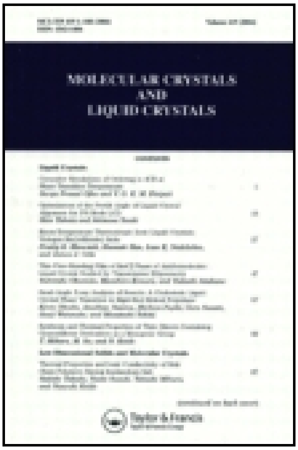

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# Synthesis and Structure of Polymeric Silver(I) Complex of Tetrakis(methylthio)-tetrathiafulvalene: The First Example of the Silver(I) Ion Coordinated Directly to TTF-Derivatives

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# SYNTHESIS AND STRUCTURE OF POLYMERIC SILVER(I) COMPLEX OF TETRAKIS(METHYLTHIO)TETRATHIAFULVALENE: THE FIRST EXAMPLE OF THE SILVER(I) ION COORDINATED DIRECTLY TO TTF-DERIVATIVES

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Abstract Reaction of silver(I) trifluoromethanesulfonate with tetrakis(methylthio)tetrathiafulvalene (TMT-TTF) yielded polynuclear silver(I) complex $[Ag(TMT\text{-}TTF)(O_3SCF_3)]$. The compound crystallizes in the orthorhombic system, space group *P*bam with cell constants $a = 14.855(5)$, $b = 22.510(3)$, $c = 13.310(8)$ Å, $Z = 8$. It is a neutral 1 : 1 metal/ligand complex in which each Ag(I) ion is six-coordinated by four sulfur atoms from the bridging TMT-TTF and two oxygen atoms from the bidentate $O_3SCF_3$ anion, which results in a two interwoven polymeric chain structure. It represents the first example of the silver(I) ion coordinated directly to TTF-derivatives. The compound is an insulator at room temperature but behaves as a semiconductor when doped with iodine.

## INTRODUCTION

A series of tetrakis(methylthio)tetrathiafulvalene (TMT-TTF) complexes exhibiting interesting physical properties such as metallic conductivity, have been appeared in literature recently.[1-6] TMT-TTF can be easily oxidized to the stable radical cation, and accordingly, its chemistry is dominated by electron-transfer processes. It reacts with organic electron acceptors, e.g., tetracyanoquinodimethane[1] and hexacyanobutadiene[2], and inorganic oxidants[3-6] to form partially or completely oxidized materials containing $TMT\text{-}TTF^{\rho+}$ where $\rho$ ranges from about 0.6 to 2.0. In most of these charge transfer compounds the donors and acceptors are stacked in segregated columns. Although some of them contain metal atoms in an anion part, these metal ions are not coordinated to the organic molecules in most cases. One of our current research interests has been focused on metallotetrathiafuvalene polymers, in which TTF and its derivatives co-ordinate directly to the metal ions. We have reported a number of copper(I) complexes with TMT-TTF[7] and $TTC_2$-TTF[8]. This paper reports the synthesis and characterization of the first silver(I) coordination polymer with TMT-TTF.

## EXPERIMENTAL

### Preparation of the Complex

TMT-TTF was purchased from Tokyo Chemical Industry Co., Japan and silver(I) trifluoromethanesulfonate was obtained from Aldrich. All solvents were dried and distilled by standard methods before use. Addition of the solution of silver(I) trifluoromethanesulfonate (6.4 mg, 0.025 mmol) in a mixed solvent of tetrahydrofuran (0.5 $cm^3$) and diethyl ether (3.0 $cm^3$) to a solution of TMT-TTF (9.7 mg, 0.025 mmol) in the same mixed solvent precipitated orange microcrystalline solid which was washed three times with diethyl ether. Single crystals for X-ray structure determination were grown by slow diffusion of diethyl ether into a thf/$CH_3CN$ solution of the complex.

