Inorg. Chem. **1996,** *35,* 4420−4426

Extensively Conjugated Dianionic Tetrathiooxalate-Bridged Copper(II) Complexes for Synthetic Metals

Anthony E. Pullen,[†] Stephan Zeltner,[‡] Ruth-Maria Olk,[‡] Eberhard Hoyer,[‡]
Khalil A. Abboud,[†] and John R. Reynolds*,[†]

Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida,
P.O. Box 117200, Gainesville, Florida 32611-7200, and Institut für Anorganische Chemie,
Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany

Received February 14, 1996[⊗]

Using a unique three-solvent biphasic method, we have prepared and characterized three new fully conjugated, chalcogen-rich, bridged copper(II) complexes for the preparation of molecular conductors and magnetic materials, having the general formula $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(L)]_2}\}$ (tto = $\mathrm{C_2S_4}^{2-}$ = tetrathiooxalato; L = mnt = $\mathrm{C_4N_2S_2}^{2-}$ = 1,2-dicyanoethene-1,2-dithiolato for complex **2**, dsit = $\mathrm{C_3Se_2S_3}^{2-}$ = 2-thioxo-1,3-dithiole-4,5-diselenolato for complex **3**, dmid = $\mathrm{C_3OS_4}^{2-}$ = 2-oxo-1,3-dithiole-4,5-dithiolato for complex **4a**). The single-crystal X-ray structures of **2** and **3** have been determined: **2**, $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$, monoclinic, space group $C2/m$, a = 19.549(4) Å, b = 13.519(3) Å, c = 10.162(2) Å, β = 90.33(1)°, Z = 2; **3**, $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$, monoclinic, space group $P2_1/c$, a = 9.903(1) Å, b = 15.589(1) Å, c = 18.218(1) Å, β = 90.40(1)°, Z = 2. Complex **2** displays perfect planarity, while **3** shows a slight tetrahedral distortion at the metal centers, resulting in a dihedral angle of 24.86(3)°. Cyclic voltammetry of $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**), $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**), and $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4a**) shows each complex to exhibit two reversible redox processes which can be attributed to $\{\mathrm{tto[Cu(L)]_2}\}^{2-} \rightleftarrows \mathrm{tto[Cu(L)]_2}\}^{-}$ and $\{\mathrm{tto[Cu(L)]_2}\}^{1-} \rightleftarrows \{\mathrm{tto[Cu(L)]_2}\}^{0}$ couples. The structural and electronic properties of **2**, **3**, and **4a** will be compared to those of the recently communicated analogous complex $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**).

Introduction

The discovery in 1973[1] of the organic conductor TTF-TCNQ displaying metallic-like electronic properties set the stage for a significant effort into the synthesis and characterization of new molecular electrically conducting materials. Many low-density organic and inorganic charge-transfer and ion radical salt systems with sulfur-rich components have been assembled that exhibit novel electronic properties, including superconductivity.[2]

An additional use of molecular electronic donors and acceptors has been for the synthesis of molecular-based magnetic materials.[3] A variety of new systems have been assembled consisting of both purely organic and transition metal based compounds, containing unpaired electrons that have exhibited novel magnetic properties such as antiferro-, ferro-, and ferrimagnetism.[3,4] Currently the material with the composition $\mathrm{V(TCNE)_2{\cdot}{}^1/_2CH_2Cl_2}$ holds the highest T_c (spin ordering transition) of 400 K.[3,5]

One set of compounds that has displayed semiconducting, metallic, and superconducting electronic properties are transition metal based anion radical salt complexes.[6] Using square planar coordinating metals bischelated with chalcogen-rich, planar 1,2-dithiolate ligands (for example, dmit = $\mathrm{C_3S_5}^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolato, dmise = $\mathrm{C_3SeS_4}^{2-}$ = 2-selenoxo-1,3-dithiole-4,5-dithiolato, dsise = $\mathrm{C_3Se_3S_2}^{2-}$ = 2-selenoxo-1,3-dithiole-4,5-diselenolato, and dsis = $\mathrm{C_3Se_5}^{2-}$ = 2-selenoxo-1,3-diselenole-4,5-diselenolato), planar complexes are assembled that allow for close-packing arrangements in the crystal lattice. This results in intrastack interactions from adjacent stacking units allowing for a completely delocalized electronic system.

Within the search for new complexes exhibiting novel electronic properties, many metals (e.g. M = Ni(II), Pt(II), Pd-

---

[*] Author to whom correspondence should be addressed.

[†] University of Florida.

[‡] Universität Leipzig.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Ferraris, J.; Cowan, D. O.; Walatka, V. J.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948.

(2) 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);* Prentice-Hall: Englewood Cliffs, NJ, 1992.

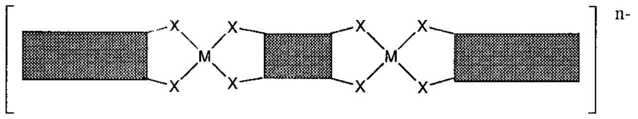
(3) Miller, J. S.; Epstein, A. J. *Chem. Eng. News* **1995**, *73* (40), 30.

(4) (a) Ovchinikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (b) Miller, J. S.; Calabrese, J. C.; Epstein, A. J.; Bigelow, R. W.; Zhang, J. H.; Reiff, W. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1026. (c) Teji, Y.; Takui, T.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147. (d) Pei, Y.; Verdaguer, M.; Kahn, O.; Sletten, J.; Renard, P. *J. Am. Chem. Soc.* **1986**, *108*, 7428. (e) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *J. Am. Chem. Soc.* **1987**, *109*, 2191. (f) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782. (g) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392. (h) Rey, P.; Laugier, J.; Caneschi, A.; Gatteschi, D. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 337. (i) Kahn, O.; Pei, Y.; Nakatani, K.; Journaux, Y. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 481. (j) Nakatani, K.; Carriot, J. Y.; Journaux, Y.; Kahn, O.; Lloret, F.; Renard, J. P.; Pei, Y.; Sletten, J.; Verdaguer, M. *J. Am. Chem. Soc.* **1989**, *111*, 5739. (k) Pei, Y.; Kahn, O.; Nakatani, K.; Codjovi, E.; Mathionere, C.; Sletten, J. *J. Am. Chem. Soc.* **1991**, *113*, 6558. (l) Kahn, O.; Stumpf, H.; Pei, Y.; Sletten, J. *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 231. (m) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447. (n) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993. (o) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 10688. (p) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635. (q) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385. (r) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866. (s) Tamura, H.; Tanaka, S.; Matsubayashi, G.; Mori, W. *Inorg. Chim. Acta* **1995**, *232*, 51. (t) Panagiotopoulos, A.; Zafiropoulos, T. F.; Perlepes, S. P.; Bakalbassis, E.; Massonramade, I.; Kahn, O.; Terzis, A.; Raptopoulou, C. P. *Inorg. Chem.* **1995**, *34*, 4918. (u) Bolvin, H.; Kahn, O. *Chem. Phys. Lett.* **1995**, *243*, 355. (v) Kahn, O. *Nature* **1995**, 667. (w) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209. (x) Vankoningsbruggen, P. J.; Haasnoot, J. G.; Vreugdenhil, W.; Reedijk, J.; Kahn, O. *Inorg. Chim. Acta* **1995**, *239*, 5.

