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Syntheses of New Multi-Sulfur 1,2-Dithiolene Complexes. Ni- and Pd-Complexes of 1,4-Dithiin-2,3-dithiolate

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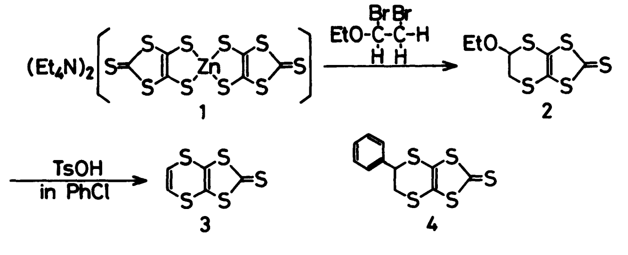
Synopsis. The title dithiolene complexes possessing eight sulfur atoms were synthesized. They are expected to give highly conductive organic salts. The improved synthesis of 4,5-(vinylenedithio)-1,3-dithiole-2-thione is also reported.

Studies on highly conductive organic materials have progressed greatly since the discovery of the low-dimensional metallic behavior of TTF·TCNQ.[1] The one-dimensional metallic system is susceptible to a metal-insulator transition due to Peierls distortion. Therefore, increase in the dimensionality was pursued. One of the most successful results along this line was achieved for BEDT–TTF salts,[2] which have a sulfur–sulfur network in the solid and exhibit two-dimensional electrical properties. BEDT–TTF salts possessing trihalide anions were found to be organic superconductors without applying pressure.[3] TTF-$[Ni(dmit)_2]_2$ was found to be a new type of organic superconductor last year.[4] Cassoux et al. postulated that this material has a three-dimensional property due to the sulfur–sulfur network in the solid.[4] Multi-sulfur 1,2-dithiolene complexes like $M(dmit)_2$ salts[5] have been postulated as promising candidates for highly conductive organic materials.[6] However, reports on the syntheses of such complexes are surprisingly few, and have appeared in recent years.[7] We have synthesized a new type of multi-sulfur dithiolene complexes (Ni- and Pd-complexes of 1,4-dithiin-2,3-dithiolate), which are also expected to give highly conductive organic complexes. The improved synthesis of 4,5-(vinylenedithio)-1,3-dithiole-2-thione, which is a starting material for the above new complexes, is also reported.

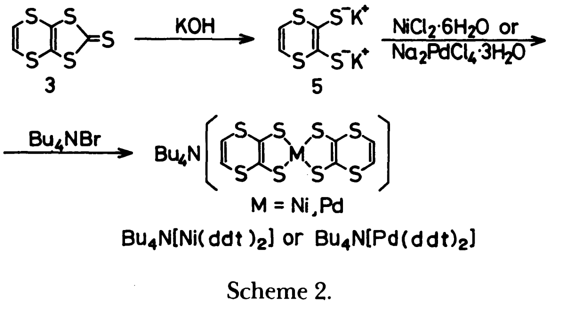
Results and Discussion

Improved Synthesis of 4,5-(Vinylenedithio)-1,3-dithiole-2-thione. 4,5-(Vinylenedithio)-1,3-dithiole-2-thione (**3**) was synthesized as a precursor to bis(vinylenedithio)tetrathiafulvalene (VT).[8] We have now found an improved synthetic method for **3**, and it is shown in Scheme 1. $(Et_4N)_2[Zn(dmit)_2]$ (**1**) was reacted with 1,2-dibromoethyl ethyl ether in acetone at room temperature, and 4,5-(ethoxyethylenedithio)-1,3-dithiole-2-thione (**2**) was obtained. Elimination of ethanol from **2** was achieved by heating the chlorobenzene solution of **2** with anhydrous *p*-toluenesulfonic acid (TsOH) to afford **3**. The currently accepted method[8] has the following drawbacks; (1) it requires expensive 1,2-dichloroethyl ethyl ether in the first step of the reaction; (2) 4,5-(phenylethylenedithio)-1,3-dithiole-2-thione (**4**) was found as a by-product in the second step of the reaction. It was produced by an electrophilic attack of the intermediate carbenium ion (resulting from the elimination of ethanol from **2**) to benzene (solvent).[9] The first drawback was overcome by using 1,2-dibromoethyl ethyl ether which can easily be synthesized on a large scale.[10] The reaction time was shortened from 24 h for the previous method to 10 h for the present method. Moreover, the reaction can be conducted at room temperature, whereas the previous method requires refluxing conditions. The second drawback was overcome by using chlorobenzene as a solvent. The reaction time was also shortened from 24 h for the previous method to 1.5 h for the present method, and the yield of **3** was improved from 23.7% to 32% owing to the absence of the side reaction. This is because the electrophilic attack of the carbenium ion[9] on chlorobenzene is suppressed as a result of the presence of the electron-withdrawing chloride group. Purification of **2** and **3** in the present method was simpler than that of the previous method. Thus, the method shown in Scheme 1 should also be used for the synthesis of VT.

