centred by Si(1) atoms. It seems possible that β-Yb_5Sb_4 (Bodnar & Steinfink, 1967) is a stacking variant of the Eu_5As_4 structure. Very recently Cromer (1977) has reported the structure of Pu_5Rh_4 and Beznosikova, Chebotarev, Luk'yanov, Shapovalov & Timofeeva (1976) those of Pu_5Rh_4 and Pu_5Ir_4; these also have tiling units similar to those in Sm_5Ge_4 and details are given by Cromer (1977).

References

Bandurkin, G. A. & Dzhurinskii, B. F. (1973). *J. Struct. Chem. (USSR)*, **14**, 271–276.

Beznosikova, A. V., Chebotarev, N. T., Luk'yanov, A. S., Shapovalov, M. P. & Timofeeva, L. F. (1976). *Sov. At. Energy*, **40**, 495–498.

Bodnar, R. E. & Steinfink, H. (1967). *Inorg. Chem.* **6**, 327–330.

Brunton, G. & Steinfink, H. (1971). *Inorg. Chem.* **10**, 2301–2303.

Cromer, D. T. (1977). *Acta Cryst.* B**33**, 1993–1995.

Demel, J. T. & Gschneidner, K. A. (1969). *Mater. Nucl. Pays-Bas*, **29**, 111–120.

Geller, S. (1955). *Acta Cryst.* **8**, 15–21.

Hulliger, F. & Mooser, E. (1965). *Prog. Solid State Chem.* **2**, 300–377.

Iandelli, A. & Palenzona, A. (1969). *J. Less-Common Met.* **18**, 221–227.

Iglesias, J. & Steinfink, H. (1972). *J. Less-Common Met.* **26**, 45–52.

Merlo, F. & Fornasini, M. L. (1969). *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.* **46**, 265–269.

Ono, S., Hui, F. L., Despault, J. G., Calvert, L. D. & Taylor, J. B. (1971). *J. Less-Common Met.* **25**, 287–294.

Pearson, W. B. (1972). *The Crystal Chemistry and Physics of Metals and Alloys*, pp. 3, 202, 605, 628. Toronto: John Wiley.

Smart, M., Calvert, L. D. & Taylor, J. B. (1978). To be published.

Smith, G. S., Johnson, Q. & Tharp, A. G. (1967). *Acta Cryst.* **22**, 269–272.

Smith, G. S., Tharp, A. G. & Johnson, Q. (1966). *Nature (London)*, **210**, 1148–1149.

Taylor, J. B., Calvert, L. D., Utsunomiya, T., Wang, Y. & Despault, J. G. (1978). *J. Less-Common Met.* **57**, 39–51.

Taylor, J. B., Calvert, L. D. & Wang, Y. (1977). *J. Appl. Cryst.* **10**, 492–494.

Wang, Y., Bodnar, R. E. & Steinfink, H. (1966). *Inorg. Chem.* **5**, 1468–1470.

Wang, Y., Gabe, E. J., Calvert, L. D. & Taylor, J. B. (1976). *Acta Cryst.* B**32**, 1440–1445.

Wang, Y., Gabe, E. J., Calvert, L. D. & Taylor, J. B. (1977). *Acta Cryst.* B**33**, 131–133.

Wang, Y., Gabe, E. J., Calvert, L. D. & Taylor, J. B. (1978). To be published.

Acta Cryst. (1978). B**34**, 1965–1968

Structural Studies of Precursor and Partially Oxidized Conducting Complexes. XIV. An X-ray Diffraction Investigation of One-Dimensional Potassium Tetracyanoplatinate Bifluoride Trihydrate*

By Richard K. Brown, Paul L. Johnson, Thomas J. Lynch† and Jack M. Williams‡

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, *USA*

(*Received* 29 *August* 1977; *accepted* 1 *February* 1978)

