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,\textsuperscript{1} nanosize self-assembling cages,\textsuperscript{2} efficient catalysts,\textsuperscript{3} nanowire precursors,\textsuperscript{4} and chemical sensors.\textsuperscript{5} Dithiolene complexes, as conducting materials, are well-known to exhibit metallic and even superconducting behavior,\textsuperscript{6} but few multimetallic complexes are known. The tetradentate bridging ligand, tto,\textsuperscript{7} has provided various multimetallic oligomer or polymer complexes that have been reported as organic conductors.\textsuperscript{8} However, their low solubility and purity have prevented studies on their physical properties based on well-defined crystal structures. Pullen and coworkers 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\textsuperscript{2} and dmise\textsuperscript{2} - ),\textsuperscript{9} which provided various multimetallic oligomer or polymer complexes that were dissolved in MeCN (acetonitrile) (50 mL) under an Ar atmosphere. For 24 h at 90 °C under Ar (Scheme 1, method (b)).

We have attempted to find a versatile method for preparation of the bimetallic complexes by a reaction of the corresponding monomolecular nickel–dithiolene complex \([\text{Ni(S-S)}]\text{)}_{n}^{+} (n = 0 or 1; \text{S} = \text{edo}^{2-}, \text{dddt}^{2-})\text{)}^{10} (\text{edo}^{2-} = 5,6-dihydro-1,4-dioxine-2,3-dithiolate; \text{dddt}^{2-} = 5,6-dihydro-1,4-dithiol-2,3-dithiolate) with a tto\textsuperscript{2-} ligand and a Ni\textsuperscript{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 \(\pi\)-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(\text{edm}^{2-} or \text{dddt}^{2-} ligand) was performed as follows. Ni(\text{edm})\text{)}_{2} (0.121 mmol), (Et\textsubscript{4}N)\text{)}\text{2} (tto) (0.242 mmol), and NiCl\text{)}\text{2} (0.128 mmol), (Et\textsubscript{4}N)\text{)}\text{2} (tto) (0.242 mmol), and NiCl\text{)}\text{2} (0.128 mmol), NiCl\text{)}\text{2} (0.242 mmol) in dimethylformamide (50 mL) were dissolved in MeCN (acetoniitride) (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 \(\mu\)m mesh membrane filter. Formation of the trimetallic [(tto)\text{2} Ni(\text{edo})\text{2}]\text{2}\text{+} (a) MeCN, r.t., under Ar, 24 h

(b) DMF, 90 °C, under Ar, 24 h

Scheme 1

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

agreement with the simulated one. Formation of the bimetallic [(tto)-Ni\text{3}(edo)\text{2}]\text{2}\text{+} was also confirmed in this reaction by the ESI-mass (\(m/z = 565.6\) for [\(\text{C}_{12}\text{H}_{8}\text{Ni}_{3}\text{O}_{4}\text{S}_{12}\text{]^{2}+}\)). The trimetallic complex 1 was separated from other byproducts using an HPLC equipped with an ODP (octadecyl polymer) column as the stationary phase and MeCN/H\textsubscript{2}O = 95:5 (v/v) as the mobile phase at rt.\textsuperscript{12} Black plates of the trimetallic complex (Et\textsubscript{4}N)\text{2}[\text{Ni}(dddt)\text{2}]\text{2} were obtained by recrystallization at \(-25^\circ\)C under Ar (yield 5.5%). The chemical formula of (Et\textsubscript{4}N)\text{2}[\text{Ni}(dddt)\text{2}]\text{2} was determined by an elemental analysis.\textsuperscript{13} Measurement of the X-ray crystal structure of (Et\textsubscript{4}N)\text{2}[\text{Ni}(dddt)\text{2}]\text{2} was not performed because of the poor crystal quality.

The trimetallic unit [(tto)\text{2} Ni(ddd)\text{2}]\text{2}\text{+} (2) was obtained by the reaction of (Bu\textsubscript{4}N)[Ni(dddt)\text{2}]\text{2} (0.121 mmol), (Et\textsubscript{4}N)\text{2}(tto) (0.242 mmol), and NiCl\textsubscript{2} (0.242 mmol) in dimethylformamide (50 mL) for 24 h at 90 °C under Ar (Scheme 1, method (b)). A bimetallic [(tto)Ni(ddd)\text{2}]\text{2} 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 [\(\text{C}_{12}\text{H}_{8}\text{Ni}_{3}\text{S}_{14}\text{]^{2}+}\); bimetallic unit, \(m/z = 629.6\) for [\(\text{C}_{12}\text{H}_{8}\text{Ni}_{3}\text{S}_{10}\text{]^{-}\}).

Figure 1. X-ray crystal structure of (Et\textsubscript{4}N)\text{2}[\text{Ni}(dddt)\text{2}]\text{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 (Et₃N)(CN). Single crystals of (Ph₄P)₂[2] were obtained as black blocks by recrystallization from MeCN with an excess amount of (Ph₄P)Br at −25 °C under Ar (yield 4.2%). The chemical formula was determined by an X-ray crystallographic analysis. The molecular structure of 2 is shown in Figure 2 with atomic labels. An inversion center is on the Ni(1) atom. Square-planar coordination is almost planar except for the terminal ethylene groups (Figure 2B). The molecular packing and overlap integrals are summarized in the 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 network. 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. These MO symmetries have also been confirmed by ab initio calculations.

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 material is available free of charge via the Internet at http://pubs.acs.org.

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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 (Ph₄P)₂[2] (PDF), CIF data (text), and temperature dependence of resistivity for (Et₃N)(CN) and (Ph₄P)₂[2]. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(13) Elemental analysis for (Et₃N)(CN). Calc. for C₆H₆N₃NiO₃Si₂: C, 32.41; H, 4.66; N, 2.70. Found: C, 32.33; H, 4.66; N, 2.66%.
(14) Crystal data of (Ph₄P)₂[2]. CuHaNi₂P₂S₂S₄. M = 516.02, monoclinic, a = 10.925(2) b = 17.691(3), c = 17.158(3) Å, β = 94.14(3)°, V = 33071(1) Å³, T = 297 K, space group P2₁/a (No. 14), Z = 2, μ(Mo Kα) = 1.433 mm⁻¹, 27 730 reflections measured, 7964 reflections (Rint = 0.070) which were used in all calculations. R(F²) = 0.0436 (final wR(F²) = 0.1367 (all data).
(17) Yamamoto, T. RIKEN. Personal communication.

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