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The Synthesis of Transition-Metal Salts of 2-Oxo-1,3-dithiole-4,5-dithiolate (dmio)

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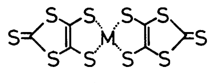
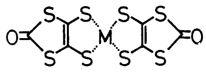
Synopsis. Transition-metal salts of 2-oxo-1,3-dithiole-4,5-dithiolate (dmio) were synthesized in order to develop highly conducting organic complexes. Their redox potentials were measured and compared with those of the related 1,2-dithiolate salts.

Most known organic superconductors are ion-radical salts expressed as D_2X; D stands for TTF derivatives, such as TMTSF, BEDT-TTF, DMET, and MDT-TTF.[1] A few transition metal salts of 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) have also given organic superconductors.[2] Coordination compounds possessing multi-chalcogen atoms in a molecule and a flat coordinated structure are expected to give a variety of new organic conductors and superconductors. Chalcogen–chalcogen networks shorter than a van der Waals distance among ligands are believed to be effective for suppressing the Peierls transition inherent in a low-dimensional solid. Cassoux et al. reported the synthesis of Ni- and Au-salts of 2-oxo-1,3-dithiole-4,5-dithiolate (abbreviated to dmio), starting from the reaction of 1,3,4,5-tetrathiapentalene-2,5-dione (TPD) with sodium methoxide.[3] However, TPD is an expensive reagent, and it sensitizes and produces skin rashes on some individuals. We have succeeded in the alternative synthesis of dmio salts by using as the starting material $Et_4N[Zn(dmit)_2]$, which can be obtained readily on a large scale at a low cost. This method is free from the above problems. The ligand dmio has a structure similar to that of dmit; the thiocarbonyl group of dmit is replaced by a carbonyl group. Thus, dmio can also be expected to give metal complexes possessing interesting electrical properties. Their redox potentials were measured and compared with those of the related 1,2-dithiolate salts previously reported.[4]



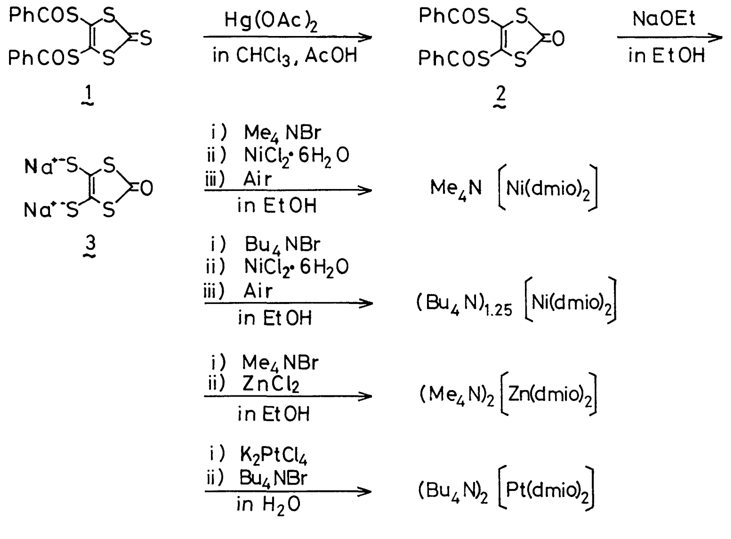
M(dmit)$_2$



M(dmio)$_2$

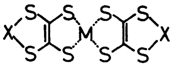
Results and Discussion

Synthesis of dmio Complexes. The route of synthesizing the transition-metal (Ni, Zn, and Pt) salts of dmio is shown in Scheme 1. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (**1**) was obtained by the method in the literature.[5] The conversion of the thiocarbonyl group of **1** to the carbonyl group was accomplished by the use of mercury(II) acetate to give 4,5-bis(benzoylthio)-1,3-dithiol-2-one (**2**). The dithiolate anion **3** was generated in an ethanol solution by treating **2** with sodium ethoxide. It was treated with tetraalkylammonium bromide and then with metal chloride ($NiCl_2 \cdot 6H_2O$ or $ZnCl_2$), followed by air oxidation. In the case of the platinum salt, K_2PtCl_4 was first added to the dithiolate (**3**) solution, and then the solution was treated with tetrabutylammonium bromide. The syntheses of Pd and Cu salts of dmio, using $Na_2PdCl_4 \cdot 3H_2O$ and $CuCl_2 \cdot 2H_2O$ respectively, were unsuccessful. $(Bu_4N)_{1.25}[Ni(dmio)_2]$ was obtained as high-quality needle crystals, which suggests it to be a single phase; several nonstoichiometric 1,2-dithiolate salts have also been found to be single crystals by X-ray



Scheme 1.

