Contribution from IBM Research Laboratory,
San Jose, California 95193

Structural Characterization of the Charge-Transfer Complex Formed by Bis(propene-3-thione-1-thiolato)platinum(II) and Tetracyanoquinodimethane, $(C_3H_3S_2)_2Pt-C_{12}H_4N_4$

J. J. MAYERLE

Received October 1, 1976 AIC607276

The crystal and molecular structure of the charge-transfer complex formed by bis(propene-3-thione-1-thiolato)platinum(II) and 7,7,8,8-tetracyanoquinodimethane has been determined from three-dimensional x-ray counter data. The material crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in a cell of dimensions a = 8.744 (5) Å, b = 9.488 (2) Å, c = 6.156 (3) Å, α = 92.10 (2)°, β = 102.73 (2)°, and γ = 105.19 (3)°. Least-squares refinement of the structure has led to a final R factor of 0.037 using 3683 independent observations. The structure consists of alternate donor and acceptor molecules stacked coplanar to each other in columns along the a axis. The mean interplanar spacing of 3.42 Å and the geometry of the TCNQ molecule suggest that the degree of charge transfer is slight. The geometry about the platinum atom is distorted square planar, with Pt–S distances of 2.282 (1) and 2.278 (1) Å.

Introduction

Complexes of dithioacetylacetone (SacSac) and related ligands have been the subjects of extensive investigation[1,2] but complexes of the parent ligand, dithiomalonaldehyde (propene-3-thione-1-thiol), have only recently been reported. As part of a study of extended interactions in molecular crystals of organometallic charge-transfer systems, workers in this laboratory have for the first time synthesized and characterized transition metal complexes of dithiomalonaldehyde.[3] In this paper we report the crystal and molecular structure of the 1:1 charge-transfer molecular compound formed between the transition metal donor complex bis(propene-3-thione-1-thiolato)platinum(II) (hereafter Pt(PTT)$_2$) and the organic acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ).

Dithiomalonaldehyde is the prototype of a common and important class of ligands. Unfortunately, the parent Pt(PTT)$_2$ complex does not form crystals of sufficient quality for a precise structure determination. Since we found the crystal structure of Pd(PTT)$_2$ to be highly disordered,[4] it appeared that the most accurate bond lengths and angles would be obtained from a compound such as the TCNQ charge-transfer complex, in which the disorder is prevented by the presence of the acceptor molecule. This expectation proved to be quite true. Since a comparison of the bond lengths of the TCNQ molecule with the bond lengths of the TCNQ molecule in other such complexes indicates that the charge-transfer interaction is slight, the geometry of the Pt(PTT)$_2$ moiety should not be much different from that of neutral Pt(PTT)$_2$ itself.

Experimental Section

Crystals of Pt(PTT)$_2$–TCNQ, grown from acetonitrile, were generously provided by Drs. A. A. Alscher and U. T. Mueller-Westerhoff of this laboratory. Observation with a transmission polarizing microscope showed most of the long, narrow platelets to be twinned or cracked. From one of the larger crystals, however, a small, centrosymmetric single crystal of approximate dimensions 0.06 × 0.20 × 0.25 mm perpendicular to the faces (010), (100), and (0$\bar{1}$2), respectively, was cleaved. The crystal was mounted on the end of a glass fiber with nail enamel and transferred to an Enraf-Nonius CAD-4 automatic diffractometer where, following machine location and centering of 15 reflections, a preliminary unit cell and orientation matrix were computed. Subsequent to this, 15 high-angle reflections were computer centered and the initial cell constants refined by least squares[5] to give a triclinic unit cell, based on Zr-filtered Mo Kα_1 radiation (λ 0.709 30 Å), with parameters a = 8.744 (5) Å, b = 9.488 (2) Å, c = 6.156 (3) Å, α = 92.10 (2)°, β = 102.73 (2)°, and γ = 105.19 (3)°. A Delaunay reduction showed no higher symmetry. The calculated density for Z = 1 is 2.10 g/cm^3 compared to an experimental density of 2.09 g/cm^3 determined by flotation in bromoform/carbon tetrachloride.

