

Toward New Electronic, Magnetic, and Optical Materials: Structure and Properties of the First Homobimetallic Tetrathiafulvalene Tetrathiolate Building Block

Richard D. McCullough,^{*,†} John A. Belot,[†]
Arnold L. Rheingold,^{*,‡} and Glen P. A. Yap[‡]

*Departments of Chemistry
Carnegie Mellon University, Pittsburgh, Pennsylvania 15213
University of Delaware, Newark, Delaware 19716*

Received April 17, 1995

One of the greatest difficulties in the design of new materials is the synthesis of building blocks that can be assembled into desirable three-dimensional architectures. Tetrathiafulvalene (TTF)-type building blocks continue to be very interesting since they can assemble into solid-state architectures which can be organic superconductors¹ or metals.² Transport, structural, and theoretical studies have provided a great wealth of fundamental information on electronic materials.^{1,2} These insights have not only allowed for a better understanding of all organic electronic materials but have also provided valuable insights into the metal oxide high T_c superconductors. One of the most interesting new directions in TTF chemistry is the cross-fertilization of the solid-state properties of TTF with metal linear chain conductors or metal high-spin materials assembled into a single building block. Despite the synthesis of multiple new TTFs,^{1a} metal dithiolenes,³ metal dmits,^{4a} and metal TTFs^{4b–e} and the allure of pioneering band structure calculations by Hoffman,⁵ the synthesis of a well-defined bimetallic TTF building block has remained elusive, until now. Reported herein are the synthesis, characterization, and first X-ray structure determination of a neutral, homobimetallic tetrathiafulvalene tetrathiolate complex (**1**) as the 1.5C₆H₆ solvate. This molecule forms stacks of a two-dimensional (2D) chain-link fence-like structure and is representative of a new class of potential building blocks for new electronic, optical, and magnetic materials.

Compound **1** may be synthesized by the addition of a solution of the golden brown tetralithiated salt of tetrathiafulvalene tetrathiolate⁶ in THF to 2.05 equiv of Ti(η^5 -i-PrC₅H₄)₂Cl₂⁷ to afford (i-PrC₅H₄)₂Ti[S₂TTFS₂Ti(i-PrC₅H₄)₂] $\cdot$ 1.5C₆H₆ (**1**) $\cdot$ 1.5C₆H₆. After Soxhlet extraction of the compound into hexanes and solvent removal, the solid was recrystallized in an inert atmosphere from benzene to give analytically pure samples in 15–35% yield as dark green crystals.⁸ This general synthesis

is expected to give a wide variety of other bimetallic tetrathiafulvalene building blocks.

The structure of (i-PrC₅H₄)₂Ti[S₂TTFS₂Ti(i-PrC₅H₄)₂] (**1**) was determined by single crystal X-ray diffraction.⁹ The molecular structure contains a planar TTFS₄ core with one of the peripheral Ti(i-PrC₅H₄)₂ groups situated above the plane of the TTFS₄ and the other below the TTFS₄ plane. It is expected that compound **1** would possess a chairlike conformation and is similar to all titanocene and vanadocene dithiolates in that the metals rest either above or below the plane of sulfur ligands and undergo a complex set of conformation equilibria.^{7,10} This behavior is driven by the electron-deficient metal centers, maximizing the amount of π donation they receive from the adjacent chalcogen atoms.⁷ The molecular structure is also similar to the very interesting, extended metal dithiolene building blocks recently reported by Rauchfuss et al.^{11a} and Reynolds et al.^{11b,c} The TTF core has essentially the same basic bond lengths and angles as a neutral TTF (Figure 1). The central alkene bond, C(3)–C(4), and the C–S bond, C(4)–S(6), distances are 1.333(10) and 1.745(8) Å, respectively. By comparison, the distances C(3)–C(4) and C(4)–S(6) in bis(ethylenedithio)tetrathiafulvalene (ET)¹² are 1.319 and 1.753 Å, respectively, and C(3)–C(4) is 1.349 Å in neutral TTF. It is well known¹ that in ET, removal of an electron from the HOMO reduces the bonding and antibonding contributions from C(3)–C(4) and C(4)–S(6) bonds, respectively, thereby lengthening the C(3)–C(4) bond and shortening the C(4)–S(6) bond. In crystallographically established titanocene thiolate complexes,¹³ where the metal exists in the 4+ oxidation state, the bond similar to S(8)–Ti(2) is 2.424 Å long, and in **1** the value is 2.427(2) Å. This is consistent with no internal oxidation of the TTF by Ti due to the mismatch in redox potentials of the Ti⁴⁺ center and the TTF core.¹⁴

Two perspectives of the crystal packing are shown in Figure 2. Perspective A shows part of the 2D stacked structure formed with perpendicular bimetallic TTFs. The herringbone structure extends in both the y and z planes, forming a chain-link fence-type structure (inset). The TTFs sit perpendicular to each other, unlike any other TTF structure we are aware of.¹ This 2D structure is similar to the τ structure¹ in ET.^{1,12} Perspective B is perspective A rotated 90° in the x–y plane and shows sheets of the 2D herringbone separated by layers of benzenes and isopropyl groups. As expected, the i-PrCp rings prevent any

[†] Carnegie Mellon University.