Abstract. $K_2[Pt(CN)_4](FHF)_{0.3}.3H_2O$, KCP(FHF) hereafter, tetragonal, $P4mm$ (C^1_{4v}), $a = 9{\cdot}850$ (2), $c = 5{\cdot}846$ (1) Å, $Z = 2$, $D_m = 2{\cdot}61$, $D_x = 2{\cdot}67$ g cm^{-3}. A room-temperature single-crystal X-ray diffraction study was performed. The structural solution was obtained by assuming KCP(FHF) to be isostructural with $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$, KCP(Br), and by using difference Fourier mapping. The absolute configuration was determined by comparison of solutions utilizing *xyz versus xy$\bar{z}$* coordinates and application of Hamilton's R-factor significance test. Refinement using full-matrix least-squares techniques led to $R(F_o^2) = 0{\cdot}036$ for 876 independent data and to $R(F_o^2) = 0{\cdot}035$ for the 740 data with $F_o^2 > 1\sigma(F_o^2)$. The main structural feature is that the $[Pt(CN)_4]^{1.7-}$ groups stack to form Pt–Pt chains, with differing intrachain separations [Pt–Pt = 2·928 (1) and 2·918 (1) Å], which are parallel to **c**, as is the disordered $(F{-}H{-}F)^-$ anion array.

---

* Work performed under the auspices of the Division of Basic Energy Sciences of the US Department of Energy.

† Research participant sponsored by the Argonne Center for Educational Affairs; from Marist College, Poughkeepsie, New York.

‡ Author to whom correspondence should be addressed.

Introduction. As part of a continuing study of partially oxidized tetracyanoplatinate (POTCP) salts, we have conducted an X-ray diffraction analysis of $K_2[Pt(CN)_4](FHF)_{0.3}.3H_2O$, KCP(FHF). A prime motivation in these studies is that comparison of the molecular structures of KCP(FHF) and the prototype one-dimensional conductor $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ may be revealing in terms of electrical-conductivity differences which arise from the different anion types which may be incorporated in the 'KCP(X)' structure, $X = Cl^-$, Br^-, or $(FHF)^-$.

A crystal of KCP(FHF) (preparation described by Lynch & Williams, 1978) was mounted on a Syntex $P2_1$ four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·71069 Å). Preliminary photographs, and the lattice constants derived from automatic reflection centering, indicated the crystal class to be tetragonal with a = 9·850 (2) Å and c = 5·846 (1) Å. This unit cell suggested that KCP(FHF) is isostructural with KCP(Br) (Williams, Petersen, Gerdes & Peterson, 1974) where a = 9·907 (3) Å, c = 5·780 (2) Å, and the space group is $P4mm$. The needle-like crystal (elongated about **c**) chosen for the X-ray diffraction work had approximate dimensions 0·06 × 0·06 × 0·22 mm. The cell constants were verified as correct from three axial photographs. All three derived axial lengths were observed to be correct rather than submultiples of the true axial lengths as frequently occurs in X-ray analyses of these systems.

Intensity data were collected using the θ–2θ scan technique. The scan range was from [2θ(Mo $K\alpha_1$) − 1·0°] to [2θ(Mo $K\alpha_2$) + 1·0°]. Backgrounds (B_1 and B_2) were measured both at the beginning and at the end of the scan, each for one-half the total scan time. 3021 reflections with $2° \leq 2\theta \leq 60°$ within the full sphere were collected and processed. Three reference reflections were monitored every 50 measurements to ensure that the crystal was neither decomposing nor drifting and the maximum deviation from the average was 3%.

The net intensity (I) and its standard deviation [$\sigma(I)$] were calculated from $I = SC - (B_1 + B_2)$ and $\sigma(I) = [SC + (B_1 + B_2) + p^2I^2]^{1/2}$, where SC is the count during the scan and p (a factor to account for systematic error) was set equal to 0·03.

