

**Crystal and Molecular Structure and EPR Properties of the 1:2 Radical Salt  
Tetraammineplatinum(II) 7,7,8,8-Tetracyanoquinodimethide,  
[Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>[(TCNQ)<sub>2</sub>]<sup>2-</sup>**

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**Abstract.** [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>[(C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>)<sub>2</sub>]<sup>2-</sup>,  $M_r = 671.60$ ,  $F(000) = 306$ , triclinic  $P\bar{1}$ ,  $a = 7.20$  (1),  $b = 14.21$  (2),  $c = 8.93$  (1) Å,  $\alpha = 127.07$  (7),  $\beta = 122.71$  (8),  $\gamma = 66.52$  (9)°,  $Z = 1$ ,  $d_c = 1.85$  g cm<sup>-3</sup>. The structure was refined to  $R = 0.049$  for 3662 counter intensities. TCNQ forms isolated  $\pi$ -dimers with an interplanar separation of 3.14 Å. The [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> cations have no remarkable contacts with one another or with the TCNQ moieties.

**Introduction.** In the course of our investigations on the structural and physical properties of the TCNQ salts of planar or nearly planar cationic transition-metal complexes (Vu Dong, Endres, Keller, Moroni & Nöthe, 1977; Endres, Keller, Moroni, Nöthe & Vu Dong, 1978), we prepared [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>[(TCNQ)<sub>2</sub>]<sup>2-</sup> (Endres, Keller, Moroni & Nöthe, 1976). Because of the pronounced brown-red metallic lustre of the compound, which hinted at strong electronic interactions, we investigated its structure. Weissenberg photographs revealed triclinic symmetry. Lattice parameters (*Abstract*) were calculated by least squares (Berdinski & Nuber, 1966) from the  $\theta$  values of 38 reflections determined on a diffractometer. Intensity measurements on an automatic single-crystal diffractometer (AED, Siemens, Mo  $K\alpha$  radiation,  $\theta$ - $2\theta$  scan, five-value method) yielded 3662 observed independent intensities up to  $2\theta = 60^\circ$ . Reflections with  $I < 2.58\sigma(I)$  were taken as unobserved. The observed intensities were corrected for Lorentz and polarization factors only.

Space group  $P\bar{1}$  was assumed and, as  $Z = 1$ , Pt was placed at 0,0,0. Fourier synthesis showed the positions of all atoms except H, which were ignored throughout. Isotropic refinement gave  $R = 0.143$ ; refinement with anisotropic temperature factors for Pt yielded  $R = 0.096$ ; anisotropic refinement resulted in  $R = 0.049$  (maximum shift/error 0.13). Atomic coordinates are listed in Table 1.\* Calculations were carried out on an

IBM 370/168 (Universitätsrechenzentrum Heidelberg) with programs of the XRAY system (Stewart, Kundell & Baldwin, 1970), and scattering factors from Hanson, Herman, Lea & Skillman (1964). EPR spectra were taken on a Bruker B-ER 418 spectrometer with an NMR gaussmeter for field calibration and a Dana 320D microwave frequency counter. A Bruker B-ST 100/700 temperature-control unit served for measurements at different temperatures.

Table 1. Atomic parameters ( $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Pt	0	0	0
N(1)	-6 (1)	101.3 (6)	284 (1)
N(2)	334 (1)	959.3 (6)	125 (1)
C(1)	155 (1)	659.4 (6)	264 (1)
C(2)	346 (1)	574.6 (7)	277 (1)
C(3)	344 (1)	474.4 (7)	261 (1)
C(4)	149 (1)	449.2 (6)	231 (1)
C(5)	40 (1)	465.8 (6)	781 (1)
C(6)	38 (1)	366.8 (6)	767 (1)
C(7)	841 (1)	235.3 (6)	716 (1)
C(8)	971 (1)	850.1 (6)	277 (1)
C(9)	354 (1)	797.9 (7)	336 (1)
C(10)	144 (1)	345.1 (7)	214 (1)
C(11)	960 (1)	324.8 (8)	202 (1)
C(12)	671 (1)	742.2 (7)	783 (1)
N(3)	822 (1)	921.6 (7)	279 (1)
N(4)	513 (1)	825.7 (8)	379 (1)
N(5)	189 (1)	689.8 (8)	803 (1)
N(6)	523 (1)	813.1 (6)	782 (1)