Table 1. Redox Potentials of dmio Salts, together with Those of the 1,2-Dithiolate Complexes Previously Reported[4]



Salts	M	X	$E_{1/2}(1)$ V vs. SCE	$E_{1/2}(2)$ V vs. SCE	ΔE V
dmio	Ni	C=O	0.25	−0.24	0.49
dmio	Pt	C=O	0.20	−0.25	0.45
dmit	Ni	C=S	0.22	−0.13	0.35
dmit	Pt	C=S	0.19	−0.13	0.32
dddt[a]	Ni	CH_2CH_2	0.06	−0.69	0.75
dddt[a]	Pt	CH_2CH_2	0.06	−0.65	0.71
dtcdt[b]	Ni	$CH_2CH_2CH_2$	0.16	−0.71	0.87
dtcdt[b]	Pt	$CH_2CH_2CH_2$	0.15	−0.64	0.79
ttcdt[c]	Ni	CH_2SCH_2	0.28	−0.59	0.87
ddt[d]	Ni	CH=CH	0.06	−0.51	0.57
ddt[d]	Pd	CH=CH	0.11	−0.37	0.43

a) 5,6-Dihydro-1,4-dithiin-2,3-dithiolate. b) 1,4-Dithiocyclohepta-2-enyl-2,3-dithiolate. c) 1,4,6-Trithiocyclohepta-2-enyl-2,3-dithiolate. d) 1,4-Dithiin-2,3-dithiolate.

crystallographic work.[6] $(Bu_4N)_{1.25}[Ni(dmio)_2]$ seems to be in a mixed valence between divalent and trivalent states. It is uncertain why $(Bu_4N)_{1.25}[Ni(dmio)_2]$ and $Me_4N[Ni(dmio)_2]$ were obtained in different compositions. The attempted synthesis of conducting dmio salts by an electrochemical method[2] has been unsuccessful thus far.

Redox Potentials of dmio Salts. Table 1 summarizes the redox potentials (vs. SCE) of dmio salts, together with those of the related 1,2-dithiolate salts.[4] The attempted measurement of the redox potentials of $Bu_4N[Zn(dmio)_2]$ was unsuccessful because of the instability of the oxidized and reduced states in the solution. $Bu_4N[M(dmio)_2]$ (M=Ni and Pt) gave similar redox potentials. Table 1 shows that $E_{1/2}(1)$ and $E_{1/2}(2)$ values are not very different when the ligands are the same, but the central metals are different. On the other hand, these values are different when the central metals are the same, but the ligands different. Thus, the $E_{1/2}(1)$ and $E_{1/2}(2)$ values are mainly determined by the kind of ligand. The $E_{1/2}(1)$ and $E_{1/2}(2)$ values of dmio salts are higher and lower respectively than those of the corresponding dmit salts. The difference between $E_{1/2}(1)$ and $E_{1/2}(2)$ ($\Delta E = E_{1/2}(1) - E_{1/2}(2)$) is a measure of an on-site Coulomb repulsion energy between conducting electrons;[7] the electron transport in the solid is believed to be retarded more strongly with the increase in the ΔE values, if the coordinated molecules are stacked one on another in the solid, as is usually found in these types of conducting metal salts.[2,8] The ΔE values of dmio salts were larger than those of the dmit salts; this fact suggests that the former salts have a larger on-site Coulomb repulsion energy than the latter in the conducting state. However, it should be noted that the electrical conductivity is also influenced by the crystal structure of the compound.

Experimental

Cyclic Voltammetries. Cyclic voltammograms of the dmio salts were measured for an acetonitrile solution containing tetrabutylammonium perchlorate as an inert electrolyte with a scan speed of 0.1 V s^{-1}. A saturated calomel electrode was used as a reference electrode, and two platinum plates, as working and counter electrodes respectively.

