

Metal Tetrathiolenes. 3. Structural Study of the First Bimetallic Tetrathiolene Complex, Tetrakis(triphenylphosphine)diplatinum Tetrathionaphthalene, $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{C}_{10}\text{H}_4\text{S}_4)$, Revealing an Unexpected Molecular Distortion

BOON-KENG TEO* and P. A. SNYDER-ROBINSON

Received June 26, 1978

The quadridentate bridging nature of the tetrathiolene ligands, "tetrathiotetracene" ($\text{C}_{18}\text{H}_8\text{S}_4$, TTT), "tetrathionaphthalene" ($\text{C}_{10}\text{H}_4\text{S}_4$, TTN), and "tetrachlorotetrathionaphthalene" ($\text{C}_{10}\text{Cl}_4\text{S}_4$, TCTTN), was confirmed by a three-dimensional single-crystal X-ray diffraction study on $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$. The red $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN}) \cdot n\text{DMF}$ (where $n = 3.55$ from density measurement and 2.74 from X-ray structural determination) crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 12.368$ (4) Å, $b = 15.799$ (9) Å, $c = 12.242$ (4) Å, $\alpha = 107.40$ (3)°, $\beta = 114.39$ (2)°, $\gamma = 84.14$ (3)°, $V = 2078$ (1) Å³, and $Z = 1$. The structure was solved by the heavy-atom method and least-squares refined to the final reliability indices of $R_1 = 5.39\%$ and $R_2 = 6.09\%$. The molecular structure involves a tetrathionaphthalene ligand bridging two bis(triphenylphosphine)platinum(II) moieties via cleavage of both sulfur-sulfur bonds to form four platinum-sulfur bonds. Each platinum atom is coordinated to two phosphorus (from two PPh_3 ligands) and two sulfur (from the bridging TTN ligand) atoms in a "square-planar" configuration with average Pt-P and Pt-S bond lengths of 2.295 (3) and 2.307 (3) Å, respectively. The bridging TTN ligand is also approximately planar with the exception of the sulfur atoms. The molecule as a whole, though it conforms to the crystallographic C_2 symmetry, is by no means planar. The unexpected molecular distortions from planarity can be described as a rotation of the sulfur atoms about the central carbon-carbon bond of the bridging ligand followed by a rotation of each of the two platinum coordination planes about the sulfur-sulfur edge, resulting in the dihedral angles of 12.6 and 38.4°, respectively. These remarkable distortions can be rationalized in terms of intramolecular angular constraints as well as steric requirements. An unusual feature of the crystal structure is that the intramolecular platinum-platinum separation of 9.043 (4) Å is 1.382 Å longer than the shortest intermolecular platinum-platinum separation of 7.662 (4) Å. The intra- and intermolecular Pt-Pt vectors form a zigzag chain of platinum atoms parallel to the diagonal of the crystallographic ac plane.

Introduction

Recently we have synthesized and successfully characterized a new series of bimetallic tetrathiolene complexes^{1,2} with the general formula $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTL})$, where TTL = tetrathiotetracene ($\text{C}_{18}\text{H}_8\text{S}_4$, TTT), tetrathionaphthalene ($\text{C}_{10}\text{H}_4\text{S}_4$, TTN), or tetrachlorotetrathionaphthalene ($\text{C}_{10}\text{Cl}_4\text{S}_4$, TCTTN). Spectroscopic measurements^{1,2} led to the conclusion that the most probable structure of these complexes involves two metal coordinations bridged by a planar tetrathiolene ligand (TTL) via oxidative cleavage of the two S-S bonds, one on each side of the TTL molecule. In order to establish unambiguously the stereochemistry of these metal tetrathiolenes, we have performed a complete three-dimensional single-crystal X-ray structural determination on $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$ which, though essentially confirms our previous prediction,^{1a} reveals additional novel stereochemical features unprecedented by other metal-organic systems involving a quadridentate or a bis bidentate ligand.

Experimental Section

The compound was prepared and characterized as previously described.^{1a} All operations were performed in an argon-filled Vacuum Atmospheres drybox.

(a) **Crystal Growth.** All solvents used in the crystal growing process were freshly distilled under nitrogen. In particular, N,N' -dimethylformamide (DMF) and acetonitrile were freshly distilled from BaO and CaH₂, respectively. Initial attempts to grow good single crystals for X-ray structural studies using various solvent combinations and different crystal growing techniques were unsuccessful. Slow diffusion of acetonitrile into a saturated solution of methylene chloride gave red spearhead-like crystals which were found not to scatter X-rays whereas similar diffusion into a saturated chloroform solution produced needle-like crystals which were too small for X-ray diffraction studies. Finally, to a saturated DMF solution was added a small amount of acetonitrile and the mixture was allowed to slowly evaporate under anaerobic condition over a period of ca. 1 month, thereby producing rectangularly shaped bright red crystals suitable for X-ray diffraction studies.

The density of several crystals was measured to be 1.559 (2) g/cm³ by the flotation method (CCl_4 /1-bromobutane). This value is sig-

nificantly higher than the calculated value of 1.512 (28) g/cm³ based on the X-ray structural determination. This discrepancy is attributed to the loss of part of the solvent molecules in the crystal during data collection (vide infra).

(b) **X-ray Diffraction Measurements.** The crystal data were measured and the X-ray diffraction data were collected and reduced to structure factors^{3,4} at Molecular Structure Corp., College Station, Texas. These data are summarized in Table Ia,b, respectively.

(c) **Solution and Refinement.** Solution and least-squares refinement of the structure were done at Bell Laboratories. The structure was solved by the heavy-atom technique. Since there is only one molecule per unit cell (triclinic, space group $P\bar{1}$ or $P1$) the asymmetric unit consists of half of the molecule (viz., one $\text{Pt}(\text{PPh}_3)_2$ moiety and half of the TTN ligand) if it is located at the crystallographic inversion symmetry $\bar{1}$ of the centrosymmetric space group $P\bar{1}$ [C_i^1 ; No. 2].⁵ This latter choice of space group was confirmed by subsequent successful least-squares refinements. An analysis of a three-dimensional Patterson map⁶ yielded the positions of the platinum atom and four sulfur/phosphorus atoms.⁷ A few cycles of Fourier synthesis⁶ revealed the positions of all 46 nonhydrogen atoms.⁷ Least-squares refinements⁸⁻¹⁰ on the positional and isotropic thermal parameters gave rise to $R_1 = 9.51\%$ and $R_2 = 11.81\%$.⁹ The conversion and the subsequent least-squares refinements of the anisotropic thermal parameters of the nonphenyl atoms yielded $R_1 = 7.06\%$ and $R_2 = 9.59\%$. A difference Fourier map at this point revealed two badly disordered solvent (DMF) molecules and 12 nonsolvent hydrogen atoms including H(4) and H(5). Three more cycles of such anisotropic-isotropic least-squares refinements with idealized phenyl hydrogen positions at C-H of 1.00 Å and assigned constant isotropic thermal parameters of 7.00 Å² and 12 partial atoms attributable to the solvent molecules found in the difference map yielded $R_1 = 5.87\%$ and $R_2 = 7.14\%$. In these three cycles of refinements, the 12 partial atoms of the solvent molecules were first assigned constant isotropic thermal parameters of 6.00 Å² and their weights refined. Their thermal parameters were then refined to the values tabulated in Table II by holding the weights constant. And finally, in order to determine the number of solvent molecules somewhat more accurately, the weights were further refined to the values listed in Table II. For the solvent molecules no attempt was made either to differentiate the type (C vs. N vs. O) of each solvent atom (all refined as carbons) or to locate the hydrogen atoms. Further least-squares refinements involving anisotropic thermal parameters for all nonhydrogen and nonsolvent atoms resulted in the final

Table I

(a) Crystal Data			
formula	$[(C_6H_5)_3P]_4Pt_2 \cdot (C_{10}H_4S_4) \cdot 2.74C_3H_7NO$	crystal dimensions, mm ³	$0.3 \times 0.3 \times 0.35$
crystal color	red	cell volume, Å ³	2078 (1)
crystal shape	rectangular prism	Z	1
cell parameters (errors)		$d(\text{calcd})$, g/cm ³	1.512 (28)
a , Å	12.368 (4)	$d(\text{obsd})$, g/cm ³ (by flotation)	1.559 (2)
b , Å	15.799 (9)	Laue symmetry	triclinic
c , Å	12.242 (4)	space group	$P\bar{1}[C_i^1; \text{No. } 2]^5$
α , deg	107.40 (3)	systematic absences	none
β , deg	114.39 (2)	equivalent positions	$\pm(x, y, z)$
γ , deg	84.14 (3)		

(b) Collection and Reduction of the X-ray Diffraction Data			
diffractometer	Enraf Nonius	scan method	$\theta-2\theta$
	CAD4	no./freq	3/100
radiation (graphite monochromated)	Mo K α	of std reflection	
temperature	ambient	intensity variation	linear
μ , cm ⁻¹	23 (1)	of std reflections	25.8% ⁴
takeoff angle, deg	2.8	2 θ limits, deg	0-45
scan speed (limits), deg/min	4-20	cutoff of obsd data	$2\sigma(I)$
scan range, deg	1.4	unique data	5405
background:scan time ratio	0.5	p	0.05

(c) Solution and Refinement			
technique of solution	heavy atom ⁶	error or fit	1.56
method of refinement	full-matrix least squares ⁸	data/parameter	4501/457
isotropic convergence	$R_1 = 9.51\%$ ⁹	anomalous dispersion cor	
isotropic-anisotropic	$R_2 = 11.81\%$	$\Delta f'$ (real) ¹⁰	-1.9 (Pt), 0.1 (P), 0.1 (S)
max shifts (Δ/σ)	$R_1 = 5.39\%$	$\Delta f''$ (imag)	9.6 (Pt), 0.2 (P), 0.2 (S)
	$R_2 = 6.09\%$	max residual intensity of final difference map, e/Å ³	<1.6 (near Pt), others <0.5

discrepancy factors of $R_1 = 5.39\%$ and $R_2 = 6.09\%$.

