

**Structural Studies of Precursor and Partially Oxidized Conducting Complexes.**  
**XVI. An X-ray Diffraction Study of Dicesium Tetracyanoplatinate Hydrogendifluoride**  
 **$\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}^*$**

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**Abstract.** Body-centered tetragonal,  $I4/mcm$ ,  $a = 13.057(2)$ ,  $c = 5.665(1)$  Å,  $Z = 4$ ,  $D_c = 3.99$  g cm<sup>-3</sup>. The structure was determined from X-ray diffraction data measured on a Syntex  $P2_1$  diffractometer. Based on 407 unique reflections, the final agreement index was  $R(F_o^2) = 0.072$ . The structure consists of linear stacks, aligned along  $c$ , of square-planar  $\text{Pt}(\text{CN})_4^{1.61-}$  groups with a Pt–Pt separation of 2.833(1) Å. Neighboring  $\text{Pt}(\text{CN})_4^{1.61-}$  groups are rotated 41.7(5)° with respect to each other. The two independent partially occupied fluorine positions generate a F(1)···F(2) distance of 2.27(7) Å with the (F–H–F) groups aligned parallel to the  $c$  direction.

**Introduction.** We have recently reported the preparation of a new series of partially oxidized tetracyanoplatinate (POTCP) complexes containing the triatomic hydrogendifluoride anion (FHF)<sup>-</sup> (Williams, Gerrity & Schultz, 1977). As part of our continuing investigation of one-dimensional conducting materials, we have determined the crystal structure of  $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$ , hereafter CsCP(FHF).

Crystals were grown electrolytically from a solution containing  $\text{Cs}_2[\text{Pt}(\text{CN})_4]$ , HF and CsF. Elemental analysis of the crystalline product is consistent with a molecular formula of  $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$  (Williams, Gerrity & Schultz, 1977). Preliminary Weissenberg photographs of CsCP(FHF) crystals exhibited body-centered tetragonal  $4/mmm$  Laue symmetry ( $h + k + l = 2n$ ) with the additional systematic absences  $l = 2n + 1$  for the  $h0l$  and  $Ok l$  reflections. The centrosymmetric space group  $I4/mcm$  ( $D_{4h}^{16}$ , No. 140) was chosen initially and was justified by the satisfactory least-squares refinement ultimately obtained. The two other possible space groups ( $I4cm$  and  $I4c2$ ) require a distortion of the  $\text{Pt}(\text{CN})_4$  moiety from  $4/m$  site symmetry, which, even if it were the case, would be difficult to observe due to the dominance of the Pt and Cs scattering.

A crystal with dimensions 0.52 × 0.06 × 0.06 mm

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was selected for data collection and sealed in a thin-walled glass capillary. Data were collected using the  $\theta$ - $2\theta$  step-scan mode on a Syntex  $P2_1$  diffractometer equipped with a graphite monochromator [Mo  $K\alpha$  X-radiation ( $\lambda = 0.7107$  Å)]. Reflections in one octant were measured out to a maximum  $2\theta$  value of 60°. The variation of the integrated intensities of three reference reflections which were measured periodically throughout the data collection was less than 2%. A set of  $F_o^2$  values were obtained by applying Lorentz, polarization and absorption corrections ( $\mu = 227.95$  cm<sup>-1</sup>) with transmission coefficients ranging from 0.21 to 0.31. Errors were assigned to the data based on standard counting statistics with  $(0.03I)^2$  added to account for systematic error. The 834 data were averaged to yield 407 independent reflections.

The initial positional parameters for the Pt, Cs, C and N atoms were taken from the isomorphous RbCP(FHF) structure (Schultz, Coffey, Lee & Williams, 1977). Refinements were carried out by full-matrix least-squares techniques with anisotropic thermal parameters. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974), including corrections for

Table 1. *Final positional and thermal parameters for  $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$*

$x, y, z$  are fractional coordinates; the isotropic temperature factor is of the form  $\exp(-B \sin^2 \theta / \lambda^2)$ .

	$x$	$y$	$z$	$B(\text{Å}^2)$
Pt	0.0	0.0	0.0	*
C	0.0550 (7)	0.1442 (7)	0.0	*
N	0.0864 (7)	0.2245 (7)	0.0	*
Cs	0.1574 (1)	0.6574	0.0	*
F(1)	0.0	0.5	0.15 (1)	3.2 (9)
F(2)	0.0	0.5	0.25	5.1 (13)

\* Anisotropic thermal parameters ( $\times 10^4$ ) of the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Pt	18.2 (5)	18.2	61 (2)	0	0	0
C	20 (5)	23 (5)	140 (29)	-1 (3)	0	0
N	45 (6)	34 (5)	203 (34)	-9 (4)	0	0
Cs	52.9 (9)	52.9	214 (4)	17.4 (5)	0	0

Table 2. Distances (Å) for  $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$ 

Superscripts refer to the following symmetry transformations of coordinates given in Table 1: (a)  $x, -y, \frac{1}{2} + z$ ; (b)  $x, 1 - y, -\frac{1}{2} + z$ ; (c)  $\frac{1}{2} - x, \frac{1}{2} + y, z$ ; (d)  $\frac{1}{2} - y, \frac{1}{2} - x, z$ .

