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SYNTHESIS OF NEW DITHIOLENE-DERIVATIVE METAL COMPLEXES

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We will report on the synthesis of some new metal-dithiolene-derivative complexes which are considered to be promising components for new organic conductors. They include 1) unsymmetrical metal-dithiolene complexes with terminal cyano groups and 2) metal-complexes with radialene-type ligands. The group 1) complexes are designed for extended intermolecular interaction via the CN groups. In the course of this study a double-decker type Ni-complex has been synthesized and structurally characterized. The group 2) complexes are designed with the expectation that the π-conjugation on a molecule expanding towards two different directions should enable two-dimensional molecular overlapping modes. Spectroscopic data and X-ray structural study have revealed that they have well-developed conjugated π-electronic systems over the whole molecule and thus good planarity.

Keywords: metal-ditholene complexes; X-ray structural study; intermolecular interaction

INTRODUCTION

Since the discovery of superconductivity in TTF[Ni(dmit)$_2$]$_2$ [1] (dmit^{2-} = 1,3-dithiol-2-thione-4,5-dithiolate; TTF = tetrathiafulvalene), the metal-dithiolene complexes are one of the most intensively studied acceptor molecules aimed for the molecular metals and superconductors [2]. Still, the common disadvantage often observed in these metal-dithiolene complexes is the one-dimensionality of the conduction path and thus metal instability in spite of their multi-dimensional chalcogen network (intermolecular S-S short contacts). Because most of unusual and interesting properties often require conduction electrons at low temperature, the chemical modifications which would lead to a stable metallic electronic structure are of general and crucial importance. One of the most effective ways for

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producing a stable metallic π-band in a molecular conductor is to utilize the molecule with extended π-orbitals and arrange them in such a way one molecule overlaps with two or more of the neighboring ones [3]. Another approach might be to utilize an unsymmetrical complex molecule with a chalcogen-donor-like ligand instead of the symmetrical dithiolene complexes [4,5]. This would avoid the cancellation of multi-dimensional intermolecular interaction via S-S short contacts. Herein are reported the results of our synthetic study along the above-mentioned two strategies of some new Ni-complex molecules.

