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Communications

The Extensively Conjugated Bimetallic (μ-Tetrathiooxalato)copper(II) Complex $(Bu_4N)_2[(C_3S_5)CuC_2S_4Cu(C_3S_5)]$ for Electrically Conducting Charge Transfer Complexes

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This article communicates a unique, reproducible, and facile synthesis of a fully conjugated, dmit-capped, tetrathiooxalate-bridged, copper(II) acceptor complex. The crystal structure and properties are reported for the complex tetrabutylammonium (μ-tetrathiooxalato)bis[(2-thioxo-1,3-dithiole-4,5-dithiolato)-cuprate(II)], $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$. The tto-bridged, bis-(copper(II)) unit, with dmit peripheral ligands, is designed to be utilized in the synthesis of new highly electrically conducting, molecular materials. The chemistry of $[M(dmit)_2]^{n-}$(where M = Ni, Pt, and Pd; dmit = $C_3S_5^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolato; $0 \le n \le 2$) complexes is a rich and highly studied area within the field of molecular electronically conducting materials. These complexes form stable dianions, monoanions and neutral species along with highly conducting mixed-valence complexes with a variety of "open" and "closed-shell" cations. In a few instances (M = Ni and Pd) and with a limited number of cations, these salts superconduct at low temperatures and/or under applied pressure, and represent the only molecular transition metal complex based superconductors.[2] This phenomenon has been attributed to several factors. Most importantly, it has been attributed to the ability for these planar acceptor ions to form close-packed segregated stacking arrangements. The incorporation of heteroatoms, such as S or Se, into the periphery of the structure stabilizes the intermolecular interactions through direct S−S or Se−Se overlap on the adjacent inter- and intrastack ions.

Other research groups are actively involved in the synthesis of bis-coordinating, sulfur-rich bridging ligands for the synthesis of electronic materials. Most recently, Rauchfuss and co-workers synthesized a C_2S_4-bridged, nickel(II) complex with $\{S_2C_2S_2C_2(CO_2Me)_2\}_2^{2-}$ as a peripheral ligand.[3a] A bridged Cu(II) complex similar to the one presented here with the peripheral dmid ligands (dmid = 2-oxo-1,3-dithiole-4,5-dithiolato) was reported, but the synthetic methodology was found to be irreproducible.[3b,c] Also, McCullough and co-workers have successfully synthesized a series of bimetallic coordination complexes with conjugation localized to the tetrathiafulvalene-tetrathiolate bridging ligand.[3d,e]

We have utilized the concepts described above for the preparation of charge-delocalized bimetallic complexes employing conjugated bridging ligands coupled with conjugated capping ligands. Addition of 2 equiv of a methanolic $CuCl_2$ solution to a stirring mixture of 2 equiv of $(Bu_4N)_2[Zn(dmit)_2]$ dissolved in CH_2Cl_2 and 1 equiv of $(Et_4N)_2tto$ in water (two-phase reaction) results in a deep purple-colored organic phase.[4,5] After separation, the solution was diluted with 2-propanol and the CH_2Cl_2 evaporated. The precipitate was purified and subsequently recrystallized by slow evaporation of a 1:1 acetone−2-propanol mixture to yield purple crystals of $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ of up to 2.5 cm in length in 25% yield.[6]

The synthetic method of simultaneous reactions leads to the formation of $\{tto[Cu(dmit)]_2\}^{2-}$ in addition to the insoluble oligomeric $[Cu(tto)]_n$ and $(Bu_4N)_2[Cu(dmit)_2]$.[7,8] This is the

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[6] Analytical results for $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ are as follows: Mp: 147−8 °C. Anal. Calcd for $C_{40}H_{72}N_2S_{14}Cu_2$: C, 41.52; H, 6.28; N, 2.42; S, 38.79; Cu, 10.99. Found: C, 41.40; H, 6.11; N, 2.39; S, 39.30; Cu, 11.36. IR KBr, cm^{-1}): ν(C=C) 1484, 1372; ν(C=S) 1065. UV−vis [acetone; nm, (log ϵ)]: 465 (4.30), 513 (4.46), 557 (4.56), 700 (4.26), 1056 (3.99), 1365 (3.72).

