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Synthesis and Structure of a Tetrahydrotrathiafulvalene–Mercuric Chloride Complex, $(\text{H}_4\text{TTF})(\text{HgCl}_2)_3$

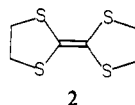
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The solid-state structure and infrared and Raman spectra of a mercuric chloride complex of tetrahydrotrathiafulvalene are reported. The compound $(\text{H}_4\text{TTF})(\text{HgCl}_2)_3$ crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 6.598$ (1) Å, $b = 7.354$ (1) Å, $c = 9.935$ (2) Å, $\alpha = 79.45$ (1)°, $\beta = 88.21$ (2)°, $\gamma = 90.59$ (2)°, and $V = 473.6$ (2) Å³. The structure is composed of polymeric chains of HgCl_2 units that are held together by bridging H_4TTF units. There are two crystallographically independent mercury atoms. One, Hg(1), sits at an inversion center and the other, Hg(2), occupies a general position within the unit cell. Hg(1) is surrounded by six chlorine atoms at distances ranging from 2.309 (5) to 3.235 (5) Å. The coordination sphere about Hg(2) comprises five chlorine atoms at distances ranging from 2.307 (5) to 3.349 (6) Å and two sulfur atoms from the H_4TTF moiety at 3.124 (4) and 3.131 (6) Å.

Introduction

As part of a research program on low-dimensional materials and as a complement to earlier studies of transition-metal derivatives of tetracyanoquinodimethan,^{1,2} a systematic study of trathiafulvalene–metal complexes has been undertaken. Trathiafulvalene (TTF) (**1**) has an E_{p1} of +0.45 V³ and forms a very stable cation radical, radical salts, and charge-transfer complexes.⁴ Tetrahydrotrathiafulvalene (H_4TTF) (**2**) has a higher oxidation potential,⁵ and it does not appear



to form stable cation radical salts as does **1** although the solution phase EPR spectrum of H_4TTF^+ has been described.⁶ It was therefore anticipated that a comparison of the chemistry of **1** and **2** would help elucidate differences between coordination complexes and materials formed by charge-transfer processes. These differences are illustrated by the products obtained from **1** and **2** and mercuric chloride. The former yields the cation radical salt $(\text{TTF})\text{HgCl}_3$ ⁷ while **2** affords $(\text{H}_4\text{TTF})(\text{HgCl}_2)_3$ (**3**), the complex which is the subject of this paper.

Experimental Section

Infrared spectra were recorded with an instrument equipped with grating optics, and peak maxima have an estimated precision of ± 5 cm⁻¹. Raman spectra were obtained with the use of spinning sample cell and 5145-Å excitation.

Tetrahydrotrathiafulvalene was prepared by the literature method and purified by recrystallization from acetone. IR (Nujol): 1410 (m), 1270 (s), 1240 (s), 1140 (w), 1100 (w), 970 (m), 950 (w), 865 (s), 840 (s), 760 (s), 675 (s), 470 (m), and 420 (m) cm⁻¹. ¹H NMR (acetone-*d*₆): δ 3.50. Electronic spectrum (KBr): λ_{max} at 298 (sh), 276, and 225 nm.

Acetonitrile, 50 mL, was added to 0.20 g of tetrahydrotrathiafulvalene (1 mmol) and 1.27 g (4.7 mmol) of mercuric chloride, whereupon a precipitate formed. The mixture was stirred, heated to boiling to dissolve the solids, and filtered. The vessel containing the pale pink filtrate was placed in a warm Dewar flask. On cooling to room temperature, block-shaped orange crystals separated. They were collected on a filter, washed with 1 mL of acetone, and dried under vacuum; yield 0.55 g. The mother liquor was set aside and, on standing, an additional 0.13 g of crystals separated. The total yield was 0.68 g (66%). Anal. Calcd for $\text{C}_6\text{H}_8\text{Cl}_6\text{Hg}_3\text{S}_4$: C, 7.1; H, 0.8; Cl, 20.7; Hg, 59.0; S, 12.5. Found: C, 7.2; H, 1.4; Cl, 20.3; Hg, 58.3; S, 12.4. IR (Nujol): 1410 (m), 1270 (s), 1240 (m),

1140 (w), 1110 (w), 970 (w), 955 (m), 870 (w), 850 (s), 775 (m), 675 (m), 670 (m), 470 (m), and 345 (s) cm⁻¹. ¹H NMR ($\text{Me}_2\text{SO}-d_6$): δ 3.48. Electronic spectrum (KBr): λ_{max} at 247 nm.

