H atoms were located as follows. Fig. 2(a) shows the difference projection from only $h0l$ data. This projection reveals the existence of H atoms but owing to considerable overlap only three of the eight, H(4), H(7) and H(8), are delineated with reasonable clarity. The other H atoms are distinguished individually, as shown in Fig. 2(b), by calculation of appropriate combinations of the first-layer ($h1l$) cosine (C_1) and sine (S_1) generalized difference projections with the zero-layer $h0l$ (designated O) difference projection. Thus, in sector A ($O + C_1 + S_1$), H(4), H(5) and H(6) attached to N, and H(7), H(8) attached to O(2), O(3) respectively are clearly portrayed. In sector B ($O - C_1 + S_1$), H(2) attached to C(3) is shown while H(3), also attached to C(3), appears clearly in sector D ($O + C_1 - S_1$). H(1) attached to C(2) is clearly depicted in sector C ($O - C_1 - S_1$).

Discussion. This work complements that on the closely-related structures of DL-aspartic acid (Amirthalingam & Ramachandran, 1955; Rao, Srinivasan & Valambal, 1968; Rao, 1973) and L-aspartic acid (Derissen, Endeman & Peerdeman, 1968). The bond lengths found in the former are consistent with those presented here, to within the limits of experimental error. The results for the latter are also consis-

tent with the present work except that the C(1)O(1)-O(2) carboxyl group is evidently ionized to form a zwitterion. In all three analyses, the C atom skeleton maintains a planar zigzag conformation.

References

AMIRTHALINGAM, V. & RAMACHANDRAN, G. N. (1955). Curr. Sci. 24, 294–295.

COCHRAN, W. & DYER, H. B. (1952). Acta Cryst. 5, 634–636.

DAWSON, B. (1953). Acta Cryst. 6, 81–87.

DAWSON, B. (1960). Acta Cryst. 13, 1034.

DAWSON, B. (1975). Advances in Structure Research by Diffraction Methods, Vol. 6, edited by R. MASON & W. HOPPE. Braunschweig: Vieweg and Pergamon Press.

DAWSON, B. & MATHIESON, A. McL. (1951). Acta Cryst. 4, 475–477.

DERISSEN, J. L., ENDEMAN, H. J. & PEERDEMAN, A. F. (1968). Acta Cryst. B24, 1349–1354.

FRIDRICHSONS, J. (1959). Amer. Min. 44, 200–201.

IUCr TENTH INTERNATIONAL CONGRESS (1975). Acta Cryst. A31, S236–S237 (especially Abstract 18.3-5).

MATHIESON, A. McL. (1952). Acta Cryst. 5, 332–341.

MATHIESON, A. McL. (1953). Acta Cryst. 6, 399–403.

RAO, S. T. (1973). Acta Cryst. B29, 1718–1720.

RAO, S. T., SRINIVASAN, R. & VALAMBAL, V. (1968). Ind. J. Pure Appl. Phys. 6, 523–529.

Structural Studies of Precursor and Partially Oxidized Conducting Complexes. III. A Neutron Diffraction Study of Barium Tetracyanoplatinate(II) Tetrahydrate*

By ROBERT L. MAFFLY,† PAUL L. JOHNSON AND JACK M. WILLIAMS‡

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

Abstract. Ba[Pt(CN)$_4$].4H$_2$O, monoclinic $C2/c$ (C_{2h}^6), $a = 12\cdot278\,(9)$, $b = 13\cdot882\,(10)$, $c = 6\cdot641\,(5)$ Å, $\beta = 107\cdot75\,(4)°$, $Z = 4$, $D_m = 3\cdot09\,(1)$, $D_x = 3\cdot13$ g cm^{-3}. A room-temperature, single-crystal neutron diffraction study was performed. The structural solution was obtained by direct methods, and refinement by full-matrix least-squares techniques gave $R(F_o^2) = 0\cdot052$ for 1437 observed reflections $> \sigma(F_o^2)$. The Pt atoms, at the centers of the planar tetracyanoplatinate anions, are arranged in a linear chain, separated by $3\cdot321\,(3)$ Å.