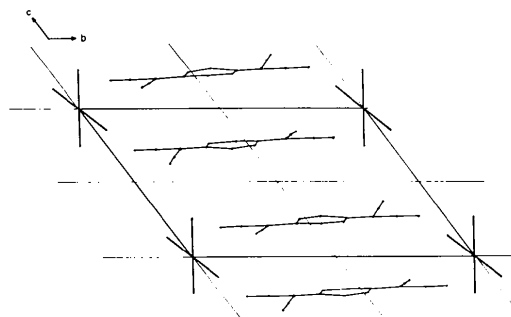
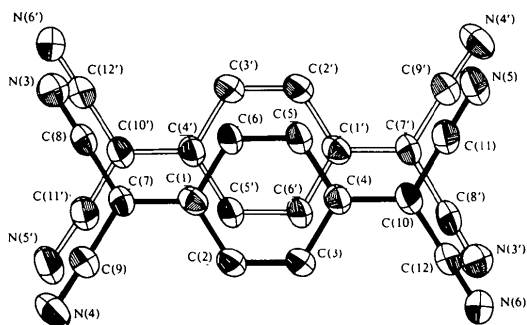


Fig. 1. Projection of the structure on the (100) plane.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33345 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 2. The mode of overlap within a (TCNQ)<sub>2</sub> dimer.Table 2. Deviations of the atoms ( $\times 10^4$ ) from the best planes through parts of the TCNQ

The equation of the plane can be expressed as  
 $PX + QY + RZ - S = 0$ .

## Benzenoid ring

C(1)	-33	C(4)	-50	$P = -1.01458$
C(2)	-10	C(5)	4	$Q = -1.0782$
C(3)	53	C(6)	36	$R = 7.19249$
				$S = 4.07084$

C(CN)<sub>2</sub> group (A)

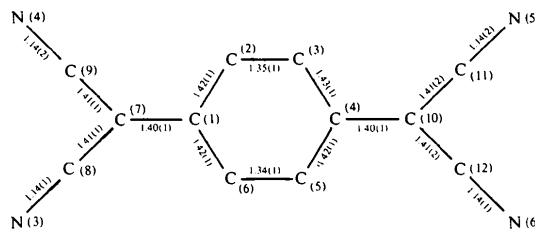
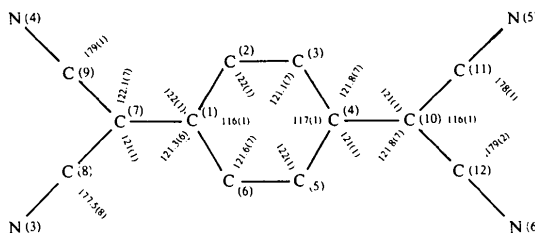
C(7)	-77	$P = -1.60657$
C(8)	147	$Q = -3.0602$
C(9)	23	$R = 7.867$
N(3)	81	$S = 3.5638$
N(4)	-12	

C(CN)<sub>2</sub> group (B)

C(10)	-23	$P = -0.4136$
C(11)	112	$Q = -0.7629$
C(12)	-54	$R = 6.887$
N(5)	-64	$S = 4.5498$
N(6)	28	

**Discussion.** Fig. 1 is a projection of the structure along *a* showing the two centrosymmetrically related TCNQ anions within the unit cell, which form isolated dimers with the corresponding anions in adjacent unit cells. The mode of overlap within a dimer is shown in Fig. 2. The interplanar distance of the benzenoid rings of a dimer is 3.14 Å. The molecular planes of all the TCNQ species are parallel. As usual, the TCNQ moieties are not completely planar; the terminal C(CN)<sub>2</sub> groups form angles of 4.8 and 8.2° with the benzenoid rings, the two terminal groups being tilted to the same side of the benzenoid ring. The deviations of the atoms from the corresponding planes are given in Table 2. The [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> cation is planar by symmetry. The angle between the planes through the cation and the benzenoid rings of TCNQ is 71.6°. The shortest contacts between anions and cations are between the amino N of the cation and cyano N atoms of TCNQ. They range from 2.09 to 3.25 Å.

Bond distances and angles in the TCNQ are given in Figs. 3 and 4. By stoichiometry, each TCNQ species carries one negative charge; a discussion of the charge distribution based on bond lengths seems not to be reasonable, because of the high standard deviations;

Fig. 3. Bond distances (Å) in TCNQ<sup>-</sup>.Fig. 4. Bond angles (°) in TCNQ<sup>-</sup>.

such a discussion for a large number of TCNQ complexes has been published by Flandrois & Chasseau (1977).

