

A Neutron Diffraction Study of Disodium Dibromotetracyanoplatinate Dihydrate*†

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Abstract. $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$, orthorhombic, *Pnma* (D_{2h}^{16}), $a = 11.949(11)$, $b = 15.124(14)$, $c = 6.487(6)$ Å, $Z = 4$, $D_m = 3.06$, $D_x = 3.065$ 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 $R(F_o^2) = 0.068$ for 1447 observed reflections $> 1\sigma(F_o^2)$. The structure consists of octahedrally coordinated platinum(IV) complex anions interacting with both the sodium cations and the waters of hydration.

Introduction. As part of a continuing study of partially oxidized tetracyanoplatinate conducting salts and their starting materials, we have performed a neutron diffraction analysis of $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$. Utilization of the compound $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_2]$ is a standard method in the preparation of the well known one-dimensional conductor $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ (Abys, Enright, Gerdes, Hall & Williams, 1976) and therefore $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$ might be expected to be the precursor of a corresponding partially oxidized, bromide-deficient compound. In fact, $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot x\text{H}_2\text{O}$ has been reported (Comès, Lambert, Launois & Zeller, 1973) although we have to date been unable to prepare a similar compound.

The compound $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ [preparation described by Koch, Abys & Williams (1976)] was used to prepare single crystals of $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$. Na_2SO_4 was added to an aqueous solution of $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$, and BaSO_4 removed by filtration. Bromine was added with stirring and heating until excess was driven off. Single, transparent, orange crystals were obtained from this aqueous solution by evaporation. Chemical analysis for Pt, C, N, Br, and O verified the compound formula given here.

Preliminary neutron observations gave the conditions for diffraction as $0kl$ ($k + l = 2n$) and $hk0$ ($h = 2n$) which determined the space group to be *Pnma* or *Pn2₁a*. The crystal selected for data collection weighed 25 mg. For protection from the atmosphere it was sealed in a lead-glass capillary and mounted for data collection on the Chemistry Division four-circle neutron diffractometer at the CP-5 research reactor. [This apparatus has been described by Peterson, Dahl & Williams (1974)]. The neutron wavelength of 1.142(1) Å was obtained with a Be crystal monochromator set at $\theta_m = 30^\circ$. The cell parameters were determined by least squares from angular measurements of 25 automatically centered reflections, chosen in the 2θ range 20–60°. 1885 data in the hkl octant, with 1447 $> \sigma(F_o^2)$, were automatically collected with the θ - 2θ scan mode, and 0.1° 2θ steps. Background intensity measurements were taken on both sides of the peak. Two reference reflections were monitored every 50 measurements to ensure that the crystal was neither decomposing nor drifting. Data collection was complete to $\sin \theta/\lambda = 0.72$. Standard errors were assigned to the data with the standard counting statistics formula, with $(0.05I)^2$ added to adjust for systematic error. Structure factors were derived by applying Lorentz and absorption corrections ($\mu = 0.905$ cm⁻¹) and the magnitude of the transmission factors ranged from 0.78 to 0.88.

The structure was solved first by *MULTAN* (Germain, Main & Woolfson, 1971) to locate the Pt atom and both CN⁻ groups and the remaining atoms were then identified with Fourier and difference-Fourier methods. Refinement was by full-matrix least-squares techniques using first isotropic and then anisotropic thermal parameters. The final $R(F_o^2) = \sum |F_o^2 - F_c^2| / \sum F_o^2$ for the 1447 data $> \sigma$ was 0.068. $R(F_o^2)$ for all data = 0.074. The final goodness-of-fit was 1.02. The successful refinement in *Pnma* was taken as confirmation of the correctness of this space group and no calculations were made in space group *Pn2₁a*. The neutron scattering amplitudes used were as follows: $b_{\text{Pt}} = 0.950$, $b_{\text{C}} = 0.663$, $b_{\text{N}} = 0.940$, $b_{\text{O}} = 0.575$, $b_{\text{H}} = -0.372$, and $b_{\text{Na}} = 0.351$, all in units of 10^{-12} cm. The refined positional and thermal parameters are given in

* Structural Studies of Precursor and Partially Oxidized Conducting Complexes. II.

