Synthesis, Structure, and Electrochemical Properties of New "Unsymmetrical" Metal Dithiolate Complexes

Reizo Kato,* Yoshiaki Kashimura, Hiroshi Sawa,† and Yoshinori Okano
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
†Department of Physics, Faculty of Science, Chiba University, Yayoi-cho, Inage-ku, Chiba 263

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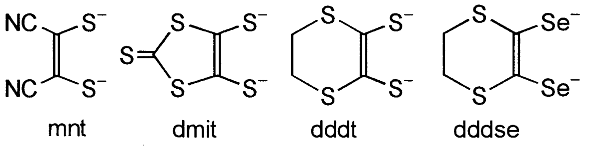
New "unsymmetrical" (mixed ligand) metal dithiolate complexes, expected as components of molecular conductors, have been obtained by a ligand-exchange reaction in refluxing acetone, followed by isolation with a preparative HPLC (ODP; acetonitrile-H_2O). Their electrochemical data suggest that the acceptor (donor) ability and the on-site Coulomb energy for the "unsymmetrical" complexes can be tuned by a combination of ligands.

There has been considerable interest in the solid-state properties of bis[(*Z*)-1,2-disubstituted ethylene-1,2-dithiolato]-metal complexes, since the discovery of one-dimensional metallic materials derived from this class of compounds.[1] Research of dithiolate complexes have grown to find several molecular superconductors with unique properties.[2] It is of prime importance to the understanding of the solid-state properties of molecular conductors that the range of materials for study should be extended. From this point of view, variety of molecular conductors based on metal dithiolate complexes is still limited. Surprisingly, there were few (systematic) attempts to examine "unsymmetrical" (mixed ligand) complexes as components of molecular conductors,[3] whereas "unsymmetrical" TTF-based donor molecules have enriched the chemistry and physics of the organic metals and superconductors.[4] Therefore we have started to develop molecular conductors based on "unsymmetrical" dithiolate complexes. We report here synthesis, structure, and electrochemical properties of new "unsymmetrical" metal (mainly nickel) dithiolate complexes derived from maleonitriledithiolate (mnt),[5] 1,3-dithiol-2-thione-4,5-dithiolate (dmit),[6] 5,6-dihydro-1,4-dithiin-2,3-dithiolate (dddt)[7] ligands (Scheme). All these ligands are known to provide highly conductive materials. In addition to these ligands, we have examined a selenium analogue of dddt, 5,6-dihydro-1,4-dithiin-2,3-diselenolate (dddse).



The dddse ligand was generated by the nucleophilic ring opening of 2,5,-dithia-7,9-diselenabicyclo[4.3.0]-non-1(6)-en-8-one,[8] and after the reaction with $NiCl_2$ the $[Ni(dddse)_2]^-$ anion was isolated as a Bu_4N salt (yield 74 %), as is the case of the dddt complex.[7] Unsymmetrical nickel dithiolate anions $[Ni(X)(Y)]^-$ (X, Y = mnt, dmit, dddt, and dddse; as Bu_4N salts) were prepared by a ligand-exchange reaction between the $[Ni(X)_2]^-$ and $[Ni(Y)_2]^-$ complexes in refluxing acetone.[9,10] As was pointed by Davison et al.,[9] in most cases, the unsymmetrical complexes were formed to an extent beyond the random reorganization (yield; 49–53 % for Se-containing complexes, 64–83 % for others). In the previous works, the unsymmetrical complexes were isolated by (repeated) recrystallization. This method is not always applicable and there should remain a possibility of contamination with "symmetrical" complexes. We have found that the unsymmetrical product can be completely separated by reversed phase column chromatography (JAIGEL-ODP, Japan Analytical