S0020-1669(96)00160-7 CCC: $12.00

(II), Cu(II)), bischelating ligands, and both "closed-shell" and "open-shell" counterions have been thoroughly studied.[6] In particular among these, the dmit based ligand complexes have displayed superconductivity.[7] The TTF-containing complex (TTF)$[\mathrm{Ni(dmit)_2}]_2$ has exhibited superconducting behavior under 7 kbar of pressure with a superconducting transition temperature (T_c) of 1.62 K.[7a,b,f] The TTF derivative complex α-(EDT-TTF)-$[\mathrm{Ni(dmit)_2}]$ superconducts at ambient pressure with a T_c of 1.3 K.[7i] Also, the $[\mathrm{Pd(dmit)_2}]$-based complex α-$(\mathrm{Me_2Et_2N})[\mathrm{Pd(dmit)_2}]_2$ has shown superconductivity at 4 K under 2.4 kbar of pressure.[7h]

Our research efforts have been directed toward the synthesis of new anionic systems similar to $[\mathrm{M(dmit)_2}]^{n-}$ but with longer conjugation lengths. In keeping with the structural requirements that have proved successful in forming electrically conducting systems with $[\mathrm{M(dmit)_2}]^{n-}$ ($0 \le n \le 2$) and other related systems, the following structural scheme is used as a template for tto (where tto = $\mathrm{C_2S_4}^{2-}$ = tetrathiooxalato) bridged bimetallic complexes as precursors to electronic and magnetic materials:



X = S, Se
M = Ni(II), Pd(II), Pt(II), Cu(II)

I

It consists of square planar coordinating transition metals "bridged" and "capped" by chalcogen-rich, fully conjugated planar ligands. This type of complex has been designed in order to extend the delocalization and to increase interactions throughout the crystal lattice.

Historically, there has been a significant effort directed toward the synthesis of bridged bimetallic complexes with various analogs of oxalato,[8abefmx] thiooxalato,[8g,n−s,w] oxamido,[c,d,k,l] and other chalcogen-rich ligands.[8t−v,y−aa] These compounds have been of interest for both their electronic and magnetic properties. While many of these provide potentially interesting materials, in these instances none of the complexes are fully planar and completely delocalized as those under study here.

Recently, we reported the synthesis of the complex $(\mathrm{Bu_4N})_2$-$\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**).[9] A unique, facile and reproducible three-solvent method was utilized in the assembly of the complex. The complex has a planar tto bridging two Cu(II) metal centers with dmit acting as a planar "capping" ligand. Cu(II) was chosen as previously mentioned because of its ability to square-planar-coordinate as seen in Ni(II), Pd(II), and Pt(II) electrically conducting dichalcogenolate complexes.[6,7] The synthetic approach developed has been used to reproducibly synthesize three new bimetallic copper(II) complexes also using tto as bridging and 1,2-dithiolates as capping ligands. The crystal structures of tetrabutylammonium (μ-tetrathiooxalato)bis[(1,2-dicyanoethene-1,2-dithiolato)cuprate(II)], $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**), and tetrabutylammonium (μ-tetrathiooxalato)bis[(2-thioxo-1,3-dithiole-4,5-diselenolato)cuprate(II)], $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**), are

---

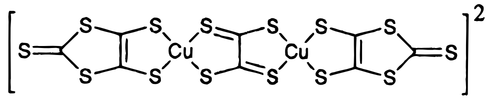
(5) Monriquez, J. M.; Yee, G. T.; McLean R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415.

(6) (a) Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Underhill, A. E.; Ahmad, M. M. *J. Chem. Soc., Chem. Commun.* **1982**, 390. (b) Ahmad, M. M.; Turner, D. J.; Underhill, A. E.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H. *J. Chem. Soc., Dalton Trans.* **1984**, 1759. (c) Matsubayashi, G.; Takahashi, K.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1988**, 967. (d) Shklover, V. E.; Nagapetyan, S. S.; Struchkov, Y. T. *Usp. Khim.* **1990**, *59*, 1179. (e) Cornelissen, J. P.; Haasnoot, J. G.; Le Loux, R.; Reedijk, J. *Synth. Met.* **1991**, *41−43*, 2315. (f) Olk, R.-M.; Olk, B.; Rohloff, J.; Reinhold, J.; Sieler, J.; Trübenbach, K.; Kirmse, R.; Hoyer, E. *Z. Anorg. Allg. Chem.* **1992**, *609*, 103. (g) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99. (h) Cornelissen, J. P.; Pomarede, B.; Spek, A. L.; Reefman, D.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1993**, *32*, 3720. (i) Faulmann, C.; Legros, J.-P.; Cassoux, P.; Cornelissen, J.; Brossard, L.; Inokuchi, M.; Tajima, H.; Tokumoto, M. *J. Chem. Soc., Dalton Trans.* **1994**, 249. (j) Svenstrup, N.; Becher, J. *Synthesis* **1995**, 215. (k) Kato, R.; Liu, Y. L.; Sawa, H.; Aonuma, S.; Ichikawa, A.; Takahashi, H.; Mori, N. *Solid State Commun.* **1995**, *94*, 973. (l) Pullen, A. E.; Piotraschke, J.; Abboud, K. A.; Reynolds, J. R.; Liu, H.-L.; Tanner, D. B. *Polym. Mater. Sci. Eng., Symp. Proc.* **1995**, *72*, 321. (m) Nakamura, T.; Underhill, A. E.; Coomber, T.; Friend, R. H.; Tajima, H.; Kobayashi, A.; Kobayashi, H. *Inorg. Chem.* **1995**, *34*, 870. (n) Nakamura, T.; Underhill, A. E.; Coomber, T.; Friend, R. H.; Tajima, H.; Kobayashi, A.; Kobayashi, H. *Synth. Met.* **1995**, *70*, 1061. (o) Liu, H.-L.; Tanner, D. B.; Pullen, A. E.; Abboud, K. A.; Reynolds, J. R. *Phys. Rev. B* **1996**, *53*, 10557. (p) Kato, R.; Liu, Y. L.; Sawa, H.; Aonuma, S.; Ichikawa, A.; Takahashi, H.; Mori, N. *Solid State Commun.* **1995**, *12*, 973. (q) Pearson, C.; Dhindsa, A. S.; Goldenberg, L. M.; Singh, R. A.; Dieing, R.; Moore, A. J.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1995**, *5*, 1601. (r) Kobayashi, A.; Sato, A.; Kawano, K.; Naito, T.; Kobayashi, H.; Watanabe, T. *J. Mater. Chem.* **1995**, *5*, 1671. (s) Tarres, J.; Mas, M.; Molins, E.; Veciana, J.; Rovira, C.; Morgado, J.; Henriques, R. T.; Almeida, M. *J. Mater. Chem.* **1995**, *5*, 1653. (t) Tomura, M.; Yamashita, Y. *J. Mater. Chem.* **1995**, *5*, 1753. (u) Liu, S. G.; Liu, Y. Q.; Liu, S. H.; Zhu, D. B. *Synth. Met.* **1995**, *74*, 137. (v) Maikawa, T.; Nakano, M.; Arakawa, R.; Matsubayashi, G. E.; Mori, W. *Z. Naturforsch., Sec. B* **1996**, *50*, 1748.

