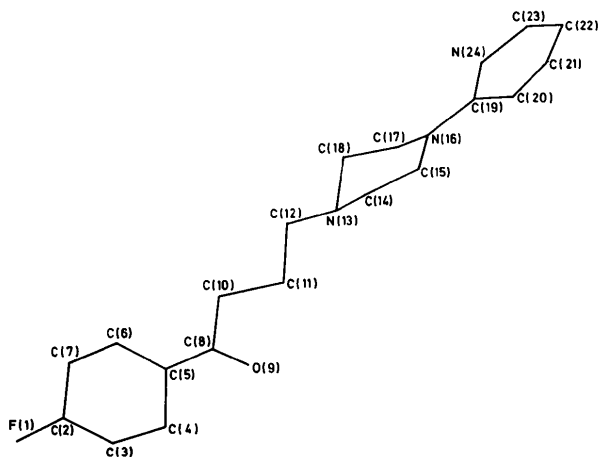


Table 4. Torsion angles defining the conformation of azaperone

C(18)–N(13)–C(12)–C(11)	–167°
N(13)–C(12)–C(11)–C(10)	–179
C(12)–C(11)–C(10)–C(8)	–171
C(11)–C(10)–C(8)–C(5)	177
C(10)–C(8)–C(5)–C(4)	–171
N(24)–C(19)–N(16)–C(15)	–164

Fig. 1. Conformation and numbering scheme of C<sub>19</sub>H<sub>22</sub>N<sub>3</sub>OF.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal least squares (Ahmed, Hall, Pippy & Huber, 1966) to a final *R* of 0.09 for all observed reflexions.\*

The scattering factors were those given in *International Tables for X-ray Crystallography* (1962).

The final coordinates are given in Table 2.

**Discussion.** The conformation of the molecule and the numbering scheme are shown in Fig. 1 and the bond distances and angles in Table 3. The torsion angles defining the conformation of the molecule are given in Table 4.

Relevant structural details are given in the *Abstract*.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32507 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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## Structural Studies of Precursor and Partially Oxidized Conducting Complexes. VII. A Neutron Diffraction Study of Disodium Tetracyanoplatinate(II) Trihydrate\*

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**Abstract.** Na<sub>2</sub>[Pt(CN)<sub>4</sub>]·3H<sub>2</sub>O, triclinic  $P\bar{1}(C_1)$ ,  $a = 15.444$  (11),  $b = 9.082$  (7),  $c = 7.350$  (5) Å,  $\alpha = 95.07$  (4),  $\beta = 92.73$  (14),  $\gamma = 89.04$  (2)°,  $Z = 4$ ,  $D_m =$

2.60,  $D_c = 2.59$  g cm<sup>-3</sup>. The structure was determined with neutron diffraction data to locate all atoms. The 4067 unique reflections were refined to an agreement index of  $R(F_o^2) = 0.067$ . For the 3188 data with  $F_o^2$  greater than one e.s.d.,  $R(F_o^2) = 0.062$ . The four independent Pt–Pt spacings are 3.651 (4), 3.691 (4), 3.745 (4) and 3.754 (4) Å along the chain formed by the Pt atoms. The C–Pt–Pt–C torsion angles average 0°. This structure contains eclipsed C–N groups which

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is opposite to the situation observed in partially oxidized compounds in which the C—N groups are staggered. The Pt chain distortion is apparently not governed by  $\text{CN}^-\cdots\text{Na}^+$  interactions and chain deformation is opposite to that found in partially oxidized tetracyanoplatinate compounds.

**Introduction.** Preliminary X-ray photographs showed triclinic symmetry and no systematic absences. These conditions allow either space group  $P\bar{1}$  or  $P1$ . Cell constants were established by centering 18 reflections and carrying out a least-squares analysis of the determined angles,  $2\theta$ ,  $\chi$ , and  $\varphi$ .