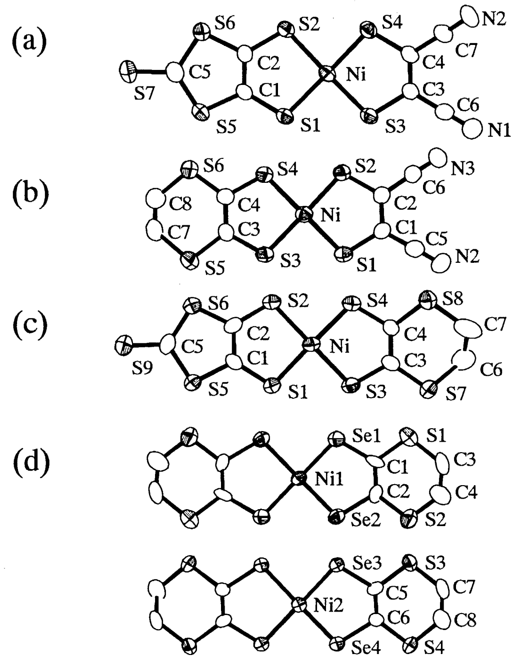


Figure 1. (a) ORTEP drawing of a $[Ni(dmit)(mnt)]^-$ unit. The selected bond distances (Å) and angles (°) are as follows; Ni-S1 = 2.163(2), Ni-S2 = 2.156(2), Ni-S3 = 2.150(2), Ni-S4 = 2.147 (2), S1-Ni-S2 = 92.65(8), S3-Ni-S4 = 92.63(8).

(b) ORTEP drawing of a $[Ni(dddt)(mnt)]^-$ unit. The selected bond distances (Å) and angles (°) are as follows; Ni-S1 = 2.149 (2), Ni-S2 = 2.142(2), Ni-S3 = 2.146(2), Ni-S4 = 2.144(2), S1-Ni-S2 = 92.85(7), S3-Ni-S4 = 90.78(7).

(c) ORTEP drawing of a $[Ni(dddt)(dmit)]^-$ unit. The selected bond distances (Å) and angles (°) are as follows; Ni-S1 = 2.143 (4), Ni-S2 = 2.163(3), Ni-S3 = 2.147(3), Ni-S4 = 2.150(3), S1-Ni-S2 = 93.7(1), S3-Ni-S4 = 91.3(1).

(d) ORTEP drawings of $[Ni(dddse)_2]^-$ units. Each of them is located on the inversion center. The selected bond distances (Å) and angles (°) are as follows; Ni1-Se1 = 2.243(3), Ni1-Se2 = 2.243(3), Ni2-Se3 = 2.252(3), Ni2-Se4 = 2.249(3), Se1-Ni1-Se2 = 91.9(1), Se3-Ni2-Se4 = 91.99(10).

Table 1. Electrochemical data for the [Ni(X)(Y)]$^-$ complexes.

	E_1 / V [a, c]	E_2 / V [b, c]	ΔE (= $E_1 - E_2$) / V
[Ni(dmit)(mnt)]$^-$	+0.32	−0.35	0.67
[Ni(dddse)(mnt)]$^-$	+0.12	−0.59	0.71
[Ni(dddt)(mnt)]$^-$	+0.10	−0.67	0.77
[Ni(dddse) (dmit)]$^-$	−0.14	−0.72	0.58
[Ni(dddt)(dmit)]$^-$	−0.18	−0.79	0.61
[Ni(mnt)$_2$]$^-$	+0.68	−0.13	0.81
[Ni(dmit)$_2$]$^-$	−0.08	−0.49	0.41
[Ni(dddse)$_2$]$^-$	−0.23	−0.97	0.74
[Ni(dddt)$_2$]$^-$	−0.32	−1.07	0.75

[a] Irreversible. [b] Reversible. [c] Measured at Pt electrode in CH_3CN, 0.1 M Bu_4NClO_4 (volts vs. 0.01 M $Ag/AgNO_3$). Temperature, 25°C.

Industry Co., Ltd.). Acetonitrile containing 5 % (v/v) water was used as an eluent. We have ascertained these procedures to be applicable for Pd and Pt complexes. It may be possible that the unsymmetrical complexes goes back into the symmetrical complexes in a solution. We have observed, however, no indication of such a disproportionation in the process of electrochemical measurement or recrystallization at room temperature.