TABLE I Crystal and final structure refinement data.

| | |
|---|---|
| Formula | $C_{11}H_{12}AgF_3O_3S_9$ |
| Formula weight | 645.62 |
| Crystal dimensions (mm) | 0.21 x 0.14 x 0.22 |
| Crystal system | orthorhombic |
| Space group | *Pbam* |
| $a$/Å | 14.855(5) |
| $b$/Å | 22.510(3) |
| $c$/Å | 13.310(8) |
| $V$/Å$^3$ | 4450(4) |
| $Z$ | 8 |
| $D_c$/g cm$^{-3}$ | 1.927 |
| $F$(000) | 2560 |
| $\mu$(Mo-K$_\alpha$)/Å | 17.44 |
| Scan type | $\omega$ - 2$\theta$ |
| Scan rate/° min$^{-1}$ | 8.0 |
| Scan width/° | (0.94 + 0.30 tan $\theta$) |
| 2$\theta_{max}$/° | 55.0 |
| No. reflections measured | 5676 |
| No. reflections observed [I>3$\sigma$(I)] | 2806 |
| $R$ | 0.067 |
| $R_w$ | 0.096 |

TABLE II Final atomic coordinates for non-hydrogen atoms.

| Atom | x | y | z |
|---|---|---|---|
| Ag(1) | 0.8872(1) | 0.15361(6) | 0.5000 |
| Ag(2) | 0.0752(1) | 0.22070(6) | 0.0000 |
| S(1) | 0.9387(2) | 0.2418(1) | 0.3713(3) |
| S(2) | 0.9542(2) | 0.3738(1) | 0.3901(3) |
| S(3) | 0.8646(2) | 0.5062(1) | 0.6101(3) |
| S(4) | 0.7262(2) | 0.6015(1) | 0.6279(3) |
| S(5) | 0.0364(2) | 0.3110(1) | -0.1270(3) |
| S(6) | 0.0763(2) | 0.4407(1) | -0.1106(3) |
| S(7) | 0.1755(2) | 0.5705(1) | 0.1103(3) |
| S(8) | 0.3217(3) | 0.6603(2) | 0.1283(3) |
| S(9) | 0.5809(4) | 0.4109(3) | 0.5000 |
| S(10) | 0.3671(4) | 0.3323(3) | 0.0000 |
| F(1) | 0.640(1) | 0.3037(8) | 0.5000 |
| F(2) | 0.7218(9) | 0.3604(5) | 0.422(1) |
| F(3) | 0.403(1) | 0.4397(9) | 0.0000 |
| F(4) | 0.291(1) | 0.4248(6) | 0.080(1) |
| O(1) | 0.5309(8) | 0.3989(5) | 0.4125(9) |
| O(2) | 0.632(1) | 0.4628(8) | 0.5000 |
| O(3) | 0.410(1) | 0.3240(7) | 0.089(1) |
| O(4) | 0.274(2) | 0.305(1) | 0.0000 |
| C(1) | 0.838(1) | 0.2579(6) | 0.291(1) |
| C(2) | 0.9393(8) | 0.3042(4) | 0.4492(9) |
| C(3) | 0.924(1) | 0.4141(7) | 0.5000 |
| C(4) | 0.888(1) | 0.4671(7) | 0.5000 |
| C(5) | 0.7886(8) | 0.5541(4) | 0.5504(9) |
| C(6) | 0.666(1) | 0.5493(7) | 0.699(1) |
| C(7) | 0.1356(10) | 0.3106(6) | -0.211(1) |
| C(8) | 0.0643(7) | 0.3718(4) | -0.0501(9) |
| C(9) | 0.111(1) | 0.4782(6) | 0.0000 |
| C(10) | 0.148(1) | 0.5319(6) | 0.0000 |
| C(11) | 0.2560(7) | 0.6160(5) | 0.0519(9) |
| C(12) | 0.381(2) | 0.608(1) | 0.189(2) |
| C(13) | 0.6637 | 0.3572 | 0.5000 |
| C(14) | 0.3422 | 0.4026 | 0.0000 |

## X-ray Structure Determination

A single orange crystal was mounted with paraffin on a thin glass fiber for X-ray structure analysis. Diffraction data were collected on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo-Ka radiation. A summary of crystallographic data is given in Table I.

The structure was solved by a direct method (MITHRIL)[9] and refined by full-matrix least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic temperature factors were refined for all non-hydrogen atoms. Isotropic hydrogen atoms were located by Fourier difference synthesis. The data were corrected for Lorentz and polarization effects. All of the calculations were performed using a TEXSAN crystallographic software package[10] on a micro VAX computer. Atomic scattering factors and anomalous dispersion terms were taken from ref. 11. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$.

