

Table 3. Unit-cell constants ( $\text{\AA}$ ) ( $\pm 0.002 \text{\AA}$ )

$Nd_3Au_3Sb_4$	9.961	$Dy_3Au_3Sb_4$	9.811
$Sm_3Au_3Sb_4$	9.909	$Ho_3Au_3Sb_4$	9.788
$Gd_3Au_3Sb_4$	9.864	$Er_3Au_3Sb_4$	9.768
$Tb_3Au_3Sb_4$	9.834	$Tm_3Au_3Sb_4$	9.752
$Y_3Au_3Sb_4$	9.821	$Lu_3Au_3Sb_4$	9.723

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## Structural Studies of Precursor and Partially Oxidized Conducting Complexes.

## V. A Neutron Diffraction Study of Dianilinium Tetracyanoplatinate(II)\*

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**Abstract.**  $(C_6H_5NH_3)_2[Pt(CN)_4]$ , triclinic,  $P\bar{1}$  ( $C^1$ ),  $a = 7.933$  (5),  $b = 10.654$  (7),  $c = 5.497$  (4)  $\text{\AA}$ ,  $\alpha = 103.24$  (3),  $\beta = 91.19$  (3),  $\gamma = 110.34$  (3)°,  $Z = 1$ ,  $D_m = 1.90$  (2),  $D_c = 1.92$   $\text{g cm}^{-3}$ . 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  $R(F_o^2) = 0.061$  for 1304 observed reflections  $> \sigma(F_o^2)$ . The structure consists of isolated tetracyanoplatinate groups interacting with the anilinium groups *via*  $N-H \cdots N \equiv C$  hydrogen bonds. No Pt–Pt chains are formed *via* overlapping  $d_{z^2}$  orbitals of the Pt atoms.

**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  $(C_6H_5NH_3)_2[Pt(CN)_4]$ . Utilization of the compound  $K_2[Pt(CN)_4] \cdot 3H_2O$  is a standard method in preparing the well known one-dimensional conductor  $K_{1.75}[Pt(CN)_4] \cdot 1.5H_2O$  (Williams, Keefer, Washecheck & Enright, 1976), and therefore  $(C_6H_5NH_3)_2[Pt(CN)_4]$  might be expected to be the precursor of a corresponding partially oxidized, aniline-deficient compound.

The compound  $Ba[Pt(CN)_4] \cdot 4H_2O$  (preparation described by Koch, Abys & Williams, 1976) was used to prepare single crystals of  $(C_6H_5NH_3)_2[Pt(CN)_4]$ . Aniline sulfate was added to a solution of  $Ba[Pt(CN)_4] \cdot 4H_2O$  and  $BaSO_4$  was removed by filtration. The pH of the filtrate was adjusted to  $\sim 2$  and

Table 1. Positional parameters for  $(C_6H_5NH_3)_2[Pt(CN)_4]$  ( $\times 10^4$ )

Here and elsewhere in this paper the e.s.d.'s in parentheses refer to the least-significant figure.

	<i>x</i>	<i>y</i>	<i>z</i>
Pt	0	0	0
C(1)	–2493 (2)	–783 (2)	–1698 (4)
C(2)	929 (2)	–905 (2)	–2942 (4)
N(1)	–3974 (2)	–1207 (2)	–2600 (4)
N(2)	1540 (2)	–1403 (2)	–4609 (3)
C(3)	–3341 (2)	–6598 (2)	–1170 (3)
C(4)	–2340 (3)	–6087 (2)	1147 (4)
C(5)	–1600 (3)	–4662 (2)	2136 (4)
C(6)	–1871 (3)	–3781 (2)	809 (4)
C(7)	–2874 (3)	–4314 (2)	–1507 (5)
C(8)	–3627 (3)	–5736 (2)	–2523 (4)
N(3)	–4075 (2)	–8092 (2)	–2265 (4)
H(1)	5583 (8)	3842 (5)	5659 (10)
H(2)	6915 (6)	1596 (4)	6847 (10)
H(3)	4930 (7)	1641 (5)	6294 (12)
H(4)	5436 (8)	1394 (5)	9028 (11)
H(5)	1280 (8)	2670 (5)	8418 (12)
H(6)	–3098 (10)	–3630 (6)	–2533 (12)
H(7)	805 (8)	4238 (6)	6050 (11)
H(8)	7880 (8)	3202 (6)	2154 (11)

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H<sub>2</sub>O<sub>2</sub> was added. Single, opaque, black crystals were obtained by slow evaporation.

