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Preparation and Characterization of Conducting Trimetallic Nickel−Dithiolene Complexes with Bridging Tetrathiooxalate Ligands

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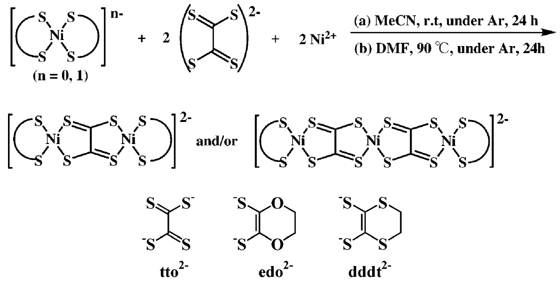
Novel trimetallic nickel(II) complexes with dithiolene ligands bridged by two tetrathiooxalate (tto) ligands have been obtained during the development of new multimetallic complexes for use as molecular conductors.

Multimetallic complexes are attracting wide interest as single-molecule magnets,[1] nanosize self-assembling cages,[2] efficient catalysts,[3] nanowire precursors,[4] and chemical sensors.[5] Dithiolene complexes, as conducting materials, are well-known to exhibit metallic and even superconducting behavior,[6] but few multimetallic complexes are known. The tetradentate bridging ligand, tto,[7] has provided various multimetallic oligomer or polymer complexes that have been reported as organic conductors.[8] However, their low solubility and purity have prevented studies on their physical properties based on well-defined crystal structures. Pullen and co-workers have reported preparations and crystal structures of a series of planar tto-bridging bimetallic Cu(II) and Ni(II) complexes with dmit or dmise ligands (dmit^{2-} = 2-thioxio-1,3-dithiole-4,5-dithiolate; dmise^{2-} = 2-selenoxio-1,3-dithiole-4,5-dithiolate).[9] However, other bimetallic complexes with the bridging tto ligand have not been obtained by their synthesis nor by conducting materials with well-defined structures.

We have attempted to find a versatile method for preparation of the bimetallic complexes by a reaction of the corresponding monometallic nickel−dithiolene complex $[\text{Ni(S−S)}_2]^{n-}$ (n = 0 or 1; S−S = edo^{2-}, dddt^{2-})[10] (edo^{2-} = 5,6-dihydro-1,4-dioxine-2,3-dithiolate; dddt^{2-} = 5,6-dihydro-1,4-dithine-2,3-dithiolate) with a tto^{2-} ligand and a Ni^{2+} cation (Scheme 1). It was found that bimetallic complexes with dithiolene ligands can be easily obtained by this reaction. In addition, this reaction unexpectedly provides *trimetallic* complexes with two tto bridging ligands together with the bimetallic complex. Metal complexes with such an extended π-conjugated system are expected to exhibit a small HOMO−LUMO gap, which is intrinsic for a single-component molecular metal, such as the case with the monometallic Ni(II) complex Ni(tmdt)_2 (tmdt^{2-} = trimethylenetetrathafulvalenedithiolate).[11] Therefore, these trimetallic complexes are promising candidates for new types of single-component molecular metals. In addition, their large/long size would provide multidimensional intermolecular interactions, new types of crystal structures, and thus interesting electronic and/or magnetic properties. In this communication, focus is made on these trimetallic Ni(II)−edo and −dddt complexes with two bridging tto ligands. To our knowledge, this is the first reported example of a conducting trimetallic complex with a well-defined structure.

The preparation of the trimetallic nickel complexes based on the edo or dddt ligand was performed as follows. Ni(edo)_2 (0.121 mmol), $(\text{Et}_4\text{N})_2(\text{tto})$ (0.242 mmol), and $\text{NiCl}_2{\cdot}6\text{H}_2\text{O}$ (0.242 mmol) were dissolved in MeCN (acetonitrile) (50 mL) under an Ar atmosphere. This solution was stirred for 24 h at rt (Scheme 1, method (a)). The resulting solution was filtered through a 0.5 μm mesh membrane filter. Formation of the trimetallic $[(\text{tto})_2\text{Ni}_3(\text{edo})_2]^{n-}$ unit (**1**) in the solution was identified by electrospray ionization mass spectrometry (ESI-mass m/z = 775.6 for $[\text{C}_{12}\text{H}_8\text{Ni}_3\text{O}_4\text{S}_{12}]^-$), as shown in Figure 1. The isotope pattern was also in perfect agreement with the simulated one. Formation of the bimetallic $[(\text{tto})\text{Ni}_2(\text{edo})_2]$ unit was also confirmed in this reaction by the ESI-mass (m/z = 565.6 for $[\text{C}_{10}\text{H}_8\text{Ni}_2\text{O}_4\text{S}_8]^-$; Supporting Information, Figure S1).