X-ray Data Collection. A suitable crystal of approximate dimensions 0.30 × 0.35 × 0.30 mm was secured with epoxy cement to the end of a thin glass fiber and then mounted on a Syntex P2₁ four-circle automatic diffractometer. Least-squares refinement of 15 reflections with a 2θ range of 24.7–30° revealed a triclinic cell with lattice constants of $a = 6.598$ (1) Å, $b = 7.354$ (1) Å, $c = 9.935$ (2) Å, $\alpha = 79.45$ (1)°, $\beta = 88.21$ (2)°, $\gamma = 90.59$ (2)°, and $V = 473.58$ (16) Å³. The calculated density for one formula unit of $\text{C}_6\text{H}_8\text{Cl}_6\text{Hg}_3\text{S}_4$ was 3.586 g/cm³, and the linear absorption coefficient was 259.99 cm⁻¹. Intensity data were collected by the θ – 2θ scan technique using Mo K α radiation ($\lambda = 0.71069$ Å) obtained with a highly oriented graphite monochromator. A scan rate of 2°/min and a scan range of 2θ (Mo K α_1) – 1.0 to 2θ (Mo K α_2) + 1.0 were used. Background counts were collected for a time equal to half the scan time, and the standard deviations on the intensities were assigned according to eq 1 where $\sigma_{\text{counter}}(I)^2 = (1 + K^2B)^{1/2}$, I is the net intensity, B is the total

$$\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.04I)^2]^{1/2} \quad (1)$$

background counts, and K is the ratio of scan time to background time. Independent data totaling 2359 reflections were collected to a maximum 2θ of 55°. The intensities of 3 standard reflections were measured every 97 reflections, and they showed no significant change in intensity throughout the data collection. Of the 2359 reflections, 1788 had $I > 2.5\sigma(I)$ and were used in the subsequent solution and refinement.

Structure Solution and Refinement. The structure was solved by conventional heavy-atom techniques⁸ in the space group $P\bar{1}$. Solution of the three-dimensional Patterson function gave the positions of the mercury atoms. Subsequent Fourier and difference syntheses established the positions of the remaining nonhydrogen atoms. Full-

- (1) A. R. Siedle, *J. Am. Chem. Soc.*, **97**, 5931 (1975).
- (2) A. R. Siedle, G. A. Candela, and T. F. Finnegan, *Inorg. Chim. Acta*, **35**, 125 (1979).
- (3) M. R. Suchanski, *J. Electrochem. Soc.*, **123**, 181c (1976).
- (4) F. Wudl, G. M. Smith and E. J. Hufnagel, *J. Chem. Soc., Chem. Commun.*, 1453 (1970).
- (5) $E_{\text{p1}} = 0.68$ V vs. SCE in acetonitrile: D. L. Coffen, J. Q. Chambers, D. R. Williams, P. T. Garrett and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971).
- (6) J. Q. Chambers, N. D. Canfield, D. R. Williams, and D. L. Coffen, *Mol. Phys.*, **19**, 581 (1970).
- (7) T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. Van Duyne, T. Cape, and A. R. Siedle, *J. Am. Chem. Soc.*, **100**, 1958 (1978).
- (8) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FORDAP, A. Zalkin's Fourier program; ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (4) ORTEP, C. K. Johnson's program for drawing crystal models. Scattering factors, including anomalous dispersion corrections for mercury, were taken from "The International Tables for X-ray Crystallography", Vol. 4, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974.