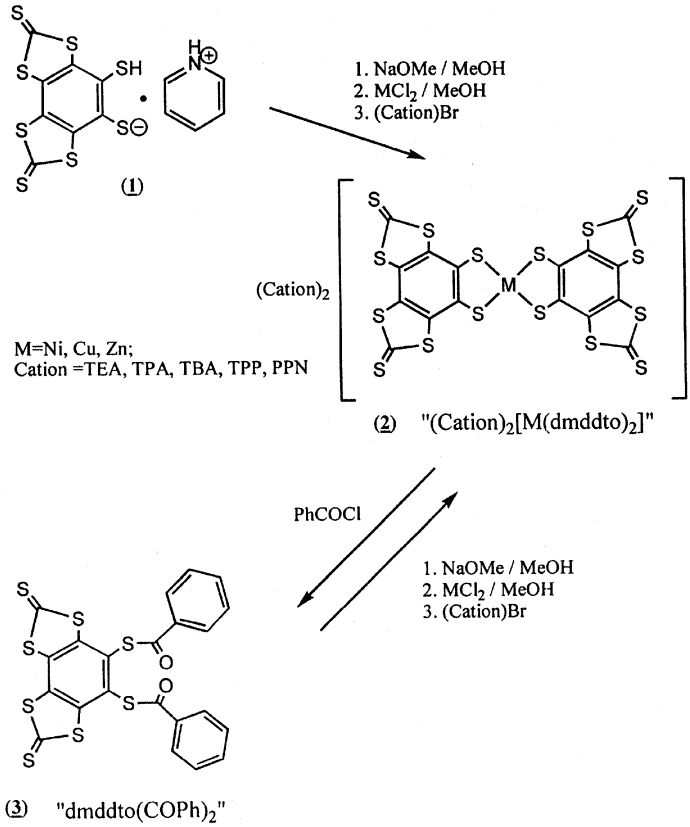
EXPERIMENTAL

The synthetic route of $\{(C_4H_9)_4N\}_2[Ni(dmddto)_2]$ (dmddto = $C_8S_8^{2-}$ and the related compounds is shown in Scheme 1. The starting material, benezenehexathiol [6], and 7-mercapto-2,5-dithioxobenzo[1,2-*d*:3,4-*d''*]bis[1,3]-dithiole-8-thiolate pyridinium salt (**1**) [7] were prepared by the reported methods. Each compound was identified by elemental analysis and IR spectroscopy: the results of selected compounds are tabulated in Table 1. The synthesis of [Ni(dmit)(*i*-mnt)] (*i*-mnt^{2-} = 1,1-dicyanoethylene-2,2-dithiolate) and the related complexes are reported elsewhere [5].

(Cation)$_2$[M(dmddto)$_2$] (2)

In a 300 ml two-necked round-bottom flask equipped with a dropping funnel and a three-way valve, the pyridinium salt (**1**) (867.5 mg; 2 mmole) was added to a methanol solution of sodium methoxide prepared from sodium metal (150 mg; 6.5 mmole) and deaerated methanol (70 ml) and dissolved with stirring under a nitrogen atmosphere at room temperature. The solution of $ZnCl_2$ (136.3 mg; 1 mmole) in methanol (20 ml) and aqueous ammonia (28%, 3 ml) was added dropwise while the solution turned orange from red. After 1 h of stirring the solution of 2 mmole of tetrabutylammonium bromide (TBA·Br 645 mg) or tetraphenylphosphonium bromide (TPP·Br 839 mg) in 50 ml methanol was slowly added. The precipitates were filtered off with suction, washed with methanol and ether, and dried *in vacuo*. The crude products were recrystallized by dissolving them in CH_2Cl_2 and diluted with ether, then chilled the solution at −30°C. The TPP salt; yield, 1.15 g (77.1%). The TBA salt; yield, 0.98 g (78.4%).

The corresponding Ni(II)- and Cu(II)-complexes were prepared by the similar procedure using $NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ and the halides of tetraethylammonium (TEA), tetrapropylammonium (TPA), TBA, TPP or bis(triphenylphosphoranylidene)ammonium (PPN). The yield was 70–80%



SCHEME 1

depending on the cation and the metal used. All the metal-complexes were obtained as analytically pure compounds.

dmddto(COPh)$_2$ (3)

$(TBA)_2[Zn(dmddto)_2]$ (1.26 g; 1 mmole) was dissolved in an acetone (70 ml) and CH_2Cl_2 (30 ml) mixed solvent. Benzoyl chloride (400 mg; 2.84 mmol) was added dropwise and the reaction mixture was refluxed for an hour. The solution was evaporated to half in its volume, and chilled in an ice bath for 2 h. The precipitates were filtered off with suction, washed with methanol and ether, and dried *in vacuo*. The recrystallization was carried out by pouring methanol (300 ml) into the hot $CHCl_3$ (65 ml) solution of the crude product. Yield 1.12 g (98%); elemental analysis for $C_{22}H_{10}O_2S_8$,

TABLE 1 Identification Data of Selected Compounds

Compounds	Elemental Analysis (%)[b]	IR (ν/cm^{-1}, KBr)
(**1**)	C 36.04/36.59, H 1.63/1.71, N 3.23/3.54, S 59.09/58.48	1655, 1631, 1535, 1483, 1332, 1305, 1280, 1196, 1164, 1125, 1062(C=S), 899, 865, 748, 678, 606, 504
(**2**) (Zn/TPP)[a]	C 53.04/52.44, H 2.78/2.64, N 0.00/0.00, S 35.40/35.92	1586, 1558, 1483, 1436, 1336, 1313, 1262, 1162, 1108, 1056(C=S), 997, 859, 752, 723, 688, 527
(**2**) (Zn/TBA)[a]	C 45.92/45.07, H 5.78/5.67, N 2.23/2.19, S 40.86/41.19	2959, 2872, 1558, 1480, 1379, 1347, 1295, 1263, 1163, 1123, 1061(C=S), 890, 860, 739, 506
(**2**) (Zn/PPN)[a]	C 57.41/55.77, H 3.28/3.57, N 1.52/1.51, S 27.87/28.14	3055, 1629, 1588, 1475, 1438, 1300, 1162, 1116, 1058(C=S), 998, 902, 745, 724, 724, 692, 547, 534, 501