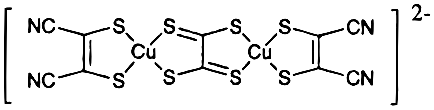
(7) (a) Brossard, L.; Ribault, M.; Valade, L.; Cassoux, P. *Physica B&C (Amsterdam)* **1986**, *143*, 378. (b) Bousseau, M.; Valade, L.; Legros, J.-P.; Cassoux, P.; Garbauskas, M.; Interrante, L. V. *J. Am. Chem. Soc.* **1986**, *108*, 1908. (c) Kobayashi, A.; Kim, H.; Sasaki, Y.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 1819. (d) Kajita, K.; Nishio, Y.; Moriyama, S.; Kato, R.; Kobayashi, H.; Sasaki, W.; Kobayashi, A.; Kim, H.; Sasaki, Y. *Solid State Commun.* **1988**, *65*, 361. (e) Brossard, L.; Ribault, M.; Valade, L.; Cassoux, P. *J. Phys. (Paris)* **1989**, *50*, 1521. (f) Brossard, L.; Ribault, M.; Valade, L.; Cassoux, P. *Phys. Rev. B.* **1990**, *42*, 3935. (g) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115. (h) Kobayashi, A.; Kato, R.; Miyamoto, A.; Naito, T.; Kobayashi, H.; Clark, R. A.; Underhill, A. E. *Chem. Lett.* **1991**, 2163. (i) Kobayashi, H.; Bun, K.; Naito, T.; Kato, R.; Kobayashi, A. *Chem. Lett.* **1992**, 1909. (j) Tajima, H.; Inokuchi, A.; Kobayashi, A.; Ohta, T.; Kato, R.; Kobayashi, H.; Kuroda, H. *Chem. Lett.* **1993**, 1235.

(8) (a) Curtis, N. F.; McCormick, R. N.; Walton, N. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1537. (b) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077. (c) Girerd, J. J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1978**, *17*, 3034. (d) Chauvel, C.; Girerd, J. J.; Jeannin, Y.; Jeannin, S.; Kahn, O. *Inorg. Chem.* **1978**, *18*, 3034. (e) Michalowicz, A.; Girerd, J. J.; Goulon, J. *Inorg. Chem.* **1979**, *18*, 3015. (f) Girerd, J. J.; Kahn, O.; Verdaguer, M. *Inorg. Chem.* **1980**, *19*, 274. (g) Maj, J. J.; Rae, D. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 4278. (h) Verdaguer, M.; Julve, M.; Michalowicz, A.; Kahn, O. *Inorg. Chem.* **1983**, *22*, 2624. (i) Julve, M.; Kahn, O. *Inorg. Chim. Acta* **1983**, *76*, L39. (j) Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y.; El Murr, N. *Inorg. Chem.* **1984**, *23*, 4484. (k) Bencini, A.; DiVaira, M.; Fabretti, A. C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 1620. (l) Bencini, A.; Benelli, D.; Gatteschi, D.; Zanchini, C.; Fabretti, A. C.; Franchini, G. C. *Inorg. Chim. Acta* **1984**, *86*, 169. (m) Julve, M.; Verdaguer, M.; Kahn, O.; Gleizes, A.; Philoche-Levisalles, M. *Inorg. Chem.* **1984**, *23*, 3808. (n) Vicente, R.; Ribas, J.; Cassoux, P.; Valade, L. *Synth. Met.* **1986**, *13*, 265. (o) Vicente, R.; Ribas, J.; Alvarez, S.; Segui, A.; Solans, X.; Verdaguer, M. *Inorg. Chem.* **1987**, *26*, 4004. (p) Harris, H. A.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1987**, *109*, 4739. (q) Harris, H. A.; Kanis, D. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 8602. (r) Dietzsch, W.; Strauch, P.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *121*, 43. (s) Strauch, P.; Münzberg, I.; Dietzsch, W.; Kirmse, R. *Z. Anorg. Allg. Chem.* **1992**, *613*, 110. (t) McCullough, R. D.; Seth, J.; Belot, J. A.; Majetich, S. A.; Carter, A. C. *Synth. Met.* **1993**, *55−57*, 1989. (u) McCullough, R. D.; Belot, J. A. *Chem. Mater.* **1994**, *6*, 1396. (v) Yang, X.; Doxsee, D. D.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1994**, 821. (w) Strauch, P.; Dietzsch, W.; Golic, L.; Sieler, J.; Franke, A.; Münzberg, I.; Trübenbach, K.; Kirmse, R.; Reinhold, R.; Hoyer, E. *Inorg. Chem.* **1995**, *34*, 763. (x) Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K. *Inorg. Chem.* **1995**, *34*, 6255. (y) McCullough, R. D.; Belot, J. A.; Rheingold, A. L.; Yap, G. P. A. *J. Am. Chem. Soc.* **1995**, *117*, 9913. (z) Szczepura, L. F.; Galloway, C. P.; Zheng, Y.; Han, P.; Rheingold, A. L.; Wilson, S. R.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1890. (aa) McCullough, R. D.; Belot, J. A.; Seth, J.; Rheingold, A. L.; Yap, G. P. A.; Cowan, D. O. *J. Mater. Chem.* **1995**, *10*, 1581.

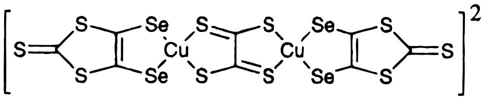
(9) Piotraschke, J.; Pullen, A. E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1995**, *34*, 4011.



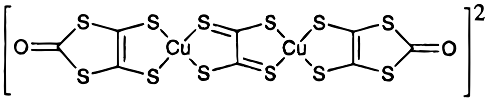
$\{tto[Cu(dmit)]_2\}^{2-}$ (**1**)



$\{tto[Cu(mnt)]_2\}^{2-}$ (**2**)



$\{tto[Cu(dsit)]_2\}^{2-}$ (**3**)



$\{tto[Cu(dmid)]_2\}^{2-}$ (**4**)

reported here. Also included is the synthesis of tetrabutylammonium (μ-tetrathiooxalato)bis[(2-oxo-1,3-dithiole-4,5-dithiolato)cuprate(II)], $(Bu_4N)_2\{tto[Cu(dmid)]_2\}$ (**4a**). The dianion of this complex has been previously synthesized and the crystal structure of $(Ph_4As)_2\{tto[Cu(dmid)]_2\}$ (**4b**) was reported, but the synthetic methodology was found to be irreproducible.[8n,o] The dianion of complex **2** displays perfect planarity, while the dianions of **1**, **3**, and **4b** show a slight tetrahedral distortion from square planarity at the metal center, resulting in dihedral angles of 18.87(3), 24.86(3), and 28.3°, respectively. The dianions in $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ (**1**) and $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) form sheets of one-dimensional chains, while the fully planar **2** exists as isolated molecular species. Cyclic voltammograms of all of the complexes show two reversible redox processes.

Experimental Section

General Procedures. Infrared spectra were recorded on a Perkin-Elmer 1725 FTIR spectrophotometer. Ultraviolet−visible spectra were obtained using a Shimadzu UV-160A UV−vis spectrophotometer. Melting points were measured using a Boetius melting point apparatus and are uncorrected. Elemental analysis for $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) was completed at Robertson Microlit Labs Inc., Madison, NJ, and for $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) and $(Bu_4N)_2\{tto[Cu(dmid)]_2\}$ (**4a**) using a Heraeus CHN rapid analyzer at the University of Leipzig.

Materials. All reactions were carried out under argon. Solvents were used as obtained (Aldrich) and degassed prior to use with argon. Water used in the synthetic procedures was purified using a Millipore Milli-Q water system.

