February, 1986] Bull. Chem. Soc. Jpn., 59, 627—630 (1986)

New Multi-Sulfur 1,2-Dithiolene Complexes. Preparation, Structure, and Electrochemical Properties

Reizo Kato,* Hayao Kobayashi, Akiko Kobayashi,† and Yukiyoshi Sasaki†
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274
†Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113
(Received September 2, 1985)

New multi-sulfur 1,2-dithiolene complexes in which the 1,2-dithiolene moiety is extended by incorporating heterorings have been prepared and characterized by IR spectroscopy, X-ray diffraction method, and cyclic voltammetry. Partial oxidation of these complexes are expected to provide the multi-dimensional molecular conductors. Electrochemical properties of these complexes are compared with those of the dmit-complexes (dmit=2-thioxo-1,3-dithiole-4,5-dithiolate).

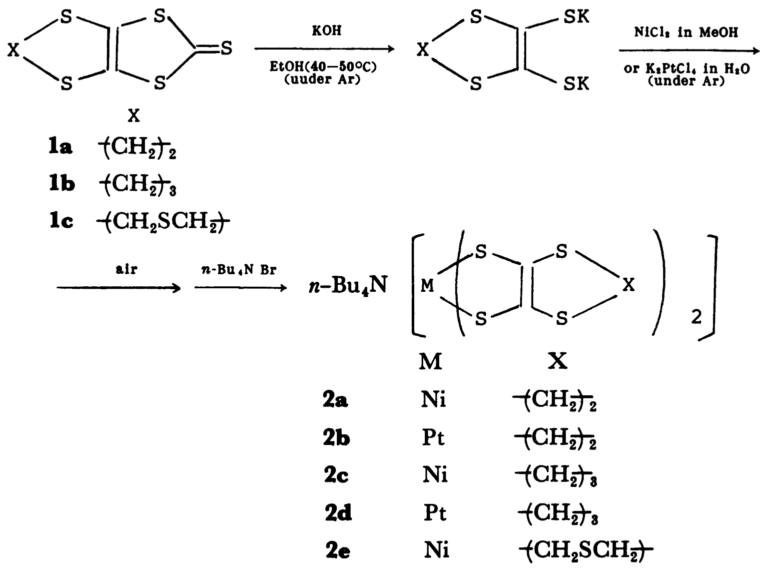
Extensive works have been carried out to synthesize and study a large range of inorganic one-dimensional metals based on the partially oxidized platinum-atom chain (for example, KCP; $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$).[1] Recent discoveries of the molecular conductors containing partially oxidized metal 1,2-dithiolene complexes have extended the range of materials for study.[2] In these compounds, the conduction pathway is formed by overlapping of ligand-centered π-system (predominantly the sulfur orbitals) and not principally of the metal orbitals. The dmit-complex (dmit=2-thioxo-1,3-dithiole-4,5-dithiolate), among others, has shown a special property, the multi-dimensional intermolecular S···S interaction, which originates from the 1,3-dithiole-2-thione rings incorporated to the 1,2-dithiolene moiety.[2] The dimensionality of the electronic structure is closely related to the stabilization of the metallic state. Although 1,2-dithiolene complexes extended by incorporating heterorings containing chalcogen atoms should be of special interest in view of the multi-dimensional molecular conductor, there was no well-characterized example except the dmit-complex and its isomer, the dmt-complex (dmt=3-thioxo-3*H*-1,2-dithiole-4,5-dithiolate).[3] In this paper, the preparation of new multi-sulfur 1,2-dithiolene ligands and their complex formation with nickel and platinum are reported.

Results and Discussion

Synthetic process is shown in the Scheme. For the preparation of the ligands, hydrolysis of 1,3-dithiole-2-thiones with base was used.[4] Hydrolysis of the 1,3-dithiole-2-thiones **1a—c** by hot ethanolic potassium hydroxide under argon provided air-sensitive dipotassium salts which were subsequently treated with $NiCl_2$ in methanol or K_2PtCl_4 in water at room temperature. After air-oxidation, addition of n-Bu_4NBr resulted in the precipitation of monoanionic species **2a—e**.

