

# Dimerization of 7,7,8,8-Tetracyanoquinodimethane (TCNQ) Radical Anions *via* $\sigma$ -Bond Formation: Crystal Structure and EPR Properties of Bis(dipyridyl)platinum(II)–TCNQ, $[\text{Pt}(2,2'\text{-dipy})_2^+(\text{TCNQ})_2^-]$

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The title compound, obtained by the reaction of  $\text{Pt}(2,2'\text{-dipy})_2\text{Cl}_2$  with  $\text{LiTCNQ}$ , crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 7.891$  (7),  $b = 14.247$  (2),  $c = 12.253$  (2) Å,  $\alpha = 130.01$  (5),  $\beta = 120.06$  (6),  $\gamma = 61.96$  (6)°,  $Z = 1$ . The structure was solved by Fourier methods and refined by least-squares to  $R = 0.059$ , based on 4122 observed reflexions. The structure consists of  $[\text{Pt}(2,2'\text{-dipy})_2]^{2+}$  cations and  $(\text{TCNQ})_2^{2-}$  anions. In the anions the unpaired electrons of two  $\text{TCNQ}^-$  radicals form a  $\sigma$ -bond of 1.65 Å between two methylene C atoms, giving a diamagnetic but easily excitable ground state. A phase transition to a paramagnetic modification is observed at 87°C.

## Introduction

Compounds crystallizing in columnar structures have received considerable attention in recent years (Shegolev, 1972; Keller, 1975; Herbststein, 1971). This interest arises because this type of structure leads to highly anisotropic physical properties, *e.g.* optical absorption, magnetism, electrical conductivity. Compounds of this kind can be found in inorganic chemistry {*e.g.*  $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.30} \cdot 3 \cdot 2\text{H}_2\text{O}$  'KCP', (Krogmann, 1969)} as well as in organic chemistry [*e.g.* *N*-methylphenazinium–TCNQ (Fritchie, 1966) or tetrathiofulvalenium–TCNQ (Phillips, Kistenmacher, Ferraris & Cowan, 1973)].

We synthesized compounds which were expected to combine in a single lattice the properties of the organic and the inorganic stacks. For this purpose we reacted the organic acceptor molecule TCNQ with planar or nearly planar  $\text{Pt}^{\text{II}}$  complexes with N-containing ligands. In segregated stacks TCNQ normally forms self-complexes leading to either equidistant stacks or stacks composed of dimers, trimers or tetramers. (Herbststein, 1971; Ashwell, Eley, Fleming, Wallwork & Willis, 1976.) Until now there has been no example of a dimerization of TCNQ radical anions *via*  $\sigma$ -bonding, which should lead to a diamagnetic state.

The compound  $\text{Pt}(2,2'\text{-dipy})_2(\text{TCNQ})_2$  can be obtained in two modifications: one is paramagnetic at room temperature, while the other is nearly diamagnetic. The crystal structure and the EPR properties of the latter modification are described below; the crystal structure of the former is under investigation.

## Experimental

$\text{Pt}(2,2'\text{-dipy})_2(\text{TCNQ})_2$  was prepared as described by Endres, Keller, Moroni & Nöthe (1976). Dark-brown shiny prismatic single crystals were obtained from a methanol–dimethyl sulphoxide mixture.

Rotation and Weissenberg photographs showed the crystals to be triclinic. The accurate  $\theta$  values of 39 reflexions were determined on a single-crystal diffractometer. Based on these, the lattice constants were calculated by least squares (Berdesinski & Nuber, 1966). Crystallographic data are summarized in Table 1.

Intensity measurements were carried out on a computer-controlled single-crystal diffractometer (Siemens) with the five-value method and a  $\theta/2\theta$  scan technique. Up to 30°  $\theta$ , 4122 independent reflexions were observed, classifying reflexions with intensity  $I < 2.58\sigma(I)$  as unobserved. The observed reflexions were corrected for polarization and Lorentz factors. No further corrections were applied. Calculations were carried out on Siemens 301 (Anorganisch-Chemisches

Table 1. *Crystal data*

Formula	$\text{Pt}(\text{C}_{10}\text{H}_{10}\text{N}_2)_2 \cdot (\text{C}_{12}\text{H}_4\text{N}_4)_2$
Triclinic $P\bar{1}$	FW 879.85
$a = 7.891$ (7) Å	$F(000) = 426$
$b = 14.247$ (2)	$V = 890 \text{ \AA}^3$
$c = 12.253$ (2)	$Z = 1$
$\alpha = 130.01$ (5)°	$d_c = 1.65 \text{ g cm}^{-3}$
$\beta = 120.06$ (6)	
$\gamma = 61.97$ (6)	

Institut Heidelberg) and IBM 370/168 (Universitätsrechenzentrum Heidelberg) computers, with programs of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964).