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Table I. Atomic Coordinates and Anisotropic Thermal Parameters for $(H_4TTF)(HgCl_2)_3^a$

	x	y	z		x	y	z	$B_{iso}, \text{Å}^2$
Hg(1)	0	0	0	C(1)	0.1373 (35)	0.8026 (30)	0.4964 (22)	
Hg(2)	0.4956 (1)	0.6825 (1)	0.1412 (1)	C(2)	0.8065 (36)	0.2471 (31)	0.3568 (22)	
Cl(1)	0.2565 (7)	0.0749 (6)	0.1341 (5)	C(3)	0.5683 (20)	0.4356 (20)	0.4876 (15)	
Cl(2)	0.2379 (6)	0.6164 (7)	0.0051 (5)	H(1)	-0.0138	0.8181	0.4881	2.74
Cl(3)	0.7706 (7)	0.7907 (7)	0.2450 (4)	H(2)	0.2057	0.9238	0.4538	2.74
S(1)	0.5460 (6)	0.3158 (6)	0.3532 (4)	H(3)	0.8980	0.3557	0.3089	2.77
S(2)	0.2236 (6)	0.6187 (6)	0.4093 (4)	H(4)	0.8296	0.1420	0.3075	2.77

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg(1)	1.50 (4)	2.76 (5)	1.86 (4)	-0.53 (3)	-0.58 (3)	-0.39 (3)
Hg(2)	1.76 (3)	3.25 (4)	1.94 (3)	-0.69 (2)	-1.01 (2)	-0.41 (3)
Cl(1)	2.23 (18)	2.96 (20)	2.23 (19)	-0.91 (15)	-1.17 (15)	-0.14 (16)
Cl(2)	1.59 (16)	3.43 (21)	2.40 (20)	0.14 (14)	-0.98 (14)	1.531 (17)
Cl(3)	2.00 (17)	1.90 (17)	1.93 (18)	0.29 (13)	-0.78 (14)	-1.20 (14)
S(1)	1.19 (14)	2.36 (18)	1.26 (16)	0.55 (13)	-0.52 (12)	-0.65 (13)
S(2)	2.05 (18)	3.92 (23)	1.74 (18)	-1.55 (16)	-0.86 (14)	-0.16 (16)
C(1)	4.70 (11)	3.5 (10)	3.1 (10)	2.73 (89)	-0.58 (87)	-1.74 (83)
C(2)	4.0 (10)	4.3 (11)	3.3 (10)	2.57 (87)	-1.41 (82)	-2.90 (89)
C(3)	0.1 (5)	1.8 (6)	1.7 (6)	0.4 (4)	0.0 (4)	0.8 (5)

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

matrix anisotropic least-squares refinement on F yielded the discrepancy factors:

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.084$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.102$$

The data were corrected for absorption by application of the Ψ -scan empirical absorption technique as originally reported by North et al.⁹ A total of 13 curves were used, covering the 2θ range 6.17–51.34°. Each reference curve was collected at 10° intervals from 0 to 350° in 2θ at 2°/min. Hydrogen atom positions were then calculated¹⁰ with positions 1.08 Å from the carbon atoms in an expected geometry. Subsequent full-matrix anisotropic least-squares refinement on the nonhydrogen atoms with fixed contributions from the hydrogen atoms yielded final values for the discrepancy factors of $R_1 = 0.067$ and $R_2 = 0.082$ and an error of fit of 2.22.

Results and Discussion

Synthesis and Spectroscopic Properties. In acetonitrile, tetrahydrotetrafulvalene does not appear to react with 2 equiv of mercuric chloride but, when an excess of the mercury salt is used, an orange precipitate is formed. Slow cooling of a solution of this material in acetonitrile affords chunky orange crystals of $(H_4TTF)(HgCl_2)_3$, whose appearance resembles that of potassium dichromate. The infrared spectra of the crystals and the crude precipitate were identical.

