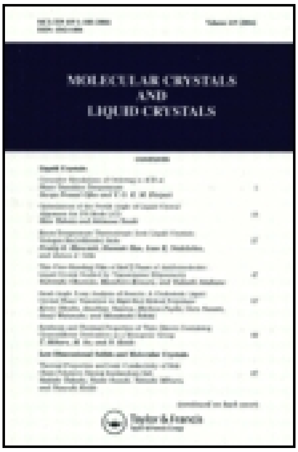

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Novel Ni-Dithiolene Complexes toward Lattice Architecture

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A novel dimerized Ni-dithiolene complex, $(n\text{-}Bu_4N)_2[Ni(dmit)(i\text{-}mnt)]_2$ (**1**), was synthesized and characterized by X-ray structure analysis. In this complex two [Ni(dmit)(*i*-mnt)] units were mutually connected by two long axial Ni–S bonds. The single crystals of TTF, BEDT-TTF and EDT-TTF salts with $[Ni(dmit)(i\text{-}mnt)]_2^{2-}$ were prepared by electrocrystallization and characterized by X-ray analyses. The Ni–S bonds of each dimer were also retained in these salts. Each salt exhibited semiconducting behavior.

Keywords Electrocrystallization; Metal-dithiolene complexes; X-ray structural determination

INTRODUCTION

To control the physical properties of the molecular crystals, construction of the aimed molecular arrangement is required. Multi-dimensional electronic structure of conducting materials is important for maintaining the metallic property down to low temperature. To design the crystal lattice for the multi–dimensional intermolecular interaction, it is useful to utilize intermolecular contacts such as hydrogen–bonding and sulfur–sulfur contacts.

On the other hand, metal-dithiolate complexes have received much attention in the solid state physics. Many salts of this system show metallic conductivity and several salts of $M(dmit)_2$ (dmit: 4,5-dimercapto-1,3-dithiole-2-thione, M= Ni, Pd) become superconductors[1]. However, in many cases, the metal complexes of mnt (mnt: malononitrile dithiolate) or dmit tend to form one–dimensional (1–D) columnar structures. We tried to develop the novel metal-dithiolate complexes with cyano groups, which would interact with neighboring molecules and counter ions [2], for it is known that the intermolecular contacts between sulfur atoms and cyano groups stabilize the crystal lattice [3]. We report here the synthesis of a novel Ni–dithiolate complex (n-Bu$_4$N)$_2$[Ni(dmit)(i-mnt)]$_2$ (**1**) (i-mnt: 1,1-dicyanoethylene-2,2-dithiolate), and the crystallization of this complex with organic donor molecules.

EXPERIMENTAL

(n-Bu$_4$N)[Ni(mnt)$_2$][4], (n-Bu$_4$N)[Ni(i-mnt)$_2$][5], and (n-Bu$_4$N)[Ni(dmit)$_2$][6] were prepared by the reported methods. Each compound was identified by IR spectroscopy and elemental analysis. (n-Bu$_4$N)[Ni(dmit)(mnt)] was prepared by the method reported by R. Kato, et al.,[7] and the purification by careful recrystallization gave the product as the single crystalline form. X-ray analyses of (n-Bu$_4$N)$_2$[Ni(dmit)(i-mnt)]$_2$ (**1**), (TTF)$_2$[Ni(dmit)(i-mnt)]$_2$ (**2**), (BEDT-TTF)$_2$[Ni(dmit)(i-mnt)]$_2$ (**3**), (EDT-TTF)$_2$[Ni(dmit)(i-mnt)]$_2$ (**4**), and (n-Bu$_4$N)$_{0.25}$[Ni(dmit)$_2$]•CH$_3$CN (**5**) were performed by a RIGAKU R–AXIS RAPID diffractometer, and their cell parameters are summarized in TABLE 1.

(n-Bu$_4$N)$_2$[Ni(dmit)(i-mnt)]$_2$ (**1**)

(n-Bu$_4$N)[Ni(i-mnt)$_2$] (2.5g, 4.3mmol) and (n-Bu$_4$N)[Ni(dmit)$_2$] (3.0g, 4.3mmol) were dissolved in acetone (350ml), and refluxed for 24 hours. The resulting solution was concentrated at 50 °C until the deposition of the microcrystals. The equal volume of 2-propanol was added to the acetone suspension, and the mixture was stood at –30 °C for 4 hours. The dark reddish brown solid (3.5g) was collected, and dried *in vacuo*. To the saturated solution of this solid, the one-third volume of acetic acid was added, and left at room temperature for 4 days. The black block–shaped single crystals were obtained quantitatively. The characterization was performed by X-ray analysis.