Crystal structures of Bu_4N[Ni(dmit)(mnt)], Bu_4N[Ni(dddt)(mnt)], Bu_4N[Ni(dddt)(dmit)], and Bu_4N[Ni(dddse)$_2$] have been determined by the single crystal X-ray diffraction method (Figure 1).[11] The salt Bu_4N[Ni(dddse)$_2$] is isostructural with the P$\bar{1}$ form of Bu_4N[Ni(dddt)$_2$].[12]

Electrochemical data of five unsymmetrical complexes along with the corresponding symmetrical ones are shown in Table 1. All these complexes were reduced in reversible one-electron step. In the oxidation, the cyclic voltammograms of all the complexes showed an irreversible wave at a sweep rate of 100–200 mVs^{-1}. The electrode potential (E_1) was determined by differential pulse polarography. The potentials E_1 and E_2 might be correlated to donor (acceptor) ability, and the ΔE (= $E_1 - E_2$) value can be a measure of the on-site Coulomb energy. Electrochemical data suggest that the acceptor (donor) ability and the on-site Coulomb energy for each "unsymmetrical" complex are intermediate between those of the corresponding symmetrical complexes respectively. This suggests that physical properties of these unsymmetrical complexes can be tuned by a combination of ligands.

We have examined salts of TTF and EDT-TTF (EDT-TTF is ethylenedithiotetrathiafulvalene) with the unsymmetrical complex, since (TTF)[Ni(dmit)$_2$]$_2$ and (EDT-TTF)[Ni(dmit)$_2$] are known to be superconductors.[2,13] Preliminary electrochemical crystallization afforded (TTF)[Ni(dmit)(mnt)] and (EDT-TTF)[Ni(dmit)(mnt)], both of which are metallic down to 20–30 K. Detailed studies are now in progress.

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11 Crystal data for Bu_4N[Ni(dmit)(mnt)] : $C_{23}H_{36}N_3S_7Ni$, F.W.=637.68, monoclinic, space group P2$_1$/a, a=23.922(4), b=11.849(3), c= 11.001(2) Å, β=96.77(2), V= 3096(1) Å^3. Z=4, D_{calc}= 1.37 g cm^{-3}, R =0.045, R_w=0.037, GOF=1.30 for independent 2247 reflections with I ≥ 3σ (I).

Crystal data for Bu_4N[Ni(dddt)(mnt)] : $C_{24}H_{40}N_3S_6Ni$, F.W.= 621.66, monoclinic, space group P2$_1$/n, a=9.007(2), b=22.612(5), c= 15.646(3) Å, β=92.10(2), V= 3184(1) Å^3. Z=4, D_{calc}= 1.33 g cm^{-3}, R =0.053, R_w=0.056, GOF=2.29 for independent 3814 reflections with I ≥ 3σ (I).

Crystal data for Bu_4N[Ni(dddt)(dmit)] : $C_{23}H_{40}NS_9Ni$, F.W.= 677.82, monoclinic, space group P2$_1$/a, a=16.486(4), b=13.397(2), c= 14.782(3) Å, β=93.26(2), V= 3260(1) Å^3. Z=4, D_{calc}= 1.38 g cm^{-3}, R =0.048, R_w=0.053, GOF=1.60 for independent 1752 reflections with I ≥ 3σ (I).

Crystal data for Bu_4N[Ni(dddse)$_2$] : $C_{24}H_{44}NS_4Se_4Ni$, F.W.=849.40, triclinic, space group P$\bar{1}$, a =13.657(4), b =14.078(7), c =9.147(4) Å, α=103.37(4), β=90.65(3), γ=87.10(3)°, V= 1708(1) Å^3. Z=2, D_{calc}= 1.65 g cm^{-3}, R=0.058, R_w=0.062, GOF=2.08 for independent 1633 reflections with I ≥ 3σ (I).

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