Perturbation of the H_4TTF moiety by incorporation into the structure of the complex **3** appears to be subtle. The ultraviolet absorption maximum is shifted to shorter wavelengths, and it lacks the fine structure seen in the spectrum of the precursor thiocarbon **2**. The orange color is due to a strong absorption, λ_{max} 247 nm, which tails into the visible. The infrared spectrum of **3** is qualitatively similar to that of H_4TTF , and the C=C stretching mode at 1558 cm^{-1} in the Raman spectrum of H_4TTF is shifted to 1580 cm^{-1} in the mercuric chloride complex. Since it is known from the work of Van Duyne and co-workers¹¹ that the frequency of the ν_3 mode, comprising primarily stretching of the central C=C bond, in partially oxidized TTF^{+p} salts is a sensitive function of ρ , the similarity between the C=C stretching frequencies in H_4TTF and $(H_4TTF)(HgCl_2)_3$ suggests that there is only little charge transfer from the thiocarbon to mercury. The Raman and

Table II. Bond Distances (Å) and Angles (Deg)

Hg(1)–Cl(1)	2.309 (5)	Hg(2)–Cl(1)''	3.349 (6)
Hg(1)–Cl(3)' ^a	2.989 (6)	Hg(2)–Cl(2)'	3.336 (5)
Hg(1)–Cl(2)'' ^b	3.235 (5)	S(1)–C(2)	1.80 (2)
Hg(2)–Cl(2)	2.307 (5)	S(1)–C(3)	1.74 (2)
Hg(2)–Cl(3)	2.319 (5)	S(2)–C(1)	1.82 (2)
Hg(2)–S(1)	3.131 (4)	S(2)–C(3)'	1.74 (2)
Hg(2)–S(2)	3.124 (6)	C(1)'–C(2)	1.50 (3)
Hg(2)–Cl(1)'	3.294 (5)	C(3)–C(3)'	1.36 (3)
C(3)–S(1)–C(2)	93.8 (8)	Cl(1)''–Hg(2)–S(2)	75.2 (1)
C(1)–S(2)–C(3)'	94.5 (9)	S(1)–Hg(2)–S(2)	61.7 (1)
S(1)–C(2)–C(1)'	108 (2)	S(1)–Hg(2)–Cl(2)'	70.5 (1)
S(2)–C(1)–C(2)'	108 (1)	Cl(1)'–Hg(2)–Cl(2)'	72.6 (1)
S(1)–C(3)–S(2)'	116.1 (8)	Cl(3)'–Hg(1)–Cl(2)''	84.6 (1)
S(1)–C(3)–C(3)'	122 (2)	Cl(3)'–Hg(1)–Cl(2)'''	95.4 (1)
S(2)–C(3)–C(3)'	121 (2)	Cl(1)–Hg(1)–Cl(2)''	94.6 (2)
Cl(3)–Hg(2)–Cl(2)	169.7 (2)	Cl(1)–Hg(1)–Cl(3)''	91.6 (1)
Cl(3)–Hg(2)–Cl(1)''	91.5 (2)	Cl(1)'–Hg(1)–Cl(2)''	85.4 (2)
Cl(3)–Hg(2)–Cl(1)'	79.9 (1)	Cl(1)'–Hg(1)–Cl(3)''	88.4 (1)
Cl(3)–Hg(2)–S(2)	93.7 (1)	Hg(2)–S(1)–C(3)	92.0 (6)
Cl(3)–Hg(2)–S(1)	85.2 (1)	Hg(2)–S(2)–C(3)'	92.4 (5)
Cl(3)–Hg(2)–Cl(2)'	95.1 (2)	Hg(2)–S(2)–C(1)	124.3 (8)
Cl(1)'–Hg(2)–Cl(1)'	82.7 (1)	Hg(2)–S(1)–C(2)	110.4 (9)

^a Generated by $1-x, 1-y, -z$. ^b Generated by $x, 1+y, z$.
^c Generated by $x, y-1, z$.