The final positional and thermal parameters, with errors estimated from the full variance-covariance matrix, are listed in Table II.¹¹ Other crystallographic details are summarized in Table Ic.

Results and Discussions

Description of the Structure of $(Ph_3P)_4Pt_2(TTN)$. The crystal structure is composed of discrete molecules (one $(Ph_3P)_4Pt_2TTN$ molecule per cell) separated by van der Waals distances. It incorporates 3.55 molecules of solvent (DMF) of crystallization per cell as determined by density measurement (flotation method). In the X-ray structural determination, however, only ca. 2.74 molecules of DMF (vide infra) (assuming each DMF molecule amounts to a total of 33 electrons) were found. The discrepancy is presumably due to the loss of solvent during data collection.

The molecular structure of $(Ph_3P)_4Pt_2TTN$ is portrayed in Figure 1a-c in three different views.¹² It involves a tetrathionaphthalene (TTN) ligand bridging two bis(triphenylphosphine)platinum moieties via cleavage of both sulfur-sulfur bonds to form four platinum-sulfur bonds. Each platinum atom is therefore coordinated to two phosphorus (from two Ph_3P ligands) and two sulfur (from the TTN ligand) atoms in a "square-planar" configuration. The platinum coordination is very nearly planar. The bridging TTN ligand is also close to planarity (except, perhaps, the sulfur atoms). The molecule as a whole, however, is by no means planar. As a result, the molecule conforms to the crystallographic $\bar{1}$ - i site symmetry

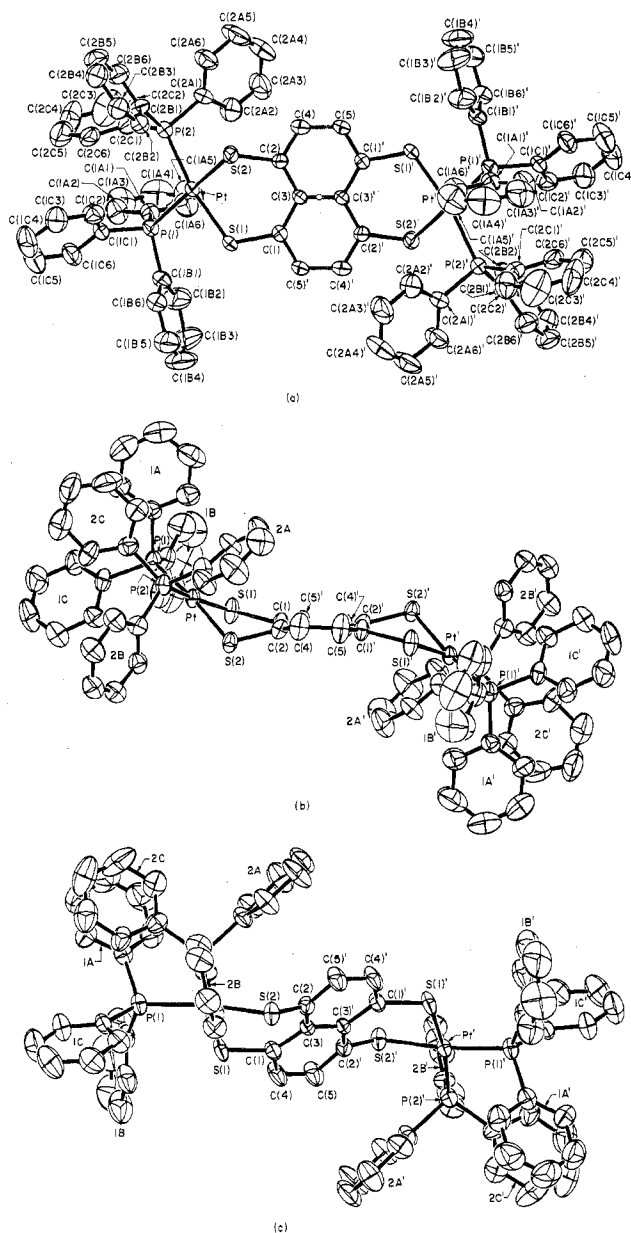


Figure 1. Stereochemistry of the $[(C_6H_5)_3P]_4Pt_2(C_{10}H_4S_4)$ molecule (ORTEP diagram, 50% probability ellipsoids, infinity projection) with crystallographic $C_i-\bar{1}$ symmetry located at the midpoint between C(3) and C(3'): (a) view along the normal of the naphthalene plane; (b) view similar to (a) but rotated 90° about the C(3)-C(3') bond; (c) general view.

in the centrosymmetric triclinic space group $P\bar{1}(C_i^1; \text{No. } 2)^5$ even though the highest possible idealized molecular symmetry is $D_{2h}-2mm$. The molecule is centrosymmetric with the center of symmetry located at the midpoint of C(3) and C(3'). The atomic labeling scheme and the anisotropic thermal ellipsoids (50%) are shown in Figure 1a.

The pertinent intramolecular distances and bond angles are tabulated in Tables III and IV, respectively.^{13,14}

Crudely speaking, the structure of $(Ph_3P)_4Pt_2(TTN)$ can be visualized as deriving from $(Ph_3P)_4Pt_2S_2$ ¹⁵ by inserting a $C_{10}H_4S_2$ group to the two bridging sulfides. The two dithio-chelating moieties (S_2C_3) of the TTN ligand are also qualitatively similar to the two PTT ligands (vide infra) in $Pt(PTT)_2^{x+}$ ¹⁶ except that they are now coordinated to two $Pt(PPh_3)_2$ groups rather than one single platinum atom. A detailed comparison of the molecular structures of these three complexes will therefore be of considerable interest (vide infra).

The molecular parameters within the platinum coordination plane appear to be normal (cf. Table III). The two Pt-P bond lengths are identical within experimental errors; the average value of 2.295 (3) Å is comparable to that of 2.260 and 2.270, 2.24(1), and 2.35 (1) Å found in $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{S}_2$, $(\text{Ph}_3\text{P})_3\text{Pt}_2\text{S}(\text{CO})$,¹⁷ and $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CS}_2)$,¹⁸ respectively. The two Pt-S distances differ by 0.017 Å which is statistically significant but probably chemically equivalent. The average value of 2.307(3) Å is somewhat longer than that of 2.280 (1) Å found in $\text{Pt}(\text{PTT})_2\text{TCNQ}$ (where PTT = bis(propene-3-thione-1-thiolato); TCNQ = tetracyanoquinodimethane)¹⁶ and that of 2.297 (7) Å found in $[\text{Pt}(\text{S}_2\text{C}_2\text{H}_2)_2]_2$ (where $\text{S}_2\text{C}_2\text{H}_2$ = ethylene-1,2-dithiolato)¹⁹ but comparable to those of 2.308 (3) and 2.312 Å found in bis(dimethyl-*o*-thiophenylarsine)platinum(II)²⁰ and PtS ,²¹ respectively. It is, however, shorter than that of 2.349 Å found in $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{S}_2$ but longer than those of 2.227 (9) and 2.218 (9) Å found in $(\text{Ph}_3\text{P})_3\text{Pt}_2\text{S}(\text{CO})$. If it is assumed that Pt-S bond lengths reflect the degree of π bonding (in addition to the σ bond) in structurally closely related systems, it is obvious that the (partial) π -bonding ability of the mercapto ligands increases from the disulfide (as in $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{S}_2$) to TTN (as in $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{TTN}$) to $\text{S}_2\text{C}_2\text{H}_2$ (as in $[\text{Pt}(\text{S}_2\text{C}_2\text{H}_2)_2]_2$) to PTT (as in $\text{Pt}(\text{PTT})_2^{x+}$). It must be emphasized, however, that this comparison is highly qualitative since the accurate structure of the neutral $\text{Pt}(\text{PTT})_2$ ¹⁶ is unknown and that in the former two structures the platinum coordination planes are not coplanar (with respect to each other as well as to the bridging ligand).