A crystal weighing 22.3 mg (approximately  $1.2 \times 1.8 \times 3.7$  mm) was mounted in a lead-glass capillary for protection against dehydration. The neutron diffraction study was carried out at the Argonne National Laboratory CP-5 reactor. A description of this facility can be found in Petersen, Dahl & Williams (1974).

Data were collected by a  $\theta$ - $2\theta$  step scan with the interval being  $0.1^\circ$  in  $2\theta$ . The scan widths were varied for different ranges of  $2\theta$  according to the observed peak breadth. The backgrounds were established by measuring the intensity at each extremity of the scan. Two standards were measured after every 50 reflections to check for crystal movement or decomposition (maximum variation = 5%).

Data were collected to a minimum  $d$  spacing of  $0.808 \text{ \AA}$  [ $\lambda = 1.142(1) \text{ \AA}$ ]. 4067 unique data were collected of which 3188 reflections were greater than  $1.0\sigma(F_o^2)$ . Structure factors were derived by applying Lorentz and absorption corrections ( $\mu = 1.28 \text{ cm}^{-1}$ ) and the magnitude of the calculated transmission factors ranged from 0.83 to 0.88. Errors were assigned to the data with the standard counting statistics formula with  $(0.05I)^2$  added to adjust for systematic error. The data were placed on an approximately absolute scale by comparison with a standard NaCl crystal.

This crystal structure has previously been solved with X-rays (Ledent, 1967, 1969, 1972). The Pt positions were taken from Ledent (1969) and the Na, C, N, and O positions from Ledent (1972). With the phases calculated from these parameters, the H atoms were located on a difference Fourier map. Refinement was carried out by full-matrix least-squares techniques with anisotropic thermal parameters and type 2 anisotropic extinction (Coppens & Hamilton, 1970). The final  $R(F_o^2) = \Sigma |F_o^2 - F_c^2| / \Sigma F_o^2$  for the 3188 data greater than  $\sigma$  was 0.062 while  $R$  based on all data was 0.067. The weighted  $R$  values were 0.095 and 0.100 for data greater than  $\sigma$  and all data respectively. The standard deviation of an observation of unit weight was 0.97 for all data. The neutron scattering amplitudes were as follows:  $b_{\text{Pt}} = 0.95$ ,  $b_{\text{C}} = 0.663$ ,  $b_{\text{N}} = 0.94$ ,  $b_{\text{O}} = 0.575$ ,  $b_{\text{H}} = -0.372$ , and  $b_{\text{Na}} = 0.351 \times 10^{-12} \text{ cm}$  (*International Tables for X-ray Crystallography*,

1974). The final positional parameters are in Table 1.\* Bond lengths and angles are in Table 2.

**Discussion.** The crystal structure consists of planar  $\text{Pt}(\text{CN})_4^{2-}$  groups stacked approximately parallel to  $c$  forming non-linear Pt—Pt chains. The C—Pt—Pt'—C' torsion angles (adjacent Pt atoms and eclipsing C

\* Lists of structure factors and anisotropic thermal parameters, with the r.m.s. component of thermal displacement along each principal axis, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32479 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ )

The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figure.