Preparation of $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (2). A 416 mg (0.500 mmol) sample of $(Bu_4N)_2[Zn(mnt)_2]$, prepared according to Gray and co-workers,[10] was dissolved in 25 mL of CH_2Cl_2. To this solution was added a solution of 103 mg (0.250 mmol) of $(Et_4N)_2tto$[11] in 25 mL of water, after which the mixture was stirred for 5 min. With a pipet, a solution of 85 mg (0.500 mmol) of $CuCl_2{\cdot}2H_2O$ dissolved in 15 mL of methanol was added rapidly in small amounts to the vigorously stirred solution. After the addition, the biphasic solution was stirred for 10 min, resulting in a deep-purple organic phase. The organic phase was removed, and the aqueous layer was washed twice with 20 mL portions of CH_2Cl_2, combined, and filtered. An equivalent amount of 2-propanol was added, and the mixture was allowed to evaporate to less than half its volume and filtered again. To the resulting precipitate was added dropwise CH_2Cl_2 until only slightly soluble product remained. The product was crystallized by slow evaporation from a 1:1 mixture of acetone/2-propanol. Crystals used for the structure determination were obtained via slow evaporation from previously crystallized material dissolved in acetone. Yield: 100 mg (19%). Mp: 192−193 °C dec. Anal. Calcd for $C_{42}H_{72}N_6Cu_2S_8$: C, 48.28; H, 6.96; N, 8.05; S, 24.55. Found: C, 48.12; H, 7.27; N, 8.08; S, 23.78. IR (KBr; cm^{-1}): ν(C−H) 2955, 2870; ν(C≡N) 2200; ν(C=C) 1448; ν(C=S) 1007. UV−vis [acetone; λ, nm (log ϵ)]: 541 (4.44), 619 (4.38), 862 (3.97).

Table 1. Crystallographic Data for $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) and $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**)

	2	**3**
empirical formula	$C_{42}H_{72}N_6S_8Cu_2$	$C_{40}H_{72}N_2Se_4S_{10}Cu_2$
fw	1044.62	1344.52
space group	*C*2/*m*	*P*2$_1$/*c*
a, Å	19.549(4)	9.903(1)
b, Å	13.519(3)	15.589(1)
c, Å	10.162(2)	18.218(1
β, deg	90.33(1)	90.40(1)
V, Å^3	2686(1)	2812.4(3)
T, °C	25	25
Z	2	2
ρ_{calc}, g cm^{-3}	1.292	1.588
μ, cm^{-1}	11.4	75.8
$R(F_o)$,^{a} %	4.90	3.59
$R_w(F_o)$,^{b} %	5.33	4.30

^{a} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

$(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (3). Complex **3** was prepared and isolated similarly to $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) using minor modifications. A solution of 565 mg (0.500 mmol) of $(Bu_4N)_2[Zn(dsit)_2]$[12] in CH_2Cl_2 was added to a solution of 103 mg (0.250 mmol) of $(Et_4N)_2tto$ in 25 mL of water, and the mixture was stirred for 5 min. With a pipet, 85 mg (0.500 mmol) of $CuCl_2{\cdot}2H_2O$ dissolved in 15 mL of methanol was added slowly directly to the organic layer of the stirring biphasic solution. The precipitate was recrystallized by slow evaporative cooling under a stream of argon in a 1:1 mixture of acetone/2-propanol, followed by refrigeration overnight. Yield: 170 mg (30%). Mp: 146−147 °C. Anal. Calcd for $C_{40}H_{72}N_2Cu_2Se_4S_{10}$: C, 35.73; H, 5.40; N, 2.08. Found: C, 35.78; H, 5.18; N, 2.11. IR (KBr; cm^{-1}): ν(C−H) 2950, 2866; ν(C=C) 1461; ν(C=S) 1052. UV−vis [methylene chloride; λ, nm (log ϵ)]: 261 (4.58), 443 (4.24), 479 (4.20), 574 (4.48), 1013 (4.06).

$(Bu_4N)_2\{tto[Cu(dmid)]_2\}$ (4a). Complex **4a** was prepared and isolated similarly to $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) with minor modifications. A solution of 455 mg (0.500 mmol) of $(Bu_4N)_2[Zn(dmid)_2]$[13] in minimal (∼10 mL) CH_2Cl_2 was added to a solution of 103 mg (0.250 mmol) of $(Et_4N)_2tto$ in 25 mL of water, and the mixture was stirred for 5 min. After 85 mg (0.500 mmol) of $CuCl_2{\cdot}2H_2O$ dissolved in 15 mL MeOH was added slowly to the organic layer, the biphasic solution was stirred for 40 min. The organic layer was then separated from the mixture and combined with two CH_2Cl_2 washings of the aqueous layer, and followed by filtration. The blue-black microcrystalline compound filtered off was recrystallized from 1:1 acetone/2-propanol. Yield: 80 mg (14%). Mp: 169−171 °C dec. Anal. Calcd for $C_{40}H_{72}N_2Cu_2O_2S_{12}$: C, 42.70; H, 6.46; N, 2.69. Found: C, 42.92; H, 6.19; N, 3.08. IR (KBr; cm^{-1}): ν(C−H) 2959, 2870; ν(C=O) 1663, 1613; ν(C=C) 1456; ν(C=S) 897 (lit.[8o] ν(C=O) 1600 and ν(C=S) 910 cm^{-1}). UV−vis [acetone; λ, nm (log ϵ)]: 460 (4.53), 555 (4.90), 700 (sh) (3.58), 1070 (4.40). (lit.[8o] 460, 560, 720 (sh), and 1100 nm).

X-ray Structure Determinations. Crystallographic data for $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) and $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) are listed in Table 1. Data were collected at room temperature on a Siemens R3m/V

---

(10) Billig, E.; Williams, R.; Bernal, I.; Waters, J. H.; Gray, H. B. *Inorg. Chem.* **1964**, *3*, 663.

(11) (a) Jeroschewski, P. *Z. Chem.* **1981**, *21*, 412. (b) Lund, H.; Hoyer, E.; Hazell-Groenbaeck, R. *Acta Chem. Scand., Ser. B* **1982**, *36*, 207.

(12) Olk, R.-M.; Röhr, A.; Sieler, J.; Köhler, K.; Kirmse, R.; Dietzsch, W.; Hoyer, E.; Olk, B. *Z. Anorg. Allg. Chem.* **1989**, *577*, 206.

(13) Olk, R.-M.; Dietzsch, W.; Köhler, K.; Kirmse, R.; Reinhold, J.; Hoyer, E.; Golic, L.; Olk, B. *Z. Anorg. Allg. Chem.* **1988**, *567*, 131.

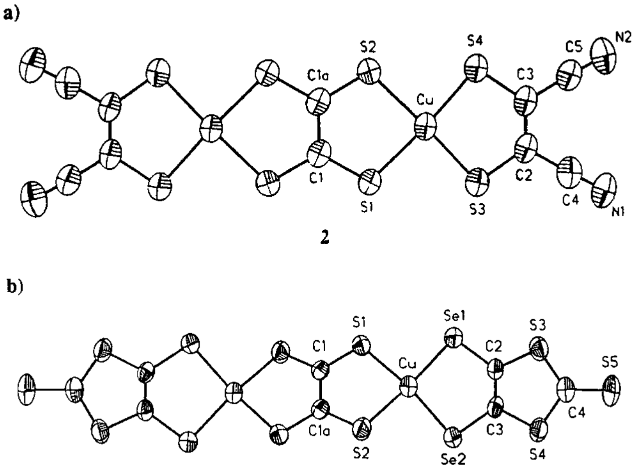


Figure 1. Thermal ellipsoid drawings (50% probability) and numbering schemes for the dianions of (a) $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) and (b) $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**).