TABLE III Selected bond lengths for the complex.

| | Bond Lengths (Å) | | Bond Lengths (Å) |
|---|---|---|---|
| Ag(1) - S(1) | 2.731(4) | Ag(2) - S(5) | 2.705(3) |
| Ag(1) - S(4) | 2.667(4) | Ag(2) - S(8) | 2.666(4) |
| Ag(1) - O(1) | 2.70(1) | Ag(2) - O(3) | 2.90(2) |
| S(1) - C(1) | 1.88(2) | S(5) - C(7) | 1.85(1) |
| S(1) - C(2) | 1.77(1) | S(5) - C(8) | 1.76(1) |
| S(2) - C(2) | 1.77(1) | S(6) - C(8) | 1.76(1) |
| S(2) - C(3) | 1.78(1) | S(6) - C(9) | 1.774(9) |
| S(3) - C(4) | 1.743(9) | S(7) - C(10) | 1.753(8) |
| S(3) - C(5) | 1.75(1) | S(7) - C(11) | 1.76(1) |
| S(4") - C(5) | 1.75(1) | S(8") - C(11) | 1.73(1) |
| S(4") - C(6) | 1.75(2) | S(8") - C(12) | 1.69(2) |
| C(2) - C(2') | 1.35(2) | C(8) - C(8') | 1.33(2) |
| C(3) - C(4) | 1.31(2) | C(9) - C(10) | 1.33(2) |
| C(5) - C(5') | 1.34(2) | C(11) - C(11') | 1.38(2) |
| S(9) - C(13) | 1.725(6) | S(10) - C(14) | 1.626(8) |
| S(9) - O(1) | 1.41(1) | S(10) - O(3) | 1.35(2) |
| S(9) - O(2) | 1.39(2) | S(10) - O(4) | 1.51(3) |
| C(13) - F(1) | 1.25(2) | C(14) - F(3) | 1.23(2) |
| C(13) - F(2) | 1.35(1) | C(14) -F(4) | 1.40(1) |

Final atomic coordinates for non-hydrogen atoms are given in Table II and selected bond lengths and bond angles are listed in Tables III and IV. The full lists of the atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated structure factors are available from the authors on request.

TABLE IV Selected bond angles for the complex.

| | Angles (°) | | Angles(°) |
|---|---|---|---|
| S(1)-Ag(1)-S(1') | 77.7(1) | S(5)-Ag(2)-S(5') | 77.3(1) |
| S(1)-Ag(1)-S(4) | 95.5(1) | S(5)-Ag(2)-S(8) | 96.0(1) |
| S(1)-Ag(1)-S(4') | 153.7(1) | S(5)-Ag(2)-S(8') | 154.9(1) |
| S(1)-Ag(1)-O(1) | 80.0(2) | S(5)-Ag(2)-O(3) | 80.0(3) |
| S(1)-Ag(1)-O(1') | 111.5(3) | S(5)-Ag(2)-O(3') | 109.5(3) |
| S(4)-Ag(1)-S(4') | 79.4(2) | S(8)-Ag(2)-S(8') | 79.6(2) |
| S(4)-Ag(1)-O(1) | 91.8(3) | S(8)-Ag(2)-O(3) | 92.8(3) |
| S(4)-Ag(1)-O(1') | 125.6(3) | S(8)-Ag(2)-O(3') | 124.7(3) |
| O(1)-Ag(1)-O(1') | 51.0(5) | O(3)-Ag(2)-O(3') | 47.9(7) |

## RESULTS AND DISCUSSION

### Crystal Structure of [Ag(TMT-TTF)($O_3SCF_3$)]

X-ray structure determination reveals that in this complex there are two crystallographically independent [Ag(TMT-TTF)($O_3SCF_3$)] units, one of which is illustrated by ORTEP view in Figure 1 together with atom numbering scheme. In each unit the Ag(I) ion is six-coordinated by four sulfur atoms from two TMT-TTF molecules and two oxygen atoms from the bidentate trifluoromethanesulfonate group. Each TMT-TTF moiety in turn bridges two metal enters with the four terminal sulfur atoms. This results in two independent polymeric chains interwoven running along the *b* axis as shown in Figure 2. The TMT-TTF molecule is in a boat-like form, Figure 1, and the four methyl groups elongate nearly perpendicular to the central $C_6S_8$ moiety. The central skeleton is appreciably non-planar. This conformation is rather analogous to that of neutral TMT-TTF molecule.[2]

It is possible to estimate the oxidation state of the donor TMT-TTF from the charge-sensitive length of the central C=C bond of the TTF core. It is known that this C=C bond distance is expected to increase with decreasing of electron density in the highest occupied (bonding) molecular orbital.[2] In the present work the average central

C=C bond length of TMT-TTF is 1.32(2) Å, and according to the correlation between the bond length and the degree of charge transfer of TTF type donors,[2] the degree of charge transfer for the ligand in the complex is close to zero. This is consistent with the determined structure and the suggested stoichiometry.