[‡] University of Delaware.

(1) (a) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Williams, J. M.; Schultz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M.; Wang, H. H.; Kwok, W.-K.; Whangbo, M.-H.; Schirber, J. E. *Science (Washington, D.C.)* **1991**, *252*, 1501. (c) Jerome, D. *Science (Washington, D.C.)* **1991**, *252*, 1509.

(2) (a) Cowan, D. O.; Wiygul, F. M. *Chem. Eng. News* **1986**, *64* (29), 28. (b) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355.

(3) (a) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (c) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295. (d) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233. (e) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1.

(4) (a) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1992**, *110*, 115. (b) Fournigue, M.; Batail, P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 29. (c) Jorgensen, T.; Hansen, T. K.; Becher, J. *Adv. Mater.* **1993**, *5*, 288. (d) Jorgensen, T.; Hansen, T.; Becher, J. *Chem. Soc. Rev.* **1994**, *41*. (e) Hansen, T.; Jorgensen, T.; Stein, P. C.; Becher, J. *J. Org. Chem.* **1992**, *57*, 6403.

(5) Alvarez, S.; Vicente, R.; Hoffman, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253.

(6) McCullough, R. D.; Belot, J. A.; Seth, J. *J. Org. Chem.* **1993**, *58*, 6480.

(7) Giolando, D. M.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1987**, *6*, 667.

(8) ¹H NMR at 300 MHz (C₆D₆, vs TMS) δ 5.20 (m, 4H), 2.6 (h, 1H), 0.8 (d, 6H). Elemental analysis: found (calcd) C, 53.70 (53.52); H, 5.24 (5.16).

(9) Crystal data for [1] $\cdot$ 1.5C₆H₆: C₄₇H₅₃S₈Ti₂, FW = 970.2, monoclinic, C2/c, a = 36.71(1), b = 17.284(9), and c = 15.113(9) Å, β = 99.79(4)°, V = 9450(2) Å³, Z = 8, μ (Mo K α) = 7.22 cm^{−1}, T = 214 K. Of 6486 data collected (Siemens P4, $2\theta_{\max}$ = 45°), 6206 were independent and 4016 were considered observed ($4\sigma F_o$). For each Ti₂ complex, three crystallographically independent half molecules of the recrystallization solvent, benzene, were located, two on two-fold axes and one on an inversion center. At convergence with all non-hydrogen atoms anisotropic and hydrogen atoms idealized; $R(F)$ = 5.23, $R_w(F)$ = 5.48. SHELXTL 4.2 software (G. Sheldrick, Siemens SRD, Madison, WI) was used for all computations. SHELXTL files were imported into Cerius² 1.0 software (Molecular Simulations Inc., Burlington, MA), which was used for graphics presentations presented here.

(10) (a) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. (b) Kopf, H.; Klapotke, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1192. (c) McCullough, R. D.; Belot, J. A. *Chem. Mater.* **1994**, *6*, 1396.

(11) (a) Yang, X.; Doherty, D. D.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1994**, 821. (b) Pullen, A. E.; Piotraschke, J.; Abboud, K. A.; Reynolds, J. R.; Liu, H.-L.; Tanner, D. B. *PMSE Prepr.* **1995**, *72*, 321. (c) Piotraschke, J.; Pullen, A. E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1995**, *34*, 4011.

(12) (a) Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 301. (b) Kini, A. M.; Gates, B. D.; Beno, M. A.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 169. (13) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422.

(14) Electrochemistry: two reversible oxidations for the TTF/TTF⁺ ($\Delta E_{1/2}$ (1) = 0.64 V) and TTF⁺/TTF²⁺ ($\Delta E_{1/2}$ (1) = 0.86 V) and two poorly resolved reduction waves for the Ti center at −0.90 V, respectively, in 0.1 M (C₄H₉)₄N⁺PF₆[−] in CH₃CN (dried and distilled from CaH₂ and then P₂O₅) vs Ag wire referenced to the ferrocene/ferrocenium couple, which appeared at 0.38 V.

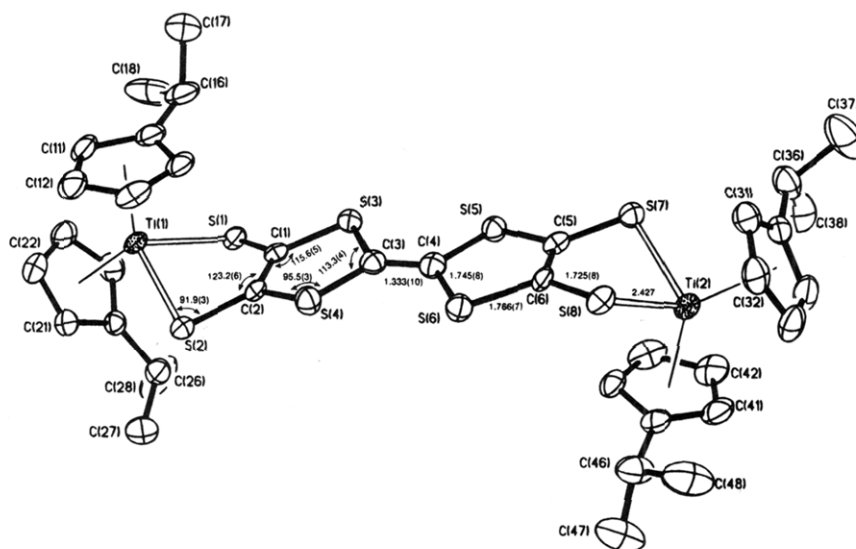


Figure 1. ORTEP diagram of the molecular structure of compound **1**. Thermal ellipsoids are drawn at the 35% probability level.