The P-Pt-P angle of 98.5 (1)° is virtually identical with that of 99.0° in $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{S}_2$. The S-Pt-S angle of 88.2 (1)° lies between that of 81.1° in $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{S}_2$ and that of 97.56 (4)° in $\text{Pt}(\text{PTT})_2^{x+}$. This latter trend can be correlated with the degree of folding of the platinum coordination plane(s) about the S...S bridge. This is not surprising because accompanying the increasing folding in going from $\text{Pt}(\text{PTT})_2^{x+}$ to $(\text{Ph}_3\text{P})_4\text{Pt}_2(\text{TTN})$ to $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{S}_2$ the S...S distance decreases dramatically from 3.430 (1) to 3.210 (4) to 3.054 Å whereas the average Pt-S distance increases from 2.280 (1) to 2.307 (3) to 2.349 Å. The two crystallographically independent P-Pt-S angles of 84.8 (1) and 89.3 (1)° are substantially different. This phenomenon, which probably stems from the low symmetry of the molecule, is also found in $(\text{Ph}_3\text{P})_4\text{Pt}_2\text{S}_2$ in which the two independent P-Pt-S angles are 87.0 and 92.6°.

The bond lengths and angles within the bridging TTN ligand are quite normal. The average S-C distance of 1.78 (1) Å is substantially longer than that of 1.665 (5), 1.685 (3), and 1.716 (13) Å in $\text{Pt}(\text{PTT})_2^{x+}$, $\text{Ni}(\text{SacSac})_2$,²² and $\text{Co}(\text{SacSac})_2$,²² respectively. The average C-C distance of 1.40 (1) Å is 0.02 Å greater than that of 1.38 Å found in the latter compounds. The expansion of the six-membered heterocyclic ring via lengthening of Pt-S, S-C, and C-C distances in going from SacSac to TTN ligand signifies the weakening of the extent of π delocalization in the same direction. In fact we believe that such expansion is one of the prime reasons for the distortion of the molecular structure from planarity (vide infra). The two independent Pt-S-C angles are significantly different: Pt-S(1)-C(1) of 115.8 (4)° is not far from the idealized trigonal value whereas Pt-S(2)-C(2) of 108.6 (3)° is close to the idealized tetrahedral value. The corresponding values (average) in $\text{Pt}(\text{PTT})_2^{x+}$, $\text{Ni}(\text{SacSac})_2$, and $\text{Co}(\text{SacSac})_2$ are 114.7 (2), 118.1 (1), and 118.7 (5)°, respectively.

The C-C bond lengths within the naphthalene group are quite normal. There exist alternations of long $C(i)-C(j) \approx 1.42$ Å for $i, j = 1, 3; 2', 3'; 4, 5'; 2, 3; 4, 5; 1', 3'$ and short $C(i)-C(j) \approx 1.36$ Å for $i, j = 1, 5'; 2', 4'; 2, 4; 1', 5$ C-C distances within each ring with the exception that the central

$C(3)-C(3')$ distance of 1.44 (2) Å turns out to be the longest. All C-C-C angles within the TTN ligand are close to the trigonal value of 120°.

The two independent triphenylphosphine ligands appear to be normal. The six phosphorus-carbon bond lengths range from 1.806 (11) to 1.858 (11) Å, averaging 1.823 Å which is comparable to the corresponding values found in other structures. The 36 independent carbon-carbon bond lengths span a range of 1.324 (18)-1.424 (16) Å with an average of 1.377 Å. The six Pt-P-C angles range from 108.13 (36) to 120.71 (38)° (average 114.45°) while the six C-P-C angles range from 101.1 (5) to 110.9 (5)° (average 104.1°). As in the cubane- or chair-like $(\text{Ph}_3\text{P})_4\text{Ag}_4\text{I}_4$ clusters,²³ the 12 P-C-C angles (cf. Table IV) can be categorized into two groups: those oriented toward the Pt-P axis are greater than 120° (122.5 (9)-125.4 (11)°) whereas those oriented otherwise are smaller than 120° (114.6 (9)-118.7 (9)°) except that both P(2)-C(2B1)-C(2B2) and P(2)-C(2B1)-C(2B6) are close to 120°. A close examination of intramolecular van der Waals contacts revealed partial hydrogen bonding interaction between H(2B2) and S(2) ($\text{S}(2)\cdots\text{H}(2\text{B}2) = 2.74$ Å) which may be the reason for the exception.

The solvent molecules, described here by 12 crystallographically independent partial carbon atoms of weights 0.511 (C(11)), 0.838 (C(12)), 0.501 (C(13)), 0.482 (C(14)), 0.712 (C(21)), 0.830 (C(22)), 0.541 (C(23)), 0.391 (C(24)), 0.631 (N(1)), 0.828 (N(2)), 0.574 (O(1)), and 0.693 (O(2)) are badly disordered and partially lost during the data collection. Assuming that a DMF molecule is equivalent to 33 electrons (excluding the hydrogen atoms), these weights correspond to a total of 1.37 independent solvent molecules, which amounts to 2.74 DMF molecules per unit cell. This latter value, when compared with the corresponding value of 3.55 obtained by a careful density measurement (floatation method) on the original crystals, suggests a loss of ca. 0.8 DMF molecule per unit cell in the process of X-ray structural data collection.

Molecular Nonplanarity. As shown in Figure 1 the most remarkable feature of the molecular structure is the distortion away from planarity, despite the fact that the two platinum coordinations and the bridging TTN ligand are not far from planarity. In fact, the platinum coordination P_2PtS_2 is roughly planar with the largest atomic displacement of 0.141 Å from the average plane (cf. Table VI). The dihedral angle between the PtP_2 and the PtS_2 planes within the platinum coordination is 9.2°. The bridging TTN ligand, however, is only approximately planar with the two crystallographically independent sulfur atoms S(1) and S(2) lying 0.461 and 0.538 Å (on opposite sides) out of the average plane of the naphthalene group (cf. Table VI). The torsional angles of C(2), C(3), C(1), S(1) and C(1), C(3), C(2), S(2) are 16.8° and -17.6°, respectively.

The overall molecular distortions from planarity can be characterized as a rotation of the sulfur atoms about the $C(3)-C(3')$ followed by a rotation of each of the two platinum coordination planes about the S...S vector, resulting in the dihedral angles of 12.6° between the average planes formed by the naphthalene group and S(1)-C(1)-C(3)-C(2)-S(2) and that of 38.4° between the average planes formed by S(1)-C(1)-C(3)-C(2)-S(2) and the PtS_2P_2 coordination, respectively. These molecular twistings are readily apparent from Figure 1 which depicts the stereochemistry of the molecule in three different views with respect to the naphthalene plane.

Nonplanar distortions of a much smaller degree have also been observed in other bi- or tetradentate ligand systems. For example, in $\text{Pt}(\text{PTT})_2^{x+}$ (which also contains a six-membered heterocyclic ring), there is a dihedral angle of 3.3° between the metal coordination plane (PtS_4) and the mean ligand plane