RESULTS AND DICUSSION

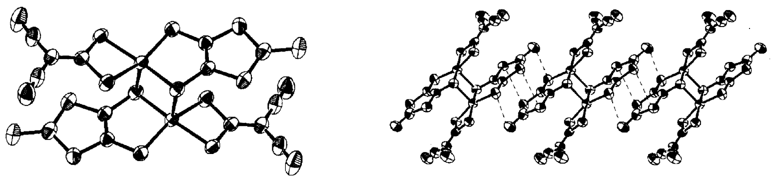
The monomeric ligand-exchanged salt (n-Bu$_4$N)[Ni(dmit)(i-mnt)]

TABLE 1 Crystal data of the $[Ni(dmit)(i\text{-}mnt)]_2$ and $[Ni(dmit)_2]$ complexes

	1	**2**	**3**	**4**	**5**
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a / Å	11.235(1)	11.353(3)	14.105(2)	13.446(1)	14.792(1)
b / Å	15.807(1)	13.205(2)	14.532(2)	13.362(1)	23.079(1)
c / Å	9.767(1)	8.993(3)	11.927(1)	13.600(1)	12.034(1)
α / °	91.55(1)	99.50(1)	104.68(1)	–	103.84(1)
β / °	113.59(1)	97.06(1)	103.26(1)	104.91(1)	96.34(1)
γ / °	105.12(1)	88.47(1)	110.68(1)	–	102.83(1)
V / Å^3	1517.6(1)	1319.6(5)	2070.7(1)	2361.1(2)	3830.9(3)
Z	2	2	4	2	2
R	0.043	0.071	0.075	0.088	0.047
Rw	0.043	0.098	0.051	0.104	0.054

was not obtained by any procedure. The dimerized salt, $(n\text{-}Bu_4N)_2[Ni(dmit)(i\text{-}mnt)]_2$ (**1**), was obtained as a single phase product after recrystallization from acetone–acetic acid (FIGURE 1(a)). The X-ray structure analysis revealed that two $[Ni(dmit)(i\text{-}mnt)]$ units were mutually connected by long axial Ni–S bonds in the black rod–like crystal of **1**.

Bond lengths of Ni–S in the square plane are 2.09 – 2.24 Å, and the axial bond is 2.45 Å. In the crystal, dimerized molecules form a 1–D chain with intracolumnar S-S short contacts (3.72, 3.85 Å) (FIGURE 1(b)). The dimerized molecule was recovered by further recrystallization from acetone. Therefore $[Ni(dmit)(i\text{-}mnt)]_2^{2-}$ is considered to be a very stable molecular unit. The cyclic voltammogram of **1** in acetone using an Ag/AgCl reference electrode and $n\text{-}Bu_4N{\bullet}PF_6$ (0.05M) as a supporting electrolyte showed a reversible oxidation peak at +0.08 V and an irreversible peak at +0.85 V. This indicates its relatively strong donor ability.



(a) (b)

FIGURE 1 (a) Molecular structure of $[Ni(dmit)(i\text{-}mnt)]_2^{2-}$, (b) 1–D chain in $(n\text{-}Bu_4N)_2[Ni(dmit)(i\text{-}mnt)]_2$.

From electrocrystallization of **1** with organic donor molecules in $CHCl_3$ or CH_3CN, black single crystals of (TTF)$_2$[Ni(dmit)(*i*-mnt)]$_2$ (**2**), (BEDT-TTF)$_2$[Ni(dmit)(*i*-mnt)]$_2$ (**3**) and (EDT-TTF)$_2$[Ni(dmit)(*i*-mnt)]$_2$ (**4**) were obtained. From their X-ray analyses, it has been found that each salt preserved dimerized structure of [Ni(dmit)(*i*-mnt)]$_2^{2-}$, and had multi-dimensional intermolecular S-S short contacts. In the TTF salt (**2**), dimerized TTF units were located between the 2-D [Ni(dmit)(*i*-mnt)]$_2^{2-}$ sheets (FIGURE 2). In the BEDT-TTF salt (**3**), [Ni(dmit)(*i*-mnt)]$_2^{2-}$ and BEDT-TTF molecules form 1-D chains, respectively. These chains are connected with intermolecular S-S short contacts, resulting in a 2-D network (FIGURE 3). In contrast to **2** and **3**, contacts between neighboring [Ni(dmit)(*i*-mnt)]$_2^{2-}$'s are very small in the EDT-TTF salt

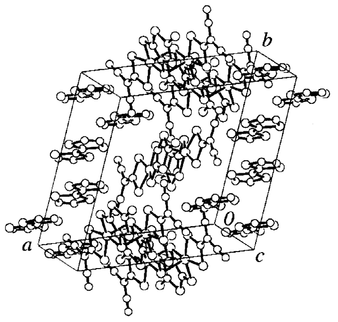


FIGURE 2 Crystal structure of the TTF salt (**2**).

