

and P-S(β)-C chelate angles in **6** also are noticeably dissimilar.

The nonbonded sulfur-sulfur distances are summarized in Table VII. The average intraligand "bite" distance is 2.97 Å, which is longer than the "bite" distance in many metal-1,1-dithiolato complexes³⁹ yet shorter than the S-S van der Waals contact distance of 3.4 Å.⁴⁰ The three sulfur atoms, S(α), covalently bonded to the phosphorus atom form a triangle with nonbonded edge distances in the range 3.067-3.138 Å in **A** and 3.083-3.131 Å in **B**. The three ionically associated sulfur atoms, S(β), form a triangle with nonbonded edge distances in the ranges 4.642-4.941 Å in **A** and 4.735-5.014 Å in **B**. The two triangles are rotated by about 45° in each molecule and the triangular S₃ planes are out of parallel by 2.9° in **A** and 4.0° in **B**.

The overall distortions in the PS₆ coordination polyhedron away from octahedral symmetry are indicated by the unequal P-S bond distances, the S-P-S and dithiocarbamate ligand bond angles, the trigonal S₃ face twist, and the large volume of coordination space between the S(β) atoms. These distortions appear to result from a combination of steric constraints imposed by the tris(dithiocarbamate) chelate structure and a balance of covalent and ionic P-S electrostatic attractions. Nonbonded S-S and S-P lone-pair van der Waals repulsions also play some role in determining the final configuration.

The geometry of the individual dithiocarbamate ligands is also of interest. The average S(α)-C distance, 1.763 Å, is significantly longer than the average S(β)-C distance, 1.666

Å, and a comparable effect is also observed in the arsenic complex: S(α)-C = 1.760 Å and S(β)-C = 1.678 Å. The average C-N bond distance, 1.33 Å, is comparable with those of most 1,1-dithiolato complexes.^{39,41} The two sulfur atoms, two nitrogen atoms, and three carbon atoms of each ligand form a plane which contains the central phosphorus atom. The equations for these planes and the atom deviations from the planes are summarized in Table VIII. The small distortions from planarity are likely a result of crystal-packing forces. The angles between the three ligand propeller blades, 78.2, 85.9, and 89.9° in **A** and 79.3, 85.6, and 87.3° in **B**, deviate from the 90° angle expected for an octahedral complex. Planes calculated for the CS₂ and NC₂ portions of each chelate ring show very small torsion angles in the S₂C-NC₂ linkage, 1.9-4.2°.

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Supplementary Material Available: Tables of mass and infrared spectrometric data (4 pages) and a table of observed and final calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, the Department of Chemistry and Materials Science Center, Northwestern University, Evanston, Illinois 60201, and the National Bureau of Standards, Washington, D. C. 20234

Crystal and Molecular Structure of an Unusual Salt Formed from the Radical Cation of Tetrathiafulvalene (TTF) and the Trichloromercurate Anion (HgCl₃), (TTF)(HgCl₃)

T. J. KISTENMACHER,*^{1a} M. ROSSI,^{1a} C. C. CHIANG,^{1a} R. P. VAN DUYN,^{1b} and A. R. SIEDLE*^{1c}

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The synthesis and crystal structure of the salt (TTF)(HgCl₃) are reported. Crystals of the salt are triclinic, of space group *P* $\bar{1}$, with *a* = 12.661 (3) Å, *b* = 15.969 (4) Å, *c* = 7.416 (2) Å, α = 98.69 (2)°, β = 95.73 (2)°, γ = 120.01 (2)°, *V* = 1256.2 Å³, mol wt ((C₆H₄S₄)(HgCl₃)) = 511.3, *Z* = 4, *D*_{meas} = 2.68 (1) g cm⁻³, and *D*_{calc} = 2.70 g cm⁻³. The structure was solved by standard Patterson and Fourier methods and has been refined by full-matrix least squares, based on 4298 counter-collected *F*_o's, to a final *R* value of 0.080. The structure can be qualitatively separated into two layers parallel to the *ac* plane. One of these layers, centered about *y* = 0.0, contains both inorganic and organic polymers propagating along the crystallographic *c* axis. The covalent inorganic polymer contains roughly trigonal-bipyramidal coordination about the Hg(II) center, with equatorial Hg-Cl bond lengths of 2.374 (5), 2.395 (5), and 2.545 (5) Å and considerably longer axial bond lengths of 2.982 (5) and 3.112 (5) Å. Collinear with this covalent inorganic polymer is a columnar array of stacked TTF radical cations. The stacking in this columnar array of TTF cations is nominally of the ring-over-bond type with a mean separation between planes of 3.6 Å. The second layer, centered about *y* = 0.5, contains solely dimeric species. The chloromercurate anion is a dimeric, edge-shared bitetrahedron, with Hg-Cl bond lengths of 2.600 (5) and 2.696 (5) Å for the bridging chloro ligands and 2.368 (5) and 2.381 (5) Å for the two independent terminal chloro ligands. The organic dimer is made up of two strongly associated and nearly eclipsed TTF cations, with a mean spacing of 3.43 Å. Resonance Raman data have been interpreted as suggesting the presence of two different kinds of TTF moieties, consistent with the X-ray data. From the Raman data it is indicated that the two different TTF species have slightly different degrees of charge transfer.