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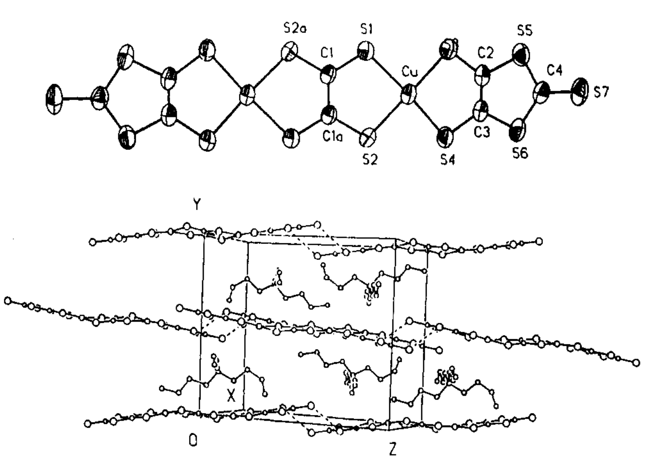

Figure 1. Molecular structure and numbering scheme for $(Bu_4N)_2$-$\{tto[Cu(dmit)]_2\}$ with 50% probability ellipsoids. Important geometric parameters include the following: S1−Cu 2.268(1) Å; S2−Cu 2.270(1) Å; S3−Cu 2.243(1) Å; S4−Cu 2.247(1) Å; C1−C1a 1.481(6) Å; C2−C3 1.339(7) Å; S1−Cu−S2 87.93(5)°; S2−Cu−S3 173.09(6)°; S3−Cu−S4 94.36(5)°; S4−Cu−S1 169.10(6)°. Packing diagram with unit cell labels of $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ showing linear chains of complex dianions separated by tetrabutylammonium cations.

result of competition between the $(Bu_4N)_2[Zn(dmit)_2]$ (metal exchange) and the tto with the Cu^{2+}. It is important to note that, in order for this method to be successful, both reactions must proceed at nearly the same rate.

The structure of the $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ was determined by single-crystal X-ray diffraction.[9] A view of the dianion and the atomic labeling are shown in Figure 1. Two Cu(dmit) units are bridged by the side on coordination of the tto ligand. The C_1-C_{1a} bond (1.481(6) Å) of the tto is comparable with the values found for the isolated ligand dianion (as its Et_4N^+ salt) (1.461(11) Å) and the $\{tto[Cu(dmid)]_2\}^{2-}$ (1.467(10) Å) but is slightly shorter than in the copper(I) complex $tto[Cu(Ph_3P)_2]$ (1.531(8) Å).[5b,10] These results indicate that the C_2S_4 moiety between both Cu centers can be considered as a tto dianion. The fact that all Cu−S bonds (2.269(1) Å) to the tto bridging ligand are equivalent indicate a fully conjugated structure. The coordination around the Cu is square planar with a slight tetrahedral distortion. The dihedral angle between the tto and dmit ligands attached to a Cu is 18.87(3)°. This is smaller than the 28° dihedral angle reported[3] for $\{tto[Cu(dmid)]_2\}^{2-}$.

Figure 1 also shows the packing of ions in the crystal. The crystal packing is characterized by sheets of anionic chains separated by sheets of isolated cations. The anion chains are formed by head-to-tail contacts between the thiole and thione groups S_6, S_7 [3.634(3) Å] of the dmit ligands on adjacent molecules related by a center of inversion. This interaction is similar to a carboxylic acid dimer.