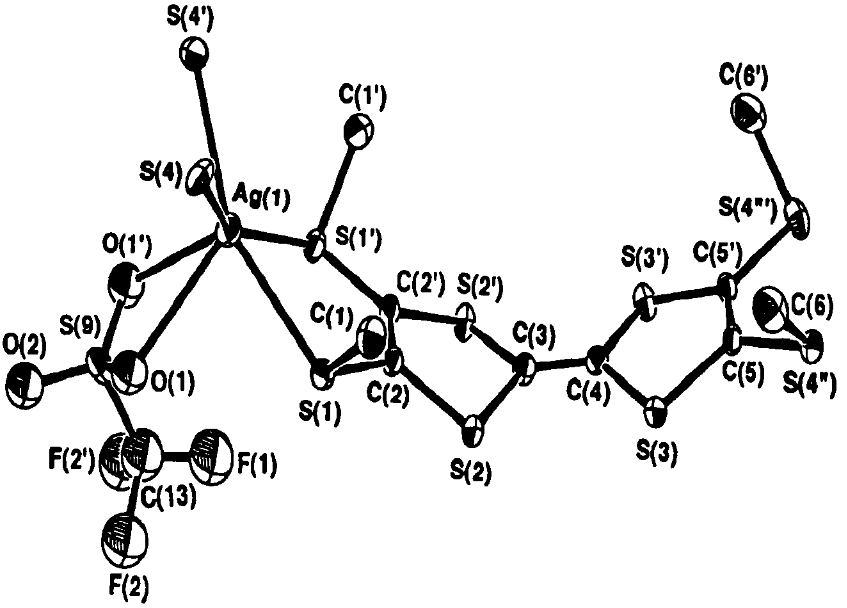

FIGURE 1 ORTEP view of one of the two crystallographically independent [Ag(TMT-TTF)($O_3SCF_3$)] units.

The coordination environment for Ag(1) and Ag(2) are very similar with comparable bond lengths and angles, Tables III and IV. However, the Ag - O bond distance of 2.70(1) Å for Ag(1) is significantly shorter than 2.90(2) Å for Ag(2). A noteworthy feature of the molecular structure is that both Ag(1) and Ag(2) involve a distorted triangular prism geometry as shown in Figure 1, with two sulfur atoms and one oxygen atom on the top triangular plane and their symmetry-related other three positions on the bottom plane. The six-coordinate silver(I) complexes most often involve a octahedral geometry and triangular prism stereochemistry observed in this complex represent a very rare example for silver(I) coordination chemistry.[12]

Although there is a large body of literature available for metal complexes involving TTF or its analogues in the search for different electrical properties, examples of coordination-bond formation between organic molecule and a metal ion are few.[7,8,13] Copper(I) and gold(I) complexes of TMT-TTF have been reported by our group[7] and others[13], in which short S•••S contacts ranging from 3.53 to 3.63 Å, results in molecular stacking leading to 2D sheet and 3D network structure. In this work the closest S•••S distance between the two chains is 4.00 Å, Figure 2, which precludes any strong S•••S contacts present. Thus, the overall structure is based on one-dimensional zigzag arrangement of Ag(1) and Ag(2) ions linked respectively by TMT-TTF molecules. The complex presented in this contribution is the first example of Ag(I) ion coordinated directly to TTF-derivatives. This study completes the systematic investigation of coordination chemistry of Group 11 univalent ions with TMT-TTF.