Table 2. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-H Atoms of $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**)

atom	x	y	z	U
Cu	0.13811(4)	0.0	0.35752(8)	0.0619(3)
S(1)	0.10329(10)	0.0	0.5688(2)	0.0827(8)
S(2)	0.02623(9)	0.0	0.2954(2)	0.0643(6)
S(2a)	−0.02623(9)	0.0	0.7046(2)	0.0643(6)
S(3)	0.24638(9)	0.0	0.4269(2)	0.0786(7)
S(4)	0.16583(9)	0.0	0.1458(2)	0.0732(7)
N(1)	0.4187(3)	0.0	0.2789(7)	0.087(3)
N(2)	0.3248(3)	0.0	−0.0531(7)	0.092(3)
C(1)	0.0185(3)	0.0	0.5639(6)	0.057(2)
C(1a)	−0.0185(3)	0.0	0.4361(6)	0.057(2)
C(2)	0.2877(3)	0.0	0.2770(7)	0.062(2)
C(3)	0.2542(3)	0.0	0.1599(7)	0.062(2)
C(4)	0.3609(4)	0.0	0.2804(7)	0.069(3)
C(5)	0.2930(3)	0.0	0.0392(8)	0.067(3)
N(3)	0.0	0.2656(3)	0.0	0.050(2)
C(11)	0.0273(2)	0.3321(3)	0.1090(4)	0.059(2)
C(11a)	−0.0273(2)	0.3321(3)	−0.1090(4)	0.059(2)
C(12)	0.0550(2)	0.2794(3)	0.2302(4)	0.066(2)
C(13)	0.0784(2)	0.3504(4)	0.3349(5)	0.077(2)
C(14)	0.1054(3)	0.2959(4)	0.4551(5)	0.097(2)
C(21)	0.0566(2)	0.1982(3)	−0.0508(4)	0.059(2)
C(21a)	−0.0566(2)	0.1982(3)	0.0508(4)	0.059(2)
C(22)	0.1176(2)	0.2487(4)	-0.1115(5)	0.069(2)
C(23)	0.1682(3)	0.1756(4)	-0.1595(5)	0.087(2)
C(24)	0.2299(3)	0.2160(4)	-0.2256(6)	0.105(3)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*A_{ij}$ where A_{ij} is the dot product of the ith and jth direct-space unit cell vectors.

diffractometer. For **2**, purple-black blocklike crystals (0.39 × 0.28 × 0.15 mm^3) were chosen for study, and for **3**, purple-black needles (0.46 × 0.09 × 0.08 mm^3) were chosen.

For **2**, the diffractometer was equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å), and for **3**, it was equipped with a Ni filter using Cu Kα radiation ($\lambda = 1.541\ 78$ Å). For $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) 32 reflections with $20.0° \leq 2\theta \leq 22.0°$ and for $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) 32 reflections with $40.0° \leq 2\theta \leq 44.0°$ were used to refine the cell parameters. For **3**, 3256 reflections were collected using the ω-scan method. For both complexes, four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was $<2\%$ for **2** and $<1\%$ for **3**). Absorption corrections were applied on the basis of measured crystal faces using SHELXTL plus.[14]

Table 3. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-H Atoms of $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**)

atom	x	y	z	U
Cu	0.89709(8)	−0.50268(5)	0.84132(4)	0.0505(3)
Se(1)	1.00266(7)	−0.50108(5)	0.72601(3)	0.0638(3)
Se(2)	0.67818(7)	−0.47784(4)	0.79585(3)	0.0577(3)
S(1)	1.1009(2)	−0.48867(10)	0.89663(8)	0.0587(6)
S(2)	0.8080(2)	−0.53131(12)	0.95284(8)	0.0648(6)
S(3)	0.8635(2)	−0.46028(11)	0.57449(8)	0.0652(6)
S(4)	0.5966(2)	−0.44394(11)	0.63227(9)	0.0657(6)
S(5)	0.6374(2)	−0.42252(12)	0.47103(9)	0.0819(8)
C(1)	1.0693(6)	−0.4908(3)	0.9871(3)	0.044(2)
C(1a)	0.9307(6)	−0.5092(3)	1.0129(3)	0.044(2)
C(2)	0.8486(6)	−0.4736(3)	0.6696(3)	0.047(2)
C(3)	0.7236(6)	−0.4649(3)	0.6960(3)	0.048(2)
C(4)	0.6951(6)	−0.4409(4)	0.5546(3)	0.058(2)
N	0.3368(5)	−0.2545(3)	0.8196(2)	0.047(2)
C(11)	0.2289(6)	−0.2033(3)	0.8583(3)	0.053(2)
C(12)	0.1073(6)	−0.2560(4)	0.8832(4)	0.072(3)
C(13)	−0.0002(7)	−0.2039(4)	0.9195(4)	0.075(3)
C(14)	−0.1123(7)	−0.2603(5)	0.9488(4)	0.098(4)
C(21)	0.3898(6)	−0.3262(3)	0.8682(3)	0.051(2)
C(22)	0.4434(7)	−0.2998(4)	0.9429(3)	0.065(3)
C(23)	0.5200(6)	−0.3726(4)	0.9769(3)	0.068(3)
C(24)	0.5672(7)	−0.3562(5)	1.0540(3)	0.094(3)
C(31)	0.2810(6)	−0.2975(3)	0.7505(3)	0.052(2)
C(32)	0.2276(7)	−0.2371(4)	0.6918(3)	0.067(3)
C(33)	0.1581(7)	−0.2863(5)	0.6302(3)	0.076(3)
C(34)	0.2433(8)	−0.3512(5)	0.5930(4)	0.102(4)
C(41)	0.4503(6)	−0.1918(3)	0.8009(3)	0.054(2)
C(42)	0.5699(6)	−0.2318(4)	0.7624(3)	0.063(2)
C(43)	0.6839(6)	−0.1692(4)	0.7522(4)	0.071(3)
C(44)	0.8035(7)	−0.2129(5)	0.7143(4)	0.095(4)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $\mathrm{U}_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*A_{ij}$ where A_{ij} is the dot product of the ith and jth direct-space unit cell vectors.

For $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) the structure was solved by the heavy-atom method and for $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) it was solved by direct methods in *SHELXTL plus*[14] from which the locations of the four Cu atoms were obtained. For both complexes, the structures were refined in SHELXTL plus.[14] The non-hydrogen atoms were treated anisotropically, whereas the positions of the hydrogen atoms were calculated in ideal positions and their isotropic thermal parameters were fixed.

For $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) 150 parameters and $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) 262 parameters were refined and $w = 1/[(\sigma|F_o)^2 + 0.0004(F_o)^2]$. For **2** and **3**, $\sum w\,(|F_o| - |F_c|)^2$ was minimized; $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity) $= (I_{peak} - I_{background})$(scan rate), $\sigma(I) = (I_{peak} + I_{bkgd})^{1/2}$(scan rate), k is the correction due to decay and Lp effects, and 0.02 is a factor used to downweight intense reflections and to account for instrument instability. The linear absorption coefficients and scattering factors for **2** and **3** were taken from ref 15.[15]

Molecular numbering schemes for the dianion of $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) and $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) are shown in Figure 1. Fractional atomic coordinates and their estimated standard deviations are collected for **2** in Table 2 and for **3** in Table 3. Selected bond lengths and angles are located for $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) in Table 4 and for $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) in Table 5.

Electrochemical Methods. Cyclic voltammetry was performed on a EG&G Princeton Applied Research 362 scanning potentiostat with a Philips X-Y PM 8120 recorder. Methylene chloride was used as received (Aldrich, 99.8%) and thoroughly degassed with argon prior to use. Ag/AgCl was used as the reference electrode with a platinum wire working electrode and a platinum foil counter electrode. Electrochemistry was completed under an argon atmosphere. Approximate concentrations of the complexes used in the cyclic voltammetry experiments were 10^{-4} M.

