	0.0000
N	0.049 (4)	0.040 (4)	0.031 (4)	-0.011 (4)	0.0000	0.0000
Cl ^c	0.09 (1)					

^a Standard deviation of the least significant digit is given in parentheses. Occupancy of the Cl^- site was refined by least-squares techniques to a value of 0.30 (2). ^b The form of the anisotropic thermal ellipsoid is given by $\exp[-\sum_i \sum_j h_i h_j r_i^* r_j^* U_{ij}]/4]$ with $i, j = 1, 2, 3$, where r_i^* is the i th reciprocal axis. ^c For the chloride ion the temperature factor is an isotropic U .

Table II. Bond Distances (Å) and Angles (deg) for the Isostructural ($I4/mcm$) Complexes $\text{Cs}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.30}$, $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$, and $\text{Rb}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.40}$ ^a

	$\text{Cs}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.30}$	$\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$	$\text{Rb}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.40}$
Pt-Pt (intra)	2.859 (1)	2.833 (1)	2.798 (1)
Pt-C	2.026 (8)	2.015 (9)	2.00 (1)
C-N	1.13 (1)	1.13 (1)	1.15 (1)
Pt-Pt (inter)	9.317	9.233	8.972
Pt-C-N	178.9 (8)		180 (1)
$[\text{Pt}(\text{CN})_4]_x$ (torsion)	41.7 (5)	41.7 (5)	40.8 (6)

^a Standard deviation of least significant digit is given in parentheses.

Structure Solution and Refinement. Coordinates for the Pt, Cs, C, and N atoms were obtained directly from a Patterson map. A difference Fourier map phased on these atoms was sufficient to locate the partially occupied Cl^- site. Several cycles of full-matrix least-squares refinement using all 427 independent reflection data led to

$$R(F_o^2) = \sum |F_o^2 - F_c^2| / \sum F_o^2 = 0.045$$

and

$$R_w(F_o^2) = [\sum w|F_o^2 - F_c^2|^2 / \sum wF_o^4]^{1/2} = 0.059$$

The quantity minimized was $\sum_i w_i |F_o^2 - S^2 F_c^2|$, where S is the scale factor, and the weight w for each reflection was calculated according to the expression

$$w_i = \frac{1}{\sigma^2(F_o^2)}$$

Atomic scattering factors were obtained from the International Tables for X-Ray Crystallography (1974),⁶ including corrections for anomalous scattering for the Pt and Cs atoms. Final positional and thermal parameters are presented in Table I. In the last cycle of least-squares refinement the largest shift to error ratio was 0.01. A final difference electron density map showed only two peaks significantly above background ($2.7 \text{ e}/\text{\AA}^3$ at 0.00, 0.08, 0.00, and 0.33, 0.17, 0.00) in the very near vicinity of the Pt and Cs atoms. The absence of any meaningful structural features in the final difference map appears to rule out the possibility of a second Cl^- site, or "defect water" molecule, in $\text{CsCP}(\text{Cl})$.⁷

Discussion

Pertinent bond distances and angles for $\text{CsCP}(\text{Cl})$ are given in Table II. The crystal structure, comprising linear chains of square-planar $\text{Pt}(\text{CN})_4^{1.70-}$ groups stacked parallel to c , is presented in Figure 1. The Pt-Pt separation is crystallo-

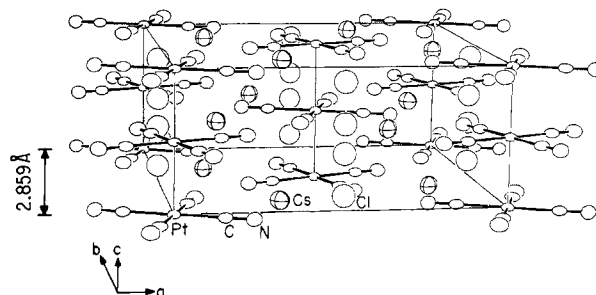


Figure 1. Perspective view of the unit cell of $\text{Cs}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.30}$. Thermal ellipsoids are shown at the 50% probability level. The Pt-Pt spacings are constrained to a value of $c/2$.