Introduction. As a result of our ongoing study of par-

tially oxidized tetracyanoplatinate conducting salts, we are able to explain why some cations are more favorable for the formation of these salts, while other cations are unsuitable. Alkali metal ions such as K$^+$ (Williams, Keefer, Washecheck & Enright, 1976; Williams, Petersen, Gerdes & Peterson, 1974) as well as the organic guanidium cation $|\mathrm{C(NH_2)_3}|^+$ (Williams, Cornish, Washecheck & Johnson, 1976), are all known to form partially oxidized tetracyanoplatinate compounds. To date, however, no such compounds with divalent cations have been prepared (Koch, Gebert & Williams, 1976). With this room-temperature, single-crystal neutron diffraction study of Ba[Pt(CN)$_4$].4H$_2$O, we are able to rationalize the non-existence of partially oxidized barium tetracyanoplatinates and, more generally, the entire series of tetracyanoplatinates which might contain divalent cations.

Ba[Pt(CN)$_4$].4H$_2$O was prepared as described by Koch, Abys & Williams (1976). Slow evaporation at room temperature of an aqueous Ba[Pt(CN)$_4$].4H$_2$O solution resulted in the formation of transparent, yellow-green single crystals. The crystal used for data collection weighed 19 mg. It was sealed in a lead-glass capillary and mounted for data collection, at the CP-5 research reactor, on the Chemistry Division fully automated four-circle neutron diffractometer. [The equipment has been described by Petersen, Dahl & Williams (1974).]

The conditions for diffraction were determined by preliminary neutron observations to be hkl ($h + k = 2n$) and $h0l$ ($l = 2n$). These conditions dictated that the space group be either $C2/c$ or Cc. The angular measurement of 25 automatically centered reflections, selected in the 2θ range 40–60°, followed by a least-squares analysis of the data, gave the lattice constants shown in the *Abstract*. These are in poor agreement with those reported for Ba[Pt(CN)$_4$].4D$_2$O in a recent two-dimensional neutron diffraction study (Dupont, Dideberg & Legrand, 1969). The final data consisted of 1670 reflections collected automatically with the θ–2θ step-scan mode, 0·1° step-scan intervals and with background measurements taken on both sides of each reflection peak. Data collection was complete to $\sin \theta/\lambda = 0·72$.

The program *MULTAN* (Germain, Main & Woolfson, 1971) was used to locate the Pt atom and both CN$^-$ ligands. A difference Fourier synthesis was used to locate the remaining atoms. Refinement was carried out by full-matrix least-squares techniques, with anisotropic thermal parameters and type 1 anisotropic extinction (Coppens & Hamilton, 1970) to $R(F_o^2) = \Sigma |F_o^2 - F_c^2|/\Sigma F_o^2 = 0·052$ for 1437 data $> \sigma(F_o^2)$. $R(F_o^2)$ for all data $= 0·054$. Space group $C2/c$ was confirmed by the successful refinement; consequently no calculations were made in the noncentrosymmetric space group Cc. The neutron scattering amplitudes used were

Table 2. *Interatomic distances* (Å) *and bond angles* (°)
for Ba[Pt(CN)$_4$].4H$_2$O

All distances are uncorrected for thermal motion unless otherwise noted.