Several open-counter ω scans gave peak widths at half-height of ~0.15°, indicating a mosaic spread acceptable for data collection. Data of the form ($\pm h,\pm k,l$) were collected using θ–2θ scans and Zr-filtered Mo K$\bar{\alpha}$ radiation to θ = 45°. The scan range was calculated according to the formula $\theta = (1.0 + 0.35 \tan \theta)°$ and was extended by 25% on each side of the scan range for background measurement. The scan rate, based on a fast prescan, was computed such that, if possible, 10^4 counts were to be obtained in the maximum time of 180 s allowed for a given reflection. The takeoff angle for the fine focus tube was set at 2.8°. An aperture with a height of 4.0 mm and a variable width of (3.0 + 2.11 tan θ) mm was placed in front of the scintillation counter at a distance of 173 mm from the crystal. Three standard reflections monitored after every 100 reflections showed no crystal or electronic instability over the course of data collection. A total of 5842 reflections were collected, of which 3683 were judged to be observed by the criterion $F^2 \geq 3\sigma(F^2)$. The value of $\sigma(F^2)$ was obtained from the equation

$$\sigma(F^2) = Lp^{-1}[E + 4(B_1 + B_2) + (\epsilon I)^2]^{1/2}$$

in which E is the total integrated count, B_1 and B_2 are the background counts at each end of the scan, ϵ is the "ignorance factor",[6] set equal to 0.04 in this case, $I = E - 2(B_1 + B_2)$, and Lp is the Lorentz–polarization factor. The intensities, I, were corrected for Lp and absorption effects. The transmission coefficients ranged between 0.221 and 0.652 based on a linear transmission coefficient μ = 78.36 cm^{-1}.

The data were placed on an absolute scale through a modification of Wilson's method,[5] which produced an estimated mean B of 1.66 and scale factor of 0.941. The scattering factors for the neutral atoms were taken from ref 7. Corrections for the anomalous dispersion of Pt and S were applied to the calculated structure factors.[8]

Since both molecules could possess a center of symmetry, $P\bar{1}$ (C_i^1, No. 2)[9] was selected as the most likely space group, a choice subsequently confirmed by the successful refinement of the structure. An origin-removed Patterson map computed[5] using the corrected data yielded the positions of the sulfur atoms. A few cycles of refinement using unit weights followed by a difference Fourier synthesis yielded the positions of the remaining atoms of the Pt(PTT)$_2$ unit and part of the TCNQ moiety. Another difference Fourier synthesis, calculated following refinement of the Pt(PTT)$_2$ molecule alone, yielded the remainder of the nonhydrogen atoms. Refinement of the entire structure using isotropic thermal parameters and the weighting scheme discussed below led to a discrepancy factor R = 0.104. At this point anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were assigned to all of the nonhydrogen atoms. Several cycles of refinement of the 123 parameters led to convergence with discrepancy indices R = 0.037 and R_w = 0.038 based on 3683 observations with $F^2 \geq 3\sigma(F^2)$. The error in an observation of unit weight was computed to be 1.07. A difference Fourier computed at this stage was essentially featureless and the structure was thus considered complete. The change in any parameter during the last cycle of refinement was at most 0.001 that of its standard deviation.

The quantity minimized in the full-matrix least-squares refinement[5] is $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated

Table I. Final Atomic Positional and Anisotropic Thermal Parameters for $Pt(S_2C_3H_3)_2$–$C_{12}H_4N_4$[a,b]

