A New Generation of Nickel−dmit-Based Molecular Conductors Based on Fully Conjugated Bimetallic Complexes

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Received August 23, 1996

This communication presents a reproducible synthesis of the complex tetrabutylammonium (μ-tetrathiooxalato)bis[(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II)], $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ (**1**). This is the first fully planar and completely delocalized complex utilizing tto as a bridging ligand of Ni(II) metal centers. These structural features are analogous to the [M(dmit)$_2$] systems (when M = Ni(II), Pd(II), Pt(II)) but with an extension of the delocalization and increased intermolecular interactions needed for molecular conductors.[1] Recently it has been shown that intermolecular interactions in transition metal bis(dithiolate) complexes of this type are also important for the assembly of molecular ferromagnets.[2]

To date, the $[M(dmit)_2]^{n-}$ (M = Ni, Pd; $0 \leq n \leq 2$) systems have yielded seven superconducting complexes.[3] These remain the only transition metal-based organic materials to exhibit superconductivity.[4] An enormous amount of research has been devoted to the study of the dmit ligand-based metal complexes with over 250 papers, including several reviews[1] published devoted to their synthesis, electrical properties and optical properties. Using square planar coordinating metal ions, the dmit-based complexes are sulfur-rich, fully conjugated and completely planar. These structural features play a crucial role in the formation of superconducting organic materials.[1,3,4]

The neutral compound $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ was first reported by Dahl and co-workers containing the planar $NiS_2C_2S_2$-Ni core, but the compound was not completely planar due to the terminal η^5-C_5Me_5 ligands.[5] Recently, McCullough reported the bimetallic $(i\text{-}PrC_5H_4)_2Ti[S_2TTFS_2]Ti(i\text{-}PrC_5H_4)_2\cdot 1.5C_6H_6$ using the tetrathiafulvalenetetrathiolate bridging ligand as a potential "building-block" for electronic materials.[6] Rauchfuss and co-workers have also synthesized a nearly planar bimetallic Ni complex, $(Et_4N)_2[Ni_2C_2S_4\{S_2C_2S_2C_2(CO_2Me)_2\}_2]$, for electronic materials, but both complexes contain bulky out-of-plane terminal groups preventing the formation of intermolecular electronic interactions.[7] We have recently synthesized a series of complexes containing a $Cu(C_2S_4)Cu$ core with a series of planar dithiolato capping ligands. The dmit-containing complex is not planar due to a tetrahedral distortion at the Cu metal centers resulting in a dihedral angle between the capping and bridging ligands of 18.87(3).[8]

$(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ (**1**) is synthesized by the addition of 2 equiv of tetrabutylammonium bromide, 2 equiv of Cs_2dmit,[9] and 1 equiv of $(Et_4N)_2$tto[10] to acetone under an argon atmosphere. After this is stirred for ∼10 min to partially dissolve $(Et_4N)_2$tto, 2 equiv of $NiCl_2\cdot 6H_2O$ dissolved in methanol is added and allowed to stir. The solution is subsequently filtered to remove insoluble oligomeric $[Ni(tto)]_n$ and unreacted $(Et_4N)_2$-tto, diluted with 2-propanol, and allowed to evaporate to less than half the initial volume. The remaining precipitate is filtered and purified by subsequent crystallizations in 1:1 acetone/2-propanol mixtures to yield $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ as brown-black air-stable platelet crystals in ∼40% yield.[11]

The structure of $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ was determined by single-crystal X-ray diffraction[12] on crystals obtained by slow evaporation of a DMF solution. A view of the dianion and the atomic labeling scheme are shown in Figure 1. Two Ni(dmit) fragments are linked by the side on coordination of a tto ligand. The C1−C1′ bond of the tto ligand is 1.416(7) Å, slightly longer than that in the Ni(II) complex $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ of 1.360-

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(11) Analytical results for $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ are as follows: Mp: 270−275 °C (dec). Anal. Calcd for $C_{40}H_{72}N_2S_{14}Ni_2$: C, 41.87; H, 6.34; N, 2.44; S, 39.12. Found: C, 41.89; H, 6.53; N, 2.49; S, 39.30. IR (KBr, cm^{-1}): υ(C=C) 1452; υ(C=S) 1080. UV−vis [acetone; nm, (log ϵ)]: 380 (4.89), 462 (4.27), 520 (4.17), 1062 (4.35).