Table II. Positional and Isotropic Thermal Parameters with Esd's

atom	x	y	z	B, Å ²
Pt	0.23059 (4)	0.33598 (3)	0.13288 (4)	a
S(1)	0.2368 (3)	0.3689 (2)	0.3314 (3)	a
S(2)	0.3156 (3)	0.4747 (2)	0.1881 (2)	a
P(1)	0.1254 (3)	0.2079 (2)	0.0793 (3)	a
P(2)	0.2575 (3)	0.3128 (2)	-0.0485 (3)	a
C(1)	0.3551 (9)	0.4415 (7)	0.4510 (9)	a
C(2)	0.4449 (9)	0.4876 (6)	0.3285 (9)	a
C(3)	0.4491 (8)	0.4820 (6)	0.4429 (9)	a
C(4)	0.5428 (11)	0.5147 (8)	0.3231 (11)	a
C(5)	0.6420 (11)	0.5538 (9)	0.4351 (10)	a
C(1A1)	0.2066 (10)	0.1085 (7)	0.0380 (10)	a
C(1A2)	0.1571 (12)	0.0339 (8)	-0.0585 (12)	a
C(1A3)	0.2291 (17)	-0.0386 (10)	-0.0751 (16)	a
C(1A4)	0.3467 (17)	-0.0372 (10)	0.0037 (17)	a
C(1A5)	0.3932 (14)	0.0367 (11)	0.0971 (17)	a
C(1A6)	0.3247 (12)	0.1111 (8)	0.1165 (13)	a
C(1B1)	0.0896 (11)	0.1893 (8)	0.1993 (10)	a
C(1B2)	0.1417 (15)	0.1290 (10)	0.2641 (14)	a
C(1B3)	0.1080 (19)	0.1216 (14)	0.3565 (17)	a
C(1B4)	0.0286 (20)	0.1769 (14)	0.3907 (16)	a
C(1B5)	-0.0218 (16)	0.2395 (12)	0.3305 (14)	a
C(1B6)	0.0061 (12)	0.2439 (9)	0.2335 (11)	a
C(1C1)	-0.0230 (9)	0.2038 (7)	-0.0414 (10)	a
C(1C2)	-0.0651 (11)	0.2803 (8)	-0.0814 (11)	a
C(1C3)	-0.1834 (12)	0.2825 (10)	-0.1651 (13)	a
C(1C4)	-0.2567 (12)	0.2105 (12)	-0.2075 (15)	a
C(1C5)	-0.2171 (13)	0.1364 (10)	-0.1695 (15)	a
C(1C6)	-0.1010 (11)	0.1342 (8)	-0.0832 (12)	a
C(2A1)	0.4181 (10)	0.3290 (7)	-0.0061 (10)	a
C(2A2)	0.4975 (11)	0.2963 (9)	0.0848 (12)	a
C(2A3)	0.6184 (12)	0.3040 (11)	0.1186 (14)	a
C(2A4)	0.6581 (12)	0.3448 (10)	0.0618 (16)	a
C(2A5)	0.5793 (12)	0.3859 (11)	-0.0248 (16)	a
C(2A6)	0.4578 (11)	0.3757 (9)	-0.0597 (13)	a
C(2B1)	0.1755 (10)	0.3854 (7)	-0.1446 (9)	a
C(2B2)	0.1072 (10)	0.4539 (8)	-0.1057 (10)	a
C(2B3)	0.0384 (11)	0.5033 (8)	-0.1817 (11)	a
C(2B4)	0.0362 (12)	0.4896 (9)	-0.2982 (12)	a
C(2B5)	0.1036 (12)	0.4217 (9)	-0.3400 (12)	a
C(2B6)	0.1724 (11)	0.3706 (9)	-0.2634 (12)	a
C(2C1)	0.2241 (11)	0.2058 (7)	-0.1641 (10)	a
C(2C2)	0.3088 (13)	0.1439 (9)	-0.1761 (13)	a
C(2C3)	0.2743 (18)	0.0630 (10)	-0.2673 (16)	a
C(2C4)	0.1618 (19)	0.0402 (11)	-0.3448 (14)	a
C(2C5)	0.0741 (15)	0.1005 (11)	-0.3326 (13)	a
C(2C6)	0.1034 (12)	0.1819 (8)	-0.2458 (10)	a
C(11)	0.4653 (44)	0.1975 (33)	-0.5168 (44)	11.9 (15) ^c
C(12)	0.4880 (32)	0.0548 (24)	-0.5675 (33)	15.3 (13)
C(13)	0.3915 (41)	0.2110 (30)	-0.4091 (41)	11.2 (16)
C(14)	0.4717 (50)	0.0723 (37)	-0.3861 (50)	13.6 (20)
C(21)	0.7137 (31)	0.1644 (22)	-0.5530 (30)	11.3 (11)
C(22)	0.7728 (22)	0.3471 (17)	-0.4613 (23)	9.8 (7)
C(23)	0.6059 (48)	0.2989 (34)	-0.5717 (46)	13.2 (14)
C(24)	0.6671 (57)	0.2561 (40)	-0.5114 (55)	9.7 (14)
N(1)	0.4447 (31)	0.1259 (25)	-0.4782 (34)	10.6 (10)
N(2)	0.7247 (25)	0.2726 (20)	-0.5231 (26)	10.1 (7)
O(1)	0.5394 (47)	0.2468 (33)	-0.5391 (44)	13.5 (15)
O(2)	0.8197 (27)	0.1767 (19)	-0.4941 (27)	9.2 (8)
H(4)	0.550 (11)	0.513 (8)	0.221 (12)	7.0 ^b
H(5)	0.714 (12)	0.581 (8)	0.421 (12)	7.0
H(1A2)	0.0711	0.0311	-0.1160	7.0
H(1A3)	0.1936	-0.0928	-0.1463	7.0
H(1A4)	0.3961	-0.0904	-0.0089	7.0
H(1A5)	0.4790	0.0393	0.1548	7.0
H(1A6)	0.3616	0.1655	0.1869	7.0
H(1B2)	0.2042	0.0896	0.2455	7.0
H(1B3)	0.1441	0.0740	0.3985	7.0
H(1B4)	0.0080	0.1712	0.4591	7.0
H(1B5)	-0.0785	0.2821	0.3556	7.0
H(1B6)	-0.0352	0.2879	0.1864	7.0
H(1C2)	-0.0106	0.3328	-0.0500	7.0
H(1C3)	-0.2131	0.3370	-0.1931	7.0
H(1C4)	-0.3410	0.2123	-0.2674	7.0
H(1C5)	-0.2710	0.0832	-0.2033	7.0
H(1C6)	-0.0746	0.0809	-0.0516	7.0

Table II (Continued)

atom	x	y	z	B, Å ²		
H(2A2)	0.4694	0.2657	0.1294	7.0		
H(2A3)	0.6749	0.2785	0.1860	7.0		
H(2A4)	0.7446	0.3464	0.0804	7.0		
H(2A5)	0.6089	0.4223	-0.0616	7.0		
H(2A6)	0.4002	0.4030	-0.1246	7.0		
H(2B2)	0.1095	0.4666	-0.0198	7.0		
H(2B3)	-0.0118	0.5504	-0.1522	7.0		
H(2B4)	-0.0125	0.5274	-0.3530	7.0		
H(2B5)	0.1019	0.4101	-0.4257	7.0		
H(2B6)	0.2208	0.3223	-0.2939	7.0		
H(2C2)	0.3945	0.1573	-0.1195	7.0		
H(2C3)	0.3380	0.0201	-0.2741	7.0		
H(2C4)	0.1397	-0.0183	-0.4102	7.0		
H(2C5)	-0.0110	0.0839	-0.3881	7.0		
H(2C6)	0.0403	0.2254	-0.2390	7.0		

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	44.6 (4)	31.8 (2)	54.2 (4)	-9.8 (2)	15.3 (3)	11.4 (2)
S(1)	59.2 (26)	57.5 (18)	61.5 (27)	-32.4 (17)	18.6 (22)	12.1 (18)
S(2)	68.9 (27)	35.2 (14)	58.2 (26)	-16.2 (16)	12.1 (22)	15.2 (16)
P(1)	60.6 (27)	37.0 (15)	67.9 (29)	-13.5 (16)	18.7 (23)	16.2 (17)
P(2)	55.9 (27)	41.4 (16)	60.2 (28)	-9.0 (16)	20.6 (23)	12.4 (17)
C(1)	49 (10)	44 (6)	58 (10)	-13 (6)	21 (8)	7 (6)
C(2)	64 (10)	33 (5)	53 (10)	-11 (6)	27 (8)	8 (6)
C(3)	42 (9)	28 (5)	55 (9)	-5 (5)	22 (7)	8 (5)
C(4)	86 (13)	67 (8)	76 (12)	-26 (8)	41 (11)	20 (8)
C(5)	69 (12)	79 (9)	67 (12)	-34 (8)	34 (10)	11 (8)
C(1A1)	65 (12)	38 (6)	86 (12)	0 (7)	23 (10)	27 (7)
C(1A2)	103 (15)	41 (7)	126 (16)	-2 (9)	44 (13)	4 (9)
C(1A3)	178 (24)	51 (9)	183 (24)	-21 (13)	83 (21)	7 (12)
C(1A4)	196 (28)	49 (9)	224 (29)	22 (13)	116 (24)	37 (14)
C(1A5)	109 (18)	81 (12)	225 (28)	30 (12)	61 (18)	63 (15)
C(1A6)	111 (16)	47 (8)	138 (17)	-1 (9)	40 (14)	38 (9)
C(1B1)	86 (13)	45 (7)	86 (13)	-28 (8)	36 (11)	14 (8)
C(1B2)	172 (21)	74 (10)	148 (19)	-16 (11)	70 (17)	54 (12)
C(1B3)	245 (32)	130 (17)	160 (25)	-8 (19)	89 (23)	94 (17)
C(1B4)	261 (35)	126 (18)	154 (24)	-69 (20)	127 (25)	32 (17)
C(1B5)	181 (24)	101 (13)	124 (19)	-59 (14)	75 (18)	13 (13)
C(1B6)	104 (15)	79 (10)	90 (14)	-40 (10)	33 (12)	22 (9)
C(1C1)	53 (11)	51 (7)	70 (12)	-20 (7)	25 (9)	4 (7)
C(1C2)	81 (13)	51 (7)	98 (14)	4 (8)	35 (11)	36 (8)
C(1C3)	84 (15)	77 (10)	123 (17)	9 (10)	24 (13)	41 (11)
C(1C4)	58 (14)	120 (15)	167 (23)	-15 (12)	-7 (14)	44 (15)
C(1C5)	88 (16)	72 (10)	186 (23)	-26 (11)	12 (16)	34 (12)
C(1C6)	76 (13)	55 (8)	116 (15)	-23 (8)	18 (12)	27 (9)
C(2A1)	60 (11)	50 (7)	86 (12)	-9 (7)	36 (10)	20 (8)
C(2A2)	73 (13)	67 (9)	122 (16)	21 (8)	26 (12)	49 (10)
C(2A3)	71 (15)	96 (11)	157 (20)	-3 (10)	16 (14)	51 (12)
C(2A4)	80 (15)	79 (10)	220 (25)	-11 (10)	78 (17)	45 (13)
C(2A5)	76 (15)	111 (13)	229 (26)	0 (11)	77 (16)	83 (15)
C(2A6)	63 (13)	77 (9)	144 (17)	2 (8)	39 (12)	57 (11)
C(2B1)	77 (12)	44 (6)	65 (12)	5 (7)	40 (10)	19 (7)
C(2B2)	64 (11)	47 (7)	87 (13)	-7 (7)	22 (10)	21 (8)
C(2B3)	86 (14)	54 (8)	106 (16)	7 (8)	35 (12)	30 (9)
C(2B4)	92 (14)	65 (9)	106 (16)	8 (9)	25 (13)	35 (10)
C(2B5)	108 (15)	77 (9)	98 (15)	12 (10)	47 (13)	50 (10)
C(2B6)	94 (14)	67 (8)	102 (15)	9 (9)	44 (12)	36 (9)
C(2C1)	97 (13)	39 (6)	71 (12)	4 (8)	40 (11)	13 (7)
C(2C2)	117 (16)	54 (8)	123 (17)	-1 (10)	29 (14)	18 (10)
C(2C3)	233 (30)	56 (10)	164 (23)	41 (14)	70 (23)	2 (13)
C(2C4)	218 (31)	74 (12)	102 (19)	-37 (16)	-15 (20)	7 (12)
C(2C5)	166 (22)	80 (11)	99 (17)	-39 (13)	31 (16)	18 (12)
C(2C6)	123 (16)	49 (7)	68 (13)	-22 (9)	43 (12)	2 (8)