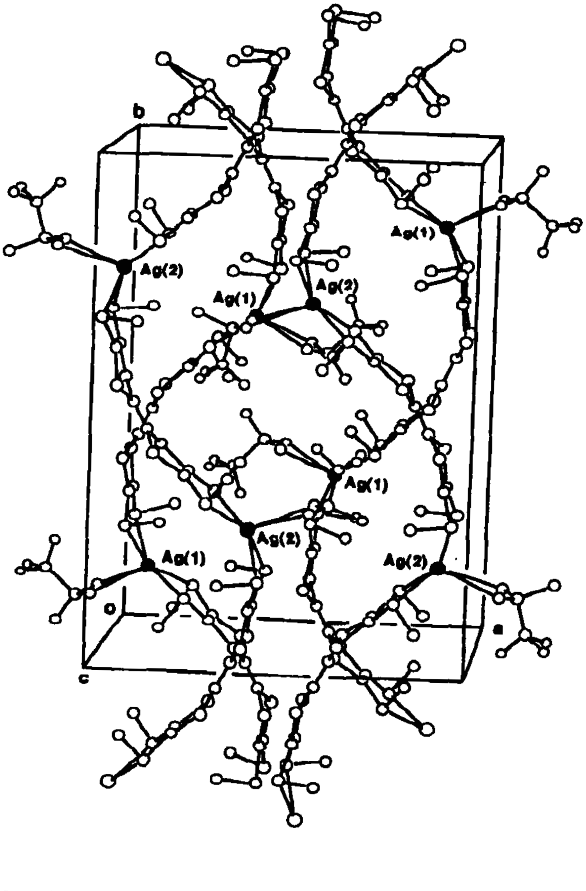

FIGURE 2 Unit cell packing diagram showing two independent polymeric chains of Ag(1) and Ag(2) interwoven along the *b* axis.

### Electrical Conductivity

Electrical resistivity of compacted pellets was measured by the conventional two-probe technique. Although the complex is an insulator at room temperature ($\sigma_{25°C} < 10^{-12}$ S cm$^{-1}$), its iodine-doped black products in powder form behave as a semiconductor with conductivity of 2.8 x $10^{-4}$ S cm$^{-1}$. Similar phenomenon has been reported in the corresponding Cu(I) complexes[7]. One of the common feature of the conducting complex is that the constituent molecules are in a mixed-valence (or partial-oxidation) state.[14] A partial oxidation can be assumed to have occurred in the present complex and ligand-ligand interactions, (TMT-TTF)$^{\bullet+}$/(TMT-TTF)$^{\bullet+}$, might cause electrical conduction pathways.[15] It might give a higher conductivity in single crystal form, unfortunately, however, all single crystals of the compound were broken in the process of iodine-doping. A detailed understanding of the conductivity observed in this partially oxidized polymer will only be possible if the structural data are available.

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## REFERENCES

1. T. Mori, P. Wu, K. Imaeda, T. Enoki, H. Inokuchi and G. Saito, Synth. Met., **19**, 545 (1987).
2. C. Katayama, M. Honda, H. Kumagai, J. Tanaka, G. Saito and H. Inokuchi, Bull. Chem. Soc. Jpn., **58**, 2272 (1985).
3. P. Wu, T. Mori, T. Enoki, K. Imaeda, G. Saito and H. Inokuchi, Bull. Chem. Soc. Jpn., **59**, 127 (1986).
4. H. Endres, Z. Naturforsch., **41B**, 1437 (1986).
5. H. Endres, Z. Naturforsch., **42B**, 5 (1987).
6. K. Honda, M. Goto, M. Kurahashi, H. Anzai, M. Tokumoto and T. Ishiguro, Bull. Chem. Soc. Jpn., **61**, 588 (1988).
7. M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota and S. Kitagawa, Inorg. Chem., **34**, 2705 (1995).
8. X. Gan, M. Munakata, T. Kuroda-Sowa, M. Maekawa and Y. Misaki, Polyhedron, **14**, 1343 (1995).
9. J. Gilmore, MITHRIL, an integrated direct method computer program, J. Appl. Crystallogr., **17**, 42 (1984).
10. TEXSAN-TEXRAY, Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985.

11. Interanational Tables for X-Ray Crystallography (Kynoch Press, Birmingham, 1974), vol. 4.
12. F. A. Cotton and G. Wikinson, Advanced Inorganic Chemistry (Wiley & Sons, New York, 5rd edn., 1972), pp. 939-945.
13. K. Brunn, H. Endres and J. Weiss, Z. Naturforsch., **43b**, 224 (1988).
14. J. B. Torrance, Acc. Chem. Res., **12**, 79 (1979); M. B. Inoue, M. Inoue, Q. Fernando and K. W. Nebesny, Inorg. Chem., **25**, 3976 (1986).
15. Extended Linear Chain Compounds, edited by J. S. Miller (Plenum Press, New York, 1982), vol. 1 and 2; (1983), vol. 3.