---

(14) Sheldrick, G. M. *SHELXTL plus*; Nicolet XRD Corp.: Madison, WI, 1990.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 55.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**)

S(1)−Cu	2.256(2)	S(2)−Cu	2.273(2)
S(3)−Cu	2.227(2)	S(4)−Cu	2.222(2)
C(1)−S(1)	1.658(6)	C(1a)−S(2)	1.680(6)
C(1)−S(2a)	1.680(6)	C(2)−S(3)	1.728(7)
C(3)−S(4)	1.733(7)	C(4)−N(1)	1.130(10)
C(5)−N(2)	1.127(10)	C(1a)−C(1)	1.483(9)
C(3)−C(2)	1.355(10)	C(4)−C(2)	1.432(10)
C(5)−C(3)	1.445(10)		
S(1)−Cu−S(2)	88.24(7)	S(1)−Cu−S(3)	89.45(8)
S(2)−Cu−S(3)	177.68(8)	S(2)−Cu−S(4)	88.32(7)
S(3)−Cu−S(4)	94.00(7)	S(4)−Cu−S(1)	176.56(9)
C(1)−S(1)−Cu	106.2(2)	C(1a)−S(2)−Cu	105.6(2)
C(2)−S(3)−Cu	99.7(2)	C(3)−S(4)−Cu	99.7(2)
C(1a)−C(1)−S(1)	120.6(5)	C(1a)−C(1)−S(2a)	119.4(5)
S(1)−C(1)−S(2a)	120.0(4)	S(2)−C(1a)−C(1)	119.4(5)
C(3)−C(2)−C(4)	119.9(6)	C(3)−C(2)−S(3)	123.3(5)
C(4)−C(2)−S(3)	116.8(5)	C(5)−C(3)−S(4)	117.2(5)
C(5)−C(3)−C(2)	119.5(6)	S(4)−C(3)−C(2)	123.2(5)
N(1)−C(4)−C(2)	177.9(8)	N(2)−C(5)−C(3)	178.2(8)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**)

Se(1)−Cu	2.353(1)	Se(2)−Cu	2.348(1)
S(1)−Cu	2.260(2)	S(2)−Cu	2.265(2)
C(2)−Se(1)	1.884(6)	C(3)−Se(2)	1.888(6)
C(1)−S(1)	1.679(6)	C(1a)−S(2)	1.666(6)
C(2)−S(3)	1.751(6)	C(4)−S(3)	1.730(6)
C(3)−S(4)	1.736(6)	C(4)−S(4)	1.725(6)
C(4)−S(5)	1.648(6)	C(1a)−C(1)	1.483(8)
C(3)−C(2)	1.338(8)		
Se(1)−Cu−Se(2)	95.63(4)	Se(1)−Cu−S(1)	89.77(5)
Se(2)−Cu−S(1)	163.94(6)	Se(2)−Cu−S(2)	89.12(5)
S(1)−Cu−S(2)	88.35(6)	S(2)−Cu−Se(1)	168.84(6)
C(2)−Se(1)−Cu	97.3(2)	C(3)−Se(2)−Cu	97.6(2)
C(1)−S(1)−Cu	105.3(2)	C(1a)−S(2)−Cu	105.2(2)
C(2)−S(3)−C(4)	98.0(3)	C(3)−S(4)−C(4)	98.2(3)
C(1a)−C(1)−S(1)	119.7(4)	S(2)−C(1a)−C(1)	120.2(4)
C(3)−C(2)−Se(1)	125.1(4)	C(3)−C(2)−S(3)	115.4(4)
Se(1)−C(2)−S(3)	119.6(3)	Se(2)−C(3)−S(4)	119.2(3)
Se(2)−C(3)−C(2)	124.3(4)	S(4)−C(3)−C(2)	116.5(4)
S(3)−C(4)−S(4)	111.9(3)	S(3)−C(4)−S(5)	123.5(4)
S(4)−C(4)−S(5)	124.6(4)		

Results and Discussion

Synthesis of $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (2), $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (3), and $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (4a). The synthesis of the complexes **2**−**4a** reported here is based on the result of competing reactions in a stirring biphasic solution. Methanolic $\mathrm{CuCl_2}$ solution is added to a biphasic solution of $(\mathrm{Et_4N})_2$tto dissolved in water and the corresponding ligand of choice as the bischelate of $\mathrm{Zn^{2+}}$ ($(\mathrm{Bu_4N})_2[\mathrm{Zn(L)_2}]$) dissolved in methylene chloride. The competing reactions are metal exchange of thiophilic $\mathrm{Cu^{2+}}$ with the zinc-containing bischelate and the $\mathrm{tto^{2-}}$. The formation of the insoluble oligomeric $[\mathrm{Cu(tto)}]_n$,[16] highly soluble bischelate, $[\mathrm{Cu(L)_2}]^{2-}$,[6c] and lesser soluble $\{\mathrm{tto[Cu(L)]_2}\}^{2-}$ allows the bimetallic complex of interest to be isolated on the basis of solubility differences as explained in the Experimental Section. The synthetic procedures are readily reproducible for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**) in 19%, $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**) in 30%, and $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4a**) in 14% yields. All of the complexes exhibit a deep-blue color in acetone and $\mathrm{CH_2Cl_2}$ solutions due to a characteristic strong absorption in the range of 541−574 nm assigned to a $\sigma(\mathrm{S}) \rightarrow \mathrm{Cu(II)}$ ligand to metal transition.[17]

Crystal and Molecular Structures of Complexes 1−4b. Comparison of the structures of $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4a**) will be discussed using results reported for the dianion as its tetraphenylarsonium salt **4b**[8n,o] along with $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**)[6l,9] and the new structures reported here, namely $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**) and $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**). As seen in Figure 1, two Cu(mnt) units in **2** and two Cu(dsit) units in **3** are bridged by the side-on coordination of the tto ligand. This is also the case for the complexes **1** and **4b**.[8o] The C(1)−C(1a) bond of tto in $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**) (1.483(9) Å) and in $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**) (1.483(8) Å) is essentially the same as we reported for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**) and as was observed for $(\mathrm{Ph_4As})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4b**) (1.467(10) Å). These bond lengths are all comparable to that of the isolated $\mathrm{tto^{2-}}$ (1.461(11) Å) as its $\mathrm{Ph_4P^+}$ salt,[18] and thus, the results indicate the $\mathrm{C_2S_4}$ bridging unit of the Cu metal centers behaves as a dianion. This is supported by the fact that these central C−C tto bonds are similar in length to that observed in the neutral Cu(I) tto complex $\mathrm{tto[Cu(Ph_3P)_2]_2}$ (1.531(8) Å).[19] If the $\mathrm{C_2S_4}$ unit behaved as a tetraanion in the form of ethylenetetrathiolate ($\mathrm{C_2S_4{}^{4-}}$), the length of the C(1)−C(1a) bond would be considerably shorter (∼1.332 Å).[8o]

The $\mathrm{Cu(C_2S_4)Cu}$ core of each complex is planar. $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**) is unique among the complexes discussed because it exhibits square planar Cu coordination resulting in a perfectly planar and highly conjugated molecule. This is the first fully planar bimetallic complex with tetrathiooxalate as a bridging ligand, which is an important structural feature for future studies in utilizing these complexes in electrically conducting materials. The coordination spheres of the Cu metal centers in $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**), $(\mathrm{Ph_4As})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4b**), and $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**) exhibit a slight tetrahedral distortion from square planar coordination at the Cu centers. This results in a twist formed between the bridging tto ligand and the capping ligands. A dihedral angle is thus formed from the planes of the tto and the capping ligands. We found the smallest dihedral angle for the tetrahedrally distorted complexes to be for the dmit derivative **1** at 18.87(3)°.[9] Complex **3** has a dihedral angle of 24.86(3)°, with that for $\{\mathrm{tto[Cu(dmid)]_2}\}^{2-}$ (**4b**) being reported as the largest at 28.3°.[8o]