Infrared spectra (KBr disk, Table 1) of these complexes show the absorptions characteristic of the bis(1,2-dithiolene) metal complexes.[5]

The structure of the $Ni(C_4H_4S_5)_2^-$ anion is shown in Fig. 1. The Ni–S distances are comparable with those found in other monoanionic nickel dithiolene complexes.[5,6] The C–S bond distances in the dithiolene group vary from 1.707 to 1.728 Å and are thus close



Scheme

Table 1. Infrared Spectra (cm^{-1}) of **2a**—**e**

	C=C	C=S	C—S	M—S
2a	1360 1280	·····	855	440
2b	1350 1280	·····	845	435
2c	1380 1270	990	860	460 395
2d	1360 1270	990	860	450
2e	1380 1210	·····	845	450

Table 2. Electrochemical Data of **2a**—**e** and M(dmit)$_2^-$ (M=Ni, Pt)[a]

Complex	E_1	E_2	$\Delta E(=E_1-E_2)$
2a	+0.06[b]	−0.69	0.75
2b	+0.06	−0.65	0.71
2c	+0.16	−0.71	0.87
2d	+0.15	−0.64	0.79
2e	+0.28[c]	−0.59	0.87
Ni(dmit)$_2^-$	+0.22[c]	−0.13	0.35
Pt(dmit)$_2^-$	+0.19[c]	−0.13	0.32

a) Measured at a glassy carbon electrode in CH_3CN, 0.1 mol dm^{-3} TBAP (volts vs. SCE); Temperature, 18 °C. b) Quasi-reversible. c) Irreversible; E_1 values were determined by differential pulse polarography, extrapolating the scan rate to 0 mV s^{-1}.

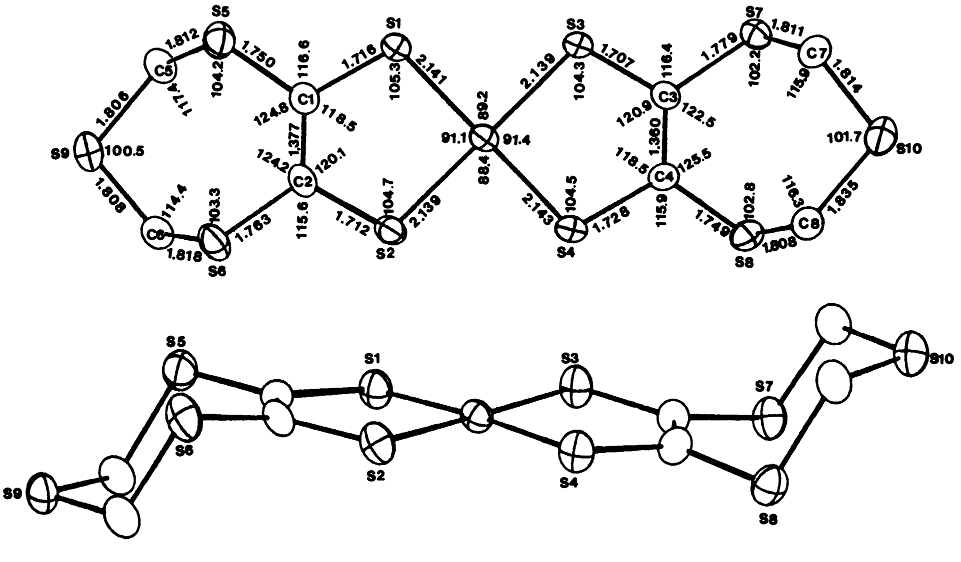


Fig. 1. Structure of Ni$(C_4H_4S_5)_2^-$. The standard deviations of the bond lengths and angles are 0.003—0.014 Å and 0.1—0.6° respectively.