EPR spectra were taken on a Bruker B-ER 418 spectrometer with an NMR gauss meter for field calibration and a DANA 320 D microwave frequency counter. Measurements at different temperatures were carried out with a Bruker B-ST 100/700 temperature control unit.

### Structure determination and refinement

As the unit cell contains only one formula unit, we placed the Pt atom at 0,0,0 and calculated a series of

Fourier syntheses in space group  $P\bar{1}$ . All atoms could be located in this way, but there was a close (1.65 Å) contact between the methylene C(17) of the two centrosymmetrically related TCNQ moieties. As we found this surprising, we changed to  $P1$ , but neither did the close contact open up significantly nor could a successful refinement be achieved (high or negative temperature factors). Therefore, we carried out the refinement in  $P\bar{1}$ . The final  $R$  for isotropic refinement was 0.121; refinement with anisotropic temperature factors for Pt yielded  $R = 0.075$ . Because of the large number of parameters the whole asymmetric unit could not be refined simultaneously with anisotropic temperature factors. Therefore, we refined either the positional parameters or the temperature factors alone. The final  $R$  was 0.059 (maximum shift/error 0.71). H atoms were ignored. Atomic positional parameters are listed in Table 2.\*

Table 2. Atomic coordinates ( $\times 10^3$ )

	x	y	z
Pt	0	0	0
C(1)	23 (1)	60 (1)	278 (1)
C(2)	70 (2)	50 (1)	398 (1)
C(3)	237 (2)	959 (1)	414 (1)
C(4)	351 (2)	887 (1)	318 (1)
C(5)	292 (1)	897 (1)	199 (1)
C(6)	874 (1)	166 (1)	263 (2)
C(7)	770 (2)	268 (1)	267 (1)
C(8)	665 (2)	374 (1)	355 (1)
C(9)	673 (1)	376 (1)	250 (1)
C(10)	775 (1)	271 (1)	147 (1)
C(11)	36 (1)	394 (1)	66 (1)
C(12)	18 (1)	454 (1)	209 (1)
C(13)	119 (1)	398 (1)	288 (1)
C(14)	244 (1)	276 (1)	232 (1)
C(15)	259 (1)	218 (1)	89 (1)
C(16)	158 (1)	272 (1)	8 (1)
C(17)	930 (1)	459 (1)	981 (2)
C(18)	874 (2)	370 (1)	820 (1)
C(19)	745 (1)	550 (1)	23 (1)
C(20)	346 (1)	218 (1)	316 (1)
C(21)	480 (1)	99 (1)	264 (1)
C(22)	312 (1)	272 (1)	448 (1)
N(1)	123 (1)	-15 (1)	177 (1)
N(2)	-135 (1)	167 (1)	150 (1)
N(3)	835 (1)	302 (1)	695 (1)
N(4)	606 (1)	620 (1)	58 (1)
N(5)	594 (1)	6 (1)	221 (1)
N(6)	279 (2)	316 (1)	555 (1)

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32485 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

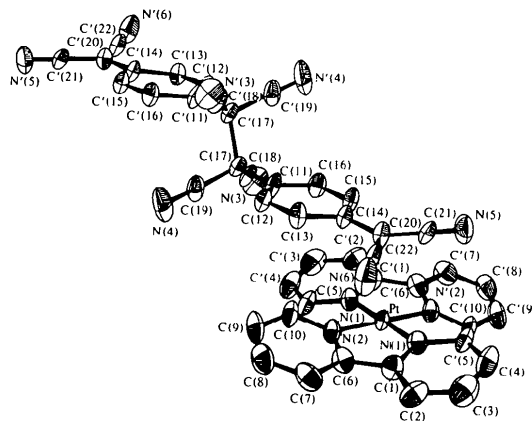


Fig. 1. ORTEP plot of the unit-cell contents of  $\text{Pt}(2,2'\text{-dipy})_2\text{-(TCNQ)}_2$ .

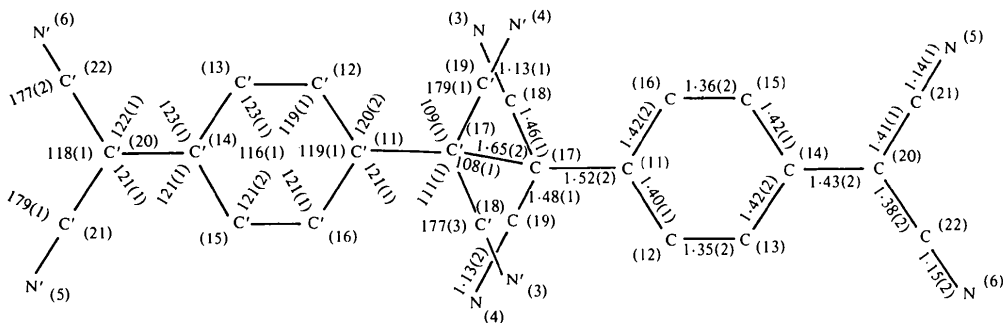


Fig. 2. Bond lengths (Å) and angles ( $^\circ$ ) in the  $(\text{TCNQ})_2^-$  dimer.