	$x$	$y$	$z$
Pt(1)	128 (1)	-123 (1)	2464 (2)
Pt(2)	4832 (1)	5131 (1)	2479 (2)
C(1)	473 (1)	-2211 (2)	2730 (3)
C(2)	-248 (1)	1952 (2)	2185 (3)
C(3)	1343 (1)	362 (2)	1983 (3)
C(4)	-1083 (1)	590 (2)	2966 (3)
C(5)	3593 (1)	4573 (2)	2357 (3)
C(6)	6069 (1)	5682 (2)	2674 (3)
C(7)	4481 (1)	7226 (2)	2306 (3)
C(8)	5198 (1)	3035 (2)	2609 (3)
N(1)	657 (1)	-3439 (2)	2884 (3)
N(2)	-489 (1)	3141 (2)	2002 (2)
N(3)	2056 (1)	643 (2)	1720 (3)
N(4)	-1789 (1)	-862 (2)	3280 (2)
N(5)	2867 (1)	4274 (2)	2331 (3)
N(6)	6790 (1)	6005 (2)	2842 (3)
N(7)	4271 (1)	8442 (2)	2173 (3)
N(8)	5434 (1)	1824 (2)	2641 (3)
O(1)	1220 (2)	4078 (3)	5052 (4)
O(2)	1424 (2)	3909 (3)	9673 (4)
O(3)	7570 (3)	2815 (4)	4885 (5)
O(4)	7383 (2)	2269 (4)	577 (5)
O(5)	3710 (2)	858 (3)	4765 (4)
O(6)	3571 (2)	1089 (3)	9481 (4)
H(1)	696 (4)	3645 (8)	5350 (11)
H(2)	1018 (4)	4756 (7)	4174 (8)
H(3)	1833 (4)	3997 (7)	10681 (8)
H(4)	1471 (5)	2925 (8)	9171 (11)
H(5)	7288 (6)	3470 (11)	5662 (12)
H(6)	8095 (5)	2647 (11)	5560 (12)
H(7)	6897 (5)	2368 (10)	-134 (11)
H(8)	7740 (6)	1594 (9)	-133 (11)
H(9)	4214 (5)	1346 (9)	5132 (13)
H(10)	3855 (4)	161 (7)	3756 (9)
H(11)	3505 (4)	2042 (7)	9076 (10)
H(12)	3125 (4)	1042 (7)	10344 (8)
Na(1)	2452 (3)	2450 (5)	4570 (5)
Na(2)	1923 (3)	5667 (5)	7607 (6)
Na(3)	3116 (3)	9279 (5)	6930 (6)
Na(4)	0 (0)	5000 (0)	0 (0)
Na(5)	5000 (0)	0 (0)	0 (0)

atoms) average  $0^\circ$  because of an inversion center midway between two Pt atoms. This compound most closely resembles  $K_2[Pt(CN)_4] \cdot 3H_2O$  (Washecheck, Peterson, Reis & Williams, 1976) which had cyanide eclipse angles of  $15.7$  and  $16.7^\circ$ . Other comparisons can be made with  $Rb_2[Pt(CN)_4] \cdot 1.5H_2O$  (Koch,

Table 2. *Interatomic distances (Å) and bond angles ( $^\circ$ ) for  $Na_2[Pt(CN)_4] \cdot 3H_2O$*

(A) Distances around platinum atoms

Pt(1)—C(1)	1.985 (3)	Pt(2)—C(7)	1.982 (3)
Pt(1)—C(2)	1.987 (3)	Pt(2)—C(8)	1.986 (3)
Pt(1)—C(3)	1.989 (3)	Pt(1)—Pt(1 <sup>xii</sup> )	3.651 (4)
Pt(1)—C(4)	1.983 (3)	Pt(1)—Pt(1 <sup>i</sup> )	3.754 (4)
Pt(2)—C(5)	1.984 (3)	Pt(2)—Pt(2 <sup>ii</sup> )	3.691 (4)
Pt(2)—C(6)	1.978 (3)	Pt(2)—Pt(2 <sup>iii</sup> )	3.745 (4)

(B) Carbon—nitrogen distances in cyanide groups

C(1)—N(1)	1.160 (3)	C(5)—N(5)	1.158 (3)
C(2)—N(2)	1.154 (3)	C(6)—N(6)	1.153 (3)
C(3)—N(3)	1.164 (3)	C(7)—N(7)	1.157 (3)
C(4)—N(4)	1.160 (3)	C(8)—N(8)	1.155 (3)