^a Anisotropic thermal parameters ($\times 10^4$) of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ are given in the second part of this table. ^b Hydrogen atoms were calculated at a C-H distance of 1.00 Å and assigned constant isotropic thermal parameters of 7.00 Å.

^c The 12 partial C, N, or O atoms attributable to the DMF molecules found in the difference map were first assigned constant isotropic thermal parameters of 6.00 Å² and their weights were refined. Their thermal parameters were then refined to these values by holding the weights constant. And finally, in order to better determine the number of DMF molecules, the weights were further refined to the following values by holding the thermal parameters constant (the scattering factor of carbon was used for all twelve atoms): C(11), 0.511; C(12), 0.838; C(13), 0.501; C(14), 0.482; C(21), 0.712; C(22), 0.830; C(23), 0.541; C(24), 0.391; N(1), 0.631; N(2), 0.828; O(1), 0.574; O(2), 0.693.

(S-C-C-C-S). Similar chair conformations have been observed in Ni(SacSac)₂ (8.6°) and Co(SacSac)₂ (ca. 6°). In Ni(Dto)₂(SnCl₄)₂²⁻ dianion,²⁴ which contains a five-membered heterocyclic ring, the central NiS₄ coordination plane makes

a dihedral angle of 9.0° with the bridging dithiooxalate (Dto) ligands which in turn make dihedral angles of 17.7° with the equatorial SnO₂Cl₂ plane of the terminal SnO₂Cl₄ complexes. It is also interesting to note that along the series²⁴ Ni(Dto)₂²⁻,

Table III. Interatomic Distances (Å) with Esd's

A. Pt-S Bond Lengths			
Pt-S(1)	2.2979 (29)	Pt-S(2)	2.3151 (30)
B. Pt-P Bond Lengths			
Pt-P(1)	2.2933 (30)	Pt-P(2)	2.2962 (29)
C. S-C Bond Lengths			
S(1)-C(1)	1.780 (10)	S(2)-C(2)	1.772 (10)
D. P-C Bond Lengths			
P(1)-C(1A1)	1.832 (11)	P(2)-C(2A1)	1.858 (11)
P(1)-C(1B1)	1.806 (11)	P(2)-C(2B1)	1.820 (11)
P(1)-C(1C1)	1.813 (11)	P(2)-C(2C1)	1.806 (11)
E. C-C (TTN) Bond Lengths			
C(3)-C(3)'	1.442 (18)	C(2)-C(4)	1.359 (14)
C(1)-C(3)	1.434 (13)	C(1)-C(5)'	1.359 (14)
C(2)-C(3)	1.408 (13)	C(4)-C(5)	1.423 (16)
F. C-C (Phenyls) Bond Lengths			
C(1A1)-C(1A2)	1.370 (15)	C(2A1)-C(2A2)	1.345 (15)
C(1A2)-C(1A3)	1.396 (19)	C(2A2)-C(2A3)	1.384 (17)
C(1A3)-C(1A4)	1.372 (22)	C(2A3)-C(2A4)	1.324 (18)
C(1A4)-C(1A5)	1.340 (21)	C(2A4)-C(2A5)	1.387 (20)
C(1A5)-C(1A6)	1.397 (19)	C(2A5)-C(2A6)	1.395 (17)
C(1A6)-C(1A1)	1.374 (16)	C(2A6)-C(2A1)	1.358 (15)
C(1B1)-C(1B2)	1.363 (17)	C(2B1)-C(2B2)	1.397 (15)
C(1B2)-C(1B3)	1.394 (21)	C(2B2)-C(2B3)	1.357 (15)
C(1B3)-C(1B4)	1.360 (27)	C(2B3)-C(2B4)	1.367 (17)
C(1B4)-C(1B5)	1.356 (25)	C(2B4)-C(2B5)	1.396 (17)
C(1B5)-C(1B6)	1.389 (18)	C(2B5)-C(2B6)	1.382 (16)
C(1B6)-C(1B1)	1.394 (17)	C(2B6)-C(2B1)	1.386 (15)
C(1C1)-C(1C2)	1.408 (15)	C(2C1)-C(2C2)	1.381 (17)
C(1C2)-C(1C3)	1.402 (17)	C(2C2)-C(2C3)	1.387 (19)
C(1C3)-C(1C4)	1.362 (20)	C(2C3)-C(2C4)	1.331 (23)
C(1C4)-C(1C5)	1.359 (21)	C(2C4)-C(2C5)	1.395 (23)
C(1C5)-C(1C6)	1.393 (18)	C(2C5)-C(2C6)	1.369 (18)
C(1C6)-C(1C1)	1.368 (15)	C(2C6)-C(2C1)	1.424 (16)
G. C-H (TTN) Bond Lengths			
C(4)-H(4)	1.29 (12)	C(5)-H(5)	1.13 (13)
H. DMF Bond Lengths (<1.90 Å)			
C(11)-O(1)	1.42 (6)	C(21)-O(2)	1.21 (4)
C(11)-N(1)	1.43 (5)	C(21)-N(2)	1.65 (4)
N(1)-C(12)	1.54 (4)	N(2)-C(22)	1.25 (3)
N(1)-C(13)	1.60 (5)	N(2)-C(23)	1.41 (5)
N(1)-C(14)	1.52 (6)	N(2)-C(24)	0.86 (6)
C(11)-C(13)	1.84 (6)	N(2)-O(2)	1.85 (4)
O(1)-C(23)	1.46 (6)	C(21)-C(24)	1.52 (6)
O(1)-C(24)	1.48 (7)	C(22)-C(24)	1.83 (6)
		C(23)-C(24)	1.14 (7)
I. Nonbonding Distances			
S(1)···S(2)	3.2110 (39)	Pt···Pt'	9.0435 (44)
P(1)···P(2)	3.4762 (41)	S(1)···H(5)'	2.71 (13)
S(1)···P(1)	3.2256 (43)	S(2)···H(4)	2.87 (12)
S(2)···P(2)	3.1096 (42)		

Ni(Dto)₂SnCl₄²⁻, and Ni(Dto)₂(SnCl₄)₂²⁻, the former increases from 1.6 to 6.3 to 9.0° whereas the latter (applicable only to the latter two anions) increases from 4.1 to 17.7°. The dihedral angle between NiS₄ and the nonbridging Dto ligand, however, is essentially unchanged in going from Ni(Dto)₂²⁻ (1.6°) to Ni(Dto)₂SnCl₄²⁻ (1.9°). Furthermore, in KSn[(C₂O₂S₂)₃Cu(P(tol)₃)]₂²⁻; ^{25a} the tin and the copper atoms are 0.111 (1) and 0.067 (1) Å above the least-squares plane of the bridging C₂O₂S₂ ligand whereas in [(Ph₃P)₂Ag]₃M-(O₂C₂S₂)₃; ^{25b} the silver (which is coordinated to the two sulfur atoms) and the M (which is coordinated to the two oxygen atoms) atoms lie 0.68, 0.64 and 0.05, 0.05 Å out of the bridging C₂O₂S₂ plane for M = Fe(III) and Al(III), respectively. For four-membered heterocyclic rings such as those observed in Ni(DED)₂²⁻ and Cu(DED)₂²⁻; ²⁶ the central MS₄ plane also forms a small dihedral angle (9.0° for Ni and 6.5° for Cu) with the "best" ligand plane, resulting in a displacement of the metal atoms of 0.266 (Ni) and 0.193 (Cu) Å from the mean ligand plane.