### Description of the structure

The triclinic unit cell contains one formula unit of  $\text{Pt}(2,2'\text{-dipy})_2^+(\text{TCNQ})_2^-$ , an *ORTEP* plot of which (Johnson, 1965) is shown in Fig. 1. Figs. 2 and 3 present the numbering scheme, bond distances and angles of the constituents. The Pt atom occupies a centre of symmetry at 0,0,0; the centre of gravity of the dimerized  $(\text{TCNQ})_2^-$  species is a centre of symmetry at  $0, \frac{1}{2}, 0$ .

Dimerization has occurred *via* an unusually long C—C bond (1.65 Å) between C(17) and C'(17), which have become tetrahedral. C(17) and its two cyano substituents lie on a plane (plane 1) which forms an angle of  $50^\circ$  with the plane through the benzene ring of the TCNQ (plane 2), which in turn forms an angle of  $7^\circ$  with the plane through the terminal  $\text{C}(\text{CN})_2$  group (plane 3). The deviations of the atoms from the respective planes are shown in Table 3.

The  $\text{Pt}(2,2'\text{-dipy})_2^+$  complex cation is not planar, but the two halves of one dipy molecule are tilted by  $22.7^\circ$  with respect to each other. Nevertheless there is a common plane through the Pt atom and its four N

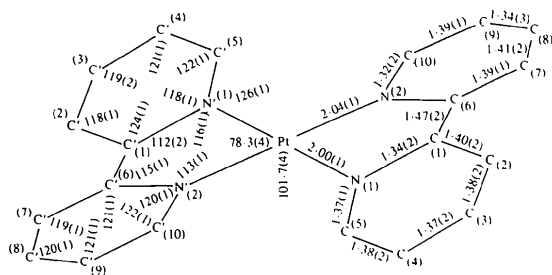


Fig. 3. Bond lengths (Å) and angles ( $^\circ$ ) in the  $[\text{Pt}(2,2'\text{-dipy})_2]^+$  cation.

Table 3. Deviations of the atoms (Å) from the best planes through parts of  $(\text{TCNQ})_2^-$

The equations of the planes are  $px + qy + rz - s = 0$ .

#### Plane 1

$$p = 4.765, q = 13.955, r = -9.231, s = 1.783$$

C(17)	-0.0014	N(3)	0.0074
C(18)	-0.0133	N(4)	-0.0093
C(19)	0.0165		

#### Plane 2

$$p = 6.980, q = 8.472, r = -2.805, s = 3.339$$

C(11)	0.007	C(14)	-0.004
C(12)	-0.005	C(15)	0.006
C(13)	0.004	C(16)	-0.007

#### Plane 3

$$p = 6.498, q = 8.227, r = -1.571, s = 3.551$$

C(20)	0.000	N(4)	0.009
C(21)	-0.017	N(5)	-0.009
C(22)	0.017		

neighbours. There are no unusual contacts between the  $(\text{TCNQ})_2^-$  dimer and the  $\text{Pt}(2,2'\text{-dipy})_2^+$  complex. The shortest distances (up to 3.4 Å) are shown in Fig. 4.

### EPR results

A signal can barely be seen at room temperature. At  $40^\circ\text{C}$  the elongated crystals show the two-line spectrum typical either of biradicals or localized triplet excitons (Frenkel excitons) (Fig. 5). Larger crystals show weak triplet lines even at room temperature. The central line (impurity signal?) has a relatively low intensity. The forbidden transition at half field cannot be seen, which is to be expected in view of the low intensity of the allowed transitions.

As the fine splitting is dependent on the orientation, anisotropy measurements were performed. The crystal was rotated parallel and perpendicular to its long axis (Fig. 6).

The measurements yielded the zero-field parameters  $D = 0.01 \text{ cm}^{-1}$ ,  $E = 0.0014 \text{ cm}^{-1}$ . The intensity of the fine-structure lines (expressed in  $I \sim \Delta^2 H_{pp} h$ ;  $\Delta H_{pp} =$  peak to peak line width,  $h =$  heights of signal) increases with increasing temperature. From  $I \sim \exp(-J/kT)$  one

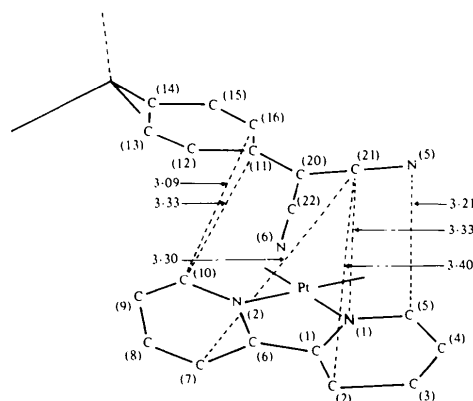


Fig. 4. Nearest contacts (up to 3.4 Å) between  $(\text{TCNQ})_2^-$  and  $[\text{Pt}(2,2'\text{-dipy})_2]^+$ .