(C) Water molecule distances

O(1)—H(1)	0.949 (8)	O(4)—H(7)	0.903 (9)
O(1)—H(2)	0.968 (7)	O(4)—H(8)	0.955 (9)
O(2)—H(3)	0.949 (7)	O(5)—H(9)	0.919 (9)
O(2)—H(4)	0.939 (9)	O(5)—H(10)	0.964 (8)
O(3)—H(5)	0.908 (11)	O(6)—H(11)	0.942 (8)
O(3)—H(6)	0.948 (9)	O(6)—H(12)	0.963 (7)

(D) Hydrogen atom interactions

H(1)—N(1 <sup>i</sup> )	2.529 (8)	O(1)—H(1)—N(1 <sup>i</sup> )	155.6 (6)
H(2)—N(1 <sup>iv</sup> )	2.023 (6)	O(1)—H(2)—N(1 <sup>iv</sup> )	165.4 (5)
H(3)—N(5 <sup>xi</sup> )	1.965 (7)	O(2)—H(3)—N(5 <sup>xi</sup> )	166.6 (5)
H(4)—N(4)	2.540 (8)	O(2)—H(4)—N(4)	155.8 (7)
H(5)—N(5 <sup>iii</sup> )	2.432 (10)	O(3)—H(5)—N(5 <sup>iii</sup> )	155.2 (8)
H(6)—N(1 <sup>vii</sup> )	2.288 (9)	O(3)—H(6)—N(1 <sup>vii</sup> )	152.3 (8)
H(7)—N(7 <sup>ii</sup> )	2.373 (8)	O(4)—H(7)—N(7 <sup>ii</sup> )	156.2 (8)
H(8)—N(3 <sup>ix</sup> )	2.276 (8)	O(4)—H(8)—N(3 <sup>ix</sup> )	150.3 (7)
H(9)—N(8)	2.754 (10)	O(5)—H(9)—N(8)	120.6 (7)
H(9)—N(7 <sup>viii</sup> )	2.991 (10)	O(5)—H(9)—N(7 <sup>viii</sup> )	145.9 (8)
H(10)—N(7 <sup>ix</sup> )	1.980 (7)	O(5)—H(10)—N(7 <sup>ix</sup> )	165.8 (6)
H(11)—N(6 <sup>iii</sup> )	2.387 (7)	O(6)—H(11)—N(6 <sup>iii</sup> )	161.6 (6)
H(12)—N(3 <sup>xii</sup> )	2.030 (6)	O(6)—H(12)—N(3 <sup>xii</sup> )	167.4 (5)

(E) Sodium ion interactions

Na(1)—O(5)	2.409 (5)	Na(3)—O(6 <sup>iv</sup> )	2.466 (6)
Na(1)—O(1)	2.410 (5)	Na(3)—N(4 <sup>x</sup> )	2.491 (5)
Na(1)—N(4 <sup>i</sup> )	2.496 (5)	Na(3)—O(4 <sup>iii</sup> )	2.560 (6)
Na(1)—N(6 <sup>iii</sup> )	2.517 (5)	Na(4)—O(2 <sup>v</sup> )	2.411 (3)
Na(1)—N(5)	2.546 (5)	Na(4)—O(2 <sup>x</sup> )	2.411 (3)
Na(1)—N(3)	2.600 (5)	Na(4)—N(2)	2.484 (2)
Na(2)—O(4 <sup>iii</sup> )	2.436 (6)	Na(4)—N(2 <sup>vi</sup> )	2.484 (2)
Na(2)—O(2)	2.455 (5)	Na(4)—N(1 <sup>ix</sup> )	2.616 (3)
Na(2)—N(2 <sup>x</sup> )	2.466 (5)	Na(4)—N(1 <sup>xii</sup> )	2.616 (3)
Na(2)—O(1)	2.484 (6)	Na(5)—O(6 <sup>v</sup> )	2.430 (3)
Na(2)—N(6 <sup>iii</sup> )	2.498 (5)	Na(5)—O(6 <sup>vii</sup> )	2.430 (3)
Na(2)—O(3 <sup>iii</sup> )	2.547 (6)	Na(5)—N(8)	2.511 (3)
Na(3)—O(3 <sup>iii</sup> )	2.450 (6)	Na(5)—N(8 <sup>viii</sup> )	2.511 (3)
Na(3)—O(5 <sup>iv</sup> )	2.454 (6)	Na(5)—N(7 <sup>ix</sup> )	2.539 (3)
Na(3)—N(8 <sup>iii</sup> )	2.456 (5)	Na(5)—N(7 <sup>ii</sup> )	2.539 (3)

Table 2 (cont.)