The folding of ligand-bridged dimeric "square-planar" d⁸ complexes across the bridging ligands appears to be quite common. In the closely related Mason structure (Ph₃P)₄Pt₂S₂, the fold across the S···S bridge amounts to 122° giving rise to a Pt···Pt distance of 3.18 Å. Similarly the two essentially planar Rh(CO)₂Cl units in [Rh(CO)₂Cl]₂ intersect at an angle of 124°, resulting in a Rh···Rh distance of 3.12 Å.²⁷ On the other hand, while [Rh(C₂H₄)₂Cl]₂²⁸ is folded (115.8°) along the Cl···Cl bridge, the Rh₂Cl₂ rhombus in [Rh(COD)Cl]₂²⁹ is strictly planar. The Rh···Rh distance of 3.02 (1) Å in the former structure is substantially shorter than the corresponding value of 3.50 Å in the latter compound. Similarly, the Pd₂Cl₂ moiety in [Pd(C₃H₉)Cl]₂³⁰ is nonplanar (150° fold) whereas the Pd₂Cl₂ rhombus in [Pd(C₃H₅)Cl]₂³¹ is strictly planar. While some, if not all, of the folding (nonplanarity) about the bridging ligands can be rationalized in terms of electronic effects such as metal-metal bonding (either through direct orbital overlap or via the bridging ligands),³² a similar argument is unlikely to be applicable in the present structure since the platinum atoms are 9.043 (4) Å apart and bridged by the TTN ligand.

The severe distortion of the present molecular structure from the expected planar conformation (viz., idealized D_{2h} symmetry for the nonphenyl atoms) can be due to a combination of various factors. It could be the result of (1) intramolecular van der Waals interactions involving either hydrogen bonding or steric repulsions, (2) stereochemical requirement of the S···S bites, with or without the involvement of the chelating S₂C₃ ring, (3) intermolecular van der Waals interactions such as crystal packing forces, (4) interactions with the solvent molecules, or (5) electronic effects.

We believe that the molecular nonplanarity of the present compound can be rationalized in the following manner. As pointed out by Beckett and Hoskins²² in their structural analysis of M(SacSac)₂ where M = Ni or Co, in order for the "square-planar" metal coordination to be coplanar with the dithiolene ligands, the sum of the internal bond angles of the six-membered heterocyclic ring must total 720°. A detailed comparison of the bond lengths and angles between M-(SacSac)₂ (M = Ni, Co) and Pt(PTT)₂^{x+} suggests that as a result of increasing M-S bond lengths in going from the former to the latter (2.156 (1) and 2.166 (3) to 2.280 (1) Å), the intraligand S···S bite distance must increase significantly (3.235 (2) and 3.242 (6) to 3.430 (1) Å) in order to maintain the same S-Pt-S angle and the planarity of the metal coordination. This then causes a drastic increase in the S-C-C angles (128.4 (3) and 128.1 (11)° to 132.4 (4)°) and a concomitant decrease in the M-S-C angles (118.1 (1) and 118.7 (5)° to 114.7 (2)°) if the metal coordination is to be approximately coplanar with the ligand. The situation is more complex in (Ph₃P)₄Pt₂(TTN) in that the opening of the S···S bite is restricted by steric factors involving both the TTN and the phosphine ligands. First consider the effect of the lengthening of the S···S distances on the ligand. As the S···S distances approach 3.04 Å, the average S···H distances approach 2.71 Å, some 0.14–0.34 Å below the sum of van der Waals radii of sulfur and hydrogen (2.85–3.05 Å). In order to further increase the S···S bite distance (note that the sum of van der Waals radius of two sulfur atoms is 3.70 Å whereas the intraligand S···S distance in a five- or six-membered heterocyclic ring is normally found to be ≥3.2 Å), the sulfur atoms move out of the naphthalene plane resulting in significant increases in both S···S (3.210 (6) Å) and S···H (average 2.79 Å) distances, thereby relieving the steric hindrance of both types. Similar steric hindrance is experienced at the metal coordination plane in that the two bulky phosphine ligands prefer to be well separated (the tendency to open up the P-Pt-P angle). The observed result, which probably