graphically constrained to a distance of $(c/2)$ 2.859(2) Å and therefore the Pt-Pt separations are crystallographically equivalent. The Pt-Pt intrachain repeat distance in $\text{CsCP}(\text{Cl})$ is very nearly that in $\text{KCP}(\text{Cl}, \text{Br})$ (2.87 (1) Å).⁷ We may therefore expect the electrical conductivities of the K and Cs salts to be very similar.¹⁸ The $\text{Pt}(\text{CN})_4$ group is also required by symmetry to be perfectly square planar. The intramolecular nonbonded C-C distance is 2.87(1) Å. Neighboring TCP groups form a staggered configuration with a 41.7 (5)^o torsion angle, and possess C-C nonbonded distances of 3.203 (8) and 3.304 (8) Å. Chloride-chloride interactions along $1/2, 0, z$ range from 1.13 (8) Å to $(c/2)$ 2.859 (2) Å. These unreasonably short derived contacts present no interpretative difficulties because they are due to the partial occupancy of the chloride ion sites. Each chloride ion has four possible nearest neighbor cesium ion interactions (two at 3.093 (7) Å and two at 3.81 (2) Å). The sum of the chloride and cesium ionic radii, as derived from the CsCl structure,⁸ is 3.56 Å. The very short cation-anion contacts are not unprecedented. In $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$ ⁷ the shortest $\text{K}\cdots\text{Br}$ distance was found to be 3.08 (5) Å, whereas the sum of the ionic radii is 3.29 Å. Due to the partial occupancy of Cl^- sites the Cs ion environment in $\text{CsCP}(\text{Cl})$ is markedly anisotropic, when compared to that in CsCl , which could give rise to atomic polarization effects similar to those expected in the vapor state where the Cs-Cl separation is known to be 2.91 Å.⁹ Unfortunately, no support for this contention can be found by examination of the thermal parameters presented in Table I and indeed we cannot rule out the possibility that partial occupancy of the Cl^- site by a trace of H_2O (vide infra) could result in the short cation-anion contacts given here. For comparative purposes the $\text{Cs}\cdots\text{O}$ distances in $\text{Cs}_2[\text{Pt}(\text{CN})_4]\cdot\text{H}_2\text{O}$ are 3.155 (8) and 3.125 (9) Å.¹⁷

The cesium cations are crystallographically constrained to lie in the plane of the TCP groups yielding two unique Cs-N contacts of 3.389 (9) and 3.617 (9) Å. There are four crystallographically equivalent interplanar Cs-N distances of 3.379 (4) Å. These values may be compared with those for $\text{Cs}_2[\text{Pt}(\text{CN})_4]\cdot\text{H}_2\text{O}$ for which the Cs-N separations range from 3.236 (5) to 3.508 (6) Å. In addition there are the four Cs-Cl contacts discussed above. The cesium ion coordination sphere is presented in Figure 2.

With the exception of the placement of a single Cl^- anion along the $0, 1/2, z$ line, $\text{CsCP}(\text{Cl})$ is isomorphous and isostructural with $\text{Rb}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.40}$ ¹⁰ and $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$.¹¹ For comparative purposes, selected bond lengths and angles for these two complexes have been included in Table II. $\text{CsCP}(\text{FHF})$ and $\text{RbCP}(\text{FHF})$ were the first examples of anhydrous partially oxidized tetracyanoplatinate complexes and the x-ray structural analysis of $\text{CsCP}(\text{Cl})$ shows no evidence for the presence of water in the crystal lattice. Both thermogravimetric and elemental analyses indicate the possibility of a trace of water. However, in the absence of a complete neutron diffraction study it is not possible to de-

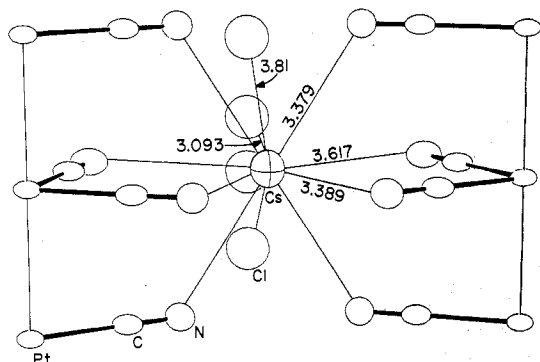


Figure 2. Perspective view showing the cesium cation coordination sphere. Distances are in angstroms.

termine if water molecules are incorporated in the crystal lattice. Without lattice water molecules, and the associated interchain hydrogen bonding, the unusually short Cs⁺...Cl⁻ contacts previously mentioned become exceedingly important with respect to maintaining crystalline integrity.