Pt—Pt <sup>a</sup>	2.833 (1)	Cs—F(2)	3.234 (1)
Pt—C	2.015 (9)	Cs—F(1) <sup>b</sup>	3.52 (4)
C—N	1.13 (1)	Cs—N <sup>b</sup>	3.355 (5)
F(1)—F(2) <sup>b</sup>	2.27 (7)	Cs—N <sup>c</sup>	3.46 (1)
Cs—F(1)	3.03 (2)	Cs—N <sup>d</sup>	3.54 (1)

anomalous scattering for Pt and Cs. The F atoms were located on a difference Fourier map and were refined with isotropic thermal parameters and site occupancies of 0.195 for each of the eight symmetry-related F(1) positions and 0.39 for each of the four F(2) positions.

The final discrepancy indices based on all 407 data are  $R(F_o) = 0.040$ ,  $R(F_o^2) = 0.072$  and  $R_w(F_o^2) = 0.084$ .\* The positional and thermal parameters obtained from the final least-squares cycle are given in Table 1. Interatomic distances and angles are presented in Table 2.

**Discussion.** CsCP(FHF) is isostructural with RbCP(FHF) (Schultz, Coffey, Lee & Williams, 1977) except for the larger cell dimensions of the  $\text{Cs}^+$  salt. The crystal structure consists of planar  $\text{Pt}(\text{CN})_4^{1-}$  groups stacked along  $c$  with a Pt—Pt separation of  $c/2 = 2.833$  (1) Å (see Fig. 1). This compares with 2.798 (1) Å for RbCP(FHF). The rotation angle between neighboring  $\text{Pt}(\text{CN})_4^{1-}$  groups is  $41.7$  (5)°. The intramolecular tetracyanoplatinate bond distances and angles all appear to be normal.

The hydrogendifluoride  $(\text{F—H—F})^-$  ions are also aligned along  $c$ , with a  $\text{F}(1) \cdots \text{F}(2)$  distance of 2.27 (7) Å between certain positions. Although short  $\text{F} \cdots \text{F}$  contacts must be prohibited, it is still crystallographically possible to have up to 0.5 hydrogendifluoride ions per Pt atom. Disorder arises from the partial occupancy of the fluorine sites since the  $(\text{FHF})^- : \text{Pt}$  ratio is only 0.39:1. The triatomic  $(\text{F—H—F})^-$  positions are not correlated between neighboring chains. A model of the

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33315 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

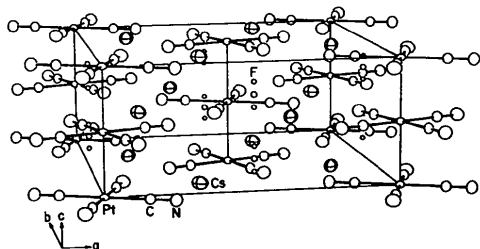


Fig. 1. Perspective view of the unit cell of  $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$ . The small circles represent the partially occupied fluorine positions. The thermal ellipsoids of the other atoms are drawn with a scale of 50% probability.

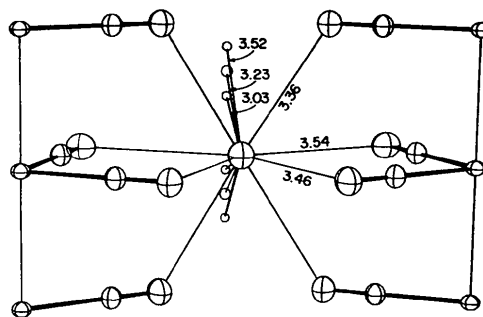


Fig. 2. A perspective view showing Coulombic  $[\text{Cs}^+ \cdots \text{X}^-]$  interactions in  $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$ .

possible positions of the  $(\text{F—H—F})^-$  anions has been previously presented in a schematic fashion (Schultz, Coffey, Lee & Williams, 1977).

CsCP(FHF) and RbCP(FHF) are the first known examples of partially oxidized tetracyanoplatinate complexes that are completely anhydrous. No evidence for water molecules was found based on the X-ray data, and this has been confirmed by thermal gravimetric analysis and IR spectroscopy (Basile, Ferraro & Williams, 1977).

In the absence of interchain hydrogen bonding in anhydrous CsCP(FHF), crystal stabilization must be due to  $\text{Cs}^+ \cdots \text{X}^-$  Coulombic interactions (see Fig. 2). From structural comparisons of CsCP(FHF) and RbCP(FHF) it appears that the Pt—Pt separation is directly related to the size of the cation. That is, the salt with the larger  $\text{Cs}^+$  cation has a longer Pt—Pt separation (2.83 vs 2.80 Å for the  $\text{Rb}^+$  salt) although both materials are otherwise isostructural and have essentially the same degree of partial oxidation ( $\sim 0.40$ , within experimental error). However, cations smaller than  $\text{Rb}^+$ , such as  $\text{K}^+$ , have a greater tendency to hydrate, which may be the reason why  $\text{K}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.30} \cdot 3\text{H}_2\text{O}$  is not isostructural with  $[\text{Cs}, \text{Rb}]\text{CP}(\text{FHF})$  and the Pt—Pt separation is relatively long at 2.91 Å (Williams, Gerrity & Schultz, 1977).

Preliminary four-probe room-temperature conductivity measurements on single crystals of CsCP(FHF) ranged from 200 to 2000  $\Omega^{-1} \text{cm}^{-1}$ , with the higher values obtained with larger, better formed crystals. This compares with our measured values of  $\sigma = 1600 \Omega^{-1} \text{cm}^{-1}$  for RbCP(FHF) and  $\sigma = 1050 \Omega^{-1} \text{cm}^{-1}$  for prototypic  $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$ .

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