Table 3. Final Atomic Coordinates (×10^4) with Estimated Standard Deviations in Parentheses for *n*-Bu $_4N[Ni(C_4H_4S_5)_2]$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	2000(1)	1345(1)	3427(1)	C(8)	481(8)	−1846(5)	1978(5)
S(1)	2893(2)	2539(1)	3523(1)	N	6749(6)	409(4)	3246(4)
S(2)	2175(2)	1506(1)	4531(1)	C(9)	6750(8)	1288(5)	3559(5)
S(3)	1851(2)	1168(1)	2331(1)	C(10)	5529(8)	1781(6)	3066(5)
S(4)	1007(2)	190(1)	3311(1)	C(11)	5735(10)	2739(7)	3305(7)
S(5)	4185(2)	3842(2)	4708(1)	C(12)	6663(8)	464(6)	2451(4)
S(6)	3534(3)	2638(2)	5850(1)	C(13)	7602(9)	1083(6)	2424(5)
S(7)	414(2)	50(1)	995(1)	C(14)	7417(10)	987(7)	1620(5)
S(8)	−453(2)	−1028(2)	2078(1)	C(15)	5632(8)	−134(6)	3100(5)
S(9)	3369(2)	4570(2)	5819(1)	C(16)	5437(9)	−224(6)	3808(5)
S(10)	433(2)	−1899(2)	1053(1)	C(17)	4282(9)	−782(6)	3555(6)
C(1)	3335(7)	2896(5)	4427(4)	C(18)	7974(7)	2(5)	3837(4)
C(2)	3032(7)	2415(5)	4883(4)	C(19)	8236(8)	−866(6)	3625(5)
C(3)	932(7)	291(5)	1969(4)	C(20)	9544(8)	−1143(6)	4303(5)
C(4)	552(7)	−156(5)	2396(4)	C(21)	4090(10)	−965(7)	4250(6)
C(5)	3206(8)	4566(6)	4876(5)	C(22)	8160(10)	1627(7)	1447(6)
C(6)	2634(8)	3572(6)	5802(5)	C(23)	6282(11)	2863(7)	4148(7)
C(7)	1233(8)	−929(5)	1066(5)	C(24)	9956(11)	−1987(7)	4143(6)

C(9)-C(24) are carbon atoms in tetrabutylammonium cation:

```
                                    C(15)-C(16)-C(17)-C(21)
                                    |
C(24)-C(20)-C(19)-C(18)-N-C(12)-C(13)-C(14)-C(22)
                                    |
                                    C(9)-C(10)-C(11)-C(23)
```

to the value 1.71 Å reported for C–S double bonds.[7] The "ethylenic" bond distances 1.360 and 1.377 Å are intermediate between double and single bond values. The external seven-membered heterorings take chair conformation, and C(5)–C(8), S(9), and S(10) largely deviate from the plane containing the rest of the anion. The C–S bond distances between the dithiolene ring and the external heteroring are slightly shorter than S(sp2)–C(sp2) distance 1.77 Å, and the remaining C–S bonds are single bonds since the usual value for a single bond is 1.81 Å.[7]

Electrochemical data of five new complexes **2a**—**e** and $(n\text{-Bu})_4N[M(dmit)_2]$ (M=Ni, Pt) are shown in Table 2. These complexes are reduced in one-electron step. This step is electrochemically reversible for all complexes. The reduction potential (E_2) values of the new complexes **2a**—**e** are comparable to those of alkyl-substituted arene-1,2-dithiolene complexes.[5] Fairly negative E_2 values explain the susceptibility to air-oxidation. The E_2 values of the dmit-complexes are less negative than those of **2a**—**e**, comparable to that of $Ni(S_2C_2(CF_3)_2)_2^-$.[5] In the 1,2-dithiolene complexes, the E_2 value is less negative when the substituted group is an electron-withdrawing group.[5] The above results suggest the electron-withdrawing property of the thioxo group in the dmit-complex. In all cases, the effect of the metal ion on the E_2 value is rather small.