Scheme 1



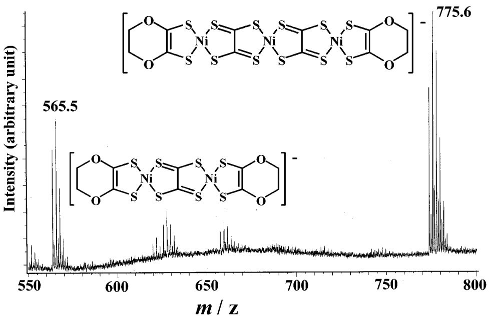


Figure 1. ESI-mass spectra of tto-bridged multimetallic complexes with edo.

The trimetallic complex **1** was separated from other byproducts using an HPLC equipped with an ODP (octadecyl polymer) column as the stationary phase and $\text{MeCN/H}_2\text{O}$ = 95:5 (v/v) as the mobile phase at rt.[12] Black plates of the trimetallic complex $(\text{Et}_4\text{N})_2[\mathbf{1}]$ were obtained by recrystallization at −25 °C under Ar (yield 5.5%). The chemical formula of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ was determined by an elemental analysis.[13] Measurement of the X-ray crystal structure of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ was not performed because of the poor crystal quality.

The trimetallic unit $[(\text{tto})_2\text{Ni}_3(\text{dddt})_2]^{n-}$ (**2**) was obtained by the reaction of $(\text{Bu}_4\text{N})[\text{Ni(dddt)}_2]$ (0.121 mmol), $(\text{Et}_4\text{N})_2(\text{tto})$ (0.242 mmol), and $\text{NiCl}_2{\cdot}6\text{H}_2\text{O}$ (0.242 mmol) in dimethylformamide (50 mL) for 24 h at 90 °C under Ar (Scheme 1, method (b)). A bimetallic $[(\text{tto})\text{Ni}_2(\text{dddt})_2]$ unit was also formed in this reaction. Formation of **2** and the bimetallic unit was verified by ESI-mass (trimetallic unit **2**, m/z = 839.4 for $[\text{C}_{12}\text{H}_8\text{Ni}_3\text{S}_{14}]^-$; bimetallic unit, m/z = 629.6 for $[\text{C}_{10}\text{H}_8\text{Ni}_2\text{S}_{10}]^-$, Supporting Information, Figure S1). This procedure is applicable to the formation of bimetallic dithiolene complexes, the results of which will be published

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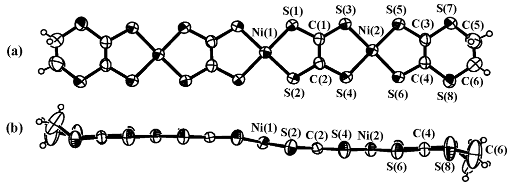

Figure 2. Molecular structure of trimetallic complex **2**.

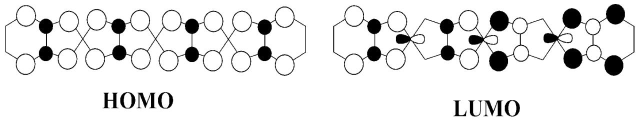

Figure 3. Schematic drawing of the HOMO and LUMO for neutral **2**.

elsewhere. Details of the reaction process are described in Supporting Information.