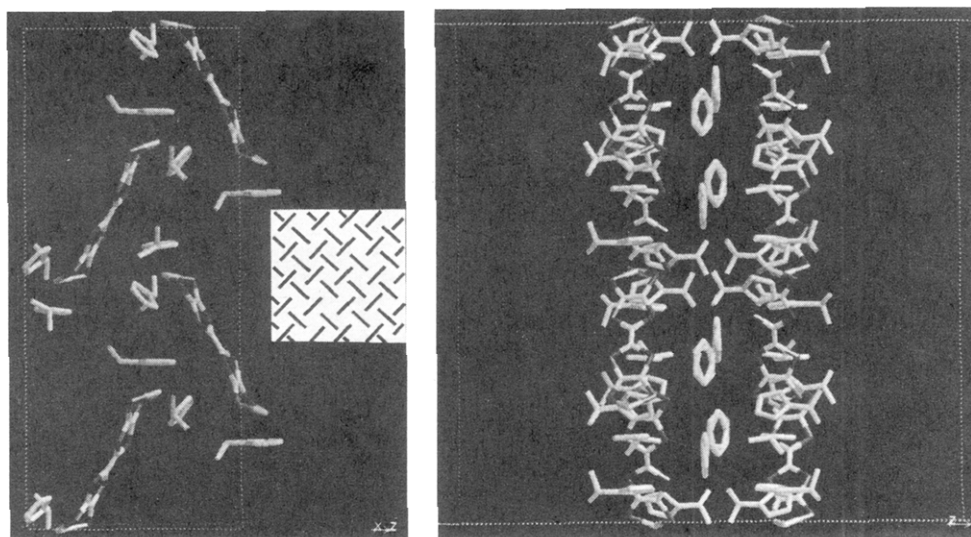


Figure 2. (Left) Perspective A. Two-dimensional stacks of perpendicular bimetallic TTFs viewed in the y - z plane. (Inset) Chain-link fence representation. (Right) Perspective B. Layers of two-dimensional sheets viewed in the y - z plane.

orbital connectivity between the TTF and the metal center. Currently, bimetallic TTF structures are being made in which metal and TTF orbitals can form networked electronic structures.

The electronic absorption spectrum of this complex exhibits a variety of excitations in THF which span the UV-vis-near-IR regions at (λ in nm (ϵ , $\times 10^3$)) 244 (53.7), 326 (20.4), 474 (2.8), and 772 (8.0). Perhaps of these four resolved excitations, the most interesting is the one at 772 nm, which bleeds well into the near-IR. This band is most probably a ligand-to-metal charge transfer (LMCT) absorbance. Given that the Ti(IV) center is formally d^0 , the low-energy absorbance therefore represents an electron from the TTF spacer being donated to the metal, forming the highly reactive Ti(III) intermediate. In addition, we have found this absorbance to be synthetically tunable, depending greatly on the steric requirements of the cyclopentadienyl rings (Cp at 760 nm, *i*-PrCp at 772 nm, and Cp* at 920 nm).¹³ Early d^0 transition metal complexes of Ti exhibiting strong low-energy LMCT absorbances are rare, and related compounds have only recently been explored for their potential as strong photochemical reductants, nonlinear optics devices, and luminescent materials.¹⁵

Presented in this Communication are the synthesis and complete characterization of the first homobimetallic tetrathia-

fulvalene tetrathiolate. Complex **1** represents a new type of building block with which new electronic, magnetic, and optical materials could be prepared. The most interesting aspect of this building block is the orbital communication afforded by the peripheral sulfur bound to the metal center. This overlap allows for electronic communication and, in systems currently under study, long-range spin communication across the TTF bridge. Further elaboration of this chemistry is in progress, including the exploration of the formation of charge transfer salts and magnetic materials, as well as the design of new building blocks via transmetalation chemistry.

Acknowledgment. This work was supported by Carnegie Mellon University "start-up" funds, NSF (CHE-9201198), and the CMU faculty development fund. We gratefully acknowledge Dr. Jyoti Seth for early work on the project.

Supporting Information Available: Synthesis and characterization of compound **1**, including tables of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951206G

(15) (a) Pfennig, B. W.; Thompson, M. E.; Bocarsly, A. B. *Organometallics* **1993**, *12*, 649. (b) Kenney, J. W., III; Boone, D. R.; Striplin, D. R.; Chen, Y.-H.; Hamar, K. B. *Organometallics* **1993**, *12*, 3671.