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Table 1. Positional ($\times 10^4$) and thermal ($\times 10^4$) parameters for $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$ and root-mean-square thermal displacements ($\text{\AA} \times 10^3$) 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 $\exp\{-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl\} \times 10^{-4}$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	μ_1	μ_2	μ_3
Pt(1)	-71 (1)	7500	5644 (2)	22 (1)	13 (1)	83 (2)	0	-5 (1)	0	120 (2)	123 (2)	138 (2)
C(1)	-1007 (1)	6567 (1)	4291 (2)	32 (1)	17 (1)	119 (3)	-3 (1)	-12 (1)	-5 (1)	127 (2)	152 (2)	171 (2)
C(2)	858 (1)	6546 (1)	6933 (2)	33 (1)	17 (1)	127 (3)	4 (1)	-14 (1)	5 (1)	124 (2)	156 (2)	177 (2)
N(1)	-1532 (1)	6028 (1)	3482 (2)	49 (1)	23 (1)	195 (3)	-8 (1)	-23 (1)	-15 (1)	133 (2)	197 (1)	219 (1)
N(2)	1380 (1)	5967 (1)	7583 (2)	55 (1)	21 (1)	196 (3)	9 (1)	-26 (1)	9 (1)	132 (2)	193 (1)	226 (1)
Br(1)	1313 (2)	2500	1305 (3)	42 (1)	41 (1)	128 (4)	0	18 (2)	0	147 (3)	189 (3)	217 (3)
Br(2)	3783 (2)	2500	7636 (3)	42 (1)	33 (1)	140 (4)	0	-25 (2)	0	143 (3)	196 (2)	199 (3)
O(1)	3947 (1)	175 (1)	7114 (3)	44 (1)	42 (1)	175 (4)	-1 (1)	-9 (2)	6 (2)	172 (2)	195 (2)	222 (2)
Na(1)	2389 (2)	247 (2)	9522 (4)	47 (2)	39 (1)	111 (5)	-5 (1)	-10 (2)	5 (2)	150 (4)	182 (3)	217 (3)
H(1)	4614 (3)	-114 (4)	7393 (9)	72 (3)	100 (3)	387 (14)	27 (3)	-27 (5)	19 (6)	200 (5)	293 (5)	354 (6)
H(2)	4151 (4)	759 (3)	6771 (9)	122 (4)	58 (2)	406 (15)	-33 (3)	15 (7)	13 (5)	211 (5)	297 (6)	331 (6)

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$) for $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$

All distances are uncorrected for thermal motion unless otherwise noted.

(a) Around Pt atoms

Pt(1)—C(1)	2.002 (2)	Pt(1)—Br(1)	2.474 (3)
Pt(1)—C(2)	2.004 (2)	Pt(1)—Br(2)	2.485 (3)

(b) Cyanide groups

C(1)—N(1)	1.155 (2)	C(2)—N(2)	1.156 (2)
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(c) Na^+ ion interactions

Na(1)—O(1 ^{vi})	2.405 (4)	Na(1)—N(2 ^{viii})	2.530 (3)
Na(1)—O(1 ⁱ)	2.433 (4)	Na(1)—N(1 ⁱⁱⁱ)	2.656 (3)
Na(1)—N(1 ⁱⁱ)	2.499 (3)	Na(1)—N(2 ^{iv})	2.700 (3)

(d) Water molecule O—H

O(1)—H(1)	0.927 (5), 0.994 (5),* 1.084 (5)†
O(1)—H(2)	0.943 (6), 1.006 (6),* 1.082 (6)†
H(1)—O(1)—H(2)	105.4 (5)

(e) H atom interactions

H(1)—N(2 ⁱⁱⁱ)	2.473 (5)	O(1)—H(1)—N(2 ⁱⁱⁱ)	168.8 (5)
H(1)—N(1 ^{iv})	2.955 (6)	O(1)—H(1)—N(1 ^{iv})	116.0 (5)
H(2)—Br(2 ⁱ)	2.729 (6)	O(1)—H(2)—Br(2 ⁱ)	144.5 (5)
H(2)—N(2 ^v)	2.808 (7)	O(1)—H(2)—N(2 ^v)	106.0 (4)

(f) Angles within the coordination sphere of Pt

C(1)—Pt(1)—C(1)′	89.6 (1)	C(2)—Pt(1)—C(2)′	92.1 (1)
C(1)—Pt(1)—C(2)	89.1 (1)	C(2)—Pt(1)—Br(1)	89.9 (1)
C(1)—Pt(1)—C(2)	178.5 (1)	C(2)—Pt(1)—Br(2)	89.1 (1)
C(1)—Pt(1)—Br(1)	90.9 (1)	Br(1)—Pt(1)—Br(2)	178.6 (1)
C(1)—Pt(1)—Br(2)	90.1 (1)		

Superscripts refer to the following symmetry transformations:

- (i) *x, y, z*; (ii) $-x, -\frac{1}{2} + y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z$; (vi) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (vii) $x, \frac{1}{2} - y, z$.