(*a*) Bond distances and angles within the |Pt(CN)$_4$|$^{2-}$ anion

Pt(1)–C(1)	1·987 (2)	C(1)–N(1)	1·157 (1)
Pt(1)–C(2)	1·988 (2)	C(2)–N(2)	1·159 (1)
C(1)–Pt(1)–C(2)	88·71 (6)	Pt(1)–C(1)–N(1)	179·15 (8)
		Pt(1)–C(2)–N(2)	177·25 (9)

(*b*) Barium ion interactions*

Ba(1)–O(1^{i,ii})	2·858 (2)	Ba(1)–O(1^{vii,viii})	2·925 (2)
Ba(1)–O(2^{iii,iv})	2·876 (3)	Ba(1)–N(1^{iii,iv})	3·038 (2)
Ba(1)–N(2^{v,vi})	2·920 (2)		

(*c*) Water molecule O–H bond distances and angles

O(1)–H(11)	0·972 (4), 0·999 (4)†
O(1)–H(12)	0·949 (3), 1·001 (3)†
O(2)–H(21)	0·939 (4), 1·002 (4)†
O(2)–H(22)	0·929 (4), 1·021 (5)†
H(11)–O(1)–H(12)	103·2 (3)
H(21)–O(2)–H(22)	102·5 (4)

(*d*) Hydrogen atom interactions

H(11)–O(2^v)	1·845 (4)	O(1)–H(11)–O(2^v)	176·9 (3)
H(12)–N(1^{ix})	2·217 (4)	O(1)–H(12)–N(1^{ix})	132·3 (3)
H(21)–N(2^{iv})	2·262 (4)	O(2)–H(21)–N(2^{iv})	151·2 (4)
H(12)–N(1^x)	2·611 (4)	O(1)–H(12)–N(1^x)	104·3 (3)
H(22)–N(2^{xi})	2·617 (6)	O(2)–H(22)–N(2^{xi})	131·0 (5)
H(21)–N(1^v)	2·696 (6)	O(2)–H(21)–N(1^v)	105·6 (4)
H(11)–O(1^{xii})	2·729 (3)	O(1)–H(11)–O(1^{xii})	90·6 (2)
H(22)–N(1^{iii})	2·767 (6)	O(2)–H(22)–N(1^{iii})	116·5 (5)
H(22)–N(2^{iii})	2·981 (5)	O(2)–H(22)–N(2^{iii})	97·6 (3)

Symmetry code

(i)	$\frac{1}{2} - x, \frac{1}{2} - y, -z$	(vii)	$x - \frac{1}{2}, \frac{1}{2} + y, z$
(ii)	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$	(viii)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
(iii)	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$	(ix)	$x, y, z - 1$
(iv)	$x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$	(x)	$x, -y, z - \frac{1}{2}$
(v)	x, y, z	(xi)	$\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$
(vi)	$-x, y, \frac{1}{2} - z$	(xii)	$1 - x, y, \frac{1}{2} - z$

* Tenfold coordination is generated by two contacts per listed atom.

† Corrected for thermal motion, H assumed to ride on O.

Table 1. *Positional* ($\times 10^4$) *and thermal* ($\times 10^4$) *parameters for* Ba[Pt(CN)$_4$].4H$_2$O *and root-mean-square thermal displacements* (*in* Å $\times 10^3$) *of atoms along their principal ellipsoidal axes*

The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figure. The form of the temperature factor is exp[$-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$].

