Structural Studies of Precursor and Partially Oxidized Conducting Complexes. XI. A Neutron Diffraction Study of Barium Dibromotetracyanoplatinate(IV) Hydrate*

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Abstract. $Ba[Pt(CN)_4Br_2].4.5H_2O$, tetragonal, $P4/mnc$ (D_{4h}^6), $a = 9.425$ (3), $c = 17.085$ (6) Å, $Z = 4$, $D_m = 2.96$, $D_c = 2.96$ g cm^{-3}. The structure was determined by direct methods. 2842 reflections were collected with single-crystal neutron-diffraction techniques and yielded 1217 independent reflections upon averaging; these were refined to an agreement factor of $R(F_o^2) = 0.056$ for all observed data and $R(F_o^2) = 0.053$ for 999 data with $F_o^2 > 1\sigma(F_o^2)$. The structure consists of octahedrally coordinated Pt^{IV} metal atoms, one Ba^{2+} ion, and two H$_2$O molecules (one O and five H atoms are in crystallographic disorder). The Ba^{2+} ion is highly coordinated with nine nearest neighbors.

Introduction. Preliminary X-ray photographs showed the crystal to be tetragonal and furnished preliminary cell constants. The following systematic absences were observed in a general survey: $0kl$ when $k + l \neq 2n$ and hhl when $l \neq 2n$. These conditions established that the space group was either centrosymmetric $P4/mnc$ or noncentrosymmetric $P4nc$. Cell constants were established by centering 30 reflections and carrying out a least-squares analysis [$\lambda = 1.142$ (1) Å] of the determined angles 2θ, χ and φ.

A large crystal (5.9 × 5.3 × 4.1 mm weighing 237 mg) was mounted in a lead-glass capillary for the neutron diffraction studies. The neutron source used was the Argonne National Laboratory CP-5 reactor; the diffractometer used was a fully automated (Sigma 5 computer control) four-circle instrument which has been described by Petersen, Dahl & Williams (1974).

Data were collected with a θ–2θ step-scan with an interval of 0.1° in 2θ. The scan widths were varied for different ranges of 2θ according to the observed peak breadth. The background was established by measuring the intensity at each extremity of the scan. Two standards were measured after every 50 reflections to monitor possible crystal movement or decomposition (maximum variation = 5%).

Data were collected to a minimum d spacing of 0.697 Å [$\lambda = 1.142$ (1) Å]. 2842 data were collected. Averaging of all data yielded 1217 independent reflections of which 999 had $F_o^2 > 1\sigma(F_o^2)$. Structure factors were derived by applying Lorentz and absorption corrections ($\mu = 1.34$ cm^{-1}). The transmission coefficients ranged from 0.31 to 0.45. Standard errors were assigned to the data with the standard counting statistics formula with $(0.05I)^2$ added to the variances to adjust for systematic error. The data were placed on an approximately absolute scale by comparison with a standard NaCl crystal.

Space group $P4/mnc$ was chosen because of the intensity statistics and the structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) to locate the Pt, C, N, Br, Ba, and O atoms. We decided at this point to adopt a model in which the O(2) site was crystallographically disordered. Because the O(2) atom was located on a fourfold rotation axis around the c crystallographic axis, full occupancy of the O(2) site would place two O atoms ~0.6 Å apart. Fourier and difference Fourier maps were then calculated. It was observed that the H atoms had alternate positions, so a

Table 1. *Fractional atomic coordinates for* $Ba[Pt(CN)_4Br_2].4.5H_2O$

The estimated deviations in parentheses for this and the following table refer to the least significant figure.

	x	y	z
Pt	0 (0)	0.5 (0)	0 (0)
C	0.1450 (1)	0.4585 (1)	0.0826 (1)
N	0.2301 (1)	0.4381 (1)	0.1294 (1)
Br	0.0804 (1)	0.7508 (1)	0 (0)
Ba	0 (0)	0 (0)	0.2988 (1)
O(1)	0.2082 (3)	0.1153 (4)	0.2021 (2)
O(2)*	0.5 (0)	0.5 (0)	0.0276 (4)
H(11a)*	0.1921 (14)	0.2095 (13)	0.1788 (9)
H(11b)*	0.2821 (12)	0.1578 (16)	0.2239 (6)
H(12a)*	0.2500 (28)	0.0578 (29)	0.1684 (16)
H(12b)*	0.2209 (18)	0.1170 (20)	0.1498 (7)
H(21)*	0.4190 (19)	0.4546 (44)	0 (0)

* This atom is in crystallographic disorder, *i.e.* all H atoms are of half occupancy.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)
for $Ba[Pt(CN)_4Br_2].4.5H_2O$

Superscripts refer to symmetry positions: (i) x,y,z; (ii) $-x, -y, z$; (iii) $-y, x, z$; (iv) $y, -x, z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vii) $-\frac{1}{2}+y, -\frac{1}{2}+x, \frac{1}{2}-z$; (viii) $\frac{1}{2}-y, \frac{1}{2}-x, \frac{1}{2}-z$; (ix) $-x, 1-y, z$; (x) $x, y, -z$; (xi) $-x, 1-y, -z$; (xii) $1-x, 1-y, z$.