Introduction

The solid-state chemistry of a wide variety of low-dimensional materials containing tetrathiafulvalene (TTF) or tet-

racyno-*p*-quinodimethane (TCNQ) has received considerable attention in the past few years. A relatively large body of literature now exists on (TTF)(TCNQ), its derivatives and analogues, simple and associated halogen salts of TTF, and ammonium, alkali-metal, and alkaline-earth salts containing TCNQ.² Less attention has been paid to simple inorganic

(1) (a) The Johns Hopkins University. (b) Northwestern University. (c) National Bureau of Standards.

Table I. Final Positional Parameters^a

atom	x	y	z	atom	x	y	z
Hg(1)	793 (1) ^b	545 (1)	2678 (1)	C(3)	474 (1)	389 (1)	826 (2)
Hg(2)	1342 (1)	4805 (1)	5164 (1)	C(4)	766 (2)	643 (1)	823 (2)
Cl(11)	-130 (3)	1106 (3)	-509 (5)	C(5)	818 (2)	610 (2)	935 (3)
Cl(12)	-943 (4)	379 (3)	3970 (6)	C(6)	590 (1)	476 (1)	844 (2)
Cl(13)	2955 (3)	1680 (3)	2953 (6)	C(21)	737 (2)	213 (1)	195 (2)
Cl(21)	-138 (5)	4763 (4)	2408 (6)	C(22)	791 (1)	162 (1)	181 (2)
Cl(22)	569 (4)	3120 (3)	5295 (7)	C(23)	559 (1)	43 (1)	42 (2)
Cl(23)	3390 (4)	6194 (3)	5610 (7)	C(31)	783 (3)	174 (3)	686 (4)
S(1)	4581 (4)	3005 (3)	9455 (6)	C(32)	721 (3)	218 (2)	681 (4)
S(2)	3402 (4)	3641 (3)	6902 (5)	C(33)	556 (2)	44 (2)	542 (4)
S(3)	7228 (4)	4984 (4)	9859 (7)	H(1)	256	155	876
S(4)	6092 (4)	5690 (3)	7385 (5)	H(2)	161	210	694
S(21)	5803 (4)	1574 (3)	1187 (6)	H(4)	817	705	786
S(22)	6905 (4)	356 (3)	787 (6)	H(5)	906	647	985
S(31)	6931 (7)	478 (7)	6013 (14)	H(21)	784	282	254
S(32)	5671 (7)	1570 (6)	5947 (13)	H(22)	882	192	225
C(1)	301 (1)	220 (1)	852 (2)	H(31)	879	217	748
C(2)	249 (1)	250 (1)	742 (2)	H(32)	763	291	732

^a Hg, Cl, and S atom parameters $\times 10^4$; C and H atom parameters $\times 10^3$. ^b The number in parentheses is the estimated standard deviation in the least-significant figure.

systems as cationic, anionic, or neutral components in such materials.

Recent work in these laboratories has focused on inorganic salts³⁻⁵ of TTF and solid solutions of coordination complexes with TTF.⁶ In one of these systems, namely, (TTF)(HgCl₃), we⁴ have found several interesting solid-state effects. X-ray crystallographic data showed the presence in the structure of two types of TTF cations; one type was associated into a columnar array similar to that found in the structure of (TTF)(TCNQ),⁷ while the second type was associated into dimeric pairs not unlike those found in (TTF)Br⁸ and (TTF)Cl.⁹ Moreover, resonance Raman data⁴ suggested that the two distinguishable TTF species in (TTF)(HgCl₃) had different degrees of charge transfer, presumably owing to solid-state effects.

In this paper we wish to give a detailed account of the synthesis and X-ray crystallographic characterization of (TTF)(HgCl₃).

Experimental Section

Preparation of (TTF)(HgCl₃). A solution of 0.43 g of mercuric chloride (1.58 mmol) in 20 mL of acetonitrile was added to 0.315 g (1.54 mmol) of tetrathiafulvalene in 30 mL of the same solvent. After 24 h, the solids were isolated by filtration and recrystallized from hot acetonitrile to give two crops, 0.10 and 0.07 g, of (TTF)(HgCl₃) as glistening black needles. Anal. Calcd for C₆H₄Cl₃HgS₄: C, 14.09; H, 0.78; Cl, 20.74; Hg, 39.33; S, 25.05. Found: C, 14.11; H, 0.57; Cl, 20.51; Hg, 40.03; S, 24.62. Electronic spectrum (KBr pellet): λ_{max} 380, 410, 530 nm. IR (Nujol mull): 3045 (w), 1490

(w), 1405 (w), 1330 (s), 1255 (w), 1250 (m), 1080 (w), 825 (s), 740 (s), 685 (s), 670 (s), 490 (s), 360 (m) cm⁻¹. ESR (solid): narrow peak with $g = 2.00$ and $\Delta H = 20$ G.

A pale pink powder, 0.15 g, insoluble in hot acetonitrile, was identified by its X-ray powder pattern as Hg₂Cl₂. Two additional lines in the observed pattern at $d = 3.54$ and 3.56 Å were unassigned.

The electrical conductivity of (TTF)(HgCl₃), measured by the microwave cavity perturbation technique on a compressed pellet, was 1×10^{-3} (Ω cm)⁻¹.

Collection and Reduction of the X-ray Intensity Data. Black crystals of (TTF)(HgCl₃) form from acetonitrile as parallelepipeds belonging to the triclinic system. Unit-cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles for 15 reflections measured on a Syntex P1 automated diffractometer. The crystal density was measured by the neutral buoyancy method in a mixture of bromoform and carbon tetrachloride. Standard crystallographic data are as follows: $a = 12.661$ (3) Å, $b = 15.969$ (4) Å, $c = 7.416$ (2) Å, $\alpha = 98.69$ (2)°, $\beta = 95.73$ (2)°, $\gamma = 120.01$ (2)°, $V = 1256.2$ Å³, mol wt = 511.30, $Z = 4$, $D_{\text{measd}} = 2.68$ (1) g cm⁻³, $D_{\text{calcd}} = 2.70$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 136.0$ cm⁻¹.

Intensity data were collected on a parallelepiped with the following crystal faces and dimensions: (010)-(010), 0.07 mm; (100)-(100), 0.15 mm; (001)-(001), 0.23 mm. The c axis of the crystal was mounted approximately along the ϕ axis of the spectrometer. The intensities of the 5223 reflections in the $+h$ hemisphere to $2\theta = 52^\circ$ were collected in the θ - 2θ scan mode, employing graphite-monochromatized Mo K α radiation ($\lambda = 0.71069$ Å). Individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning ranged from 2 to 12° min⁻¹. The intensities of three standards were monitored after every 100 reflections and showed no systematic variation over the course of the experiment.

The measured intensities were assigned observational variances on the basis of the counting statistics plus a term $(pI)^2$, where p was taken to be 0.03 and represents the expected error proportional to the diffracted intensity.¹⁰ The intensities and their standard deviations were corrected for Lorentz, polarization, and absorption effects (maximum and minimum transmission factors were 0.44 and 0.12, respectively). The data were subsequently reduced to 4298 independent reflections with $I \geq \sigma_f$. An approximate absolute scale was determined by the method of Wilson.¹¹

Solution and Refinement of the Structure. Positional parameters for the two independent Hg atoms were readily determined from a Patterson synthesis. A subsequent structure factor Fourier synthesis yielded atomic positional parameters for all the remaining nonhydrogen atoms. Hydrogen atom positions were determined on the basis of geometric considerations as well as a difference-Fourier synthesis at an intermediate stage in the analysis. Five cycles of isotropic refinement followed by five cycles of anisotropic refinement, minimizing

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Table II. Final Nonhydrogen Bond Angles (Deg)

(A) Tetrathiofulvalinium Cations			
C(1)-S(1)-C(3)	95.2 (8)	C(21)-S(21)-C(23)	93.8 (9)
C(2)-S(2)-C(3)	94.1 (8)	C(22)-S(22)-C(23)	95.0 (8)
C(5)-S(3)-C(6)	94.3 (9)	C(31)-S(31)-C(33)	95.4 (17)
C(4)-S(4)-C(6)	95.2 (9)	C(32)-S(32)-C(33)	92.8 (17)
S(1)-C(1)-C(2)	116.3 (14)	S(21)-C(21)-C(22)	121.4 (16)
S(2)-C(2)-C(1)	118.8 (14)	S(22)-C(22)-C(21)	114.1 (15)
S(3)-C(5)-C(4)	117.6 (16)	S(31)-C(31)-C(32)	113.9 (29)
S(4)-C(4)-C(5)	117.3 (16)	S(32)-C(32)-C(31)	122.8 (29)
S(1)-C(3)-S(2)	115.5 (9)	S(21)-C(23)-S(22)	115.7 (9)
S(3)-C(6)-S(4)	115.4 (9)	S(31)-C(33)-S(32)	115.0 (18)
S(1)-C(3)-C(6)	121.4 (12)	S(21)-C(23)-C(23')	123.7 (19)
S(2)-C(3)-C(6)	123.0 (12)	S(22)-C(23)-C(23')	120.6 (19)
S(3)-C(6)-C(3)	121.4 (12)	S(31)-C(33)-C(33')	121.9 (19)
S(4)-C(6)-C(3)	123.2 (12)	S(32)-C(33)-C(33')	123.1 (19)
(B) Hg ₂ Cl ₆ ²⁻			
Cl(21)-Hg(2)-Cl(21')	90.1 (2)	Cl(22)-Hg(2)-Cl(21')	98.9 (2)
Cl(21)-Hg(2)-Cl(22)	106.4 (2)	Cl(22)-Hg(2)-Cl(23)	132.2 (2)
Cl(21)-Hg(2)-Cl(23)	111.3 (2)	Cl(23)-Hg(2)-Cl(21')	109.1 (2)
(C) (HgCl ₃) _n Polymeric Chain			
Cl(11)-Hg(1)-Cl(11')	88.9 (2)	Cl(12')-Hg(1)-Cl(11')	88.3 (2)
Cl(11)-Hg(1)-Cl(12)	87.9 (2)	Cl(12)-Hg(1)-Cl(12')	77.6 (2)
Cl(11)-Hg(1)-Cl(12')	163.4 (2)	Cl(12)-Hg(1)-Cl(13)	141.0 (2)
Cl(11)-Hg(1)-Cl(13)	97.6 (2)	Cl(13)-Hg(1)-Cl(11')	109.9 (2)
Cl(12)-Hg(1)-Cl(11')	108.8 (2)	Cl(13)-Hg(1)-Cl(12')	98.7 (2)

Table III. Variation in the Geometry of the TTF Donor as a Function of Charge Transfer [*mmm* (*D*_{2h}) Point Group Symmetry Imposed]

compd	"a", Å	"b", Å	"c", Å	"d", Å	estd CT, e	ref
TTF ⁰	1.349 (4)	1.757 (2)	1.726 (2)	1.314 (3)	0.0	18
(TTF)(TCNQ)	1.372 (4)	1.745 (3)	1.739 (3)	1.326 (4)	~0.6	2
(TTF)Cl _{0.67}	1.38 (1)	1.720 (5)	1.719 (5)	1.32 (1)	~0.7	19
(TTF)(HgCl ₃)	1.41 (1)	1.72 (1)	1.71 (1)	1.31 (1)	~1.0	this work

the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma_{F_o}^2$, led to a final *R* value ($\sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.080. The final weighted *R* value [$(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$] and goodness of fit [$(\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV}))^{1/2}$, where NO = 4298 observations and NV = 253 variables] were 0.083 and 2.8, respectively. No attempt was made to refine the hydrogen atom parameters at any stage of the analysis. A final difference-Fourier synthesis was essentially featureless, except for peaks at $\pm 2 e/\text{\AA}^3$ near the Hg atoms. Neutral scattering factor curves for the nonhydrogen¹² and hydrogen¹³ atoms were taken from common sources. Anomalous dispersion corrections¹⁴ were applied to the scattering curves for all the nonhydrogen atoms. Final atomic positional parameters are collected in Table I. Tables of thermal parameters and final observed and calculated structure-factor amplitudes are available.¹⁵ The crystallographic computations were performed with a standard set of computer programs.¹⁶

Results and Discussion

(A) The Tetrathiofulvalene Cations. The molecular geometry and dimensions for the three independent TTF cations are presented in Figure 1 and Table II. Two of the TTF cations (B and C, Figure 1) are required by crystallographic considerations to have at least $\bar{1}$ (*C*_i) molecular symmetry (with

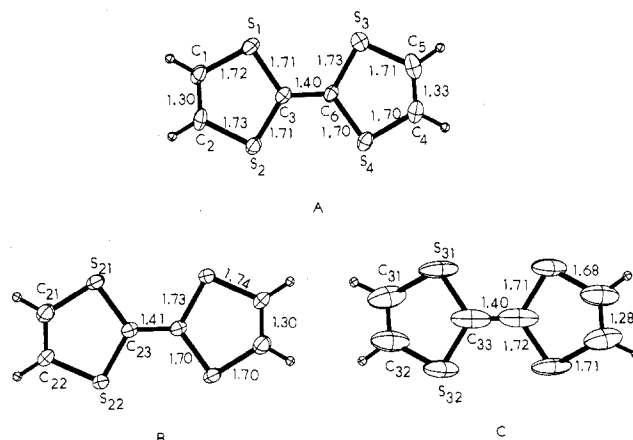


Figure 1. Molecular structure and dimensions for the three unique TTF cations. Cations B and C have their centroids coincident with crystallographic centers of symmetry, while cation A has no required crystallographic symmetry. The esd's in the bond lengths are in the range 0.01–0.02 Å.

the $\bar{1}$ crystallographic symmetry element coincident with the midpoint of the central C=C double bond in each case), while the third TTF cation (A, Figure 1) has no imposed symmetry requirements. Each cation displays, however, essentially *mmm* (*D*_{2h}) molecular symmetry.

The molecular dimensions of the three independent TTF cations are internally self-consistent and appear capable of qualitatively yielding a measure of the charge transfer in the complex. In Table III, we present a comparison of the average (imposing rigorous *mmm* (*D*_{2h}) molecular symmetry) dimensions for the three TTF cations with those in several other

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- (17) We do not have a detailed explanation for the somewhat elongated thermal ellipsoids exhibited by the TTF cation labeled C in Figure 1. We speculate that the crystal employed in data collection was, in fact, not a single crystal but a very intimate lattice twin, with only the TTF cation C sensitive to the alternative twin domains.

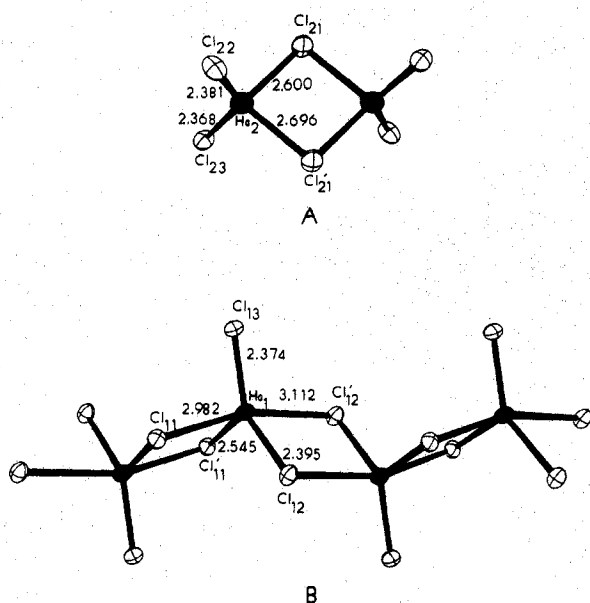


Figure 2. The two chloromercurate species: (A) the edge-bridged bitetrahedron (Hg_2Cl_6)²⁻; (B) the polymeric (HgCl_3^-)_n chain. The esd's in the Hg-Cl bond lengths are 0.005 Å.

systems, including neutral TTF,¹⁸ (TTF)Cl_{0.67},¹⁹ where the charge transfer is assumed from the stoichiometry of the material, and (TTF)(TCNQ), where the charge transfer is known from diffuse X-ray scattering experiments.² Smooth trends, notably in the length of the C=C central bond length "a" and the C-S bond length "b", in the molecular geometry of the TTF cation are displayed as a function of charge transfer. Each of these trends is consistent with expectations from simple molecular-orbital calculations²⁰ and serves to indicate that the charge transfer in (TTF)(HgCl₃) is near unity. As noted in our earlier report,⁴ the resonance Raman spectrum of (TTF)(HgCl₃) is consistent with this deduction. The ν_3 mode in TTF (predominantly a stretching of the central C=C bond "a") undergoes large frequency shifts on electron transfer. For example, ν_3 occurs at 1515 cm⁻¹ in neutral TTF^{21,22} and is seen at 1413 cm⁻¹ in (TTF)Br (assumed to be fully charge transferred).^{3,21} The resonance Raman spectrum of crystalline (TTF)(HgCl₃)⁴ reveals two bands at 1415 and 1424 cm⁻¹ with a 1:1 intensity ratio. These ν_3 bands are in the range typical for fully charge-transferred TTF compounds. The presence of two ν_3 bands, however, suggests that there exist in the solid two different environments for TTF⁺ such that the charge densities on the thia carbon in them are slightly different. Van Duyne and co-workers²¹ have studied the resonance Raman spectra of a wide variety of salts in which the TTF was in different partial oxidation states, and a linear relationship between ρ in TTF^{+ ρ} and ν_3 was observed. Application of this relationship leads to an approximate difference in the degree of charge transfer of 0.1 e between the two sites in the trichloromercurate salt.

(B) The Chloromercurate Anions. Two types of chloromercurate anions are found in the crystalline structure of (TTF)(HgCl₃). One anion is a dimeric, edge-shared bitet-

rahedron, (Hg_2Cl_6)²⁻, with its center of mass coincident with a crystallographic center of symmetry, Figure 2A. The two independent Hg-Cl bridging distances at 2.600 (5) and 2.696 (5) Å lead to a slightly asymmetric bridging system reminiscent of that found in the discrete chloro-bridged dimer in $\text{PPh}_3\text{-HgCl}_2$ (Hg-Cl bridging bond lengths of 2.62 (1) and 2.66 (1) Å).²³ The Hg-Cl bond lengths to the two independent terminal chloro ligands in the dimer are substantially shorter at 2.386 (5) and 2.381 (5) Å. Similar terminal Hg-Cl distances are observed, for example, in $\text{Me}_3\text{P-HgCl}_2$, 2.36 (1) Å,²⁴ and $\text{Et}_3\text{P-HgCl}_2$, 2.40 (1) Å,²⁵ and in the complex 1,4,8,11-tetrathiacyclotetradecane- HgCl_2 , 2.41 and 2.42 Å.²⁶

The second chloromercurate(II) species is a polymer of HgCl_3^- , with its propagation direction parallel to the crystallographic *c* axis (Figure 2B and Figure 3). In this polymeric system, the coordination about the Hg(II) ion is roughly trigonal bipyramidal, with three relatively short equatorial Hg-Cl bonds and two rather long axial Hg-Cl interactions. One of the chloro ligands, Cl(13), bonds solely at a terminal site with a Hg-Cl bond length, 2.374 (5) Å, which is very similar to those observed for the terminal chloro ligands in the $\text{Hg}_2\text{Cl}_6^{2-}$ dimer described above. The other two chloro ligands in the (HgCl_3^-)_n polymer act as bridging ligands with very asymmetric Hg-Cl bond lengths. The chloro ligand Cl(12) has a strong equatorial bond at 2.395 (5) Å and a substantially weaker axial interaction at 3.112 (5) Å (Figure 2B). A similar situation obtains for the chloro ligand Cl(11), which forms a somewhat less asymmetric bridging system with a Hg-Cl equatorial bond length at 2.545 (5) Å and an axial Hg-Cl interaction at 2.982 (5) Å.

The formation of two such diverse chloromercurate(II) anionic systems is, to our knowledge, unique to the present case.

(C) Crystal Structure. Qualitatively, the crystal structure of (TTF)(HgCl₃) can be separated into two types of two-dimensional nets (Figure 3) lying parallel to the crystallographic *ac* plane. One of these layers, centered about *y* = 0.0, contains the polymeric (HgCl_3^-)_n chloromercurate(II) anion, and parallel to this is a column of TTF cations (Figure 3). The TTF columnar array is comprised of the TTF cations labeled B and C in Figure 1 in an alternating fashion. Within these columnar arrays of TTF cations there is substantial molecular overlap (Figure 4) nominally of the ring-over-bond type and with a mean separation between approximately parallel (dihedral angle = 4.9°) planes of 3.6 Å. The mean separation observed here is considerably longer than in (TTF)(TCNQ) (3.48 Å)⁷ but similar to those observed in (TTF)(DETCNQ) (3.60 Å)²⁷ and the eclipsed columnar arrays in (TTF)Cl_{0.92} (3.59 Å)²⁸ and (TTF)Br_{0.79} (3.57 Å).²⁹

The second type of layer parallel to the *ac* plane and centered about *y* = 0.5 contains solely dimeric species (Figure 3). The (Hg_2Cl_6)²⁻ edge-shaped bitetrahedron in this layer has been described above. Coupled with this chloromercurate(II) dimer is a pair of TTF cations, of the type labeled A in Figure 1, strongly associated about crystallographic centers of symmetry. The molecular overlap in these TTF cation dimers is nearly eclipsed with a slight lateral shift

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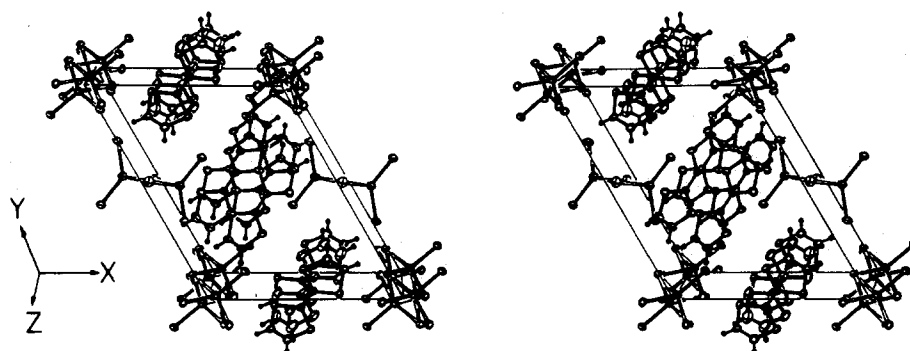


Figure 3. Stereoview of the crystal packing in $(\text{TTF})(\text{HgCl}_3)$. Note in particular the qualitative separation of the structure into layers parallel to the crystallographic ac plane.

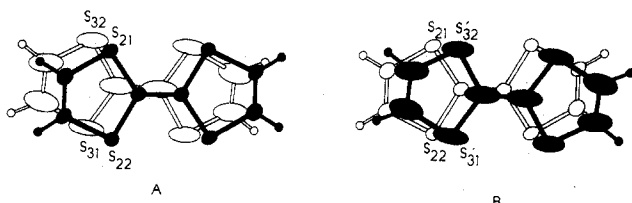


Figure 4. Molecular stacking patterns in the columnar array of TTF cations. The mean stacking distance is about 3.6 Å in each case.

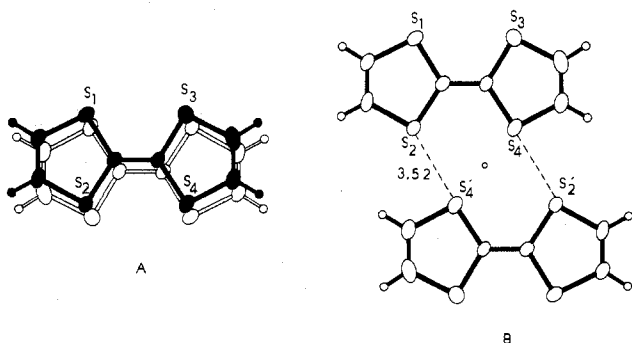


Figure 5. (A) Molecular overlap in the dimeric TTF cations (mean stacking distance 3.43 Å). (B) S...S contacts coupling dimeric TTF cations along the c axis (see text).

along the short in-plane molecular axis (Figure 5A). The mean stacking distance in these TTF dimers is short at 3.43 Å. The molecular overlap and spacing found here are virtually identical with those found in the salt $(\text{TTF})\text{Br}$.⁸ Coupling between dimeric species along the c axis is mainly accomplished through the $\text{S}(2)\cdots\text{S}(4)$ ($1-x, 1-y, 2-z$) contact illustrated in Figure 5B.

The intraplane and interplane interactions between the TTF cations and the chloromercurate anions are dominated by $\text{Cl}\cdots\text{S}$ contacts (Table IV). Within the layer centered about $y = 0.0$, the polymeric $(\text{HgCl}_3^-)_n$ entity and the columnar TTF column are coupled via the $\text{Cl}(12)\cdots\text{S}(31)$ and $\text{Cl}(12)\cdots\text{S}(22)$ contacts at 3.276 (8) and 3.404 (8) Å, respectively. Similarly, a short $\text{Cl}(22)\cdots\text{S}(2)$ contact, 3.292 (8) Å, couples the dimeric $(\text{Hg}_2\text{Cl}_6)^{2-}$ and the $(\text{TTF})_2^{2+}$ dimer in the layer centered about $y = 0.5$. These three intraplane $\text{Cl}\cdots\text{S}$ contacts are all substantially shorter than the sum (3.65 Å) of the van der Waals radii for chlorine (1.8 Å) and S (1.85 Å), suggesting that

Table IV. Selected Interatomic Contacts (Å)^a

	(a) $\text{Cl}\cdots\text{S}$		
$\text{Cl}(12)\cdots\text{S}(31)^{\text{i}}$	3.28 (1)	$\text{Cl}(23)\cdots\text{S}(21)^{\text{iii}}$	3.56 (1)
$\text{Cl}(22)\cdots\text{S}(2)^{\text{ii}}$	3.29 (1)	$\text{Cl}(23)\cdots\text{S}(32)^{\text{iii}}$	3.57 (2)
$\text{Cl}(12)\cdots\text{S}(22)^{\text{j}}$	3.40 (1)	$\text{Cl}(11)\cdots\text{S}(22)^{\text{i}}$	3.61 (1)
	(b) $\text{S}\cdots\text{S}$		
$\text{S}(1)\cdots\text{S}(4)^{\text{iv b}}$	3.36 (2)	$\text{S}(1)\cdots\text{S}(21)^{\text{v}}$	3.65 (2)
$\text{S}(2)\cdots\text{S}(3)^{\text{iv b}}$	3.43 (2)	$\text{S}(21)\cdots\text{S}(32)^{\text{ii c}}$	3.55 (3)
$\text{S}(2)\cdots\text{S}(4)^{\text{iii}}$	3.52 (2)	$\text{S}(22)\cdots\text{S}(31)^{\text{vi c}}$	3.58 (3)
	(c) $\text{C}\cdots\text{C}$		
$\text{C}(3)\cdots\text{C}(6)^{\text{iv b}}$	3.45 (2)	$\text{C}(2)\cdots\text{C}(5)^{\text{iv b}}$	3.49 (2)
$\text{C}(1)\cdots\text{C}(4)^{\text{iv b}}$	3.47 (2)	$\text{C}(2)\cdots\text{C}(4)^{\text{iv b}}$	3.49 (2)

^a Symmetry transforms: (i) $-1+x, y, z$; (ii) x, y, z ; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 1-y, 2-z$; (v) $x, y, 1+z$; (vi) $x, y, -1+z$. ^b Intradimer stacking. ^c Intracolumn stacking.

something in addition to long-range dipolar forces is operative in these interactions. As a significant portion of the positive charge on the TTF cations is expected to reside on the S atoms²⁰ and the chloro ligands surely retain some measure of negative charge, we expect that these contacts contain a significant degree of electrostatic interaction.

The predominant interlayer interactions are again of the $\text{Cl}\cdots\text{S}$ type (Table IV), and we expect these interactions also contain a significant electrostatic component.

Finally, it is tempting to try to decide which of the TTF species is more highly charged as indicated by the Raman data. It may be argued that TTF dimers are expected from their eclipsed stacking mode to carry a larger positive charge than the TTF columns.³⁰ One might also expect that the polymeric HgCl_3^- system is more robust than the $\text{Hg}_2\text{Cl}_6^{2-}$ dimer in accepting more than unit negative charge, owing to the possibility of extensive delocalization of the charge density.

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Registry No. $(\text{TTF})(\text{HgCl}_3)$, 75046-09-2.

Supplementary Material Available: Tables of atomic thermal parameters and observed and calculated structure-factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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