In oxidation the cyclic voltammograms of **2b**, **c**, and **d** show a reversible oxidation to the neutral species at potentials (E_1) in the range of 0.06—0.28 V. At slow sweep rates (50 mV s^{-1}) the oxidation of **2a** is irreversible, at faster sweep rates becomes reversible (Fig. 2). At all sweep rates (50—200 mV s^{-1}), the oxidation of **2e** and $M(dmit)_2^-$ is irreversible (Fig. 2).

The $\Delta E(=E_1-E_2)$ values of the dmit-complex are ca. 0.3 V, while those for other 1,2-dithiolene complexes including **2a**—**e** are larger than 0.7 V.[5] This suggests that in the case of the dmit-complex the intermolecular Coulomb repulsion energy in the conducting state is smaller than that in other 1,2-dithiolene complexes.[8]

The ability of **2a**—**e** to form the conducting partially oxidized salt is suggested by the fact that the E_1 and E_2 values of **2a**—**e** are close to those of the unsubstituted 1,2-dithiolene complex $Ni(C_2H_2S_2)_2$ (E_1=0.09, E_2=−0.95 V vs. SCE) which provides the conducting compounds with the organic donors (TTF; Tetrathiafulvalene and TTT; Tetrathiotetracene(5, 6: 11,12-bis(epithio)naphthacene)).[9]

Experimental

1,3-Dithiole-2-thiones **1a**—**c** were synthesized from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione and corresponding dibromoalkanes or bis(chloromethyl) sulfide.[10]

Preparation of Complexes. **$n\text{-}Bu_4N[Ni(C_4H_4S_4)_2]$ 2a**: A mixture of 20 ml of ethanol, 2.0 g (36 mmol) of potassium hydroxide, and 1.0 g (4.5 mmol) of 2,5,7,9-tetrathia-