Syntheses of Ni- and Pd-Complexes of 1,4-Dithiin-2,3-dithiolate. The synthetic route of Ni- and Pd-complexes of 1,4-dithiin-2,3-dithiolate is shown in Scheme 2. 4,5-(Vinylenedithio)-1,3-dithiole-2-thione (**3**) was reacted with KOH in ethanol to give a potassium salt (**5**) The salt was then reacted with $NiCl_2·6H_2O$ or $Na_2PdCl_4·3H_2O$; the product was oxidized by air, and subsequently reacted with

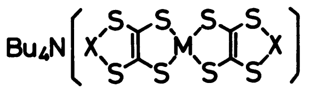


Scheme 1.



Scheme 2.

Table 1. Electrochemical Data for $Bu_4N[Ni(ddt)_2]$ and $Bu_4N[Pd(ddt)_2]$, Together with Those of the 1,2-Dithiolene Complexes Reported



Complex	M	X	E_1 V vs. SCE	E_2 V vs. SCE	$\Delta E(E_1-E_2)$ V
$Ni(ddt)_2$	Ni	-CH=CH-	0.06	−0.51	0.57
$Pd(ddt)_2$	Pd	-CH=CH-	0.11	−0.37	0.43
a	Ni	$-CH_2CH_2-$	0.06	−0.69	0.75
b	Ni	$-CH_2CH_2CH_2-$	0.16	−0.71	0.87
c	Ni	$-CH_2SCH_2-$	0.28	−0.59	0.87
$Ni(dmit)_2$	Ni	C=S	0.22	−0.13	0.35
$Pt(dmit)_2$	Pt	C=S	0.19	−0.13	0.32

tetrabutylammonium bromide to give the new multi-sulfur dithiolene complexes ($Bu_4N[Ni(ddt)_2]$, $Bu_4N[Pd(ddt)_2]$). Here, the ligand portion (1,4-dithiin-2,3-dithiolate) is abbreviated as ddt as shown in Scheme 2. The synthetic approach to $Bu_4N[Pt(ddt)_2]$ by using K_2PtCl_4[7] was unsuccessful. The redox potentials of the dithiolene complexes obtained by the cyclic voltammograms vs. SCE in acetonitrile are shown in Table 1, together with those of the other multi-sulfur 1,2-dithiolene complexes reported[7] for the sake of comparison. The redox waves in the negative potential range were reversible. However, those in the positive potential range were irreversible. In spite of this, E_1 and E_2 of the present complexes were defined as the middle points between the redox peak potentials. The $\Delta E(=E_1-E_2)$ values of the present complexes are 0.43—0.57 V, while those for **a**—**c**, and $M(dmit)_2$ complexes in Table 1 are 0.75—0.87 V and 0.32—0.35 V respectively. This suggests that in the case of the present complexes the intermolecular Coulomb repulsion energy in the conducting state lies between that of $M(dmit)_2$ complexes and other 1,2-dithiolene complexes **a**—**c**.[11]