Preliminary neutron observations determined the

Table 2. *Interatomic distances (Å) and bond angles (°) for (C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>[Pt(CN)<sub>4</sub>]*

(a) Distances around Pt atoms

Pt—C(1) 1.974 (2) P—C(2) 1.979 (2)

(b) C—N distances in cyanide groups

C(1)—N(1) 1.155 (2) C(2)—N(2) 1.154 (2)

(c) C—C distances in the anilinium ion

C(3)—C(4) 1.374 (3) C(8)—C(3) 1.378 (3)  
 C(4)—C(5) 1.391 (3) C(3)—N(3) 1.462 (3)  
 C(6)—C(7) 1.375 (3) C(5)—C(6) 1.381 (3)  
 C(7)—C(8) 1.390 (3)

(d) C—H and N—H distances in the anilinium ion

C(4)—H(8) 1.091 (6) C(8)—H(1) 1.080 (6)  
 C(5)—H(7) 1.080 (6) N(3)—H(4) 0.999 (7)  
 C(6)—H(5) 1.085 (6) N(3)—H(3) 1.023 (7)  
 C(7)—H(6) 1.075 (6) N(3)—H(2) 1.043 (4)

(e) Angles in the platynocyanide groups

C(1)—Pt—C(2) 92.3 (1)  
 Pt—C(2)—N(2) 177.2 (2)  
 Pt—C(1)—N(1) 177.0 (2)

(f) Angles within the anilinium ion

C(3)—C(4)—C(5) 118.8 (2) C(3)—C(4)—H(8) 119.8 (4)  
 C(4)—C(5)—C(6) 120.4 (2) H(8)—C(4)—C(5) 121.4 (4)  
 C(5)—C(6)—C(7) 119.8 (2) C(4)—C(5)—H(7) 120.0 (4)  
 C(6)—C(7)—C(8) 120.5 (2) H(7)—C(5)—C(6) 119.6 (4)  
 C(7)—C(8)—C(3) 118.8 (2) C(5)—C(6)—H(5) 120.1 (4)  
 C(8)—C(3)—C(4) 121.7 (2) H(5)—C(6)—C(7) 120.0 (4)  
 N(3)—C(3)—C(8) 119.1 (2) C(6)—C(7)—H(6) 119.9 (4)  
 N(3)—C(3)—C(4) 119.2 (2) H(6)—C(7)—C(8) 119.6 (4)  
 C(3)—N(3)—H(4) 111.3 (3) C(7)—C(8)—H(1) 120.7 (3)  
 C(3)—N(3)—H(3) 111.5 (3) H(1)—C(8)—C(3) 120.5 (3)  
 C(3)—N(3)—H(2) 109.7 (3)

space group to be *P*1 or *P* $\bar{1}$ . The crystal selected for data collection weighed 7.55 mg. 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 well described by Petersen, Dahl & Williams (1974).] The neutron wavelength of 1.142 (1) Å was obtained with a Be crystal monochromator set at  $\theta_m = 30^\circ$ . The cell parameters were determined from angular measurements of 30 automatically centered reflections chosen in the  $2\theta$  range 40–60°. A least-squares analysis gave the lattice constants. 1678 data, with 1304  $> \sigma(F_o^2)$ , were automatically collected with the  $\theta$ – $2\theta$  step-scan mode, and 0.1° scan intervals. Reference reflections were taken every 80 measurements to determine whether the crystal was decomposing or drifting. These intensities did not vary more than 6% during data collection. Data collection was complete to  $2\theta = 90^\circ$ .

The structure was solved first with the program *MULTAN* (Germain, Main & Woolfson, 1971) to locate the Pt atom, both CN<sup>–</sup> groups and the anilinium C and N atoms. The H atoms were located by Fourier and difference-Fourier methods. Refinement was carried out by full-matrix least-squares techniques, first with isotropic then anisotropic thermal parameters, as well as isotropic extinction ( $g = 0.004$ ). The final  $R(F_o^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$  for the 1304 data  $> \sigma(F_o^2)$  was 0.061.  $R(F_o^2)$  for all data was 0.068. The largest peak in the difference-Fourier map was a peak 1.6% of a Pt peak and 0.94 Å away from C(8) and 1.240 Å from C(3). We attributed this to background noise. The successful refinement in space group *P* $\bar{1}$  was taken as confirmation of the appropriateness of its choice as the space group and consequently no calculations were made in space group *P*1. The neutron scattering amplitudes used were as follows:  $b_{Pt} = 0.950$ ,  $b_C = 0.663$ ,  $b_N = 0.940$  and  $b_H = -0.372$ , all  $\times 10^{-12}$  cm. The refined positional parameters are given in Table 1 and