It should be noted that within this new three-membered series of anhydrous and isomorphous tetracyanoplatinate complexes, RbCP(FHF), CsCP(FHF), and CsCP(Cl), that as the *interchain* Pt-Pt distances decrease there is a linear (within experimental error) decrease in the *intrachain* Pt-Pt separation (see Table II). The interchain separations also appear to be dependent, at least partially, on the cation and anion size. Another closely related series of partially oxidized tetracyanoplatinates comprises K₂[Pt(CN)₄]Cl_{0.3}·3H₂O,¹³ K₂[Pt(CN)₄]Br_{0.3}·3H₂O,⁷ and Rb₂[Pt(CN)₄]Cl_{0.3}·3.0H₂O,¹² all of which are isomorphous (space group *P4mm*). Here again there is a linear relationship between inter- and intrachain Pt-Pt separations. As the cation size is increased upon progressing from KCP(Cl) to RbCP(Cl), both inter- and intrachain Pt-Pt separations increase. A similar, but slight (~0.01 Å), increase in Pt-Pt separations is observed upon increasing the anion size from Cl⁻ to Br⁻ in KCP(Cl, Br).⁷

Another important factor with respect to the *intrachain* Pt-Pt separation, which has been discussed previously, is the degree of partial oxidation (DPO) of the Pt atoms. For Cs₂[Pt(CN)₄]Cl_{0.30(2)} the platinum oxidation state is 2.30, hence the DPO is 0.30. This value was obtained by varying the occupancy factor of the Cl⁻ site in the least-squares refinement of the x-ray data. Inspection of the values listed in Table II shows that as the DPO is increased upon progressing from CsCP(Cl) to CsCP(FHF) there is a concomitant decrease in the *intrachain* Pt-Pt separation. This is a particularly illuminating comparison in that the two materials are isomorphous and contain the same cation. A value of 2.859 (1) Å for the Pt-Pt spacing in CsCP(Cl) is also in good agreement with the value of 2.88 Å for KCP(Br) where the Pt-atom DPO is 0.30.⁷ If the Cl⁻ sites in CsCP(Cl) were partially occupied by H₂O molecules, the DPO of the platinum atoms would be reduced and it seems likely that a larger Pt-Pt separation than that observed would result.

In view of the fact that all three of the known anhydrous partially oxidized tetracyanoplatinates possess Pt-Pt separations which are shorter than any of the previously char-

acterized (POTCP) complexes, it appears likely that future investigations of anhydrous (POTCP) salts may yield Pt-Pt separations very near that found in Pt metal (2.78 Å).

It is generally agreed that the tendency toward hydration is not solely dependent on either the cation or anion alone but rather on the particular combination of cation and anion.^{14,15} Ions such as Na⁺, K⁺, and Mg²⁺, which have a high (*z*²/*r*) value, are generally hydrated to a much larger extent than ions such as Rb⁺ or Cs⁺. The MCP(X) salts, where M = K or Rb and X = Cl or Br, all of which are isolated as hydrates, exemplify this point. Hydration normally improves the matching of cation and anion size.¹⁴ Therefore, one might expect salts having a large disparity in their cation vs. anion size to be hydrated, and salts containing ions of equal size to be anhydrous. This may explain why RbCP(Cl), with *r*_{Rb⁺}/*r*_{Cl⁻} = 0.81, is hydrated whereas CsCP(Cl), with *r*_{Cs⁺}/*r*_{Cl⁻} = 0.93, is anhydrous.

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Supplementary Material Available: A listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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