(F) Angles of Pt chain and bonded atoms

Pt(1)—Pt(1)—Pt(1)	166.04 (8)	C(2)—Pt(1)—C(3)	90.8 (1)
Pt(2)—Pt(2)—Pt(2)	162.48 (8)	C(2)—Pt(1)—C(4)	88.9 (1)
Pt(1)—C(1)—N(1)	178.6 (2)	C(5)—Pt(2)—C(7)	89.6 (1)
Pt(1)—C(2)—N(2)	178.0 (2)	C(5)—Pt(2)—C(8)	91.0 (1)
Pt(1)—C(3)—N(3)	179.3 (2)	C(6)—Pt(2)—C(7)	90.7 (1)
Pt(1)—C(4)—N(4)	179.3 (2)	C(6)—Pt(2)—C(8)	88.7 (1)
Pt(2)—C(5)—N(5)	178.0 (2)	H(1)—O(1)—H(2)	102.2 (9)
Pt(2)—C(6)—N(6)	178.0 (2)	H(3)—O(2)—H(4)	105.5 (6)
Pt(2)—C(7)—N(7)	178.7 (2)	H(5)—O(3)—H(6)	102.2 (9)
Pt(2)—C(8)—N(8)	177.5 (2)	H(7)—O(4)—H(8)	104.6 (9)
C(1)—Pt(1)—C(3)	90.5 (1)	H(9)—O(5)—H(10)	106.1 (7)
C(1)—Pt(1)—C(4)	89.8 (1)	H(11)—O(6)—H(12)	104.2 (6)

Superscripts refer to the following symmetry positions. If no superscript appears (x, y, z) is implied. (i) -x, -y, 1-z; (ii) 1-x, 1-y, -z; (iii) 1-x, 1-y, 1-z; (iv) x, 1+y, z; (v) x, y, z-1; (vi) -x, 1-y, -z; (vii) 1-x, -y, 1-z; (viii) 1-x, -y, -z; (ix) x, y-1, z; (x) -x, 1-y, 1-z; (xi) x, y, 1+z; (xii) -x, -y, -z.

Johnson & Williams, 1977), where the torsion angles range from  $29.47$  to  $35.24^\circ$ , and  $Cs_2[Pt(CN)_4] \cdot H_2O$  (Johnson, Koch & Williams, 1977) where the range is  $30.4$  to  $34.8^\circ$ .

The Pt(1)—Pt(1')—Pt(1'') angle is  $166.04(8)^\circ$  and the Pt(2)—Pt(2')—Pt(2'') angle is  $162.48(8)^\circ$ . The four separate Pt—Pt interactions (see Table 1) average  $3.7 \text{ \AA}$ .

The average Pt—C bond length is  $1.984(8) \text{ \AA}$  and the average C—N bond length is  $1.158(8) \text{ \AA}$ . The Pt—C—N angle averages  $178.4(6)^\circ$ . Pt(1) and Pt(2) are  $0.000(2)$  and  $0.005(2) \text{ \AA}$  away from the planes formed by C(1)—C(2)—C(3)—C(4) and C(5)—C(6)—C(7)—C(8), respectively, the dihedral angle between which is  $14.1(2)^\circ$ . It should be noted that these planes are crystallographically distinct and correspond to chains of Pt atoms running through the origin and the center of the cell (see Fig. 1). If one calculates the angle between planes along Pt(1)—Pt(1')—Pt(1''), the dihedral angle is  $0^\circ$  because of the center of symmetry midway between two Pt(1) atoms. There is also a center of symmetry between Pt(2) and Pt(2') so the dihedral angle between planes along this chain is also  $0^\circ$ .