Structure factors were derived by applying Lorentz, polarization, and absorption corrections. For absorption corrections μ_{calc} = 138·2 cm^{-1} and the minimum and maximum transmission factors were 0·37 and 0·48 respectively. Structure factor averaging, based on the crystallographic fourfold axis and mirror planes bisecting the a and b axes, was carried out to yield 876 symmetry-independent reflections. Agreement factors after averaging were $R(F_o^2) = \sum (F_{ave}^2 - F_o^2)/\sum F_o^2 = 0{\cdot}033$ and $R_w(F_o^2) = [\sum w(F_{ave}^2 - F_o^2)^2/\sum wF_o^4]^{1/2} = 0{\cdot}055$.

Initial Fourier calculations, phased using only the Pt atom positions previously derived for KCP(Br), resulted in K, C, and N positional parameters consistent with the KCP(Br) structure. Water molecule O atom and possible F atom locations were obtained from difference maps. The resulting molecular structure is different from KCP(Br) only in that the F atom positional parameters, at ($\frac{1}{2},\frac{1}{2},z$), of the $(FHF)^-$ ion have different z values from those of Br^- in KCP(Br). The final positional coordinates are given in Table 1. The structure is illustrated in Fig. 1.

The final $R(F_o^2) = \sum |F_o^2 - F_c^2|/\sum F_o^2$ for the 740 data with $F_o^2 > 1{\cdot}0\sigma F_o^2$ was 0·035. $R(F_o^2)$ for all data = 0·036. $R_w(F_o^2)$ for the configuration corresponding to the values given in Table 1 was 0·0697 and that for the mirror-image model was 0·0802. According to the Hamilton R-factor ratio test (Hamilton, 1965), this difference is highly significant even at the 0·005 level.*

Table 1. *Positional parameters for* $K_2[Pt(CN)_4](FHF)_{0.3}.3H_2O$

The estimated standard deviations in parentheses here and in Table 2 refer to the least significant figures.

	x	y	z
Pt(1)	0·0000	0·0000	0·0000
Pt(2)	0·0000	0·0000	0·5009 (2)
C(1)	0·205 (1)	0·0000	−0·004 (3)
C(2)	0·141 (2)	0·141	0·495 (2)
N(1)	0·319 (1)	0·0000	
N(2)	0·227 (2)	0·227	0·512 (3)
K	0·1968 (3)	0·5000	0·741 (1)
O(1)	0·5000	0	0·405 (2)
O(2)	0·346 (2)	0·346	0·078 (2)
F(1)$^{(a)}$	0·5000	0·5000	0·67 (1)
F(2)$^{(a)}$	0·5000	0·5000	0·49 (1)
F(3)$^{(a)}$	0·5000	0·5000	0·34 (2)
F(4)$^{(a)}$	0·5000	0·5000	0·92 (3)

(a) The F atoms of $(FHF)^-$ are crystallographically disordered. The total chemical occupancy was refined by least squares to a value of 0·35 (2).

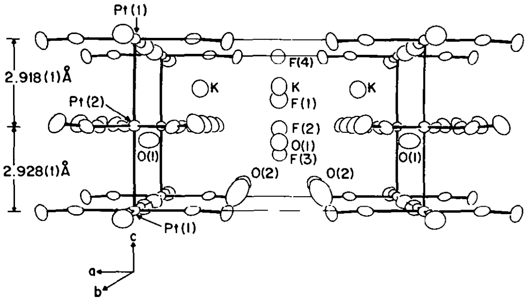

Fig. 1. Drawing of the unit cell of $K_2[Pt(CN)_4](FHF)_{0.3}.3H_2O$ showing the Pt atom chain and the unequal Pt–Pt distances. Hydrogen atoms are not shown.