The trimetallic complex **2** was recrystallized after HPLC separation under the same conditions as those used for $(Et_4N)_2$[**1**]. Single crystals of $(Ph_4P)_2$[**2**] were obtained as black blocks by recrystallization from MeCN with an excess amount of $(Ph_4P)Br$ at -25 °C under Ar (yield 4.2%). The chemical formula was determined by an X-ray crystallographic analysis.[14]

The molecular structure of **2** is shown in Figure 2 with atomic labels. An inversion center is on the Ni(1) atom. Square-planar coordinations are formed around the Ni(1) and Ni(2) atoms, as expected for d^8 complexes. The distances of the Ni$-$S and C$-$C bonds are close to those observed for other bimetallic nickel complexes (Supporting Information, Table S1).[9,15] The molecule is almost planar except for the terminal ethylene groups (Figure 2b). The molecular packing and overlap integrals are summarized in the Supporting Information.

The temperature dependence of resistivity was measured for single crystals of $(Et_4N)_2$[**1**] and $(Ph_4P)_2$[**2**] from 290 to 170 K using the standard four- or two-probe DC method. The salts exhibited moderate conduction (($(Et_4N)_2$[**1**]: $\rho_{rt} = 1.5 \times 10^3\ \Omega$ cm, $E_a = 0.12$ eV; $(Ph_4P)_2$[**2**]: $\rho_{rt} = 1.0 \times 10^4\ \Omega$ cm, $E_a = 0.28$ eV; Supporting Information, Figure S6).

To reveal electronic features of the trimetallic complexes, the extended Hückel molecular orbital (MO) calculations were performed on the basis of the crystal structure. Atomic parameters given in ref 16 were adopted for the calculation. Figure 3 shows the calculated HOMO and LUMO for **2** in a neutral state. The nickel d orbital's contribution was found only in the LUMO. The highly symmetric HOMO and LUMO of **2** resemble those of $Ni(tmdt)_2$, which allows a three-dimensional (3D) π band.[11] The calculated HOMO$-$LUMO energy gap of **2** is 0.15 eV. Although the gap of **2** is slightly larger than that of $Ni(tmdt)_2$ (0.10 eV), a trimetallic complex with a very small HOMO$-$LUMO energy gap and a good HOMO/LUMO symmetry similar to $Ni(tmdt)_2$ seems to be suitable for the formation of a single-component molecular metal.[11] These MO symmetries have also been confirmed by ab initio calculations.[17]

In conclusion, the development of multimetallic complexes with tto bridging ligands has led to the preparation of novel *trimetallic* nickel complexes. Our synthesis has yielded crystals of conducting trimetallic complexes. Although the yields of the trimetallic complexes require improvement, it was revealed that the side reaction polymerization can be reduced by mixing the corresponding monometallic complex and tto ligand. These new trimetallic complexes are good candidates for single-component molecular metals: the calculated HOMO$-$LUMO gap of **2** is very small (0.15 eV), and the HOMO and the LUMO of **2** have a symmetry similar to $Ni(tmdt)_2$. Electrochemical crystallization or chemical oxidation of the trimetallic complexes, $(Et_4N)_2$[**1**] and $(Ph_4P)_2$[**2**], is now in progress.

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Supporting Information Available: ESI-mass spectra and the isotope simulations of each trimetallic and bimetallic complex, X-ray crystallographic information for $(Ph_4P)_2$[**2**] (PDF), CIF data (text), and temperature dependence of resistivity for $(Et_4N)_2$[**1**] and $(Ph_4P)_2$[**2**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Elemental analysis for $(Et_4N)_2$[**1**]. Calcd for $C_{28}H_{48}N_2Ni_3O_4S_{12}$: C, 32.41; H, 4.66; N, 2.70. Found: C, 32.33; H, 4.60; N, 2.66%.

(14) Crystal data of $(Ph_4P)_2$[**3**]: $C_{60}H_{44}Ni_3P_2S_{16}$, $M = 1516.02$, monoclinic, $a = 10.925(2)$, $b = 17.691(3)$, $c = 17.158(3)$ Å, $\beta = 94.143(3)°$, $V = 3307(1)$ Å^3, $T = 297$ K, space group $P2_1/n$ (No. 14), $Z = 2$, μ(Mo Kα) $= 1.437$ mm^{-1}, 27 730 reflections measured, 7560 unique ($R_{int} = 0.079$) which were used in all calculations. $R(F^2)$ ($I > 2.00\sigma(I)$) $= 0.0436$. The final $wR(F_2)$ was 0.1367 (all data).

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