Experimental

4,5-(Ethoxyethylenedithio)-1,3-dithiole-2-thione (2). To the acetone solution (1.8 L) of $(Et_4N)_2[Zn(dmit)_2]$ (**1**) (25 g) was added dropwise an acetone solution (200 cm^3) of 1,2-dibromoethyl ethyl ether (17 g) for a 6-h period with stirring at room temperature, and the mixture was stirred for another 4 h. The orange powder was filtered off, and the solvent removed to obtain an orange solid. It was extracted with benzene, washed with aqueous sodium hydrogencarbonate, and then with water. After drying over Na_2SO_4, the benzene was evaporated, and the residue recrystallized from a mixed solvent of hexane and chloroform (1 : 1) to give **2** (51% yield based on **1**). Its ^1H NMR, mass spectrum, and melting point were identical to those reported previously.[8] Elemental analyses gave satisfactory results.

4,5-(Vinylenedithio)-1,3-dithiole-2-thione (3). The reaction was conducted under nitrogen atmosphere. *p*-Toluenesulfonic acid monohydrate ($TsOH\cdot H_2O$, 7.09 g) was added to a mixed solvent of chlorobenzene (100 cm^3) and benzene (100 cm^3). Water in the solution was eliminated by azeotropic distillation of benzene. The above solution was heated to 120 °C and chlorobenzene solution (200 cm^3) of **2** (5 g) was added. The mixture was stirred for 1.5 h at 110 °C. After filtering off TsOH, the filtrate was washed with aqueous sodium hydrogencarbonate, and then with water. After drying over Na_2SO_4, the solvent was distilled under vacuum. The black solid was chromatographed on silica gel using hexane and chloroform (4:1) as eluent, and the first reddish yellow fraction gave **3** (32% yield). Its ^1H NMR, mass spectrum, and melting point were identical to those reported previously.[8] Elemental analyses gave satisfactory results.

Preparation of Complexes. $Bu_4N[Ni(ddt)_2]$. An ethanol solution (20 cm^3) of **3** (1 g) and KOH (2 g) was stirred at 40—45 °C for 2 h under nitrogen atmosphere. The potassium salt **5** precipitated was collected in a hurry, washed with ethanol under nitrogen atmosphere, and dried in vacuum. It was then dissolved in methanol (10 cm^3), and a methanol solution (20 cm^3) of $NiCl_2\cdot 6H_2O$ (0.4 g) was added. The solution was stirred for 2 h at room temperature under a nitrogen atmosphere. After air-bubbling for 15 min, tetrabutylammonium bromide (2 g) was added to the solution. The dark purple precipitate was collected, washed with methanol, dissolved into acetone (65 cm^3), and the solution filtered. To the filtrate was added isopropyl alcohol (65 cm^3), the solution was concentrated by rotary evaporator, and $Bu_4N[Ni(ddt)_2]$ was crystallized out. It was collected, washed with methanol and diethyl ether, and dried in vacuum (0.45 g, 73% yield). 135 °C (decomp). Found: C, 43.42; H, 6.08; N, 2.02; S, 38.92%. Calcd for $C_{24}H_{40}NNiS_8$: C, 43.82; H, 6.13; N, 2.13; S, 38.99%. $\lambda_{max}^{CH_3CN}$ ($\log\varepsilon$): 252 nm (4.42); 316 nm (4.40); 564 nm (3.11).

$Bu_4N[Pd(ddt)_2]$. Using $Na_2PdCl_4\cdot 3H_2O$ (0.6 g) instead of $NiCl_2\cdot 6H_2O$ in the above reaction, $Bu_4N[Pd(ddt)_2]$ was obtained as black needles (32% yield). 133 °C (decomp). Found: C, 40.30; H, 5.72; N, 1.86; S, 35.88%. Calcd for $C_{24}H_{40}NPdS_8$: C, 40.86; H, 5.72; N, 1.99; S, 36.33%. $\lambda_{max}^{CH_3CN}$ ($\log\varepsilon$): 258 nm (4.57); 289 nm (4.55); 549 nm (3.16).

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