Table IV. Bond Angles (Deg) with Esd's

A. Pt Coordination			
S(1)-Pt-S(2)	88.23 (10)	S(1)-Pt-P(1)	89.27 (11)
P(1)-Pt-P(2)	98.48 (11)	S(2)-Pt-P(2)	84.80 (10)
S(1)-Pt-P(2)	170.05 (10)	S(2)-Pt-P(1)	172.79 (11)
B. Pt-S-C Angles			
Pt-S(1)-C(1)	115.78 (35)	Pt-S(2)-C(2)	108.61 (34)
C. Pt-P-C Angles			
Pt-P(1)-C(1A1)	112.23 (36)	Pt-P(2)-C(2A1)	108.13 (36)
Pt-P(1)-C(1B1)	116.37 (37)	Pt-P(2)-C(2B1)	115.49 (36)
Pt-P(1)-C(1C1)	113.79 (38)	Pt-P(2)-C(2C1)	120.71 (38)
D. C-P-C Angles			
C(1A1)-P(1)-C(1B1)	103.0 (5)	C(2A1)-P(2)-C(2B1)	107.7 (5)
C(1A1)-P(1)-C(1C1)	110.9 (5)	C(2A1)-P(2)-C(2C1)	102.4 (5)
C(1B1)-P(1)-C(1C1)	99.5 (5)	C(2B1)-P(2)-C(2C1)	101.1 (5)
E. S-C-C Angles			
S(1)-C(1)-C(3)	129.7 (8)	S(2)-C(2)-C(3)	125.7 (7)
S(1)-C(1)-C(5)'	109.8 (8)	S(2)-C(2)-C(4)	113.8 (8)
F. P-C-C Angles			
P(1)-C(1A1)-C(1A2)	125.0 (9)	P(2)-C(2A1)-C(2A2)	118.4 (9)
P(1)-C(1A1)-C(1A6)	114.6 (9)	P(2)-C(2A1)-C(2A6)	122.5 (9)
P(1)-C(1B1)-C(1B2)	125.4 (11)	P(2)-C(2B1)-C(2B2)	121.6 (8)
P(1)-C(1B1)-C(1B6)	117.7 (9)	P(2)-C(2B1)-C(2B6)	120.8 (9)
P(1)-C(1C1)-C(1C2)	118.4 (8)	P(2)-C(2C1)-C(2C2)	123.8 (10)
P(1)-C(1C1)-C(1C6)	122.6 (9)	P(2)-C(2C1)-C(2C6)	118.7 (9)
G. C-C-C (TTN) Angles			
C(1)-C(3)-C(2)	122.4 (8)	C(3)-C(1)-C(5)'	119.9 (9)
C(1)-C(3)-C(3)'	117.9 (10)	C(3)-C(2)-C(4)	120.0 (9)
C(2)-C(3)-C(3)'	119.7 (10)	C(2)-C(4)-C(5)	120.2 (10)
		C(4)-C(5)-C(1)'	121.1 (10)
H. C-C-C (Phenyl) Angles			
C(1A6)-C(1A1)-C(1A2)	120.3 (11)	C(2A6)-C(2A1)-C(2A2)	119.0 (11)
C(1A1)-C(1A2)-C(1A3)	118.6 (13)	C(2A1)-C(2A2)-C(2A3)	121.3 (13)
C(1A2)-C(1A3)-C(1A4)	121.7 (14)	C(2A2)-C(2A3)-C(2A4)	120.1 (14)
C(1A3)-C(1A4)-C(1A5)	118.6 (15)	C(2A3)-C(2A4)-C(2A5)	120.1 (13)
C(1A4)-C(1A5)-C(1A6)	121.7 (15)	C(2A4)-C(2A5)-C(2A6)	118.7 (13)
C(1A5)-C(1A6)-C(1A1)	119.2 (13)	C(2A5)-C(2A6)-C(2A1)	120.4 (12)
C(1B6)-C(1B1)-C(1B2)	116.8 (12)	C(2B6)-C(2B1)-C(2B2)	117.4 (10)
C(1B1)-C(1B2)-C(1B3)	120.3 (16)	C(2B1)-C(2B2)-C(2B3)	121.6 (11)
C(1B2)-C(1B3)-C(1B4)	122.0 (17)	C(2B2)-C(2B3)-C(2B4)	121.1 (12)
C(1B3)-C(1B4)-C(1B5)	118.8 (15)	C(2B3)-C(2B4)-C(2B5)	118.8 (11)
C(1B4)-C(1B5)-C(1B6)	119.5 (17)	C(2B4)-C(2B5)-C(2B6)	120.1 (12)
C(1B5)-C(1B6)-C(1B1)	122.4 (14)	C(2B5)-C(2B6)-C(2B1)	120.9 (12)
C(1C6)-C(1C1)-C(1C2)	118.4 (11)	C(2C6)-C(2C1)-C(2C2)	117.4 (11)
C(1C1)-C(1C2)-C(1C3)	119.8 (11)	C(2C1)-C(2C2)-C(2C3)	119.6 (14)
C(1C2)-C(1C3)-C(1C4)	119.7 (13)	C(2C2)-C(2C3)-C(2C4)	123.5 (17)
C(1C3)-C(1C4)-C(1C5)	121.0 (13)	C(2C3)-C(2C4)-C(2C5)	118.1 (15)
C(1C4)-C(1C5)-C(1C6)	120.0 (13)	C(2C4)-C(2C5)-C(2C6)	120.8 (15)
C(1C5)-C(1C6)-C(1C1)	120.9 (12)	C(2C5)-C(2C6)-C(2C1)	120.5 (13)
I. C-C-H (TTN) Angles			
C(2)-C(4)-H(4)	124.0 (56)	C(1)'-C(5)-H(5)	124.2 (65)
C(5)-C(4)-H(4)	115.6 (55)	C(4)-C(5)-H(5)	114.7 (65)
J. DMF Angles			
O(1)-C(11)-N(1)	151.6 (48)	O(2)-C(21)-N(2)	79.1 (26)
C(11)-N(1)-C(12)	94.0 (32)	C(21)-N(2)-C(22)	154.1 (30)
C(11)-N(1)-C(13)	74.8 (30)	C(21)-N(2)-C(23)	103.9 (32)
C(11)-N(1)-C(14)	153.6 (41)	C(21)-N(2)-C(24)	66.5 (51)
C(12)-N(1)-C(14)	94.5 (32)	C(22)-N(2)-C(23)	98.7 (32)
C(13)-N(1)-C(14)	98.4 (35)	C(22)-N(2)-C(24)	119.5 (58)
C(12)-N(1)-C(13)	167.1 (36)	C(23)-N(2)-C(24)	54.2 (47)
C(11)-O(1)-C(23)	174.7 (53)	O(2)-C(21)-C(24)	101.6 (37)
C(11)-O(1)-C(24)	139.2 (51)	N(2)-C(21)-C(24)	31.2 (23)
C(23)-O(1)-C(24)	45.8 (31)	N(2)-C(24)-C(21)	82.2 (57)
O(1)-C(23)-C(24)	68.5 (45)	N(2)-C(24)-C(23)	88.2 (63)
O(1)-C(23)-N(2)	105.9 (43)	C(21)-C(24)-C(23)	128.7 (58)
C(24)-C(23)-N(2)	37.6 (35)	O(1)-C(24)-C(21)	108.6 (46)
O(1)-C(24)-C(23)	65.8 (46)	O(1)-C(24)-N(2)	153.2 (76)

represents a compromise between various steric factors, is that $P-Pt-P = 98.5 (1)^\circ$ is greater than both $P-Pt-S = 89.3 (1)$ and $84.8 (1)^\circ$ and $S-Pt-S = 88.2 (1)^\circ$ and that the non-bonding $P \cdots P = 3.476 (4) \text{ \AA}$ is greater than both $P \cdots S = 3.226$

(4) and $3.110 (4) \text{ \AA}$ and $S \cdots S = 3.211 (4) \text{ \AA}$. Concomitant to the opening of the $S \cdots S$ bite distance is the increase of the average $S-C-C$ angle to 127.7° . In order for the six-membered $Pt_2S_2C_2$ ring to be planar with the observed $S-Pt-S$,

Table V. Nonbonding Distances

A. Intramolecular Pt···H (<3.80 Å), S···H (<3.50 Å), H(4)···H(5) and (Ph)H···H(Ph') (<2.80 Å) Contacts ^a			
Pt···H(1C2)	2.89	H(4)···H(5)	2.45 (18)
Pt···H(2B2)	3.06	H(1A2)···H(1C6)	2.24
Pt···H(2A2)	3.06	H(1A6)···H(2A2)	2.58
Pt···H(1A6)	3.10	H(1C2)···H(2B2)	2.56
Pt···H(2B3)	3.14	H(1C2)···H(2C6)	2.69
Pt···H(1B6)	3.80	H(2A6)···H(2B6)	2.46
S(1)···H(5)	2.71		
S(1)···H(1B6)	3.27		
S(2)···H(4)	2.87		
S(2)···H(2B2)	2.74		
B. Intermolecular Pt···H (<3.80 Å), S···H (<3.50 Å), (H(4), H(5))···H(Ph) and (Ph)H···H(Ph') (<2.80 Å) Contacts ^a			
Pt···H(2B3) ⁱ	3.14	H(1A4)···H(2C2) ⁱⁱⁱ	2.71
S(1)···H(2B4) ⁱ	3.14	H(1A5)···H(2C3) ⁱⁱⁱ	2.41
S(1)···H(2B3) ⁱ	3.17	H(1B2)···H(1C5) ^{iv}	2.73
S(2)···H(2A5) ⁱⁱ	2.99	H(1B4)···H(2C5) ^v	2.72
S(2)···H(1C3) ⁱ	3.11	H(1B6)···H(2A4) ^{vi}	2.69
H(4)···H(2A6) ⁱⁱ	2.28	H(1C2)···H(2B3) ⁱ	2.53
H(4)···H(2A5) ⁱⁱ	2.52	H(2C4)···H(2C5) ^{vii}	2.29
H(5)···H(2B5) ⁱⁱ	2.27		
C. Intermolecular S···X (<4.20 Å), C(n)···X (<4.20 Å) and X···H(Ph) (<3.40 Å) (where n = 1-5, X = C, N, or O of DMF) ^a			
S(1)···O(1) ^v	3.96 (5)	C(11)···H(1C4) ^{viii}	2.96
S(1)···C(11) ^v	3.99 (5)	C(11)···H(1A6) ^{ix}	3.20
S(2)···C(22) ⁱⁱ	4.13 (3)	C(12)···H(1A5) ^{ix}	3.29
C(1)···C(22) ⁱⁱ	3.54 (3)	C(12)···H(1C5) ^{vii}	3.34
C(1)···O(1) ^v	3.64 (5)	C(12)···H(2C3) ^x	3.37
C(1)···C(23) ^v	3.70 (5)	C(13)···H(1C4) ^{viii}	3.03
C(1)···C(23) ⁱⁱ	3.93 (5)	C(13)···H(2B6)	3.12
C(1)···C(11) ^v	4.03 (5)	C(14)···H(2C3)	2.85
C(2)···C(23) ^v	3.65 (5)	C(14)···H(1C4) ^{viii}	2.95
C(2)···C(23) ⁱⁱ	3.97 (5)	C(14)···H(1C5) ^{viii}	3.03
C(2)···C(22) ⁱⁱ	4.04 (3)	C(22)···H(1C3) ^{viii}	3.27
C(2)···O(1) ⁱⁱ	4.19 (5)	C(22)···H(1B5) ^{xi}	3.33
C(3)···C(23) ^v	3.32 (5)	C(23)···H(2A2) ^{ix}	3.23
C(3)···C(23) ⁱⁱ	3.48 (5)	C(23)···H(2A3) ^{ix}	3.33
C(3)···C(22) ⁱⁱ	3.67 (3)	C(24)···H(1C4) ^{viii}	3.30
C(3)···O(1) ^v	3.81 (5)	N(1)···H(1C4) ^{viii}	2.92
C(3)···O(1) ⁱⁱ	4.09 (5)	N(1)···H(1B2) ^{ix}	3.39
C(4)···C(23) ^v	3.89 (6)	N(2)···H(1B5) ^{xi}	3.37
C(5)···C(13) ⁱⁱ	3.79 (5)	N(2)···H(2A3) ^{ix}	3.38
C(5)···C(22) ^v	3.82 (3)	O(1)···H(1A6) ^{ix}	3.11
C(5)···O(1) ⁱⁱ	3.89 (5)	O(1)···H(1C4) ^{viii}	3.23
C(5)···C(11) ⁱⁱ	3.99 (5)	O(2)···H(2C4) ^x	2.52
C(5)···C(23) ^v	4.07 (5)	O(2)···H(2C5) ^{viii}	2.55
		O(2)···H(1B4) ^{xi}	2.60
		O(2)···H(2C6) ^{viii}	3.12

^a The superscripts refer to the following symmetry transformations: (prime) 1-x, 1-y, 1-z; (i) -x, 1-y, -z; (ii) 1-x, 1-y, -z; (iii) 1-x, -y, -z; (iv) -x, -y, -z; (v) x, y, 1+z; (vi) -1+x, y, z; (vii) -x, -y, -1-z; (viii) 1+x, y, z; (ix) x, y, -1+z; (x) 1-x, -y, -1-z; (xi) 1+x, y, -1+z.