The coordination sphere around each of the five independent Na atoms is sixfold. The contact distances are listed in Table 2. The geometries are all approximately octahedral with the most regular angles being about Na(4) where the largest deviations are found to be  $94.4(1)$  and  $85.6(1)^\circ$  for adjacent atoms in the octahedral figure. The largest deviations from perfect octahedral symmetry are found around Na(2) where bond angles of  $99.4(2)$  and  $78.7(2)^\circ$  are calculated for adjacent atoms in the octahedron.

The average intramolecular bond angle for the six water molecules is  $104.1(19)^\circ$ . The average O—H

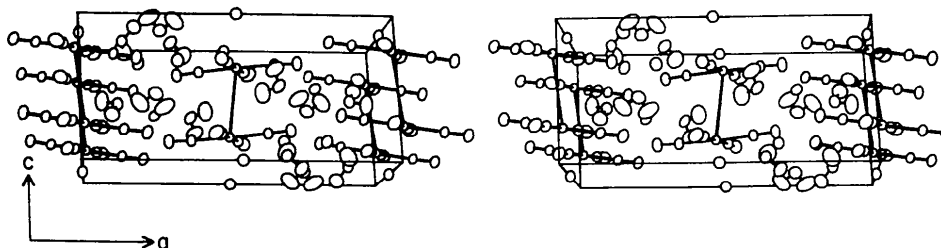


Fig. 1. Stereoscopic drawing (Johnson, 1965) of the unit cell of  $\text{Na}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$  with thermal ellipsoids drawn on a 50% probability scale.

bond length is 0.942 (29) Å. When a correction for the effects of thermal motion is carried out, the average becomes 0.996 (22) and 1.080 (23) Å, respectively, for one model where H rides on O and a second model where they move independently.

All H atoms participate in O—H...N hydrogen bonds with the exception of H(9) which has a bifur-

cated hydrogen bond to N(7) and N(8) (Table 2D). This fits the definition of hydrogen bonding as stated by Hamilton & Ibers (1968).

The partially oxidized compound,  $\text{K}_{1.75}[\text{Pt}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$ , shows an interesting chain distortion which is ascribed to an asymmetric  $\text{K}^+$  distribution about  $\text{CN}^-$  (Reis, Peterson, Washecheck & Miller, 1976; Williams, Keefer, Washecheck & Enright, 1976). This compound also shows an asymmetric crystalline environment as illustrated in Figs. 2 and 3. However, the Pt chain distortion in the opposite direction to that found in  $\text{K}_{1.75}[\text{Pt}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$  in that the distortion is toward  $\text{K}^+$  in the former, and away from  $\text{Na}^+$  in  $\text{Na}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ .

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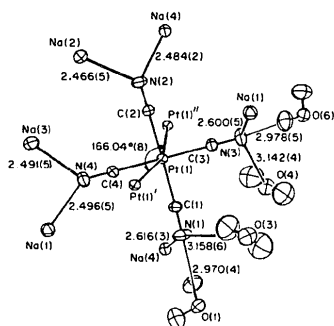


Fig. 2. Diagram of the asymmetric environment about Pt(1) in  $\text{Na}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ .

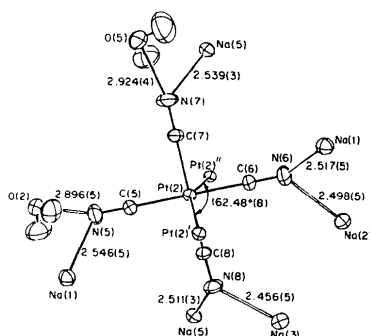


Fig. 3. Diagram of the asymmetric environment about Pt(2) in  $\text{Na}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ .