

METALLOTETRATHIAETHYLENES*

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Discovery of unusual electrical transport properties of the 1:1 donor-acceptor complex formed from tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) has stimulated an intense study of materials prepared from other cyano-carbon acceptors. Less, however, is known about the complex chemistry of TTF, and only recently has a series of metal dithiolenes derivatives such as $(\text{TTF})_2\text{-}[(\text{C}_2\text{H}_2\text{S}_2)_2\text{Ni}]$ been reported.^{1,2} To obtain further insight into the fundamental chemistry of such tetrathiaethylenes, we have carried out an extensive study of their complexes with transition metal halides. Several types of materials have been prepared, and they are surveyed here.

Metal halide complexes of tetrathiaethylenes may be considered members of three general classes: (1) crystal complexes, (2) charge-transfer or donor-acceptor complexes, and (3) salts.

Crystal complexes may be formed by cocrystallization of the thiacyanone with some metal derivatives. The x-ray powder diffraction patterns are unique, but optical and vibrational spectroscopic properties are the sum of minimally perturbed component molecules. Such materials are usually insulators.

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Donor-acceptor complexes comprise a broad and fascinating class of materials. We consider them complexes in which low energy-excited states, formed by electron transfer from the thiaethylene to a metal center, is mixed with a neutral, uncharged ground state. These compounds have new infrared and electronic-spectroscopic properties relative to the starting materials. They are usually semiconductors, although, in favorable cases, rather high conductivity may be observed. TTF-TCNQ is probably the most spectacular member of this class.

Salts of tetrathiaethylenes are formed by complete electron transfer to the thiocarbon and so are ionic in character. Some cation-anion interaction, in addition to electrostatic forces, may be observed. Microwave conductivity of pressed powdered samples is usually in the semiconductor-insulator range.³

The reaction chemistry of conjugated tetrathiaethylenes, notably TTF, which forms a stable cation radical, is dominated by electron-transfer processes. This is illustrated by a comparison of the products formed from mercuric chloride and TTF or 4,4',5,5'-tetrahydrotetrathiafulvalene, (H_4 TTF). TTF is oxidized by mercuric chloride in acetonitrile to afford the cation radical salt $TTF^+HgCl_3^-$ and mercurous chloride. Two-probe conductivity measurements on single crystals of this salt reveal that it is an insulator, $\sigma = 1 \times 10^{-7}$ (ohm cm)⁻¹ at room temperature. An x-ray structure determination reveals two kinds of TTF cation radical dimers and polymeric $HgCl_3$ chains. The magnetic susceptibility χ_C^M is 300×10^{-6} cm³ mole⁻¹ at 51°K, or about 4% of the value expected for a simple radical salt. Strong coupling between oxidized TTF moieties appears to be a general phenomenon, at least in compounds that crystallize in segregated stacks, c.f. TTF-TCNQ⁴ and TTF subhalides.^{5,6} Cooling solutions containing H_4 TTF and excess mercuric chloride produces, in contrast, $(H_4TTF)(HgCl_2)_3$. The structure of this material has been determined by x-ray diffraction methods. It is a crystal complex containing molecules of H_4 TTF and polymeric $HgCl_2$ units (FIGURE 1). The shortest Hg—S distance is 3.133 Å. The electronic spectrum shows absorption maxima at 33,560, 36,200, and 44,400 cm⁻¹, compared with 40,480 cm⁻¹ in the starting thioethylene, confirming minimal interactions between the lattice components. The structure of this compound is important because it demonstrates the ability of TTF analogs to form crystal complexes and discloses that the sulfur atoms in these molecules have a surprisingly low nucleophilicity. The 1:1 complex $(TTF)[Pd(C_5H_7O_2)_2]$, formed by slow evaporation of solutions of TTF and palladium bis(acetylacetonate), appears to be another member of this class.

The TTF-Cu⁺⁺ system is interesting and has yielded several novel materials. The detailed course of the reactions of TTF with CuX_2 depends on both the nature of X and the solvent. Addition of TTF to $CuCl_2 \cdot 2H_2O$ in ethanol yields $(TTF)_3-(CuCl_2)_3$, about which more will be said later; recrystallization of this compound from acetonitrile produces $(TTF)_2CuCl_4$. The influence of the solvent on the course of the reaction, demonstrated by the isolation of $(TTF)CuCl_4$ from $CuCl_2 \cdot 2H_2O$ and TTF in acetonitrile, arises from the stronger solvation of Cu^+ by acetonitrile than ethanol.

Raman spectroscopy has proved extremely valuable in studying metallotetrathiaethylenes. Of the seven Ag normal modes in TTF, the ν_3 mode, which is predominantly the central C=C stretch, undergoes the largest frequency shift on oxidation and shifts from 1515 cm⁻¹ in neutral TTF to 1413 and 1323 cm⁻¹ in

TTF⁺ and TTF⁺⁺ derivatives, respectively. This mode is observed at 1419 cm⁻¹ in (TTF)₂CuCl₄ and at 1313 cm⁻¹ in (TTF)CuCl₄. Electron spin resonance parameters for the former are $g \parallel 2.323(5)$; $g \perp 2.053(5)$; $\Delta H \parallel 43$ G; $\Delta H \perp 41$ G. For (TTF)CuCl₄, $g \parallel 2.476(5)$; $g \perp 2.123(6)$; $\Delta H \parallel 69$ G; $\Delta H \perp 175$ G. The relatively narrow lines and spread of g values in (TTF)₂CuCl₄ are suggestive of a

ANGLE	DEGREE(°)
CL(1)--Hg(1)--CL(1')	180.00
CL(1)--Hg(1)--CL(6)	93.71
CL(1)--Hg(1)--CL(6')	86.29
CL(1)--Hg(1)--CL(2)	83.52
CL(1)--Hg(1)--CL(2')	96.48
CL(6)--Hg(1)--CL(2)	86.15
CL(2)--Hg(1)--CL(6')	93.85
CL(6)--Hg(1)--CL(2')	93.85
CL(6')--Hg(1)--CL(2')	86.15
CL(6)--Hg(2)--S(3)	84.85
CL(6)--Hg(2)--S(4)	96.19
CL(6)--Hg(2)--CL(2)	170.04
CL(6)--Hg(2)--CL(1)	93.66
CL(6)--Hg(2)--CL(1')	78.14
CL(6)--Hg(2)--CL(2')	92.34
S(3)--Hg(2)--S(4)	62.71
S(3)--Hg(2)--CL(2')	70.43
CL(2')--Hg(2)--CL(1')	71.41
CL(1')--Hg(2)--CL(1)	84.31
S(4)--Hg(2)--CL(1)	73.96

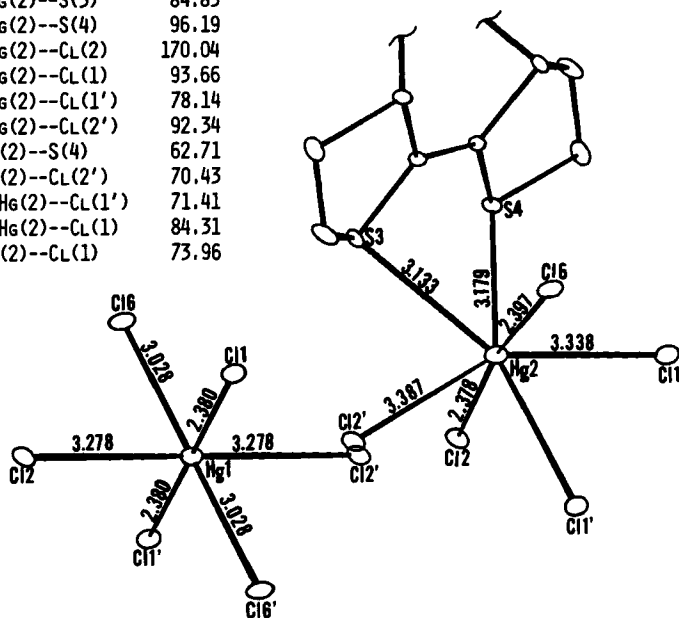


FIGURE 1.

parallel arrangement of square planar CuCl_4^{2-} units, but in (TTF)CuCl₄, the data are more consistent with a flattened tetrahedral geometry about copper. From these data and the experimental values of θ , exchange fields of about 10^4 G were calculated, based on three dimensional magnetic interactions.^{7,8} Thus, in contrast to $[(\text{CF}_3)_2\text{C}_2\text{S}_2]_2\text{Cu}(\text{TTF})$, where evidence for the presence of linear, one-dimensional antiferromagnetic Heisenberg chains has been adduced,⁹ significant

exchange fields are observed in all three dimensions in these TTF tetrachlorocuprates.

$(\text{TTF})_3(\text{CuCl}_2)_5$ is only weakly paramagnetic and does not show an ESR spectrum at room temperature. Its Raman spectrum reveals bands at 1456, 1422, and 1306 cm^{-1} and the material therefore contains both the dication and cation radical of TTF. We suggest that this compound is a mixed-valence salt containing chlorine bridged copper(I) centers, c.f. (paraquat) $(\text{CuCl}_2)_2$.¹⁰

Formation of ionic complexes from TTF and metal halides appears to be a general reaction, and as additional examples, $(\text{TTF})(\text{TiCl}_4)_2$, $(\text{TTF})_2\text{SnCl}_6$, and $(\text{TTF})_2\text{FeCl}_4$ prepared from TiCl_4 , SnCl_4 , and FeCl_3 , respectively, may be mentioned. Cobalt(II) chloride represents an unusual case: acetonitrile solutions of TTF and anhydrous CoCl_2 yield no solid product, but when air is injected into the system, crystals separate, the analysis of which corresponds to $(\text{TTF})_{2.4}\text{CoCl}_3$.

Group VIII metal-halide-TTF complexes of the type $(\text{TTF})_2\text{MX}_2$ ($\text{M}=\text{Pd}$, Pt ; $\text{X}=\text{Cl}$, Br) are particularly interesting and have been studied in some detail.

TABLE I

Compound	$\nu_{\text{M-Cl}}$ cm^{-1}	Raman $\Delta\nu$, cm^{-1}	Absorption Maxima, nm	Conductivity (ohm, cm) $^{-1}$	Core Level Binding Energies, eV		
					$\Delta(\text{Cl-S})$	$\Delta(\text{S-M})$	$\Delta(\text{Cl-M})$
$(\text{TTF})_2\text{PdCl}_2$	330	1489, 1425	830, 240	2×10^{-4}	34.1	-137.6	-139.5
$(\text{TTF})_2\text{PtCl}_2$	340	1499, 1425	550, 340	6×10^{-4}	34.0	91.6	125.6
K_2PdCl_4	336	—	—	—	—	—	-139.6
K_2PtCl_4	321	—	—	—	—	—	126.1
$(\text{TTF})\text{HgCl}_3$	360	1419	530, 380, 410, 280	$1 \times 10^{-7(\text{A})}$	33.4	63.8	97.2
$(\text{H}_4\text{TTF})_2\text{PdCl}_2$	345	1543, 1528	650, 427, 380, 345, 280	4×10^{-4}	34.3	-173.9	-139.6
$(\text{H}_4\text{TTF})_2\text{PtCl}_2$	342	1537	530(w), 400	2×10^{-4}	34.5	91.2	125.7

Measured on single crystal by two-probe dc method. All other conductivities were obtained by the microwave method.³

They are readily prepared in high yield from the reaction in acetonitrile of TTF with $\text{KPtCl}_3(\text{C}_2\text{H}_4)$, K_2PtCl_4 , or $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$. These materials are intensely colored and show long wavelength absorptions in their electronic spectra that are attributed to $\text{M} \leftarrow \text{L}$ charge-transfer processes. Raman bands in $(\text{TTF})_2\text{PdCl}_2$, and $(\text{TTF})_2\text{PtCl}_2$ are observed at 1489, 1425 cm^{-1} , and 1499, 1425 cm^{-1} , respectively. These, therefore, are mixed-valence compounds in that they contain both TTF^0 and TTF^+ . In the platinum chloride compound, an absorption in the far infrared at 340 cm^{-1} is observed. This band shifts on substitution of bromine for chlorine and is thus assigned to $\nu_{\text{Pt-Cl}}$. These results exclude the otherwise attractive formulation $[(\text{TTF})_2\text{Pt}]^{++}\text{Cl}_2$ which might have been anticipated from earlier work on metal complexes of 2,2'-bimidazoly.¹¹

X-ray photoelectron spectroscopy (ESCA) has provided additional insight into the nature of these materials, and some of these results are shown in TABLE I. Core-level binding energies are expressed in terms of differences between Cl_{2p} S_{2p} , S_{2p} -metal, and Cl_{2p} -metal energies so that shifts due to charging of the samples,

a severe problem with the K_2PdCl_4 and K_2PtCl_4 references, will be less important. In the $TTF-PdCl_2$ and $PtCl_2$ complexes, the separation between the Cl_{2p} and $Pd\ 3d_{5/2}$ or $Pt\ 4f_{7/2}$ levels is changed by only a small amount relative to the MCl_4^{2-} salts. Further, the sulfur $2p$ binding energies fall in the range 162.6–163.5 eV (relative to C_{1s} from the graphite sample holder at 284.0 eV), compared with 163.9 eV in the salt $TTF^+ HgCl_3^-$. These data indicate that small changes in the $M-Cl$ bond polarity have resulted from the interaction of the MCl_2 unit with TTF and that in the cases studied, the sulfurs are less positively charged than in TTF^+ . These data appear consistent with the formulation of the palladium(II) and platinum(II) chloride-TTF compounds and donor-acceptor or charge-transfer complexes.

The present, incomplete, picture of the bonding in these palladium and platinum complexes of TTF involves stacks of TTF molecules with linear MX_2 units in the channels. Weak sulfur-metal coordination through the lone pair of electrons on sulfur or back bonding into the ligand π system may also be possible. Partial electron transfer from TTF to the metal center generates mixed-valence materials (on the Raman time scale) containing $TTF^{0,+1}$, but the precise degree of electron transfer has yet to be established. The electrons involved in the charge-transfer process are delocalized over the ten-atom TTF moiety and have only a small effect on the sulfur core-level energies. These are dominated by localized lone electron pairs, as is illustrated by comparison of the ESCA data for $(TTF)_2-PdCl_2$ and $(H_4TTF)_2PdCl_2$.

It is clear that additional data will be needed to delineate the structure and bonding in these TTF-metal complexes. The scope and diversity of the chemistry is extremely large. It is probable that within the donor-acceptor class of complexes, gradations in bonding features will continue to be observed among different metal complexes, and that new materials will emerge that have novel chemical and physical properties.

NOTES AND REFERENCES

1. INTERRANTE, L. V., K. W. BROWALL, H. R. HART, JR., I. S. JACOBS, G. D. WATKINS & S. H. WEE. 1975. *J. Amer. Chem. Soc.* **97**: 889.
2. WUDL, F. 1977. *J. Amer. Chem. Soc.* **97**: 1962.
3. Unless otherwise noted, conductivities reported herein were measured by the micro-wave cavity perturbation method on thin compressed pellets.
4. SCOTT, J. C., A. F. GARITO & A. J. HEEGER. 1974. *Phys. Rev.* **B10**: 3131.
5. SOMOANO, R. B., A. GUPTA, V. HADEK, M. JONES, T. DATTA, R. DECK & A. M. HERMANN. 1977. *Phys. Rev.* **B15**: 595.
6. WUDL, F., D. E. SCHAFER, W. M. WALSH, JR., L. W. RUPP, F. J. DISALVO, J. V. WASCZAK, M. L. KAPLAN & G. A. THOMAS. 1977. *J. Chem. Phys.* **66**: 377.
7. GAURA, R., G. KOKOSZKA, K. HYDE & R. LANCIONE. 1976. *Coord. Chem.* **5**: 105.
8. KOKOSZKA, G. 1974. *In Low Dimensional Cooperative Phenomena*. H. J. Keller, Ed.: 171. Plenum Press. New York, N.Y.
9. BRAY, J. W., H. R. HART, JR., L. V. INTERRANTE, I. S. JACOBS, J. S. KASPER, G. D. WATKINS, S. H. WEE & J. C. BONNER. 1975. *Phys. Rev. Lett.* **35**: 744.
10. PROUT, C. K. & P. MURRAY-RUST. 1969. *J. Chem. Soc. (A)*: 1520.
11. KAISER, S. W., R. B. SAILLANT, W. M. BUTLER & P. G. RASMUSSEN. 1976. *Inorg. Chem.* **15**: 2681, 2688.