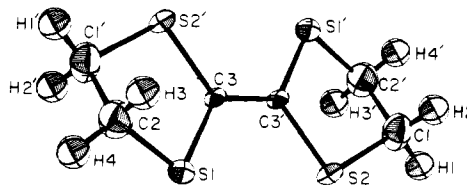


Figure 1. ORTEP drawing of the H_4TTF moiety. The thermal parameters are represented by 30% probability ellipsoids.

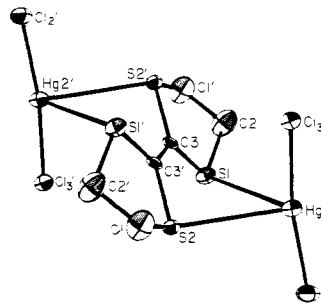


Figure 2. ORTEP drawing of the coordination of the H_4TTF moiety within the $HgCl_2$ net.

- (9) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24A**, 351 (1968).
(10) Ideal positions for the hydrogen atoms were calculated with A. Zalkin's HFINDR program as modified by Dr. T. J. Anderson.
(11) A. R. Siedle, G. A. Candela, T. F. Finnegan, R. P. Van Duyne, T. Cape, G. F. Koksza, and P. M. Woyciesjes, *J. Chem. Soc., Chem. Commun.*, 69 (1978).

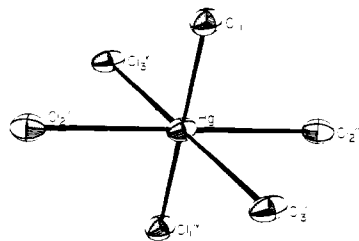


Figure 3. ORTEP representation of the coordination sphere about Hg(1).

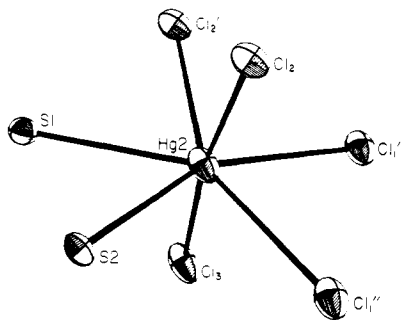


Figure 4. ORTEP representation of the coordination sphere about Hg(2).

infrared spectra of **3** also reveal respectively strong bands at 290 and 345 cm⁻¹ which may be assigned to the ν_1 and ν_3 modes in the HgCl₂ units. The ν_1 band is shifted 23 cm⁻¹ to shorter wavelength and ν_3 by -33 cm⁻¹ with respect to HgCl₂,¹² which is not unexpected since ν_1 is known¹³ to be sensitive to environmental effects. Consistent with the weak metal-ligand interactions observed in the crystal, **3** appears to dissociate in dimethyl sulfoxide since, in this solvent, its ¹H NMR spectrum is that of **2**.

Description of the Solid-State Structure. Atomic positional and thermal parameters for (H₄TTF)(HgCl₂)₃ are presented in Table I. Bond distances and angles are shown in Table II, and Table III gives the equations of planes and dihedral angles for the H₄TTF moiety. Figures 1 and 2 display views of the H₄TTF unit and its mode of coordination to the HgCl₂ groups, respectively. Figures 3 and 4 show the effective coordination sphere about each of the crystallographically independent mercury atoms. Figure 5 presents a stereoview of the packing of the H₄TTF moieties within the mercuric chloride net.