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

† Corrected for thermal motion, atoms assumed to move independently.

Table 1 and important bond lengths and angles in Table 2.*

Discussion. The interatomic distances between the Pt, C and N atoms are in close agreement with values previously reported for tetracyanoplatinates (e.g. Washecheck, Petersen, Reis & Williams, 1976; Williams, Keefer, Washecheck & Enright, 1976). The cyanides form a planar arrangement around the central Pt. Br atoms occupy axial positions about the Pt.

The Na^+ ion interacts with only two species, the cyanide N atoms and the O atoms of water. The resulting coordination sphere is a distorted octahedron with cyanide N atoms occupying the equatorial positions, and water O atoms occupying axial positions. The water molecules present in the structure seem to serve as cross-linking agents as shown in Fig. 1. The O atoms interact with the Na^+ cations, and the H atoms interact with the Br and N atoms, to create water bridges between the Na^+ ions and the $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$ anions.

As expected, the non-equivalent Pt(1)—C(1) and Pt(1)—C(2) bonds are of equal length, within one standard deviation, though not required to be so. Similarly, the lengths of the non-equivalent C(1)—N(1) and C(2)—N(2) bonds, and the Pt(1)—Br(1) and Pt(1)—Br(2) bonds, are in agreement within statistical limits.

Thus it seems that the $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$ structure may be very stable owing to the cross-linking discussed above. It may be that because of high stabilities of the Pt^{IV} and Pt^{II} forms of the Na compounds, they are preferentially formed over the perhaps less stable

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32141 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

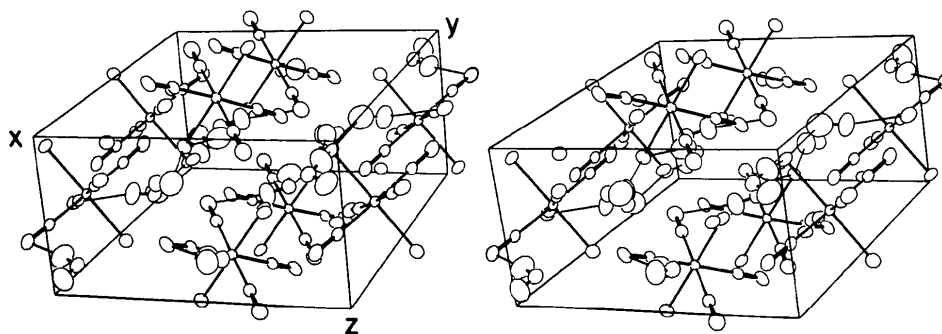


Fig. 1. A stereoview of the unit cell of $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$ with the ellipsoids shown at 50% probability. Hydrogen-bonding interactions are weak and are indicated with thin lines.

partially oxidized compounds. A study of potassium tetracyanoplatinate(IV) dibromide may reveal why $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_{0.3}] \cdot 3\text{H}_2\text{O}$ is preferentially formed.

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Sodium 2-Methyl-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylate trihydrate*†

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Abstract. $\text{C}_9\text{H}_{13}\text{O}_3\text{Na} \cdot 3\text{H}_2\text{O}$, monoclinic, $P2_1/c$; $a = 15.887$ (8), $b = 6.459$ (4), $c = 11.829$ (6) Å, $\beta = 106.60$ (5)°, $Z = 4$, $D_x = 1.406$ (2), $D_m = 1.399$ (7) g cm⁻³, at 23 °C. For 1357 reflections with $I > 3\sigma$, $R = 0.036$ and $R_w = 0.032$. Each Na ion is coordinated by five water molecules and an alcohol O atom. Hydrogen bonds between water and the carboxyl groups tie the molecules together in a layer structure. The carboxyl C and hydroxyl O atoms are 2.783 (3) Å from each

other, and bond angles indicate that the molecule has been deformed to avoid a closer contact.

Introduction. The title compound is one of several derivatives of norbornane which we have studied to obtain accurate molecular dimensions for the framework and for the attached groups. These data were desired for the interpretation of geometrical effects on rates of intramolecular reactions, such as lactonization, which have been studied with several such derivatives (Storm & Koshland, 1972; Hackney, 1975). The structure of one of the related lactones was reported earlier (Chapuis, Zalkin & Templeton, 1973).

* Structures of Bicyclo[2.2.1] Systems. II.

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