4,5-Bis(benzoylthio)-1,3-dithiol-2-one (2). 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (**1**) (0.82 g, 2.0 mmol), obtained by a method reported elsewhere,[5] was dissolved in a solvent mixture of chloroform (80 cm^3) and acetic acid (80 cm^3), and then mercury(II) acetate (1.27 g, 4.0 mmol) was added. The solution was stirred for 30 min at room temperature to obtain a white dispersion. The precipitate was then filtered off, and the filtrate was treated with aqueous sodium hydrogencarbonate. The organic layer was separated and then dried by anhydrous sodium sulfate. The solvent was removed, and the residue was recrystallized from a mixed solvent of chloroform and methanol to obtain white needles (0.564 g; 72.3% yield). Mp 115—116 °C. MS *m/z* 390 (M^+). Calcd for $C_{17}H_{10}S_4O_3$: C, 52.28; H, 2.58; S, 32.85%. Found: C, 51.79; H, 2.55; S, 33.13%.

$(Bu_4N)_{1.25}[Ni(dmio)_2]$. To an ethanol solution (5 cm^3) of **2** (0.39 g, 1.0 mmol), we added, under a nitrogen atmosphere, an ethanol solution (20 cm^3) of sodium ethoxide which had previously been prepared by adding sodium metal (0.046 g, 2.0 mmol) to ethanol. The solution was stirred for 20 min, and then an ethanol solution (30 cm^3) of $NiCl_2 \cdot 6H_2O$ (0.16 g) was added. The new mixture was stirred for 15 min and then bubbled with air. A small amount of a precipitate was filtered off, and tetrabutylammonium bromide (0.355 g, 1.1 mmol) was added to the filtrate. The solution was stirred for 4 h at room temperature. The precipitate was collected, washed with isopropyl alcohol, and recrystallized three times from a solvent mixture of acetone and isopropyl alcohol to obtain black needles (0.232 g; 64% yield). Mp 260 °C (decomp). Calcd for $C_{26}H_{45}N_{1.25}NiO_2S_8$: C, 43.22; H, 6.27; N, 2.42; S, 35.50%. Found: C, 43.10; H, 6.50; N, 2.39; S, 34.54%.

$Me_4N[Ni(dmio)_2]$ and $(Me_4N)_2[Zn(dmio)_2]$. Almost the same procedures as those used for the synthesis of $(Bu_4N)_{1.25}[Ni(dmio)_2]$ were adopted. Tetramethylammonium bromide and $NiCl_2 \cdot 6H_2O$ were used for the synthesis of

$Me_4N[Ni(dmio)_2]$ and tetramethylammonium bromide, and $ZnCl_2$, for the synthesis of $(Me_4N)_2[Zn(dmio)_2]$. $Me_4N[Ni(dmio)_2]$: Yield, 16%. Mp>270 °C. Calcd for $C_{10}H_{12}NNiO_2S_8$: C, 24.34; H, 2.45; N, 2.84; S, 51.99%. Found: C, 24.37; H, 2.44; N, 2.75; S, 51.53%. $(Me_4N)_2[Zn(dmio)_2]$: Yield, 72%. Mp 225 °C (decomp). Calcd for $C_{14}H_{24}N_2O_2S_8Zn$: C, 29.27; H, 4.21; N, 4.88; S, 44.67%. Found: C, 29.26; H, 4.21; N, 4.69; S, 43.89%.

$Bu_4N[Pt(dmio)_2]$. An ethanol solution of disodium 2-oxo-1,3-dithiole-4,5-dithiolate (**3**) was obtained by the same method as that described for the synthesis of $(Bu_4N)_{1.25}[Ni(dmio)_2]$; sodium (0.046 g, 2.0 mmol) and **2** (0.39 g, 1.0 mmol) were used. After that, ethanol was hurriedly removed by means of a rotary evaporator, and the residual dithiolate was extracted with water (50 cm^3); the ethanol and aqueous solutions of **3** should not be in contact with air for a long time. To this aqueous solution, we added aqueous solutions of K_2PtCl_4 (0.278 g, 0.67 mmol) and then Bu_4NBr (0.355 g, 1.1 mmol). The solution was stirred for 8 h to obtain a brown precipitate. It was collected and then dissolved in a solvent mixture of acetone and isopropyl alcohol. The subsequent concentration of the solution by the use of a rotary evaporator gave microcrystals of $Bu_4N[Pt(dmio)_2]$. Yield, 51%. Mp 156 °C (decomp). Calcd for $C_{24}H_{36}NO_2PtS_8$: C, 43.85; H, 6.97; N, 2.69; S, 24.65%. Found: C, 43.99; H, 6.99; N, 2.64; S, 24.65%.

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