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0	0	0	7.33 (2)	6.88 (2)	11.87 (3)	2.30 (2)	1.05 (2)	1.42 (2)
S(1)	0.1364 (1)	−0.1559 (1)	0.1714 (2)	12.2 (1)	9.4 (1)	16.1 (2)	4.8 (1)	0.0 (1)	1.8 (1)
S(2)	−0.1063 (1)	−0.1346 (1)	−0.3396 (2)	13.0 (1)	9.6 (1)	14.0 (2)	4.2 (1)	−0.9 (1)	0.0 (1)
C(A)	0.1287 (6)	−0.3018 (5)	0.0070 (8)	13.1 (6)	9.1 (5)	22.8 (11)	5.3 (5)	3.9 (6)	3.2 (6)
C(B)	0.0503 (7)	−0.3501 (6)	−0.2155 (9)	16.4 (8)	9.8 (5)	24.3 (12)	5.7 (5)	2.5 (8)	−0.2 (6)
C(C)	−0.0498 (7)	−0.2881 (6)	−0.3617 (7)	15.4 (7)	10.4 (5)	18.6 (10)	3.6 (5)	1.9 (7)	−2.0 (6)
N(1)	0.3945 (10)	−0.3776 (7)	−0.5627 (9)	30.2 (13)	16.4 (8)	23.9 (12)	12.7 (9)	−7.0 (1)	−5.4 (8)
N(2)	0.7136 (6)	−0.4040 (5)	0.0899 (6)	14.6 (6)	10.9 (5)	25.3 (11)	5.5 (5)	−0.9 (6)	−1.9 (9)
C(1)	0.4584 (7)	−0.3301 (5)	−0.3831 (8)	15.9 (5)	9.5 (5)	20.6 (10)	6.6 (5)	−1.5 (7)	−1.7 (6)
C(2)	0.6347 (5)	−0.3426 (5)	−0.0219 (7)	11.0 (5)	7.0 (4)	19.2 (9)	2.6 (4)	0.4 (5)	0.1 (5)
C(3)	0.5358 (5)	−0.2662 (5)	−0.1585 (7)	10.6 (5)	7.7 (4)	17.7 (9)	3.4 (4)	0.3 (5)	0.3 (5)
C(4)	0.5175 (4)	−0.1348 (4)	−0.0810 (6)	8.6 (4)	7.1 (4)	16.0 (8)	3.1 (3)	0.7 (5)	0.9 (4)
C(5)	0.4196 (5)	−0.0580 (5)	−0.2216 (6)	10.5 (5)	9.4 (5)	13.5 (7)	3.8 (4)	−0.5 (5)	0.6 (5)
C(6)	0.4027 (5)	0.0697 (5)	−0.1462 (6)	9.6 (5)	8.5 (4)	15.6 (8)	3.5 (4)	−0.5 (5)	1.2 (5)

[a] Atoms are labeled as indicated in Figures 1 and 2. [b] Standard deviations in the least significant figure are given in parentheses. [c] The form of the anisotropic thermal ellipsoids is given in the text; values here are × 10^3.

Table II. Interatomic Distances (Å) and Angles (deg) in $Pt(S_2C_3H_3)_2$–$C_{12}H_4N_4$[a]

Atoms	Distance	Atoms	Angle
Pt–S(1)	2.282 (1)	S(1)–Pt–S(2)	97.56 (4)
Pt–S(2)	2.278 (1)	S(1)–Pt–S(2′)	82.44 (4)
S(1)–C(A)	1.663 (5)	Pt–S(1)–C(A)	114.7 (2)
S(2)–C(C)	1.666 (5)	Pt–S(2)–C(C)	114.6 (2)
C(A)–C(B)	1.389 (7)	S(1)–C(A)–C(B)	132.1 (4)
C(B)–C(C)	1.373 (8)	S(2)–C(C)–C(B)	132.7 (4)
		C(A)–C(B)–C(C)	128.1 (5)
N(1)–C(1)	1.139 (7)	N(1)–C(1)–C(3)	177.9 (5)
N(2)–C(2)	1.149 (6)	N(2)–C(2)–C(3)	179.4 (13)
C(1)–C(3)	1.431 (6)	C(1)–C(3)–C(2)	117.1 (4)
C(2)–C(3)	1.426 (6)	C(1)–C(3)–C(4)	120.9 (3)
C(3)–C(4)	1.380 (6)	C(2)–C(3)–C(4)	121.9 (3)
C(4)–C(5)	1.435 (5)	C(3)–C(4)–C(5)	121.4 (3)
C(4)–C(6′)	1.451 (5)	C(3)–C(4)–C(6′)	120.8 (3)
C(5)–C(6)	1.337 (6)	C(4)–C(5)–C(6)	121.2 (3)
		C(4)–C(6′)–C(5′)	121.0 (3)
		C(5)–C(4)–C(6′)	117.8 (3)
S(1)···S(2)	3.430 (1)		
S(1)···S(2′)	3.005 (2)		

[a] See footnote *b* of Table I.