(12) Crystal data for **1**: orthorhombic, $P2_12_12_1$, brown-black platelet crystal, $a = 9.8188(3)$ Å, $b = 16.1038(4)$ Å, $c = 34.1910(9)$ Å; $Z = 4$; $R_1 = 4.96$ [F, for 6054 reflections $> 2\sigma(I)$], w$R_2 = 8.91$ [F^2, for 7015 reflections], GOF$(F^2) = 1.471$.

S0020-1669(96)01038-5 CCC: $14.00

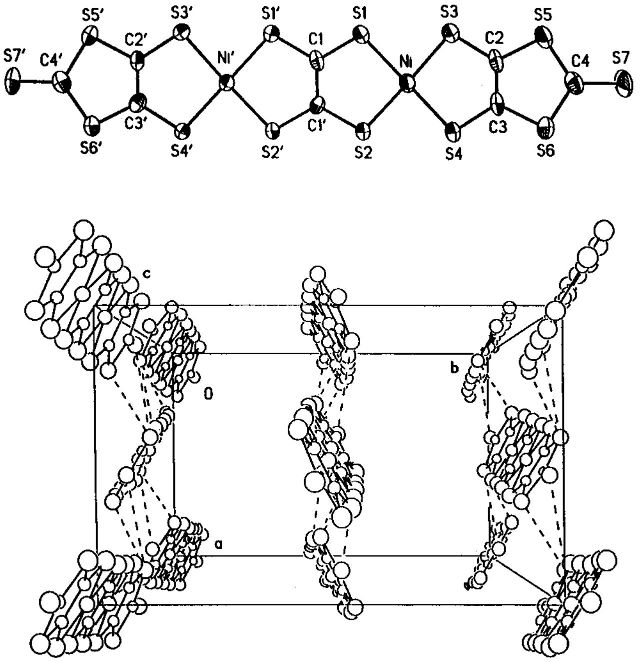

Figure 1. Top: Molecular structure and numbering scheme for $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ (**1**) with 50% probability ellipsoids. Important geometric parameters include the following: C1−C1′ 1.416(7) Å; C2−C3 1.365(9) Å; Ni−S1 2.145(2) Å; Ni−S2 2.163(2) Å; Ni−S3 2.162(2) Å; Ni−S4 2.161(2) Å; S1−Ni−S2 91.35(7)°; S1−Ni−S4 178.35(8)°; S4−Ni−S3 93.58(7)°; S3−Ni−S2 178.58(8)°. Bottom: View of the packing diagram along the c axis with unit cell labels showing sheets of canted dianions. Tetrabutylammonium cations have been omitted for clarity.

(11) Å and also comparable to 1.461(11) Å seen for the isolated tto ligand dianion.[13] The π system of the tto bridging ligand is highly delocalized and results in a planar structure as the Ni−S (2.158(4) Å) and C−S (1.706(12) Å) bond lengths are comparable to those found for $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ of 2.122(1) and 1.718(3) Å, respectively. The coordination about the d^8 Ni(II) metal centers is essentially square planar with S1−Ni−S2 and S1−Ni−S3 bond angles being 91.35(7) and 87.55(8)° respectively.

A perspective of the crystal packing is also given in Figure 1. This view shows a significant amount of two-dimensional nonbonding orbital interactions of thioxo−thiole (3.532−3.572 Å) and thiole−thiole atoms (3.438−3.484 Å) of the dianionic units arranged in a canted fashion resulting in each bimetallic unit to interact with four adjacent bimetallic units. The crystal packing is characterized by sheets of dianions with nonbonding S···S interactions in two dimensions, separated by sheets of tetrabutylammonium cations. Using a smaller cation, we have also synthesized the Me_4N^+ salt of this complex, which exhibits intermolecular orbital overlap in three dimensions including not only S−S interactions but also Ni−S orbital interactions.