[a] Metal/Cation. For abbreviations of the cations, see text.
[b] calc/found.

calculated (%); C 50.22, H 2.48, N 0.00, S 39.43: found (%); C 51.75, H 2.56, N 0.00, S 38.20.

$(TBA)_2[Ni(dmddto)_2]$ from $dmddto(COPh)_2$ (3)

In a 300 ml two-necked round-bottom flask equipped with a dropping funnel and a three-way valve, $dmddto(COPh)_2$ (**3**) (1.12 g; 2 mmole) was treated with sodium methoxide in methanol prepared from sodium (200 mg; 8.7 mmole) and deaerated methanol (70 ml) under a nitrogen atmosphere. The solution of $NiCl_2{\cdot}6H_2O$ (237.7 mg; 1 mmole) in methanol (20 ml) was added dropwise while the color changed to black from red. After 1 h stirring at room temperature, the solution of tetrabutylammonium bromide (TBA·Br 645 mg; 2 mmole) in 50 ml methanol was slowly added. The precipitates were filtered off with suction, washed with methanol and ether, and dried *in vacuo*. Yield, 1.03 g (82.3%); elemental analysis for $C_{48}H_{72}N_2S_{16}Ni$, calculated (%); C 46.17, H 5.81, N 2.24, S 41.08: found (%); C 45.29, H 5.77, N 2.20, S 41.87.

RESULTS AND DISCUSSION

The reactivity and spectroscopic properties indicated that the dithiolate anion $dmddto^{2-}$ behaves similarly as other known dithiolate anions. Yet the

new Ni-complex $[Ni(dmddto)_2]^{2-}$ is characterized with its well-delocalized π-orbitals on the whole ligands. Such conclusion is supported by the molecular planarity and the strong inclination to overlap the ligands between the neighboring molecules in the crystal. The molecular structure is consisitent with the result of the molecular orbital calculation. In contrast to $(TBA)_2[Ni(dmit)_2]$ [8], $(TBA)_2[Ni(dmddto)_2]$ has a one-dimensional (1D) chain along the molecular "diagonal" direction (Figure 1) with partial overlap of the ligands (interplanar distance = 3.49 Å). With appropriate oxidants $[Ni(dmddto)_2]^{2-}$ was oxidized to yield charge transfer salts as black powder with semiconducting properties (e.g. for $(TPP)_{1.3}[Ni(dmddto)_2]$, $\sigma_{RT} \sim 3 \times 10^{-3}\,S\,cm^{-1}$, $E_a = 0.13\,eV$). Further study on other related charge transfer salts is now under way.

In our previous work [4] on $(TBA)_n[Ni(C_8H_4S_8)(CN)_2]$ (n = 1,2), we at first expected intermolecular interactions via the CN groups in the solid state in addition to the well-known S-S network. However, the complexes have turned out to have markedly different molecular orbitals from the structurally-related chalcogen donor molecules and easily decomposed when they were oxidized beyond the mono-radical species (n = 1). Recently a double-decker type new Ni-complex molecule $[Ni(dmit)(i\text{-mnt})]_2^{2-}$ has been synthesized (Figure 2), which can be oxidized without