Table III. Root-Mean-Square Amplitudes of Vibration (Å)[a]

Atom	Min	Intermed	Max
Pt	0.1392 (2)	0.1657 (2)	0.1705 (2)
S(1)	0.152 (1)	0.192 (1)	0.223 (1)
S(2)	0.150 (1)	0.192 (1)	0.231 (1)
C(A)	0.168 (5)	0.205 (5)	0.220 (5)
C(B)	0.184 (6)	0.207 (5)	0.250 (6)
C(C)	0.170 (5)	0.218 (5)	0.238 (5)
N(1)	0.182 (5)	0.217 (6)	0.373 (6)
N(2)	0.176 (5)	0.215 (5)	0.257 (5)
C(1)	0.169 (5)	0.178 (5)	0.269 (6)
C(2)	0.169 (5)	0.175 (4)	0.215 (5)
C(3)	0.165 (4)	0.175 (5)	0.211 (5)
C(4)	0.152 (4)	0.171 (5)	0.191 (4)
C(5)	0.145 (4)	0.189 (5)	0.213 (5)
C(6)	0.147 (4)	0.186 (5)	0.207 (5)

[a] See footnote *b* of Table I.

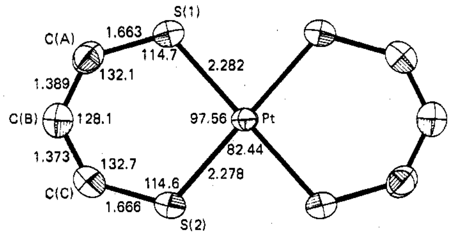

Figure 1. The $Pt(PTT)_2$ molecule. The 50% probability ellipsoids are depicted.

structure amplitudes. The weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$. The discrepancy indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o)^{1/2}$.

Table I contains the final positional and thermal parameters for all atoms, with their standard deviations derived from the inverse matrix of the last least-squares cycle. Bond distances and angles are listed in Table II, while Table III contains the root-mean-square amplitudes of thermal vibration.

Description of Structure and Discussion

Crystals of $Pt(PTT)_2$–TCNQ consist of individual centrosymmetric $Pt(PTT)_2$ and TCNQ molecules stacked approximately coplanar to each other in a D–A–D–A arrangement along the *a* axis, a common mode of stacking for 1:1 charge-transfer complexes and a feature of the structure that will be discussed below.

The atom-labeling scheme and the anisotropic thermal ellipsoids of the $Pt(PTT)_2$ molecule are shown in Figure 1. Bond distances and angles are listed in Table II. Since $Z = 1$, both the $Pt(PTT)_2$ and TCNQ molecules are required to be centrosymmetric and, because of this, the coordination about the Pt atom ($Pt–S_4$) is rigidly planar. Such is not the case for the entire molecule. There is a dihedral angle of 3.3° between the plane defined by S(1)–Pt–S(2) and the mean ligand plane defined by S(1)–C(A)–C(B)–C(C)–S(2), Table IV. This chair conformation is seen also in the square-planar complex bis(dithioacetylacetonato)nickel(II)[10] (hereafter $Ni(SacSac)_2$) and is apparently a common feature in metal complexes of β-keto enolates.[11] The angle subtended at the platinum atom by sulfur atoms of the same ligand is 97.56°. This and the interligand S(1)–Pt–S(2′) angle of 82.44° are very similar to the corresponding values of 97.20 and 82.80° found for $Ni(SacSac)_2$.[10] Thus the stereochemistry about the platinum atom is best described as slightly distorted square planar. The Pt–S distances of 2.282 (1) and 2.278 (1) Å are rather short compared to the average values of 2.305 and 2.289 Å found in bis(ethylene-1,2-dithiolato)platinum[12] and those of 2.308 and 2.312 Å found in bis(dimethyl-*o*-thiolophenylarsine)platinum(II)[13] and PtS,[14] respectively. A short Pt–S distance of 2.27 Å has been reported for the compound bis(8-mercaptoquinolinato)platinum(II).[15]

Although there is no crystallographic symmetry imposed on the ligand, the first fact to be noted about the chelate ring is that the values of chemically equivalent bond lengths and angles within the ring are essentially identical. Since accurate structural information on simple $M(PTT)_2$ complexes is not available, the geometry within the chelate ring may be compared to the geometry found in square-planar complexes of dithioacetylacetone, in particular to that of $Ni(SacSac)_2$.[10] The C–S bond lengths of 1.663 (5) and 1.665 (5) Å are significantly shorter than that of 1.685 (3) Å found in Ni-

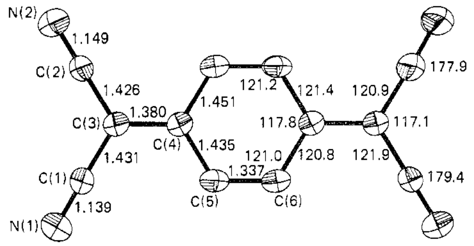

Figure 2. The TCNQ molecule. The 50% probability ellipsoids are depicted.