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	μ_1	μ_2	μ_3
Pt(1)	0	0	5000	22 (1)	17 (1)	92 (2)	1 (1)	9 (1)	–2 (1)	123 (1)	126 (1)	143 (1)
C(1)	1547 (1)	592 (1)	5871 (2)	25 (1)	25 (1)	139 (2)	–2 (1)	11 (1)	–2 (1)	131 (1)	158 (1)	174 (1)
C(2)	–667 (1)	1315 (1)	4464 (2)	32 (1)	19 (1)	156 (2)	3 (1)	20 (1)	6 (1)	130 (1)	151 (1)	181 (1)
N(1)	2442 (1)	947 (1)	6364 (2)	30 (1)	40 (1)	239 (2)	–9 (1)	13 (1)	–9 (1)	136 (1)	203 (1)	229 (1)
N(2)	–1021 (1)	2092 (1)	4120 (2)	56 (1)	22 (1)	300 (3)	8 (1)	47 (1)	21 (1)	135 (1)	195 (1)	251 (1)
Ba(1)	0	3699 (1)	2500	45 (1)	20 (1)	111 (3)	0	30 (2)	0	141 (2)	142 (3)	177 (2)
O(1)	4039 (1)	527 (1)	570 (2)	40 (1)	35 (1)	151 (3)	–1 (1)	22 (1)	7 (1)	166 (2)	170 (2)	190 (2)
O(2)	3613 (1)	1897 (1)	3367 (2)	47 (1)	37 (1)	203 (3)	5 (1)	15 (1)	11 (1)	167 (2)	196 (2)	217 (2)
H(11)	3921 (2)	1006 (2)	1553 (4)	75 (2)	55 (1)	218 (6)	5 (1)	41 (3)	–13 (3)	199 (4)	224 (3)	243 (3)
H(12)	3293 (2)	430 (3)	–375 (6)	52 (2)	81 (2)	348 (10)	–3 (1)	3 (3)	–36 (4)	181 (3)	258 (4)	310 (4)
H(21)	2816 (3)	1896 (3)	3094 (8)	58 (2)	96 (3)	493 (14)	8 (2)	46 (4)	–66 (5)	194 (4)	260 (4)	363 (5)
H(22)	3739 (4)	2483 (3)	2799 (9)	149 (4)	56 (2)	587 (18)	–1 (2)	43 (7)	86 (5)	192 (5)	314 (5)	391 (7)

as follows: $b_{Pt} = 0.950$, $b_C = 0.663$, $b_N = 0.940$, $b_{Ba} = 0.520$, $b_H = -0.372$ and $b_O = 0.575$, all in units of 10^{-12} cm. The refined positional and thermal parameters are listed in Table 1. Important bond lengths and angles are given in Table 2.*

Discussion. The crystal structure consists of nearly square-planar $[Pt(CN)_4]^{2-}$ anions stacked upon one another at the edges and center of the cell such that linear Pt chains are formed parallel to **c**. All Pt atoms are equivalent, having $\bar{1}$ site symmetry and occupying the fourfold site (a). The Pt—Pt distance is 3.321 (3) Å, half the length of the cell in the **c** direction. The $[Pt(CN)_4]^{2-}$ groups are tilted by $\sim 3°$ with respect to the **c** axis, as can be determined from the bond angles in Table 3. Adjacent $[Pt(CN)_4]^{2-}$ groups are almost totally staggered with torsion angles of nearly 45° in all

---

Table 3. *Torsion and tilt angles between adjacent* $[Pt(CN)_4]^{2-}$ *groups* (°)

(a) Torsion angles

C(2)—Pt(1)—Pt(1)—C(2)'	46.27 (7)
C(2)'—Pt(1)—Pt(1)—C(1)	42.44 (4)
C(1)—Pt(1)—Pt(1)—C(1)'	48.85 (7)

(b) Tilt of CN⁻ groups with respect to the c axis

C(1)—Pt(1)—Pt(1)'	89.99 (5)
C(2)—Pt(1)—Pt(1)'	86.94 (4)

cases (see Table 3). This is unusual in that we have previously observed fully staggered cyanide groups in the partially oxidized compounds only when the Pt—Pt distance is much shorter (*e.g.* 2.96 Å in $K_{1.75}[Pt(CN)_4].1.5H_2O$). The more eclipsed configurations observed in Pt^{II} compounds generally accompany longer Pt—Pt separations, *e.g.* 3.48 Å in $K_2[Pt(CN)_4].3H_2O$.