As we previously reported for dmit complex **1**, the equal lengths of the Cu−S bonds (2.269(1) Å) to the tto ligand indicate a fully conjugated Cu−tto−Cu system. This is also seen in the dsit-capped chelate **3** (2.262(2) Å). In contrast to this, $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**) behaves similarly to $(\mathrm{Ph_4As})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4b**), where two different types of Cu−tto bonds are observed. In **4b**, the bond lengths are 2.258(2) and 2.245(2) Å for the chemically equivalent bonds, and in complex **2**, they are 2.256(2) and 2.273(2) Å.[8o] This was also observed for the copper(I) complex $\mathrm{tto[Cu(Ph_3P)_2]_2}$.[19]

An interesting relationship between the ethylene bond lengths (C(2)−C(3)) of the capping ligands and the dihedral angles resulting from the slight tetrahedral distortion was found. As the length of the bond increases, the dihedral angle decreases.

---

[16] (a) Strauch, P.; Dietzsch, W.; Hoyer, E. *Z. Chem.* **1983**, *23*, 448. (b) Hoyer, E. *Comments Inorg. Chem.* **1983**, *2*, 261. (c) Polescher, H.; John, W.; Hoppe, F.; Fanghänel, E.; Roth, S. *J. Prakt. Chem.* **1983**, *325*, 957. (d) Reynolds, J. R.; Karasz, F. E.; Lillya, C. P.; Chien, J. C. W. *J. Chem. Soc., Chem. Commun.* **1985**, 268. (e) Reynolds, J. R.; Chien, J. C. W.; Lillya, C. P. *Macromolecules* **1987**, *20*, 1184. (f) Vogt, T.; Faulmann, C.; Soules, R.; Lecante, P.; Mosset, A.; Castan, P.; Cassoux, P.; Galy, J. *J. Am. Chem. Soc.* **1988**, *110*, 1833. (g) Jolly, C. A.; Wang, F.; Krichene, S.; Reynolds, J. R.; Cassoux, P.; Faulmann, C. *Synth. Met.* **1989**, *29*, F189. (h) Reynolds, J. R.; Jolly, C. A.; Krichene, S.; Cassoux, P.; Faulmann, C. *Synth. Met.* **1989**, *31*, 109. (i) Jolly, C. A.; Reynolds, J. R. *Chem. Mater.* **1990**, *2*, 479.

[17] Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

[18] Lund, H.; Hoyer, E.; Groenbaeck-Hazell, R. *Acta Chem. Scand., Ser. B* **1982**, *36*, 207.

[19] Hansen, L. K.; Sieler, J.; Strauch, P.; Dietzsch, W.; Hoyer, E. *Acta Chem. Scand., Ser. A* **1985**, *39*, 571.

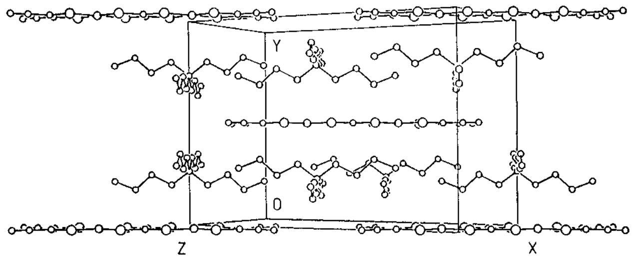


Figure 2. Packing diagram of $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) showing sheets of planar dianions separated by tetrabutylammonium cations.

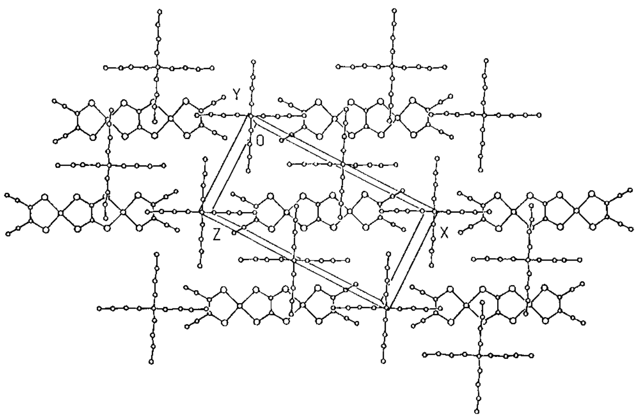


Figure 3. View down the *y* axis of $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**).

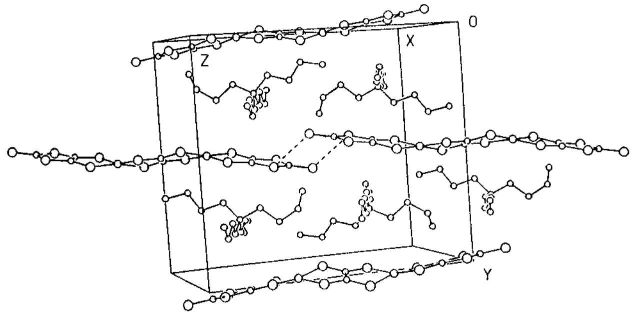


Figure 4. Packing diagram showing sheets of one-dimensional chains of the dianion of $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) formed from nonbonding interactions separated by tetrabutylammonium cations.

In $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**), the bond length of 1.355(10) Å corresponds to a planar structure with dihedral angle of 0° whereas, in $(Ph_4As)_2\{tto[Cu(dmid)]_2\}$ (**4b**), the bond distance of 1.326(8) Å leads to the largest dihedral angle value of 28.3°.[8o]

Figures 2 and 3 show two views of the packing of the chelate anions for $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**), and Figure 4 shows a view of the anion for $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**). Complex **2** exhibits packing of sheets of isolated planar dianions separated by sheets of isolated cations. For complex **4b** it was reported that the dianions were surrounded by six tetraphenylarsonium cations.[8o] Complex **3** exhibits a packing scheme different from those of $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) and $(Ph_4As)_2\{tto[Cu(dmid)]_2\}$ (**4b**), but of the same type we communicated for $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ (**1**).[9] The packing is exhibited as sheets of one-dimensional chains of dianions separated by isolated tetrabutylammonium cations. The dianion chains of $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) are formed from interactions of thioxo (S5)−thiole (S4) groups on adjacent molecules (3.631(3) Å). In $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ (**1**), the distance is essentially identical at 3.634(3) Å.[9] The distances are shorter than the sum of the van der Waals radii of sulfur (3.70 Å).[20]

On the basis of the crystal structures discussed, $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ (**1**) and $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**) are isostructural. The intermolecular contacts lead to one-dimensional chains. These interactions may prove important for future electrical conductivity studies. $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) is unique because of its planarity but displays no intermolecular interactions as seen in **1**[9] and **3**. The dianion of $(Ph_4As)_2\{tto[Cu(dmid)]_2\}$ (**4b**) exhibits neither intramolecular planarity as seen for the dianions of **1** and **3** nor intermolecular interactions as seen for the dianionic unit of **2**.[8o]

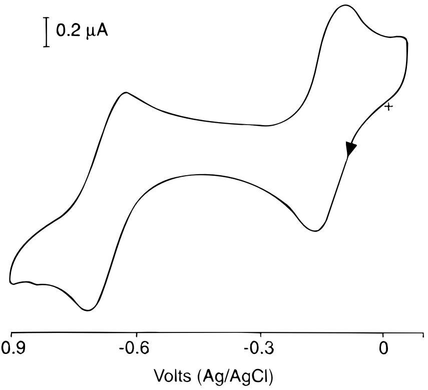


Figure 5. Cyclic voltammogram of $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**). Conditions: scan rate, 100 mV/s; reference electrode, Ag/AgCl; counter electrode, Pt foil; working electrode, Pt wire; 0.1 M Bu_4NClO_4 in CH_2Cl_2 under Ar at room temperature.