Table IV. Least-Squares Planes for $Pt(S_2C_3H_3)_2$-$C_{12}H_4N_4$[a]

Atom	Dev,[b] Å Plane 1	Plane 2	Plane 3	Plane 4
Pt	0		0.0018	
S(1)	0	−0.0002	−0.0070	
S(2)	0	0.0003	−0.0063	
C(A)		0.0056	0.0822	
C(B)		0.0130	0.1213	
C(C)		−0.0224	0.0545	
N(1)				0.0063
N(2)				0.0057
C(1)				0.0005
C(2)				0.0042
C(3)				−0.0109
C(4)				−0.0072
C(5)				−0.0012
C(6)				0.0083

Coefficients of Planes

Coeff	Plane 1	Plane 2	Plane 3	Plane 4
A	0.8068	0.7820	0.8044	0.7878
B	0.5038	0.5523	0.5086	0.5311
C	−0.3087	−0.2889	−0.3070	−0.3119
D	0.0000	−0.0871	−0.0018	3.4436

Interplanar Dihedral Angles, Deg

Plane 1-plane 2	3.32	Plane 3-plane 4	1.63
Plane 2-plane 4	1.82		

[a] Equation of the plane is $AX + BY + CZ - D = 0$ referred to orthogonal coordinates in which X is along a, Y is in the ab plane, and Z is along the c^* axis. [b] Deviation from the plane; indicates atoms making up the planes.

$(SacSac)_2$ or that of 1.716 (13) Å found in $Co(SacSac)_2$.[10] This, the rather short Pt–S bond lengths, and the small dihedral angle between the S–Pt–S and mean ligand planes may reflect the large degree of delocalization associated with this complex.[3] The average C–C distance of 1.381 (6) Å is typical of the values found in complexes of β-keto enolates and is close to that expected for an aromatic system. The intraligand angles are not significantly different from those found in dithioacetylacetone complexes. The exception is the average S–C–C angle of 132.4 (3)°, which is 4° larger than the corresponding angles in $Ni(SacSac)_2$. The cause of this is the expansion of the ring necessary to accommodate the platinum atom. This is further reflected in the large ligand "bite" distance of 3.430 (1) Å, which is 0.195 Å greater than the value of 3.235 Å found in $Ni(SacSac)_2$. Interestingly enough, in going from $Ni(SacSac)_2$ to $Pt(PTT)_2$ the angles about the metal atom essentially remain the same, as does the C–C–C angle, and the increase in the size of the metal atom is accommodated by an increase of the C–C–S angles and a decrease of the C–S–M angles. A similar expansion of the ring occurs in $Pd(PTT)_2$,[4] in which the C–C–C angle remains at ~128° while the C–C–S angles increase to ~133°. The interligand S–S distance in the present complex is 3.004 (2) Å. Although 0.5–0.7 Å shorter than twice the van der Waals radius of multiply bonded sulfur,[16,17] it is significantly longer than the corresponding distance of 2.852 (2) Å found in $Ni(SacSac)_2$. This also is due to the difference in size of the metal atoms.

The atom-labeling scheme and the anisotropic thermal ellipsoids of the TCNQ molecule are shown in Figure 2. The only symmetry possessed by the molecule is a center of symmetry, imposed crystallographically. An examination of Table IV reveals the molecule to deviate only slightly from strict planarity, in contrast to the distinct nonplanarity, usually the result of deviation of the cyano groups from the quininoid plane, often found in TCNQ salts.