---

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33389 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *for* $K_2[Pt(CN)_4](FHF)_{0.3}.3H_2O$

(*a*) Distances around Pt atoms			
Pt(1)–C(1)	2·02 (1)	Pt(1)–Pt(2)	2·928 (1)
Pt(2)–C(2)	1·96 (1)	$Pt(1)–Pt(2)^{I}$	2·918 (1)
(*b*) C–N distances in cyanide groups			
C(1)–N(1)	1·12 (1)	C(2)–N(2)	1·19 (2)
(*c*) K^+ ion interactions			
$K–O(1)^{II}$	2·76 (1)	K–N(2)	3·02 (1)
$K–O(2)^{III}$	2·88 (1)	$K–N(2)^{VII}$	3·02 (1)
$K–O(2)^{IV}$	2·88 (1)	K–F(1)	3·00 (2)
$K–N(1)^{V}$	2·99 (1)	K–F(2)	3·32 (2)
$K–N(1)^{VI}$	2·99 (1)	K–F(4)	3·15 (6)
(*d*) O atom interactions			
$O(1)–K^{II}$	2·76 (1)	$O(2)–O(2)^{XI}$	3·02 (2)
$O(1)–K^{VIII}$	2·76 (1)	$O(2)–O(2)^{VII}$	3·02 (2)
O(1)–N(1)	3·03 (2)	O(2)–F(1)	3·17 (3)
$O(1)–N(1)^{IX}$	3·03 (2)	$O(2)–F(2)^{I}$	3·21 (3)
$O(2)–K^{I}$	2·88 (1)	O(2)–F(3)	2·62 (7)
$O(2)–K^{X}$	2·88 (1)	$O(2)–F(4)^{I}$	2·33 (7)
O(2)–N(2)	3·03 (2)		
(*e*) F atom interactions*			
F(1)–F(2)	1·10 (5)	F(2)–F(3)	0·9 (1)
F(1)–F(3)	2·0 (1)	F(2)–F(4)	2·5 (2)
F(1)–F(4)	1·4 (2)	$F(2)–K^{II}$	3·32 (2)
F(1)–O(2)	3·17 (3)	$F(2)–K^{XIII}$	3·32 (2)
$F(1)–O(2)^{IX}$	3·17 (3)	$F(2)–O(2)^{III}$	3·21 (3)
$F(1)–O(2)^{XI}$	3·17 (3)	$F(2)–O(2)^{XIV}$	3·21 (3)
$F(1)–O(2)^{VII}$	3·17 (3)	$F(2)–O(2)^{XV}$	3·21 (3)
F(1)–K	3·00 (1)	$F(2)–O(2)^{IV}$	3·21 (3)
$F(1)–K^{XII}$	3·00 (1)	$F(3)–F(4)^{I}$	2·5 (2)
$F(1)–K^{II}$	3·00 (1)	F(3)–F(4)	3·4 (2)
$F(1)–K^{XIII}$	3·00 (1)	F(3)–O(2)	2·62 (7)
F(2)–K	3·32 (2)	$F(3)–O(2)^{XII}$	2·62 (7)
$F(2)–K^{XII}$	3·32 (2)	$F(3)–O(2)^{XI}$	2·62 (7)
		$F(3)–O(2)^{VII}$	2·62 (7)
(*f*) Angles of Pt chain and bonded atoms			
Pt(2)–Pt(1)–Pt(2)	180	$C(1)–Pt(1)–C(1)^{II}$	90·0 (1)
Pt(1)–C(1)–N(1)	177·5 (13)	$C(2)–Pt(2)–C(2)^{II}$	90·0 (7)
Pt(2)–C(2)–N(2)	174·5 (13)		

Symmetry code [if no superscript appears, (x,y,z) is implied]

(I)	$x, y, z-1$	(IX)	$1-x, -y, z$
(II)	y, x, z	(X)	$y, x, z-1$
(III)	$x, y, z+1$	(XI)	$1-x, y, z$
(IV)	$x, 1-y, z+1$	(XII)	$1-x, 1-y, z$
(V)	$y, x, z+1$	(XIII)	$1-y, 1-x, z$
(VI)	$-y, 1-x, z+1$	(XIV)	$1-x, 1-y, z+1$
(VII)	$x, 1-y, z$	(XV)	$1-x, y, z+1$
(VIII)	$1-y, -x, z$		

* These atoms are in crystallographic disorder and the shortest derived F···F separations are given. The two independent bifluoride anions correspond to F(1) with F(3) and F(2) with F(4).