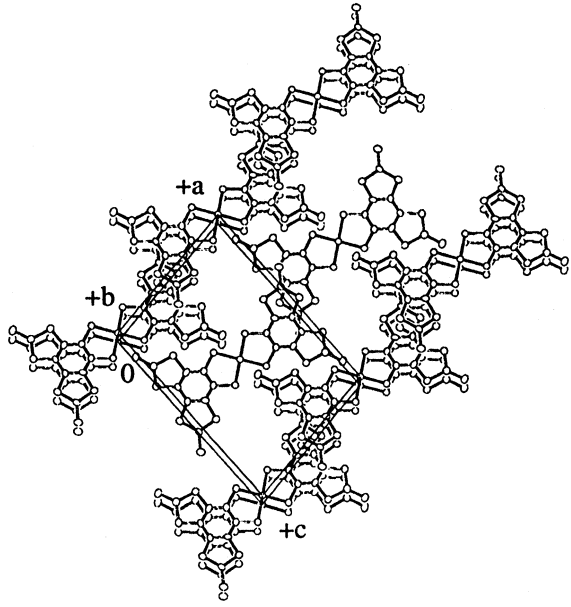


FIGURE 1 Molecular arrangement of the Ni-complex in $(TBA)_2[Ni(dmddto)_2]$.

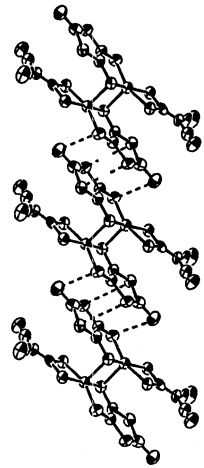


FIGURE 2 1D chain of $[Ni(dmit)(i\text{-mnt})]_2^{2-}$ in $(TBA)_2[Ni(dmit)(i\text{-mnt})]_2$.

decomposition and can interact through the CN group as well as peripheral sulfur atoms. This Ni-complex crystallizes with some chalcogen donor radical cations to yield semiconducting solids (e.g. $\rho_{RT} = 10^2\,\Omega$ cm, Ea = 0.13 eV for $(C_{10}H_8S_8)_2[Ni(dmit)(i\text{-mnt})]_2$). The X-ray structural study on these salts revealed many intermolecular short S-S and CN-S was observed. Therefore one could expect that highly conducting solids with stable metallic bands would be obtained from this kind of salts in due course.

What is more this complex molecule could induce a direct interaction between conduction and localized electrons through coordination bonds (CN—M) if a transition metal cation and cyano-ligands are located in a favorable way in the crystal. Such study is also under way.

REFERENCES

[1] Brossard, L., Ribault, M., Valade, L., & Cassoux, P. (1986). *Physica B&C (Amsterdam)*, *143*, 378.
[2] For example, see Cassoux, P., Valade, L., Kobayashi, H., Kobayashi, A., Clark, R. A., & Underhill, A. E. (1991). *Coord. Chem. Rev.*, *110*, 115.
[3] Kato, R., Kobayashi, H., Kim, H., Kobayashi, A., Sasaki, Y., Mori, T., & Inokuchi, H. (1988). *Chem. Lett.*, *865*; Inabe, T., & Maruyama, Y. (1990). *Bull. Chem. Soc. Jpn.*, *63*, 2273.
[4] Naito, T., Kobayashi, N., & Inabe, T. (1998). *Chem. Lett.*, *8*, 723; Naito, T., Kobayashi, N., Inabe, T. (1999). *Synth. Met.*, *102*, 1687.
[5] Kobayashi, N., Naito, T., & Inabe, T. Pacifichem 2000. Symposium #13.
[6] Richter, A. M., Engels, V. Beye, N., & Fanghänel, E. (1989). *Z. Chem.*, *29*, 444.
[7] Richter, A. M., Beye, N., & Fanghänel, E. (1990). *Synthesis*, 1149.
[8] Lindqvist, O., Sjolin, L., Sieler, J., Steimecke, G., & Hoyer, E. (1979). *Acta Chim. Scand. A*, *33*, 445.