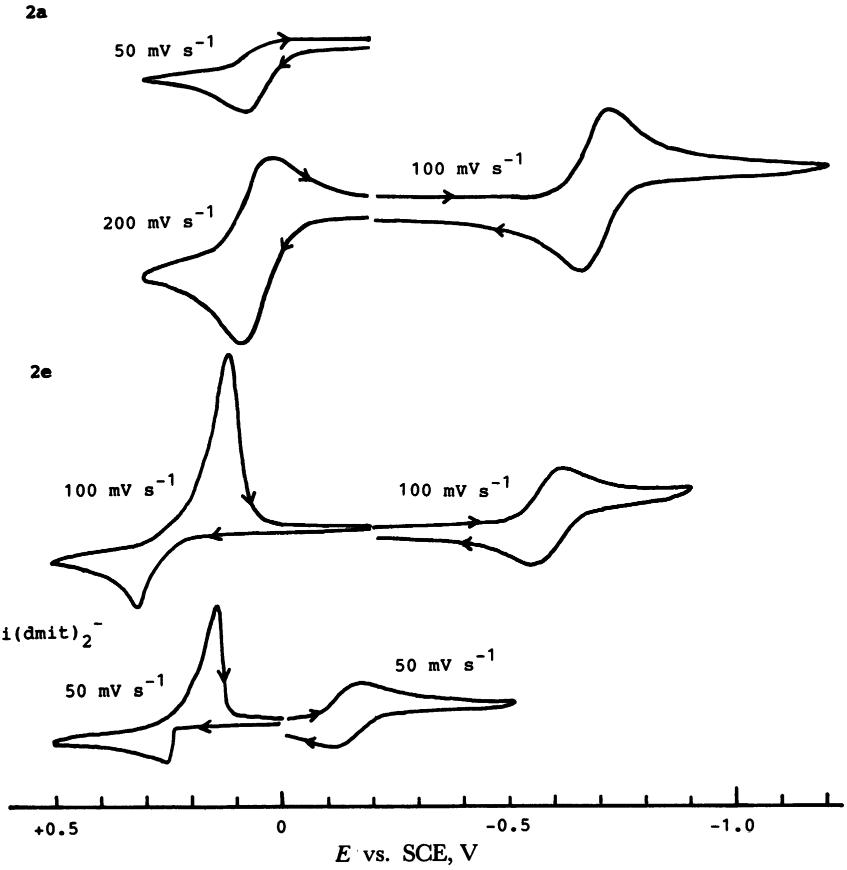


Fig. 2. Cyclic voltammograms of **2a**, **2e**, and $Ni(dmit)_2^-$.

bicyclo[4.3.0]non-1(6)-ene-8-thione **1a** was stirred for 1.5 h at 40—45 °C (water bath temperature) under argon. The resulting pale yellow micro crystals of the dipotassium salt were isolated by filtration, washed with a 4 ml portion of ethanol twice under argon, and dried in vacuo. The salt was dissolved in 20 ml of methanol and treated with 0.3 g (1.3 mmol) of $NiCl_2 \cdot 6H_2O$ in 20 ml of methanol. Stirring was continued overnight at room temperature under argon. Air was bubbled through the reaction mixture for 15 min. After filtration (yellow residue), to the dark green filtrate was added 2.0 g of tetrabutylammonium bromide. The dark green precipitate was isolated by filtration with suction, washed with methanol, and air-dried at room temperature. The crude complex was dissolved in 65 ml of acetone. After filtration, to the filtrate was added 65 ml of 2-propanol. Concentration of the solution with a rotary evaporator gave dark green crystals of **2a**, which were isolated by filtration, washed with methanol and ether, and dried in vacuo. Yield 0.45 g (54% based on Ni). Found: C, 43.39; H,7.13; N,2.00; S, 37.36%. Calcd for $C_{24}H_{44}NS_8Ni$: C, 43.55; H,6.70; N, 2.12; S, 38.76%.

Other complexes (**2b**, **2c**, **2d** and **2e**) were prepared analogously.

***n*-Bu$_4$N[Pt(C$_4$H$_4$S$_4$)$_2$] 2b:** Yield 26% based on Pt. Found: C, 35.88; H, 5.83; N, 1.67; S, 31.91%. Calcd for $C_{24}H_{44}NS_8Pt$: C, 36.11; H, 5.56; N, 1.67; S, 31.91%.

***n*-Bu$_4$N[Ni(C$_5$H$_6$S$_4$)$_2$] 2c:** Yield 34% based on Ni. Found: C, 44.98; H, 7.60; N, 1.90; S, 36.37%. Calcd for $C_{26}H_{48}NS_8Ni$: C, 45.27; H, 7.01; N, 2.03; S, 37.18%.

***n*-Bu$_4$N[Pt(C$_5$H$_6$S$_4$)$_2$] 2d:** Yield 4% based on Pt. Found: C, 37.57; H, 6.23; N, 1.62; S, 31.07%. Calcd for $C_{25}H_{48}NS_8Pt$: C, 37.79; H, 5.85; N, 1.70; S, 31.04%.

***n*-Bu$_4$N[Ni(C$_4$H$_4$S$_5$)$_2$] 2e:** Yield 46% based on Ni. Found: C, 39.72; H, 6.28; N, 1.69; S, 42.76%. Calcd for $C_{24}H_{44}NS_{10}Ni$: C, 39.71; H, 6.11; N, 1.93; S, 44.16%. To date, attempts to prepare *n*-$Bu_4N[Pt(C_4H_4S_5)_2]$ have been unsuccessful.

Infrared Spectra. Spectra of compounds pressed in KBr disks were recorded on a model 260-30 Hitachi infrared spectrophotometer over the range 400—4000 cm^{-1}.