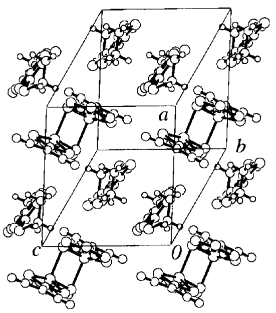


FIGURE 3 Crystal structure of the BEDT-TTF salt (**3**).

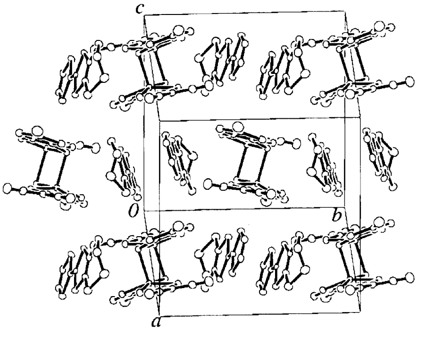


FIGURE 4 Crystal structure of the EDT-TTF salt (**4**).

(**4**), but there are short contacts between $[Ni(dmit)(\textit{i}\text{-mnt})]_2^{2-}$ and the dimerized EDT-TTF units like κ-phase of the superconducting BEDT-TTF salts (FIGURE 4). Usually, unsymmetrical complexes take head-to-tail and parallel stacking arrangement in the crystal [8]. However, in these salts **2**, **3** and, **4**, molecular planes of the cation and dianion are not parallel but almost perpendicular. Electrical resistivities were measured by 4- and 2-probe methods. They exhibited the room–temperature resistivities of 1.8×10^4 Ωcm (**2**), 1.0×10^2 Ωcm (**3**), and 2.1×10^3 Ωcm (**4**), respectively, with semiconducting behavior. The activation energies were 0.33, 0.12 and 0.27 eV, respectively.

On the cation–exchange reactions of $(\textit{n}\text{-Bu}_4N)[Ni(dmit)(mnt)]$ toward the construction of crystals with interactions between cyano groups and transition ions, the $[Ni(dmit)_2]$ salts with varied stoichiometry were obtained possibly due to the ligand–exchange reactions in the solution. Among these salts, a stoichiometrically novel complex $(\textit{n}\text{-Bu}_4N)_{0.25}[Ni(dmit)_2]\bullet CH_3CN$ (**5**) was characterized (FIGURE 5(a)). The $\textit{n}\text{-Bu}_4N$ cation and CH_3CN molecules separate the $[Ni(dmit)_2]$ sheets (FIGURE 5(b)). Electrical resistivity measurement showed its semiconducting behavior with room–temperature resistivity ρ = 30 Ωcm. The activation energy was 0.28 eV (FIGURE 6).

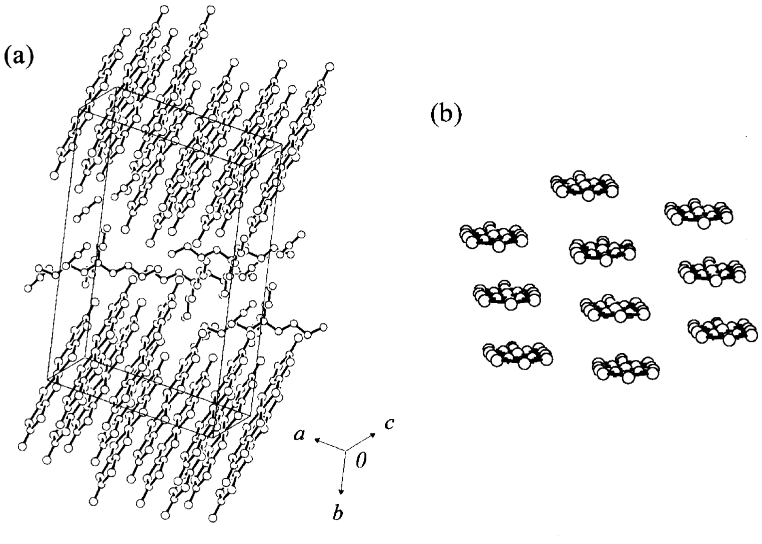


FIGURE 5 (a) Crystal structure of (**5**), (b) 2–D sheet of the $[Ni(dmit)_2]$ molecules viewed along the *ac* plane.

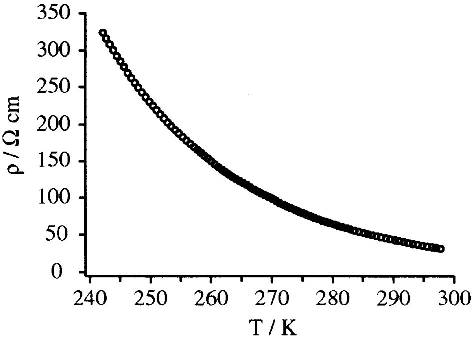


FIGURE 6 Temperature dependence of the electrical resistivity of **5**.

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