A most useful piece of information to be obtained from a structural determination such as this is the degree of charge transfer as judged by comparison of the bond lengths and angles in the TCNQ molecule with the same molecular parameters in structures in which the charge on the TCNQ moiety is known. A survey of the literature indicates that such comparisons, although numerous, are at best difficult to make. Although it is true that the various averaged bond lengths, as compiled by Herbstein,[18] do show a correlation with the degree of charge transfer, the differences in a given bond length in going from $TCNQ^0$ to $TCNQ^{0.5-}$ to $TCNQ^-$ are often on the order of only one or two standard deviations, making the results of comparison for any single structure somewhat ambiguous. However, the length of the C(3)–C(4) bond seems to be particularly sensitive to the degree of charge transfer,[18,19] ranging from 1.374 Å in $TCNQ^0$ to 1.396 Å in $TCNQ^{0.5-}$ to 1.401 Å in $TCNQ^-$. The value of 1.380 (6) Å in the present compound seems to indicate that the charge-transfer interaction is slight. That this is so is further indicated by the interplanar spacing of ~3.4 Å, which is essentially the van der Waals spacing of aromatic molecules and is rather large compared to the distance in compounds in which the charge-transfer interaction is thought to be significant (vide infra).

The values of the other TCNQ molecular parameters are, with one exception, quite ordinary and, to a lesser degree than the C(3)–C(4) bond length, indicate the degree of charge

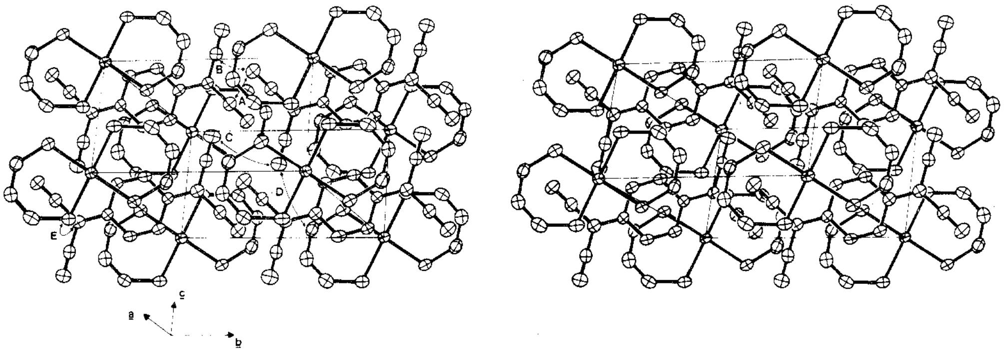

Figure 3. A stereoscopic view of the contents of one unit cell of $Pt(PTT)_2$–TCNQ. The arrows showing short non-bonded interactions are discussed in the text.

transfer to be slight. The CN bond lengths of 1.139 (7) and 1.149 (6) Å are equal, within their standard deviations, to the values found in other structures. The somewhat short value of 1.139 Å is most probably due to the anomalously large thermal motion exhibited by N(1), Table III. This thermal motion, in a direction approximately perpendicular to the TCNQ plane, is not unusual for TCNQ complexes. However, the fact that N(2) does not also exhibit this large thermal motion is somewhat surprising and may indicate that it is an artifact of the data. It should be pointed out that N(2) is pinned down to a greater degree than N(1) by interstack CN–CN coupling and short intrastack CN–PTT contacts. Long and co-workers[20] have estimated the correction for thermal motion for the CN bond lengths in neutral TCNQ to be as much as 0.01 Å. The values of 1.431 (6) and 1.426 (6) Å for the C(1)–C(3) and C(2)–C(3) bond lengths, respectively, fall within the range reported for TCNQ complexes. The C(5)–C(6) bond length of 1.337 (6) Å, which is among the shortest reported, is close to the value of 1.340 Å found in the phenazine complex of TCNQ.[21] Values of this bond length as high as 1.356 Å have been reported. The C(4)–C(5) and C(4)–C(6′) bond lengths of 1.435 (5) Å and 1.451 (5) Å give rise to the only large deviation from approximate *mmm* symmetry in the molecule.