The redox behavior of $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ has been examined by cyclic voltammetry (CV) in 0.08 M TBAP/CH_3CN at a Pt working electrode. The CV data show interesting yet complex electrochemical behavior. Two low-potential anodic processes ($E_{p,a} = -0.35$, and -0.04 V vs Ag/Ag^+) are observed. These anodic processes are correlated with two cathodic processes ($E_{p,c} = -0.65$ and -0.36 V). Scan rate dependence studies (25−250 mV s^{-1}) show all of the peak currents to scale with the square root of the scan rate, as expected for diffusion of the electroactive species to the electrode surface. Studies of the redox behavior of $[Ni(dmit)_2]^{n-}$ show that these types of reactions play an important role in electrocrystallization and the formation of highly conducting complexes.[11] Initial constant current electrocrystallization experiments carried out on $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ show the deposition of insoluble powder on the electrode surface but, as yet, no well-defined crystals.

Reactions of $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$ with varied amounts of NaI/I_2 in acetone followed by precipitation with methanol were carried out to examine the feasibility of isolating higher oxidation states and to determine the conductivity of partially oxidized complexes. The dianionic complex is insulating as expected with single-crystal conductivities $<10^{-10}$ S cm^{-1}, comparable to $[Cu(dmit)_2]^{2-}$. To date these reactions have yielded black powders with pressed pellet conductivities up to 10^{-2} S cm^{-1}. Elemental analysis was completed on the product obtained from the oxidation of the dianionic complex with 1 equiv of Na/I_2 oxidizing agent. The analysis shows the formation of a complex with the approximate stoichiometry $(Bu_4N)_{0.33}\{tto[Cu(dmit)]_2\}$.[12]

On the basis of the elemental analysis data, this new acceptor has the capability of forming complexes with partial oxidation states. As seen in the literature, this is a prerequisite for the formation of highly conducting complexes.[3] We are currently attempting electrocrystallization and slow interdiffusion experiments with a variety of counterions to synthesize new charge-transfer complexes. This new fully conjugated, bridged bimetallic complex may pave the way for a new family of highly conducting and potentially superconducting materials.

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Supporting Information Available: Text describing detailed synthetic procedures and tables of crystallographic data, atomic coordinates, bond lengths and angles, and isotropic and anisotropic thermal parameters (10 pages). Ordering information is given on any current masthead page.

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(9) Crystals of the complex obtained after recrystallization are black needles, with formula $(C_8S_{14}Cu_2)(NC_{16}H_{36})_2$, monoclinic, M_r = 1156.92, $P2_1/c$, $a = 9.941(1)$ Å, $b = 15.304(2)$ Å, $c = 18.084(2)$ Å, $\beta = 90.92(1)°$, $V = 2750.9(5)$ Å^3, $Z = 2$, $D_{calc.} = 1.397$ g cm^{-3}, T = 298 K. Data were collected with a crystal of dimensions 0.55 × 0.13 × 0.13 mm^3 on a Siemens P3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\,73$ Å). A total of 32 reflections with $20.0° \le 2\theta \le 22.0°$ were used to refine the cell parameters. A total of 5042 reflections (h, $0 \rightarrow 11$; k, $0 \rightarrow 18$; l, $-21 \rightarrow 21$) were collected using the ω-scan method ($2\theta_{max} = 50°$). After merging of the equivalent reflections, 4859 were unique and had an $R_{int.}$ of 1.56%. The structure was solved by direct methods and refined in *SHELXTL* plus using full-matrix least squares (Sheldrick, G. M. *SHELXTL plus*; Nicolet XRD Corp.: Madison, WI, 1990). The non-H atoms were treated anisotropically, whereas the positions of the hydrogen atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. In the final cycle of refinement 262 parameters and 2773 reflections [with $I > 2\sigma(I)$] gave R and wR of 0.0387 and 0.0396, respectively.

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(12) Elemental analysis results for $(Bu_4N)_{0.33}\{tto[Cu(dmit)]_2\}$ are as follows. Calcd for $C_{13.33}H_{12}N_{0.33}S_{14}Cu_2$: C, 21.27; H, 1.61; N, 0.62; S, 59.63; Cu, 16.88. Found: C, 22.05; H, 1.83; N, 0.63; S, 57.50; Cu, 16.89.