(a) Distances around the Pt atom and the C—N distance in the cyanide group

Pt–C	2.003 (1)	Pt–Br	2.482 (1)
Pt–N	3.152 (1)	C–N	1.149 (1)

(b) Water molecule distances

O(1)–H(11a)*	0.985 (12)	O(1)–H(12b)*	0.903 (12)
O(1)–H(11b)*	0.885 (12)	O(2)*–H(21)*	0.994 (14)
O(1)–H(12a)*	0.884 (21)		

(c) Barium ion interactions

Ba–O(1^i)	2.785 (2)	Ba–N^{vi}	2.884 (1)
Ba–O(1^{ii})	2.785 (2)	Ba–N^{vii}	2.884 (1)
Ba–O(1^{iii})	2.785 (2)	Ba–N^{viii}	2.884 (1)
Ba–O(1^{iv})	2.785 (2)	Ba–O(2^v)	2.967 (8)
Ba–N	2.884 (1)		

(d) Angles of bonded atoms

C^i–Pt–C^{ix}	90.41 (6)	H(11a)*–O(1)–H(12a)*	111 (2)
C^i–Pt–C^x	89.59 (6)	H(11b)*–O(1)–H(12b)*	108 (1)
C^i–Pt–C^{xi}	180.0 (0)	H(21^i)*–O(2)*–H(21^{xii})*	123.3 (9)
Pt–C–N	178.08 (9)		

* This atom is in crystallographic disorder. Only the chemically reasonable (water molecule) bond angles and distances are given.

disordered model for the H atoms was adopted. Refinement was carried out with full-matrix least-squares techniques with anisotropic thermal parameters. The final $R(F_o^2) = \Sigma |F_o^2 - F_c^2|/\Sigma F_o^2$ for the 999 data $>1.0\sigma$ was 0.053 while $R(F_o^2)$ for all 1217 data was 0.056. The standard deviation of an observation of unit weight was 1.07 with all data. The neutron scattering amplitudes were as follows: $b_{Pt} = 0.95$, $b_C = 0.665$, $b_N = 0.94$, $b_{Br} = 0.68$, $b_{Ba} = 0.52$, $b_O = 0.58$, and $b_H = -0.374$ all in units of 10^{-12} cm (Bacon, 1972).

Since a very satisfactory solution was reached in the space group $P4/mnc$, no refinement was attempted in the space group $P4nc$. The refined positional parameters are in Table 1,* bond lengths and angles in Table 2.

Discussion. There has been considerable recent interest in platinocyanide complexes which form unusual Pt–Pt metal atom chains. However, as we have recently reported (Koch, Gebert & Williams, 1976), there has as yet been no partially oxidized tetracyanoplatinate (POTCP) complex prepared which contains a *divalent*
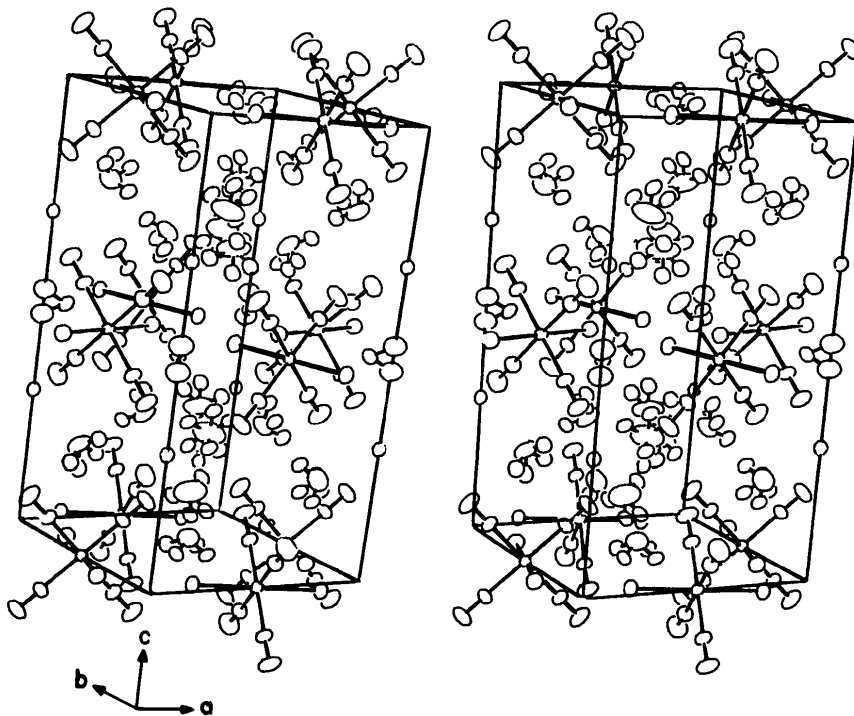
Fig. 1. Stereoscopic drawing of the unit cell of $Ba[Pt(CN)_4Br_2].4.5H_2O$. For clarity, the thermal ellipsoids of the H atoms have been reduced.