The packing arrangement of the molecules within the unit cell, shown in Figure 3, is one of alternate donor and acceptor molecules stacked approximately plane to plane along the *a* axis. The $Pt(PTT)_2$ molecule is located at (0, 0, 0) and the TCNQ molecule is centered at ($^1/_2$, 0, 0). This D–A–D–A stacking sequence is a common feature of π molecular complexes and is the feature of the structure responsible for the high resistivity,[3] segregated stacks of donors and acceptors being one of the necessary conditions for metallic electrical behavior. There is a slight dihedral angle of 1.8° between the molecular planes, indicating perhaps some small degree of interaction between the donor and acceptor molecules. The molecular planes are tilted with respect to the stacking axis, the mean PTT plane being tilted 38.6° and the TCNQ plane being tilted 38.0°. The average perpendicular interplanar spacing is ~3.42 Å. Compared to intrastack contacts of 3.3 Å or less found in the TCNQ complexes of *N,N′*-dimethyldihydrophenazine[22] or *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine,[23] this intrastack distance is rather large and is another feature of the structure that suggests a weak charge-transfer interaction. A weak interaction was also postulated for the TCNQ complex of dibenzo-*p*-dioxin,[24] in which the interplanar spacing is 3.46 Å. Figure 3, in which the molecular planes lie in the plane of the paper, shows that the main intrastack interactions are such that electron-deficient C(3) lies under electron-rich S(2), indicated by the arrow labeled E, while the quininoid ring is situated such that S(1) atoms of different $Pt(PTT)_2$ molecules lie above and below it in a centrosymmetric manner. The C–N(2) group of the TCNQ molecule lies below the PTT ligand.

Short intermolecular contacts between like molecules in adjacent stacks are more numerous and probably more significant than those between different molecules in the same stack. These interstack contacts are dominated by close approaches of cyano groups which link the TCNQ molecules into a two-dimensional network. The short CN(2)–CN(2) contact of 3.218 Å and the CN(1)–CN(2) contact of 3.381 Å, indicated by arrows A and B, respectively, in Figure 3, link the TCNQ molecules in chains along the *b* axis. A CN(1)–CN(1) contact of 3.338 Å, arrow C in Figure 3, forms the cross-link between the chains. As in the phenazine complex of TCNQ,[21] this network of close approaches between cyano groups suggests that dipole–dipole interactions may be of importance in stabilizing the observed packing arrangement. The arrow labeled D in Figure 3 indicates a short (3.353 Å) contact between a cyano group and a PTT ligand in adjacent stacks.

Registry No. $Pt(PTT)_2$–TCNQ, 61505-68-8.

Supplementary Material Available: Table V, a listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A. R. Hendrickson and R. L. Martin, *Inorg. Chem.*, **14**, 979 (1975), and references therein.
(2) For a review see S. W. Schneller, *Int. J. Sulfur Chem., Part B*, **7**, 295 (1972).
(3) A. A. Alscher and U. T. Mueller-Westerhoff, unpublished results.
(4) J. J. Mayerle, unpublished results.
(5) Calculations were performed on an IBM 360-195 computer using the following programs: LSCELL, Corfield's adaptation of the Brookhaven cell parameter refinement program MODE; DATAB, Corfield's adaptation of the Brookhaven absorption program of the same name; XDATA, the Brookhaven Wilson plot and scaling program; FOURIER, by Dellaca and Robinson; BUGLS, the Brown University version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS) modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; and ORTEP-II, Johnson's thermal ellipsoid plotting program; various local programs.
(6) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(7) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A.
(8) D. T. Cromer, "International Tables for X-Ray Crystallography", Vol. IV, Birmingham, England, 1974, Table 2.3.1.
(9) "International Tables for X-Ray Crystallography", Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, p 75.
(10) R. Becket and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 662 (1974).
(11) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).
(12) K. W. Browall, T. Bursh, L. V. Interrante, and J. S. Kasper, *Inorg. Chem.*, **11**, 1800 (1972).
(13) J. P. Beale and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **27**, 73 (1971).
(14) F. Grønvold, H. Haraldsen, and A. Kjekshus, *Acta Chem. Scand.*, **14**, 1879 (1960).
(15) A. Ozola, L. Pecs, J. Ozols, and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 373 (1970); *Chem. Abstr.*, **73**, 81 735 (1970).
(16) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, p 260.
(17) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(18) F. H. Herbstein, *Perspect. Struct. Chem.*, **4**, 166–395 (1971).
(19) A. Hoekstra, T. Spoelder, and A. Vos, *Acta Crystallogr., Sect. B*, **28**, 14 (1972).
(20) R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, **18**, 932 (1965).
(21) I. Goldberg and U. Shmueli, *Acta Crystallogr., Sect. B*, **29**, 440 (1973).
(22) I. Goldberg and U. Shmueli, *Acta Crystallogr., Sect. B*, **29**, 421 (1973).
(23) A. W. Hanson, *Acta Crystallogr.*, **19**, 610 (1965).
(24) I. Goldberg and U. Shmueli, *Acta Crystallogr., Sect. B*, **29**, 432 (1973).