The redox behavior of $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ (**1**) has been examined by cyclic voltammetry (CV) in 0.08 M tetramethylammonium perchlorate (TMAP)/CH_3CN at a Pt button working electrode using a Pt foil counter electrode. The CV results

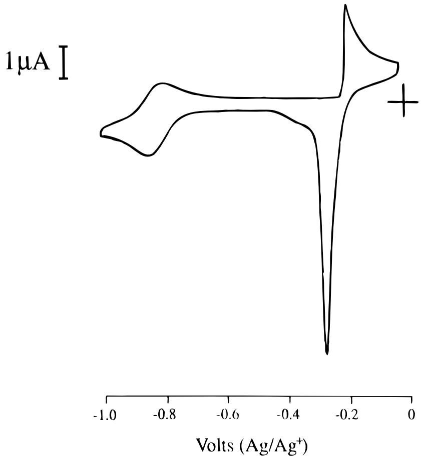

Figure 2. Cyclic voltammogram of $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ (**1**). Conditions: scan rate, 50 mV/s; reference electrode, Ag/Ag^+; counter electrode, Pt foil; working electrode, Pt button; 0.08 M Me_4NClO_4 in CH_3CN under Ar at room temperature.

(Figure 2) show starting at potentials at ~ -0.90 V, a low-potential, reversible couple ($E_{1/2} = -0.83$ V vs Ag/Ag^+), which may be attributed to the formation of the monoanionic species. This first redox couple is diffusion controlled as the peak currents are proportional to the square root of the scan rate. A second non-Nernstian-shaped redox couple is also observed at a higher potential ($E_{p,a} = -0.20$, $E_{p,c} = -0.25$ V). The shape of the second redox couple is very similar to the second redox couples also seen for the bischelate complexes of $[Ni(dmit)_2]^{2-}$ and $[Ni(dsit)_2]^{2-}$ (dsit = $C_3Se_2S_3{}^{2-}$ = 2-thioxo-1,3-dithiole-4,5-diselenolato).[14,15] This may be attributed to the formation of the neutral species. The reduction peak of the second redox couple is characteristic of a redissolution process. As reported in a thorough study of the mechanism of electrocrystallization, the redissolution process may be that of a noninteger oxidation state material formed on the electrode from the reaction of neutral species with charged species in the diffusion layer.[14] This electrochemical behavior is needed for the assembly of noninteger oxidation state electrically conducting and superconducting molecular materials via electrocrystallization, the most general and widely used technique today.[4,14−16]

We have allowed a slight excess of $(TTF)_3(BF_4)_2$[17] to react with $(Bu_4N)_2\{tto[Ni(dmit)]_2\}$ (**1**) in acetonitrile−acetone (1:1). A black insoluble precipitate formed which exhibited a pressed-pellet, two-probe room temperature conductivity of 0.4 S/cm. We have also electrocrystallized **1** in CH_3CN/DMF in the presence of an excess of Bu_4NBr using a constant current density of 0.5 $\mu A/cm^2$. A black, shiny, microcrystalline material was harvested from the electrode. Pressed-pellet electrical conductivity measurements of the material yielded an even higher conductivity of 0.5 S/cm. Current work is underway using electrocrystallization and also slow interdiffusion experiments to synthesize partial oxidation state materials with a variety of counterions.

Acknowledgment. This work was funded by grants from the Air Force Office of Scientific Research (F49620-96-1-0067 and F49620-93-1-0322) and the IAESTE program at the University of Leipzig, Leipzig, Germany (Reference No. 951405-R).

Supporting Information Available: Text describing detailed synthetic procedures and full tables of crystallographic data, atomic coordinates, bond lengths and angles, and isotropic and anisotropic thermal parameters (15 pages). Ordering information is given on any current masthead page.

IC9610389

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