The important bond lengths and angles are given in Table 2.

Atomic scattering factors were as listed in *International Tables for X-ray Crystallography* (1974*a*). For the Pt and K atoms, the anomalous-dispersion factors were applied as listed in *International Tables for X-ray Crystallography* (1974*b*).

Discussion. The columnar stacking of the square-planar $[Pt(CN)_4]^{1.7-}$ groups results in Pt atom chain formation parallel to **c**. The most striking finding is that the two crystallographically independent Pt–Pt distances are different [2·928 (1) and 2·918 (1) Å] and much longer than in KCP(Br) [2·88 (1) Å]. Therefore, although identical cations are involved in these two isostructural materials which both contain disordered anion arrays aligned parallel to **c**, it appears that the presence of the triatomic $(FHF)^-$ ion is the driving force behind the increased Pt–Pt chain distance. Since the degrees of partial oxidation (DPO) of the Pt atoms in KCP(Br) and KCP(FHF) also appear equal at 0·30, the increased Pt–Pt separations in the latter do not appear to be due to a decreased DPO.

Neighboring TCP groups in KCP(FHF) possess a staggered configuration with a 45° torsion angle. The Pt–C and C–N interatomic distances are in close agreement with values previously reported for tetracyanoplatinates. The important intramolecular bond lengths and angles are: Pt(1)–C(1) = 2·015 (12), Pt(2)–C(2) = 1·958 (12) Å; C(1)–N(1) = 1·119 (13), C(2)–N(2) = 1·189 (15) Å; and Pt(1)–C(1)–N(1) = 177·5 (13), Pt(2)–C(2)–N(2) = 174·5 (12)°.

From infrared spectroscopic measurements we have verified conclusively that this salt contains the $(F–H–F)^-$ ion (Basile, Ferraro & Williams, 1977). However, the precise location of the $(FHF)^-$ ion is difficult to assess because the expected Fourier map peak heights would be only approximately 1·5 times that of a H atom. Examination of a difference electron density map, phased on all atoms except F and H, yielded a series of peaks along the $\frac{1}{2},\frac{1}{2},z$ line. The observed z coordinates were 0·02, 0·49, 0·65, and 0·84. This corresponds to a disordered model for the bifluoride anion with both F–F distances being approximately 2·2 Å. This is in good agreement with the normal F–F separation of 2·26 Å in $(F–H–F)^-$ (see Williams & Schneemeyer, 1973). As might be expected, least-squares refinement of these positions gave rise to large coordinate shifts and errors (comparable to those of a H atom in the presence of Pt). Final parameters for the bifluoride anion are included in Tables 1 and 2. The derived structure is therefore similar to that of anhydrous $Rb_2[Pt(CN)_4](FHF)_{0.40}$ (Schultz, Coffey, Lee & Williams, 1977) in that both salts contain an $(F–H–F)^-$ ion array which is itself parallel to the Pt–Pt chain. The presence of water in KCP(FHF) is in marked contrast to the case of $Rb_2[Pt(CN)_4](FHF)_{0.40}$. Since no H atoms were located in this study, we can only speculate that the close isomorphism of KCP(Br) and KCP(FHF) results in the same pattern of hydrogen bonding. A more detailed analysis of hydrogen-bonding effects, water content, and bifluoride anion structure will have to await a neutron diffraction study.

In KCP(FHF), there are nine K^+ ion nearest neighbors with K—*X* distances ranging from 2·76 (1) to 3·32 (1) Å (see Table 2*c*). The O atom interactions are presented in Table 2(*d*) and range in distance from 2·76 (1) to 3·21 (3) Å.