All Ba cations are crystallographically equivalent and occupy the fourfold sites (e) with a site symmetry of 2. Surrounding each Ba^{2+} cation are six water molecules and four cyanides (see Table 2 for interaction distances). All these near neighbors are at distances roughly equal to those predicted by van der Waals radii. The ten coordinating groups are three more than surround K^+ in $K_2[Pt(CN)_4].3H_2O$ (Washecheck, Peterson, Reis & Williams, 1976). This difference is not surprising, and is apparently a result of the dipositive charge on Ba^{2+}, compared with a monopositive charge on K^+. This additional charge also provides the driving force for higher cation—water coordination numbers in divalent Pt^{II} cyanides, *e.g.* $Mg[Pt(CN)_4].7H_2O$, $Sr[Pt(CN)_4].5H_2O$, and $Ca[Pt(CN)_4].5H_2O$ (Moreau-Colin, 1972). The water molecules also interact extensively with the cyanide groups, as shown in Fig. 1. H(11), H(12), and H(21) all form single, strong hydrogen bonds and also weaker interactions $(H \cdots X \ 2.6 \ Å)$ which are listed in Table 2(d). H(22) has no strong hydrogen bonds but there are three weaker interactions involving this atom. Because of the electrostatic $CN^- \cdots Ba^{2+}$ and dipolar $CN^- \cdots H_2O$ interactions, the cyanides are forced into the aforementioned non-eclipsed configuration. It appears that partially oxidized Ba tetracyanoplatinates do not form because the steric interactions between the bulky ten-coordinate Ba^{2+} ions (see Table 2b) favor larger $(> 3.2 \ Å)$ Pt—Pt separations.
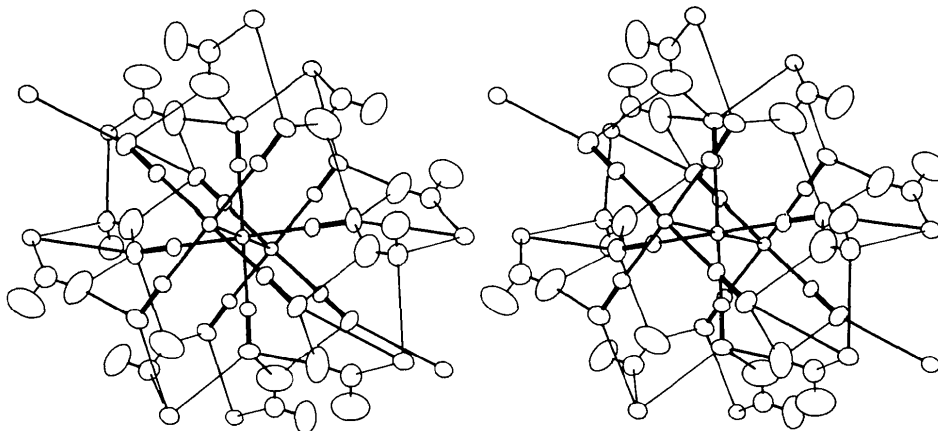

Fig. 1. A stereo view of Pt—Pt chain (c axis) and the water molecule interactions between the cyanide groups and the Ba ions. Ellipsoids are shown at 50% probability.

References

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.

DUPONT, L., DIDEBERG, O. & LEGRAND, E. (1969). *Bull. Soc. Roy. Sci. Liège*, 38, 503–508.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

KOCH, T. R., ABYS, J. A. & WILLIAMS, J. M. (1976). *Inorg. Synth.* 19. In the press.

KOCH, T. R., GEBERT, E. & WILLIAMS, J. M. (1976). *J. Amer. Chem. Soc.* 98, 4017–4018.

MOREAU-COLIN, M. L. (1972). *Struct. Bond.* 10, 167–190.

PETERSEN, J. L., DAHL, L. F. & WILLIAMS, J. M. (1974). *J. Amer. Chem. Soc.* 96, 6610–6620.

WASHECHECK, D. M., PETERSON, S. W., REIS, A. H. JR & WILLIAMS, J. M. (1976). *Inorg. Chem.* 15, 74–78.