Structural Study. The crystal of **2e** has been investigated by X-ray diffraction. The crystal data are: monoclinic, space group $P2_1/c$, a=12.374(3), b=15.748(4), c=20.127(5) Å, β=119.54(2)°, V=3412.2 Å^3, Z=4. A total of 4501 independent reflections ($2\theta \leq 60°$, $|F_o|>3\sigma(|F_o|)$) were recorded on a Rigaku automatic four-circle diffractometer using Mo$K\alpha$ radiation. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. The structure was solved by the direct method and refined by the block-diagonal least-squares method on a PANAFACOM U-1300 computer by the use of a local version of the UNICS-III programs.[11] Scattering factors were taken from Ref. 12. The weighting scheme, $w=1/(\sigma(F_o)^2+0.0001|F_o|^2)$ was employed. The final discrepancy factors were $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.067$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.074$. The final atomic coordinates are listed in Table 3. A list of the final F_o-F_c table, and anisotropic temperature factors are deposited as Document No.8618 at the office of Bull. Chem. Soc. Jpn.

Electrochemical Study. Electrochemical measurements were performed with a YANACO polarographic analyzer P-1100 at 18 °C. Tetrabutylammonium perchlorate was used as a supporting electrolyte. A glassy carbon was employed as a working electrode. The counter electrode was a platinum wire which was immersed directly in the electrolysis solution. An aqueous saturated calomel electrode (SCE) was separated from the test solution by a fine-porosity glass frit and a salt bridge filled with the solution under study. All potentials are reported vs. an aqueous SCE.

References

1) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976); A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, **9**, 429 (1980).

2) A. E. Underhill and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, **1981**, 67; L. Valade, J. Bousseau, A. Gleizes, and P. Cassoux, ibid., **1983**, 110; R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, and H. Kobayashi, *Chem. Lett.*, **1984**, 1; P. Cassoux, L. Valade, M. Bousseau, J-P. Legros, M. Garbauskas, and L. Interrante, *Mol. Cryst. Liq. Cryst.*, **120**, 377 (1985); R. Kato, H. Kobayashi, A. Kobayashi, and Y. Sasaki, *Chem. Lett.*, **1985**, 131; H. Kobayashi, R. Kato, A. Kobayashi, and Y. Sasaki, ibid., **1985**, 191, 535.

3) G. Steimecke, J. Sieler, R. Kirmse, W. Dietzsch, and E. Hoyer, *Phosphorus and Sulfur*, **12**, 237 (1982).

4) M. Mizuno, M. P. Cava, and A. F. Garito, *J. Org. Chem.*, **41**, 1484 (1976).

5) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968); R. P. Burns, and C. A. Mcauliffe, *Adv. Inorg. Radiochem.*, **22**, 303 (1979).

6) A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **50**, 2650 (1977).

7) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham (1962), Vol. III, p. 276.

8) A. W. Addison, J. P. Barnier, V. Gujval, Y. Hoyano, S. Huizinga, and L. Weiler, "Molecular Metals," ed by W. E. Hatfield, Plenum Press, New York (1979), p. 15.

9) L. V. Interrante, K. W. Browall, H. R. Hart, Jr., I. S. Jacobs, G. D. Watkins, and S. H. Wee, *J. Am. Chem. Soc.*, **97**, 889 (1975); J. S. Kasper, L. V. Interrante, and C. A. Secaur, ibid., **97**, 890 (1975); J. W. Bray, H. R. Hart, Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper, P. A. Piacente, and G. D. Watkins, *Phys. Rev. B*, **16**, 6359 (1977).

10) G. Steimecke, H. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus and Sulfur*, **7**, 49 (1979).

11) T. Sakurai and K. Kobayashi, *Rep. Inst. Phy. Chem. Res.*, **55**, 69 (1979).

12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.