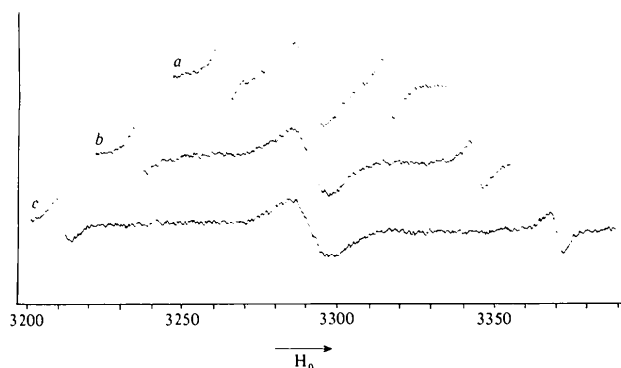


Fig. 5. EPR spectrum of  $\text{Pt}(2,2'\text{-dipy})_2(\text{TCNQ})_2$  single crystals at three different orientations.

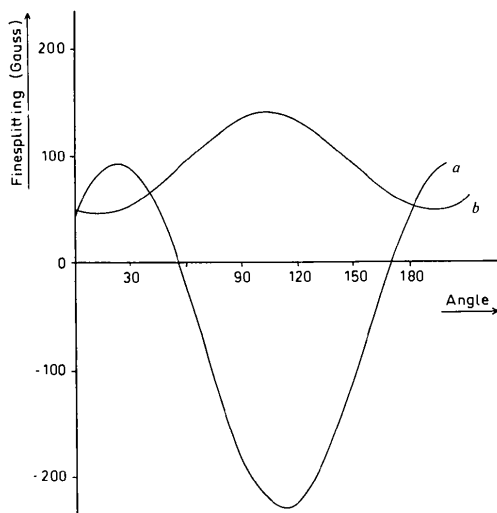


Fig. 6. Angular dependence of fine splitting: (a) rotation parallel to prism axis, (b) rotation perpendicular to prism axis.

can estimate the activation energy  $J$  for the paramagnetism to be 0.25 eV.

At about 75°C the fine-structure lines start to broaden. At 87°C the lines suddenly coincide to a single new line, the intensity of which is three orders of magnitude larger. This phase transition from a nearly diamagnetic to a paramagnetic modification is accompanied by a change in colour from grey green to grass green in powder samples.

Hyperfine splittings cannot be observed below or above the transition temperature.

### Discussion

The crystal structure clearly shows that two TCNQ anion radicals form a dimer which is held together by a C—C  $\sigma$ -bond with the unusual length of 1.65 Å. To our knowledge this is the first case where TCNQ radicals dimerize by forming a  $\sigma$ -bond in an analogous way as, for example, triphenylmethyl radicals form hexaphenylethane.

The activation energy necessary for exciting the electrons to a triplet state (0.25 eV) is large compared with the values observed in known TCNQ  $\pi$ -complexes. This can be understood from the presence of a  $\sigma$ -bond instead of a  $\pi$ -bonding mechanism which is normally observed in this class of compounds. Yet, speaking in terms of normal C—C  $\sigma$ -bonds, the bond strength is rather weak so that the triplet state is readily accessible. The lack of hyperfine structure shows that the triplet excitons can interact with one another despite the fact that no close dimer-dimer contacts exist in the lattice.

From the known spin-density distribution (Lowitz, 1967; Jonkman, van der Velde & Nievwoort, 1974) and taking into account only the spin density on the methylene C(17), a zero-field parameter  $D$  is calculated which is about a factor of three larger than that observed. Therefore, one can conclude that the spin-density distribution in our case is different from that normally found in TCNQ radical anions. This indicates that the geometry also in the excited triplet state differs from the usual (planar) arrangement.

At the transition temperature of 87°C an enormous increase in paramagnetism is observed accompanied by a colour change and sometimes by a macroscopic destruction of the crystals. We propose that at this point the  $\sigma$ -bond breaks and that the TCNQ radicals adopt their normal planar geometry. This is supported by the magnetic data (Endres, Keller, Moroni & Nöthe, 1976) which show that above the transition temperature the magnetic moment is 2.35 BM, which corresponds to two unpaired electrons per formula unit.

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