WILLIAMS, J. M., CORNISH, T. F., WASHECHECK, D. M. & JOHNSON, P. L. (1976). Amer. Cryst. Assoc. Meeting, Aug. 9–12, Abstract G1.

WILLIAMS, J. M., KEEFER, K. D., WASHECHECK, D. M. & ENRIGHT, N. P. (1976). *Inorg. Chem.* 15, 2446–2455.

WILLIAMS, J. M., PETERSEN, J. L., GERDES, H. M. & PETERSON, S. W. (1974). *Phys. Rev. Lett.* 33, 1079–1081.

Structural Studies of Precursor and Partially Oxidized Conducting Complexes. IV. A Neutron Diffraction Study of Dirubidium Tetracyanoplatinate(IV) Dibromide*

BY GREGORY F. NEEDHAM,† PAUL L. JOHNSON, THOMAS F. CORNISH† AND JACK M. WILLIAMS‡

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

Abstract. $Rb_2[Pt(CN)_4Br_2]$, monoclinic, $P2_1/c$ (C_{2h}^5), $a = 7.281$ (3), $b = 9.271$ (4), $c = 8.960$ (3) Å, $\beta = 106.65$ (2)°, $Z = 2$, $D_m = 3.5$ (1), $D_c = 3.61$ g cm^{-3}. A room-temperature, single-crystal neutron diffraction study was performed. The structure was solved by direct methods and refined by full-matrix least-squares techniques to $R(F_o^2) = 0.038$ for 1322 observed reflections $> \sigma(F_o^2)$. The structure consists of octahedrally coordinated platinum(IV) groups interacting with the rubidium ions.

Introduction. As part of a continuing study of partially oxidized tetracyanoplatinate conducting salts, and their starting materials, we have performed a room-temperature neutron diffraction analysis of $Rb_2[Pt(CN)_4Br_2]$. Use of the analogous compound $K_2[Pt(CN)_4Br_2]$ is a standard method in preparing the well-known one-dimensional conductor $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ (Abys, Enright, Gerdes, Hall & Williams, 1976) and therefore $Rb_2[Pt(CN)_4Br_2]$ is expected to be the precursor of a corresponding partially oxidized Br-deficient compound.

The compound $Ba[Pt(CN)_4]\cdot4H_2O$ [preparation described by Koch, Abys & Williams (1976)] was used to prepare single crystals of $Rb_2[Pt(CN)_4Br_2]$ by adding Rb_2SO_4 to a solution of $Ba[Pt(CN)_4]\cdot4H_2O$ heated to 70°C. After stirring, the $BaSO_4$ was removed by filtration. Br_2 was then added and the excess was driven off. Single, transparent, orange crystals were obtained from aqueous solution by slow evaporation.

Preliminary neutron observations gave the conditions for diffraction as $h0l$ ($l = 2n$) and $0k0$ ($k = 2n$) which fixed the space group as $P2_1/c$. The crystal selected for data collection weighed 96 mg. After being sealed in a lead-glass capillary it was mounted on the Chemistry Division four-circle neutron diffractometer at the CP-5 research reactor. [This apparatus has been described by Petersen, Dahl & Williams (1974).] The neutron wavelength of 1.142 (1) Å was obtained with a Be crystal monochromator set at $\theta_m = 30°$. The cell parameters were determined from angular measurement of 30 automatically centered reflections, chosen in the 2θ range 40–60°. The least-squares-determined lattice parameters are given in the *Abstract*. 1557 data in the *hkl* octant, with 1322 $> \sigma(F_o^2)$, were automatically collected by the θ–2θ scan mode with 0.1° step-scan intervals. Background intensity measurements were taken on both sides of the peak. Two reference reflections were monitored every 80 measurements to assure that the crystal was neither decomposing nor drifting. These observations deviated only 1.5% from the mean. Data collection was complete out to $2\theta = 100°$. Structure factors were derived by applying Lorentz and ab-

---