Table 6. Cyclic Voltammetric Peak Potentials (V) for Complexes **1**−**3** and **4a**[a]

complex	$E_{p,a}$	$E_{p,c}$	$E_{1/2}$
$(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ (**1**)	−0.08	−0.15	−0.12
	−0.66	−0.73	−0.70
$(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**)	+0.03	−0.03	0.00
	−0.59	−0.67	−0.63
$(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**)	−0.11	−0.17	−0.14
	−0.63	−0.71	−0.67
$(Bu_4N)_2\{tto[Cu(dmid)]_2\}$ (**4a**)	−0.13	−0.18	−0.15
	−0.76	−0.82	−0.79

[a] Conditions: scan rate, 200 mV/s; reference electrode, Ag/AgCl; counter electrode, Pt foil; working electrode, Pt wire; 0.1 M Bu_4NClO_4 electrolyte in CH_2Cl_2 under Ar at room temperature.

Redox Properties. All of the complexes exhibit similar redox behaviors with two separate reversible redox processes. Each complex is dianionic and stable in argon-purged CH_3CN- and CH_2Cl_2-based electrolytes. A cyclic voltammogram of $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**), representative for all complexes, is shown in Figure 5. A compilation of the cyclic voltammetric results is given in Table 6.

At potentials equal to −0.8 V, the complexes are stable and remain in their dianionic state. Scanning anodically, each complex exhibits a first low-potential redox couple with $E_{1/2}$ values in the range −0.79 to −0.63 V. $(Bu_4N)_2\{tto[Cu(dmid)]_2\}$ (**4a**) oxidizes with a peak at the lowest potential of −0.76 V, with $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**) having a first peak oxidation at the highest potential of −0.59 V. This is expected for **2** because of the highly electronegative terminal cyano groups. The first process for all of the complexes is reversible with observed peak-to-peak separations of 70 mV for $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ (**1**), 80 mV for $(Bu_4N)_2\{tto[Cu(mnt)]_2\}$ (**2**), 80 mV for $(Bu_4N)_2\{tto[Cu(dsit)]_2\}$ (**3**), and 60 mV for $(Bu_4N)_2\{tto[Cu(dmid)]_2\}$ (**4b**). This first redox process seen for all complexes may be assigned to the one-electron oxidation of the dianionic to the monoanionic species:

---

(20) Pauling, L. *Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

$$\{\mathrm{tto[Cu(L)]_2}\}^{2-} \rightleftarrows \{\mathrm{tto[Cu(L)]_2}\}^{-} + \mathrm{e}^{-}$$

Scanning to higher potentials, a second redox process is exhibited for each complex. $E_{1/2}$ values for this process range from −0.15 to 0.00 V. Complex **4a** again oxidizes with a peak at the lowest potential of −0.18 V, while **2** again oxidizes with a peak at the highest potential of +0.03 V. This second redox process for all complexes is also reversible with observed peak-to-peak separations of 70 mV for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**), 60 mV for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**), 60 mV for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**), and 50 mV for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4a**) and may be assigned to the one-electron oxidation of the monoanion to the neutral species:

$$\{\mathrm{tto[Cu(L)]_2}\}^{-} \rightleftarrows \{\mathrm{tto[Cu(L)]_2}\}^{0} + \mathrm{e}^{-}$$

Scan rate dependence studies (50−200 mV/s) show that all of the peak currents scale with the square root of the scan rate, as expected for diffusion of the electroactive species to the electrode surface when the switching potential is maintained at <+0.20 V; this indicates that, within this potential range and at these scan rates, the electroactive species remains in solution.

Upon anodic scans to higher potentials, further oxidation processes are observed at approximately +0.20 and +0.45 V for all compounds studied. Switching at +0.90 V and scanning cathodically, a large peak at −0.12 V dominates the cathodic process as shown for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**) in Figure 6. This behavior is observed for all the compounds studied and, as we reported earlier, for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**).[9] Upon scans to higher anodic potentials, an increase in the current for the cathodic wave is observed. This is characteristic of a redissolution process, as the redissolution peak intensity is related to the amount of material deposited on the electrode.[21]

It has previously been reported[8o,22] that the carbon−carbon π-bonding orbital ($2b_{1u}$) of the C_2S_4 bridging ligand is the HOMO for this class of complexes. Oxidation of the complexes may result in the C_2S_4 unit becoming neutral, resulting in cleavage of the carbon−carbon bond producing carbon disulfide, thereby ultimately resulting in the decomposition of the bimetallic bridged complex. This is not observed, as the redox behavior presented indicates the stability of the complexes in solution in their dianionic, monoanionic, and neutral forms.

Conclusions

Using a unique, reproducible, three-solvent method, we have synthesized three new extensively conjugated, sulfur-rich bimetallic copper(II) complexes. For $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**) and as previously reported for $(\mathrm{Ph_4As})_2\{\mathrm{tto[Cu(dmid)]_2}\}$ (**4b**), the dianion exhibits a slight tetrahedral distortion at the metal centers, while $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(mnt)]_2}\}$ (**2**) is planar with a dihedral angle of 0°.

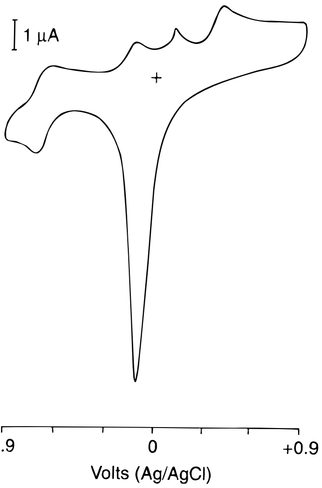


Figure 6. Cyclic voltammogram of $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dsit)]_2}\}$ (**3**) showing a large cathodic wave upon anodically scanning to high potentials. Conditions: scan rate, 200 mV/s; reference electrode, Ag/AgCl; counter electrode, Pt foil; working electrode, Pt wire; 0.1 M $\mathrm{Bu_4NClO_4}$ in $\mathrm{CH_2Cl_2}$ under Ar at room temperature.

Cyclic voltammetry results for all complexes show two reversible redox couples are accessible, and upon scans to higher potentials, a large cathodic wave is observed. This is indicative of stripping of a deposit from the working electrode surface. As previously reported for $(\mathrm{Bu_4N})_2\{\mathrm{tto[Cu(dmit)]_2}\}$ (**1**),[6l,9] the complex can be chemically oxidized to give highly conducting powders. These topics will be a focus of future studies. Other systems with different ligands and metals will also be investigated to further search for superior structural and electronic properties.

Acknowledgment. This work was funded by grants from the Air Force Office of Scientific Research (F49620-93-1-0322 and F49620-J-0509), the National Science Foundation (CHE 9307732), and the IAESTE program in Leipzig, Germany (951405-R).

Supporting Information Available: Text presenting X-ray experimental details and full tables of crystallographic data, hydrogen atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters (16 pages). Ordering information is given on any current masthead page.

IC9601605

---

(21) Tommasino, J.-B.; Pomarede, B.; Medus, D.; de Montauzon, D.; Cassoux, P. *Mol. Cryst. Liq. Cryst.* **1993**, *237*, 445.

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