The solid-state structure of (H₄TTF)(HgCl₂)₃ is composed of polymeric chains of HgCl₂ units that are held together by bridging H₄TTF units. The structure contains two crystallographically independent mercury atoms in the asymmetric unit. The environment about each is shown in Figure 3. One mercury atom, Hg(1), is located at the origin of the cell; the H₄TTF molecule is located on the inversion center at 1/2, 1/2, 1/2. The environment about Hg(1) comprises six chlorine atoms at distances ranging from 2.309 (5) to 3.235 (5) Å. There are two strongly bonded chlorine atoms at 2.309 (5) Å which make up the basic HgCl₂ unit. This distance appears to be typical of a covalent Hg-Cl bond as indicated by comparison with structural parameters for some related compounds (Table IV). Since Hg(1) sits on a crystallographic inversion center, the Cl(1)-Hg(1)-Cl(1) angle is constrained to be 180°. In addition, there are four additional chlorine atoms that are more weakly bonded to Hg(1): two at 2.989 (6) Å and two at 3.235 (5) Å. Each of these distances is greater than the sum of the covalent radii but are within the van der Waals interactive distance (i.e., 3.20-3.40 Å) and are, therefore, considered as weakly bonding. Taking these chlorine atoms into consideration, it is possible to describe the effective co-

Table III. Equations of Planes and Dihedral Angles for the Tetrahydrotetrafulvalene Molecule^a

plane	atoms	A	B	C	D
P1	C(3)', C(3), S(1)	0.5148	0.6145	-0.5979	1.6598
P2	C(3)', C(3), S(2)'	0.5170	0.6157	-0.5946	1.6892
P3	C(3), S(1), C(2)	0.2227	0.7245	-0.6523	0.7213
P4	C(3), S(2)', C(1)'	0.5073	0.5568	-0.6577	1.1099
P5	S(1), C(2), C(1)'	0.1408	0.4242	-0.8946	-1.3067
P6	S(2)', C(1)', C(2)	0.2989	0.5492	-0.7804	0.2551
P7	S(1), C(3), S(2)'	0.5167	0.6134	-0.5972	1.6660
P8	S(1), C(3), S(2)', C(1)	0.5220	0.5903	-0.6157	1.5228

planes	angles, deg	planes	angles, deg
P1/P2	0.2	P3/P5	22.8
P1/P3	18.2	P3/P6	13.2
P1/P4	4.8	P4/P5	26.4
P1/P5	29.8	P4/P6	13.9
P1/P6	16.7	P5/P6	13.3
P2/P3	18.4	P6/P7	16.8
P2/P4	5.0	P7/P1	0.1
P2/P5	30.0	P7/P2	0.2
P2/P6	16.9	P7/P3	18.4
P5/P8	29.0	P7/P4	4.8
P3/P4	19.0	P7/P5	29.9

^a The equation of the plane is the form $AX + BY + CZ - D = 0$, where A , B , C , and D are constants and X , Y , and Z are orthogonalized coordinates.

Table IV. Selected Structural Parameters for Mercury-Sulfur Compounds

compd	$d(\text{Hg-Cl})$, Å	$d(\text{Hg-S})$, Å	ref
HgCl ₂ ·C ₄ H ₈ S	2.30, 2.62, 2.83, 3.07	2.40, 3.89	<i>a</i>
2HgCl ₂ ·(C ₂ H ₅) ₂ S	2.35, 2.33, 2.30, 2.70, 2.85, 2.88, 3.55, 3.00, 3.06, 3.16	2.41	<i>b</i>
HgCl ₂	2.26		<i>c</i>
ClHgSCN	2.29, 3.08	2.31	<i>d</i>
HgS (red)		2.36	<i>e</i>
HgS (black)		2.53	<i>e</i>
Hg(C ₁₃ H ₁₁ N ₄ S) ₂ ·2C ₂ H ₅ N		2.42	<i>f</i>
(TTF)HgCl ₂	2.374 (5)-2.545 (5) (equatorial) 2.982 (5)-3.112 (5) (axial), 2.600 (5), 2.696 (5), 2.368 (5), 2.381 (1)		<i>g</i>
HgCl ₂ ·3SC(NH ₂) ₂	2.24, 2.36	2.37, 2.61, 3.10	<i>h</i>