References

Basile, L. J., Ferraro, J. R. & Williams, J. M. (1977). *J. Phys. Chem.* **66**, 4941–4942.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
International Tables for X-ray Crystallography (1974*a*). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974*b*). Vol. IV, pp. 149–150. Birmingham: Kynoch Press.
Lynch, T. J. & Williams, J. M. (1978). *Inorg. Synth.* **20**. In the press.
Schultz, A. J., Coffey, C. C., Lee, G. C. & Williams, J. M. (1977). *Inorg. Chem.* **16**, 2129–2131.
Williams, J. M., Petersen, J. L., Gerdes, H. M. & Peterson, S. W. (1974). *Phys. Rev. Lett.* **33**, 1079–1081.
Williams, J. M. & Schneemeyer, L. S. (1973). *J. Am. Chem. Soc.* **95**, 5780–5781.

Acta Cryst. (1978). B**34**, 1968–1969

Mercury(II) Chromate

By Claes Stålhandske

Inorganic Chemistry 2, *Chemical Center, University of Lund, PO Box* 740, *S*-220 07 *Lund* 7, *Sweden*

(*Received* 30 *January* 1978; *accepted* 21 *February* 1978)

Abstract. $HgCrO_4$, monoclinic, space group $P2_1/n$, $a = 7{\cdot}342\,(1)$, $b = 8{\cdot}522\,(1)$, $c = 5{\cdot}202\,(1)$ Å, $\beta = 94{\cdot}00\,(2)°$, $V = 343{\cdot}4$ Å^3, $Z = 4$, $D_x = 6{\cdot}12$ g cm^{-3}. The structure was refined to a final *R* of 0·049 for 1163 counter reflections. Each Hg atom is almost linearly bonded to two O atoms [Hg—O 2·10 (1), 2·12 (1) Å] of different chromate tetrahedra forming endless zigzag chains. The Cr—O distances are 1·70 (bridging) and 1·61 Å (terminal).

Introduction. This investigation is part of a research project on inorganic Hg^{II} compounds. At least three different Hg^{II} chromates exist, $HgCrO_4$, $HgCrO_4.\frac{1}{2}H_2O$ and $Hg_3O_2CrO_4$ (Aurivillius & Malmros, 1961). Commercially available Hg^{II} chromates often consist of mixtures of these three phases. $HgCrO_4.\frac{1}{2}H_2O$ has been studied both by X-rays and neutrons (Aurivillius, 1972; Aurivillius & Stålhandske, 1975). $Hg_3O_2CrO_4$ (and $Hg_3O_2SeO_4$) are isotypic with $Hg_3O_2SO_4$ (Aurivillius & Malmros, 1961); the latter was studied by Nagorsen, Lyng, Weiss & Weiss (1962).

Cell dimensions for $HgCrO_4$, determined from powder photographs, are in good agreement with those given by Aurivillius & Malmros (1961). A single crystal, 0·12 × 0·14 × 0·25 mm, was picked out from a commercial product and used in the data collection. The intensities were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The ω–2θ scan technique was used with a scan interval $\Delta\omega = (0{\cdot}8 + 0{\cdot}5 \tan\theta)°$ and a maximum time of 3·5 min for each reflexion. Of the 1508 reflexions with $\theta < 35°$ in one quadrant of reciprocal space, 1163 with $I > 3\sigma(I)$ were used in the structure analysis. Corrections were applied for Lorentz–polarization and absorption effects (μ = 487 cm^{-1}). The transmission factors, evaluated by numerical integration, varied from 0·009 to 0·056. The atomic positions were determined by Patterson and Fourier techniques. Full-matrix least-squares refinement was performed with anisotropic temperature factors for Hg and Cr and isotropic for O and with a parameter to correct for secondary extinction (Zachariasen, 1967). The form factors of Doyle & Turner (1968) were used with the anomalous dispersion

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	*y*	*z*
Hg	1583 (1)	366 (1)	2525 (1)
Cr	6637 (2)	1889 (2)	2766 (3)
O(1)	6055 (13)	3622 (11)	4078 (18)
O(2)	8471 (11)	1118 (11)	4388 (15)
O(3)	4934 (14)	711 (12)	2648 (20)
O(4)	7229 (12)	2215 (10)	37 (17)