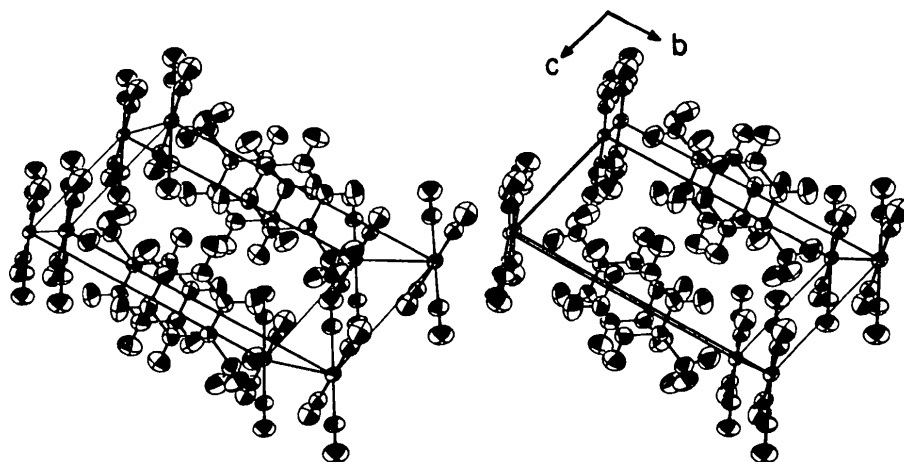


Fig. 1. Stereoscopic drawing of the unit cell of dianilinium tetracyanoplatinate(II).

important bond lengths and angles in Table 2. A stereo-drawing of the unit cell is shown in Fig. 1.\*

**Discussion.** As expected, the crystallographically non-equivalent Pt—C(1), Pt—C(2), and C(1)—N(1), C(2)—N(2) distances, are equal to within one e.s.d. These distances are in close agreement with those reported previously (e.g. Washecheck, Peterson, Reis & Williams, 1976; Williams, Keefer, Washecheck & Enright, 1976; Needham, Johnson, Cornish & Williams, 1977). The cyanides form a planar arrangement around the central Pt atom, although they do not form a square.

The anilinium ion interacts with the platinocyanide group mainly through N—H...N≡C hydrogen bonds. The dihedral angle between the planes of these two groups is 78°. It appears two bonds in the ring of the anilinium ion [C(4)—C(5), C(8)—C(7)] are longer by four times the standard deviation of the other C—C bonds. The distance between nearest-neighbor anilinium groups is 4.25 Å. The anilinium ion stacking is such that the benzene rings are eclipsed and the nitrogens point toward opposite ends of the unit cell (see Fig. 1).

No Pt—Pt bonds exist in this compound, probably

\* Lists of structure factors, anisotropic thermal parameters and r.m.s. thermal displacements have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32408 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

because of the steric hindrance imposed by the anilinium ions. This interaction is probably the reason why attempts to synthesize partially oxidized anilinium tetracyanoplatinate have as yet been unsuccessful. This cation hindrance has been previously observed in Ba[Pt(CN)<sub>4</sub>].4H<sub>2</sub>O (Maffly, Johnson & Williams, 1977). However, in that case a Pt—Pt chain was formed, probably because of the smaller cation. It appears that partially oxidized anilinium tetracyanoplatinate did not form in this case because the steric interactions between the anilinium ions favor larger (>5 Å) Pt—Pt separations.

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## Calcium Nitrate Tetraurea

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**Abstract.** Ca(NO<sub>3</sub>)<sub>2</sub>.4CO(NH<sub>2</sub>)<sub>2</sub> is monoclinic, space group  $P2_1/c$ ,  $a = 9.246(1)$ ,  $b = 12.668(1)$ ,  $c = 7.684(1)$  Å,  $\beta = 113.51(1)^\circ$ ,  $Z = 2$ ,  $D_m = 1.63$ ,  $D_c = 1.63$  g cm<sup>-3</sup>. The Ca<sup>2+</sup> ions are octahedrally coordinated by O atoms from two NO<sub>3</sub><sup>-</sup> ions and four urea molecules. The discrete, neutral complexes are linked with hydrogen bonds.

**Introduction.** Crystals of the title compound were grown by slow evaporation of an aqueous solution of CaNO<sub>3</sub> and urea in a molar ratio 1:4. A crystal ground to the shape of a sphere of diameter 0.20 mm was used

to collect intensity data on an Enraf–Nonius CAD-4 diffractometer. The lattice constants were obtained by least-squares refinement from the setting angles of the reflexions used in the auto-indexing procedure. They agreed with those previously reported (Chojnacki, Lebioda & Weber, 1969).

Three-dimensional diffraction data out to  $\theta = 30^\circ$  were recorded with graphite-monochromated Mo K $\alpha$  radiation and a  $\theta/2\theta$  scan mode. The scan range over the peak was  $0.60^\circ + 0.42^\circ \tan \theta$ . Background was measured at both sides of each reflexion over one fourth of the scan range. A standard reflexion was