^a C. I. Branden, *Ark. Kemi*, **22**, 495 (1964). ^b C. I. Branden, *Ark. Kemi*, **22**, 83 (1964). ^c D. R. Grdenic, *Ark. Kemi*, **22**, 14 (1950). ^d Z. V. Zvonkova and G. S. Zhdanov, *Zh. Fiz. Khim. SSSR*, **26**, 586 (1952). ^e K. Aurivillius, *Acta Chem. Scand.*, **4**, 1413 (1950). ^f M. M. Harding, *J. Chem. Soc.*, 4136 (1958). ^g T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. Van Duyne, T. Cape, and A. R. Siedle, *J. Am. Chem. Soc.*, **100**, 1958 (1978). ^h "Comprehensive Inorganic Chemistry", Vol. 3, A. F. Trotman-Dickenson, Ed., Pergamon Press, New York, p 327.

ordination sphere about Hg(1) as a distorted octahedron, as is reflected in the Cl-Hg-Cl angles (Table II).

The coordination sphere about Hg(2) (Figure 4) has five chlorine atoms at distances ranging from 2.307 (5) to 3.349 (6) Å and two sulfurs in the H₄TTF molecule at distances of 3.124 (4) and 3.131 (6) Å. These Hg-S contacts are somewhat longer than those observed in coordination compounds of mercuric chloride with sulfur donors (cf. Table IV). However, they are within the van der Waals contact distance (ca. 3.30 Å), and, although weak, they appear to be of sufficient magnitude to influence the stereochemistry about Hg(2). This influence is manifested in the deviation from linearity of the Cl(3)-Hg(2)-Cl(2) angle of the basic HgCl₂ unit. The chlorine atoms are bent away from the H₄TTF by 5°. As with Hg(1), there are two chlorine atoms, Cl(2) and

(12) G. J. Janz and D. W. James, *J. Chem. Phys.*, **38**, 902 (1963).

(13) G. Allen and E. Warhurst, *Trans. Faraday Soc.*, **54**, 1786 (1958).

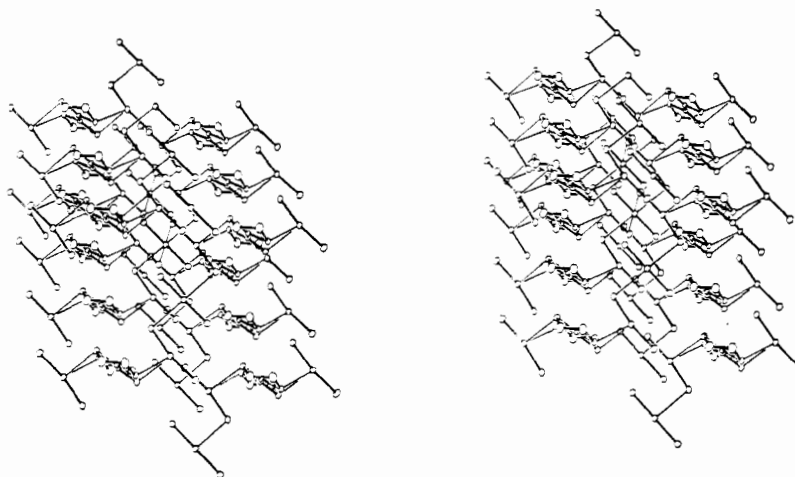


Figure 5. Stereoview showing the packing of the H_4TTF moieties within the $HgCl_2$ network.

Cl(3), bonded to Hg(2) at distances of 2.307 (5) and 2.319 (5) Å, respectively, which make up the second basic $HgCl_2$ unit. This unit, unlike Cl(1)–Hg(1)–Cl(1), is nonlinear, and the Cl(3)–Hg(2)–Cl(2) angle is 169.7 (2)°, a result, as indicated above, of the weak Hg–S interactions. Also coordinated to Hg(2) are three additional chlorine atoms, Cl(1)', Cl(2)', and Cl(1)'', with Hg–Cl separations of 3.294 (5), 3.336 (5), and 3.349 (6) Å, respectively. These distances are at the limit of the van der Waals contact distance and, as a result, the influence of these Hg–Cl interactions is difficult to completely ascertain. The problem is compounded by lack of agreement on a value for the van der Waals contact distance for mercury. Grdenic¹⁴ gives a value of 3.30 Å. However, with use of values for the van der Waals radii listed by Huheey,¹⁵ a range of 3.20–3.40 Å is obtained. It is therefore debatable whether the above distances can be considered as interactive. If we take these contacts into account, the effective coordination sphere about Hg(2) can be described as a highly distorted pentagonal bipyramid. However, there is still a marked propensity toward retention of the basic, linear $HgCl_2$ unit, a common feature in the rather complicated structural chemistry of mercuric chloride coordination compounds.¹⁴