The EPR spectra of polycrystalline samples as well as of single crystals show one exchange-narrowed line of about 5 G width. This value is quite high for a TCNQ anion radical but it may reflect the fact that the dimers are relatively far apart, hence showing only small interpair exchange. Nevertheless the exchange is strong enough to average out any hyperfine interactions. Such averaging has been observed even in [Pt(dipy)<sub>2</sub>](TCNQ)<sub>2</sub> (Vu Dong, Endres, Keller, Moroni & Nöthe, 1977), where  $\sigma$ -bonded (TCNQ)<sub>2</sub> dimers are separated from each other by the metal complexes. In contrast to the findings in that compound we could not detect fine-structure lines in [Pt(NH<sub>3</sub>)<sub>4</sub>](TCNQ)<sub>2</sub>, but temperature-dependent measurements show that the EPR intensity as measured by the product  $(\Delta H)^2 h$  ( $\Delta H$  = peak to peak linewidth,  $h$  = peak height) does not follow a Curie law. The paramagnetism increases with rising temperature. Assuming that a thermally accessible triplet state becomes occupied, one can calculate an activation or exchange energy of the order of 0.05 eV.

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## Structure of Manganese Dihydrogen Diphthalate Dihydrate

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**Abstract.** Mn(C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, monoclinic, *P*2<sub>1</sub>/*c*, *Z* = 2, *a* = 13·018 (6), *b* = 5·158 (1), *c* = 12·940 (6) Å, β = 113·90 (3)°, *V* = 794·4 (6) Å<sup>3</sup> at 293 K, *D<sub>c</sub>* = 1·761 g cm<sup>-3</sup>; single-crystal diffractometer data up to sin θ/λ = 0·65 Å<sup>-1</sup>. The two carboxyl groups of the phthalate group are mutually orthogonal. Their relative orientation is determined by packing effects rather than by conjugation.

**Introduction.** Colourless, plate-shaped crystals were obtained from an aqueous solution of manganese carbonate and an excess of phthalic acid. A crystal 0·25 × 0·12 × 0·09 mm cut from a larger specimen was selected.

Data were collected in two quadrants of reciprocal space, up to sin θ/λ = 0·65 and 0·36 Å<sup>-1</sup>, respectively, on a Syntex *P*2<sub>1</sub> diffractometer with Nb-filtered Mo *K*α radiation and a step-scanning mode. 2215 reflections were obtained of which 1837 were unique. The step-scan data were analysed by profile analysis (Blessing, Coppens & Becker, 1974). Three standard reflections observed after every 50 reflections showed no significant fluctuations. The data were corrected for absorption ( $\mu = 9\cdot26 \text{ cm}^{-1}$ ); the transmission factor ranged from 0·892 to 0·930. A weight was assigned to each observation according to  $w(I) = [\sigma^2(I)_{\text{counting}} + (0\cdot02I)^2]^{-1}$ . After equivalent reflections had been averaged, 1541 reflections had  $F_o^2 > 0$  and were used for the structure refinement. The structure was determined by direct methods with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Initial attempts failed because the Mn atom occupies a special position, resulting in a non-uniform distribution of *E* values over the parity groups. However, after the *E* values had been rescaled to approach the values proposed by Main (1976), a solution was obtained. Scattering factors were from *International Tables for X-ray Crystallography* (1974), except those for H which were from Stewart, Davidson & Simpson (1965). For the Mn atom the anomalous-dispersion factors of Cromer & Liberman (1970) were applied. Extinction was found to be negligible. The final *R*(*F*) = 10·7%.

Table 1. *Positional parameters*

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0·5	0·0	0·0
C(1)	0·2206 (3)	0·3372 (7)	0·8396 (3)
C(2)	0·1412 (3)	0·1396 (8)	0·8062 (4)
C(3)	0·0730 (3)	0·1044 (9)	0·6930 (4)
C(4)	0·0848 (3)	0·2601 (9)	0·6129 (4)
C(5)	0·1658 (3)	0·4528 (9)	0·6453 (3)
C(6)	0·2342 (3)	0·4929 (8)	0·7582 (3)
C(7)	0·2850 (3)	0·3769 (8)	0·9641 (3)
C(8)	0·3214 (3)	0·7068 (7)	0·7934 (3)
O(1)	0·3695 (2)	0·2599 (5)	0·0237 (2)
O(2)	0·2317 (2)	0·5392 (6)	0·0040 (2)
O(3)	0·3720 (2)	0·7451 (5)	0·8972 (2)
O(4)	0·3385 (2)	0·8329 (5)	0·7178 (2)
O(5)	0·4830 (3)	0·2027 (6)	0·8469 (2)
H(1)	0·132 (2)	0·051 (7)	0·863 (2)
H(2)	0·018 (3)	−0·026 (7)	0·672 (2)
H(3)	0·038 (2)	0·235 (6)	0·534 (2)
H(4)	0·178 (3)	0·546 (7)	0·589 (3)
H(5)	0·265 (3)	0·568 (8)	0·078 (3)
H(6)	0·433 (3)	0·121 (8)	0·787 (3)
H(7)	0·537 (3)	0·207 (9)	0·830 (3)

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