cation. We have therefore undertaken the study of the molecular structures of platinocyanide complexes containing divalent cations in order to compare their structures with those of platinocyanide complexes containing *monovalent* cations. Within this class of compounds, we have recently reported a complete molecular study of $Ba[Pt(CN)_4].4H_2O$ (Maffly, Johnson & Williams, 1977).

The crystal structure of $Ba[Pt(CN)_4Br_2].4\cdot5H_2O$ consists of octahedrally coordinated Pt^{IV} atoms in which the cyanide groups form a nearly square planar configuration around the Pt atom, and the Br atoms occupy the axial positions. There are also two independent H_2O sites (one O and five H atoms are in disorder) and one Ba^{2+} ion in the structure. A stereoview of the unit cell (*ORTEP*, Johnson, 1965) is shown in Fig. 1.

The Ba^{2+} ion is highly coordinated with nine nearest neighbors. In the corresponding Pt^{II} complex, $Ba[Pt(CN)_4].4H_2O$, we also observed a highly coordinated Ba^{2+} ion with ten nearest neighbors.

In this hydrated complex, both independent H_2O sites contain atoms which are in crystallographic disorder. The O(1) atom is in a fully occupied site; the $H_2O(1)$ molecule appears to pivot about the fixed O(1) atom which results in four H atoms of $H_2O(1)$ in crystallographic disorder. The $H_2O(2)$ molecule contains one H and one O atom in disorder. Because of these disordered atoms, the H—O—H bond angles in both H_2O molecules are not accurately determined (see Table 2*d*).

Two precursor Pt^{IV} complexes containing *monovalent* cations which are important in the preparation of POTCP salts are $K_2[Pt(CN)_4Br_2]$ and $Rb_2[Pt(CN)_4Cl_2]$. From these salts the partially oxidized complexes $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ (Abys, Enright, Hall, Gerdes & Williams, 1977) and $Rb_2[Pt(CN)_4]Cl_{0.3}.3H_2O$ have been prepared (Coffey & Williams, 1977).

As we have previously noted, $Ba[Pt(CN)_4Br_2].4\cdot5H_2O$ is *not* a precursor in the formation of any known POTCP complex. In contrast, both $K_2[Pt(CN)_4Br_2]$ and $Rb_2[Pt(CN)_4Cl_2]$ are anhydrous in the solid state. It is also interesting that in $K_2[Pt(CN)_4Br_2]$ two Br^- ions lie within the eightfold coordination sphere of the K^+ ion (Washecheck, Johnson, Koch & Williams, 1977). However, the Ba^{2+} ion in the complex

$Ba[Pt(CN)_4Br_2].4\cdot5H_2O$ has *no* Br^- ion within its nearest neighbor coordination sphere of nine atoms (see Table 2*c*). Similarly, in another hydrated Pt^{IV} complex, $Na_2[Pt(CN)_4Br_2].2H_2O$, we have *not* observed Br^- in the sixfold coordination sphere of the Na^+ ion (Maffly, Johnson, Koch & Williams, 1977). In keeping with this finding we have been unable to prepare $Na_2[Pt(CN)_4]X_{0.3}.yH_2O$ ($X = Cl, Br$).

Since these preparative reactions are carried out in aqueous solution, the cation–halide separation in the precursor crystal might appear to be unimportant. However, we have observed a novel solid-state auto-reduction reaction in which the compound $K_2[Pt(CN)_4Br_2]$ slowly decomposes (in the presence of H_2O vapor) to form the POTCP complex $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ (Washecheck, Johnson, Koch & Williams, 1977). It is likely that H_2O diffuses into the crystal and that Br_2 is released from the lattice with concomitant reduction of Pt^{4+} to $Pt^{2\cdot3+}$. These results suggest that the crystal structures of these Pt^{IV} complexes may be most important in predicting the possible formation of one-dimensional POTCP conductors containing halide ion.

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