The geometry of the H_4TTF molecule in **3** is similar to that reported for the fully conjugated analogue, TTF.¹⁶ The average S–C distances are 1.74 (2) Å for $S-C_{sp^2}$ and 1.81 (2) Å for $S-C_{sp^3}$, i.e., the shorter S–C distances are adjacent to the central C=C double bond. These shorter S–C separations are similar to the (average) 1.76 Å in 1-[2-(1,3-dithiolanylidine)]-2,3,6,9-tetrathiaspiro[4.4]nonane¹⁷ and 1.756 (2) Å in TTF itself.¹⁶ The C=C bond distance of 1.364 (3) Å is approximately the same as the 1.349 (3) Å of TTF but the 1.50 (3)-Å C–C bond distance is typical of a C–C bond. The S–C–C angles average 108 (2)° and are normal for tetrahedral carbon. The C–S–C angles of 93.8 (8) and 94.5 (9)° agree well with the 94.3° reported for TTF and reflect the effect of participation of sulfur p orbitals in bonding. Each of the five-membered rings in H_4TTF adopts the half-chain conformation with a seat-to-back angle of ca. 29° (cf. Table III).

Discussion

Tetrathiaethylenes such as TTF and tetrakis(methylthio)ethylene¹⁸ often react with oxidizing metal ions by electron transfer. An additional reaction pathway for the latter compound, with (triethylphosphine)platinum dichloride dimer, involves carbon–sulfur bond fission and the formation of a platinum–sulfur chelate.¹⁹ Electron-rich olefins which contain an ethylene unit substituted with four alkylamino groups typically react with transition-metal derivatives by chelate formation and/or cleavage of the carbon–carbon double bond to afford metal–carbene complexes.¹⁹ The tetrathiaethylenes TTF and H_4TTF , however, have not been observed to follow either of these reaction pathways. As noted above, TTF is oxidized by mercuric chloride to form the cation radical salt $(TTF)HgCl_3$.⁷ It has such long mercury–sulfur contacts as to preclude strong bonding between these elements. It could be that the weak Hg–S interaction is due, in part, to the fact that the potential TTF^+ ligand carries unit positive charge, but this explanation is not applicable to $(H_4TTF)(HgCl_2)_3$. There is no evidence for charge transfer in the tetrahydro-tetrathiafulvalene complex, and it may be considered to be a member of the thus far small class of metallotetrathiaethylene crystal complexes of which other examples are $TTF \cdot M(acac)_2$ ($M = Pd, Pt$).²⁰ The mercury–sulfur contacts in $(H_4TTF)(HgCl_2)_3$ may be described as weakly bonding at best, their principle effect being to perturb the stereochemistry of the mercury coordination sphere. Thus, in both $(TTF^+)HgCl_3$ and $(H_4TTF)(HgCl_2)_3$, one finds that chloride is a better ligand toward mercury(II) than the tetrathiaethylene sulfurs. A definitive explanation for the apparent lack of basic character on sulfur is not available, but it may be due to extensive delocalization of the sulfur lone pairs into the C=C double bond. The similarity between C=C stretching frequencies in TTF and H_4TTF , 1515¹⁰ and 1585 cm^{-1} , respectively, and the C=C distances, 1.349 (3) and 1.364 (3) Å, respectively, are consistent with this.

Registry No. 3, 78421-00-8.

Supplementary Material Available: Structure factor tables (8 pages). Ordering information is given on any current masthead page.

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