S-C-C, and C-C-C angles, the average Pt-S-C angle must be ca. 127.0°. This value is even higher than the idealized value of 120° expected for highly delocalized π systems (with partial double bond character in C-S bonds such as that in Pt(PTT)₂^{x+}, Ni(SacSac)₂, and Co(SacSac)₂ where the reported values are 114.7, 118.1 (1), and 118.7 (5)°, respectively). A natural consequence is to fold along the (already twisted) S···S vector, resulting in the observed Pt-S-C angles of 115.8 (4) and 108.6 (3)° (average 112.2°). From another angle, it can be argued that the stereochemical requirement of the M-S-C angles in mercapto ligands is that they prefer to be close to the idealized tetrahedral value of 109.5° except in cases where strong and delocalized metal-ligand π -bonding forces the metal to be coplanar with the chelating ligand(s). The former is exemplified by the terminal Pd-S-C angles of 106.0 (2) and 106.5 (11)° observed in the two crystal forms of [(Ph₃P)Pd(SC₆F₅)₂]₂³³ whereas the latter is illustrated by the Pt-S-C angle of 114.7 (2) observed in Pt(PTT)₂^{x+}. It is

Table VI. Equations of Least-Squares Planes, Perpendicular Distances (Å) of Selected Atoms from These Planes, and Dihedral Angles between Normals of Planes^a

(a) Plane I through C(1), C(2), C(3), C(4), and C(5)			
$0.4154X - 0.9051Y - 0.0911Z + 4.3150 = 0$			
C(1)	0.059	Pt	0.917
C(2)	-0.078	P(1)	2.124
C(3)	-0.005	P(2)	1.408
C(4)	0.057	S(1)	0.461
C(5)	0.014	S(2)	-0.538
(b) Plane II through S(1), S(2), C(1), C(2), and C(3)			
$0.5555X - 0.8007Y - 0.2242Z + 3.7265 = 0$			
S(1)	0.156	S(1)'	-0.194
S(2)	-0.156	S(2)'	0.118
C(1)	-0.200	C(1)'	0.162
C(2)	0.206	C(2)'	-0.244
C(3)	-0.006	C(3)'	-0.032
C(4)	0.575	C(4)'	-0.613
C(5)	0.501	C(5)'	-0.539
Pt	1.028	Pt'	-1.066
P(1)	1.946	P(1)'	-1.984
P(2)	1.969	P(2)'	-2.007
(c) Plane III through Pt, P(1), P(2), S(1), and S(2)			
$-0.7593X + 0.5497Y - 0.3482Z - 0.1098 = 0$			
Pt	0.000	S(1)	-0.136
P(1)	0.125	S(2)	0.141
P(2)	-0.130		
(d) Plane IV through Pt, P(1), and P(2)			
$-0.7095X + 0.5938Y - 0.3795Z - 0.4159 = 0$			
(e) Plane V through Pt, S(1), and S(2)			
$-0.8125X + 0.4944Y - 0.3088Z + 0.2475 = 0$			
Dihedral Angles (deg) between Planes			
plane I and plane II		12.6	
plane I and plane III		38.6	
plane II and plane III		38.4	
plane IV and plane V		9.2	

^a The equation of the plane is of the form $A^*X + B^*Y + C^*Z + D = 0$ where A, B, C, and D are constants and X, Y, and Z are orthogonal coordinates which are related to the triclinic cell coordinates by the transformation: $X = ax + b(\cos \gamma)y + c(\cos \beta)z$, $Y = b(\sin \gamma)y + [c(\cos \alpha - \cos \beta \cos \gamma)\sin \gamma]z$, and $Z = [V/(ab \sin \gamma)]z$ where $V = abc(1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma)^{1/2}$.

then not surprising that the molecule folds along the S···S edges such as to reduce the Pt-S-C angles from the expected 127.0° to the observed average value of 112.2°.

The close intramolecular van der Waals contacts are tabulated in Table Va. No abnormally short distances are observed. However, the relatively short S(2)···H(2B2) and H(1A2)···H(1C6) distances of 2.74 and 2.24 Å, which are 0.31 and 0.16 Å, respectively, shorter than the sum of van der Waals radii (3.05 and 2.40 Å),³⁴ signify a significant degree of intramolecular van der Waals interaction. It is not unreasonable to propose that both attractive (partial) hydrogen bondings and repulsive steric requirements contribute significantly to the realization of the observed molecular nonplanarity.

On the other hand, it should be emphasized that given the present physical evidence we cannot rule out the possibility of electronic effects causing the nonplanar distortions (or twistings) of the molecular structure of dimetal-tetrathiolene complexes. Structural details of other tetrathiolene complexes are needed to assess the relative importance of steric vs. electronic effects.

Crystal Structure: Zigzag Chains of Platinum Atoms. An interesting observation of the crystal structure is that the intramolecular Pt···Pt' distance of 9.043 (4) Å is substantially greater than the closest intermolecular Pt···Pt' separation of 7.662 (4) Å by 1.382 Å. The intra- and intermolecular Pt···Pt vectors form a zigzag array of platinum chains parallel to the

diagonal of the crystallographic *ac* plane. The platinum atoms of the intramolecular Pt...Pt' pairs are related by inversion symmetry at positions ($n/2, 1/2, n/2$) with $n = \pm 1, \pm 3, \pm 5, \dots$, whereas the platinum atoms in the adjacent intermolecular Pt...Pt pairs are related by the same symmetry but at $n = 0, \pm 2, \pm 4, \dots$.

The close intermolecular van der Waals contacts are listed in Table Vb. The closest H(5)...H(2B5)ⁱⁱ, H(4)...H(2A6)ⁱⁱ, and H(2C4)...H(2C5)^{vii} distances of 2.27, 2.28, and 2.29 Å, respectively, are ca. 0.12 Å shorter than the sum of van der Waals radii of 2.40 Å. These values are larger than the corresponding intramolecular contacts. Though these intermolecular van der Waals contacts appear to be normal, anisotropic crystal packing which favors a nonplanar structure as observed here cannot be ruled out completely.

The shape of the (Ph₃P)₄Pt₂(TTN) molecule resembles a dumbbell. The void space near the central bridging ligand can accommodate solvent molecules as indicated by close C(3)...C(23)^v, C(3)...C(23)ⁱⁱ, C(1)...C(22)ⁱⁱ, C(1)...O(1)^v, C(2)...C(23)^v, and C(3)...C(22)ⁱⁱ of 3.32–3.67 Å which are smaller than the sum of van der Waals radii of 3.70 Å for (Ph)C...CH₃. The solvent molecules also form partial hydrogen bonding with the phenyl groups. This is evidenced by the short O(2)...H(2C4)^x, O(2)...H(2C5)^{viii}, and O(2)...H(1B4)^{xi} contacts of 2.52, 2.55, and 2.60 Å, respectively, which are shorter than the sum of van der Waals radii of 2.60–2.70 Å for X...H (where X = O or N) as well as a spectrum of (solvent) C...H (phenyl) contacts which are smaller than the van der Waals contact of 3.20 Å for CH₃...H.

Acknowledgment. We are grateful to Mr. J. L. Bernstein for programming assistance.

Registry No. (Ph₃P)₄Pt₂(TTN), 62767-35-5.

Supplementary Material Available: A listing of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

References and Notes

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- (3) The intensity *I* was calculated according to the expression $I = S(C - RB)$ where *S* is the scan rate, *C* is the total integrated peak count, *R* is the ratio of scan time to background counting time, and *B* is the total background count. The standard deviation of *I* was calculated as $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$ where $p = 0.05$. The data were also corrected for Lorentz and polarization effects to yield the observed structure factor $|F_o| = [I/(Lp)]^{1/2}$ and its standard deviation $\sigma(F_o) = \sigma(I)/(2 \times |F_o| \times (Lp))$. No extinction or absorption correction was necessary.
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