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Reizo Kato^a, Eiji Watanabe^b, Masahiro Fujiwara^b, Yoshiaki Kashimura^b, Yoshinori Okano^b & Jun-Ichi Yamaura^b

^a RIKEN (The Institute of Physical and Chemical Research), Hirosawa, Wako-shi, Saitama, 351-0198, Japan

^b The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo, 106-8666, Japan

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REIZO KATO^a, EIJI WATANABE^b, MASAHIRO FUJIWARA^b,
 YOSHIKI KASHIMURA^b, YOSHINORI OKANO^b and
 JUN-ICHI YAMAURA^b

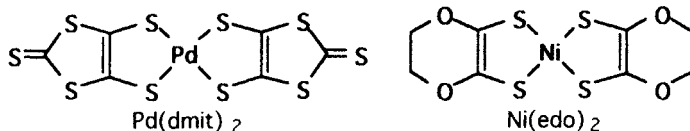
^aRIKEN (The Institute of Physical and Chemical Research), Hirosawa, Wako-shi,
 Saitama, 351-0198, Japan and ^bThe Institute for Solid State Physics,
 The University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan

Assembled metal complexes, where organic π electrons and metal d electrons coexist, form one important class of materials in the field of molecular "metals" and "superconductors". Among them, molecular conductors based on metal-dithiolene complexes are known to exhibit various conducting properties. Recent studies on molecular conductors based on the acceptor-type $\text{Pd}(\text{dmit})_2$ [dmit=2-thioxo-1,3-dithiol-4,5-dithiolate] and the donor-type $\text{Ni}(\text{edo})_2$ [edo = ethylenedioxydithiolate] and related materials are described.

Keywords: molecular conductor; metal dithiolene complex; resistivity; crystal structure; pressure effect; band calculation

INTRODUCTION

Electrical conduction is one of the most prominent functionalities of the assembled system. Assembled metal complexes are known to exhibit various conducting properties [1]. In this paper, we will focus on two types of metal dithiolene-complexes as components of molecular metals and superconductors. The one is an electron acceptor $\text{Pd}(\text{dmit})_2$, and the other is an electron donor $\text{Ni}(\text{edo})_2$.



SUPERCONDUCTING Pd(dmit)₂ SALTS AND RELATED SYSTEMS

An isostructural series of β' -type Pd(dmit)₂ salts with closed-shell cations ($\text{Me}_4\text{Z}'$ and $\text{Et}_2\text{Me}_2\text{Z}'$; $\text{Z} = \text{P, As, Sb}$) with the tetrahedral coordination geometry is considered a unique "two-band" system containing two bands with different characters near the Fermi level (2-dimensional HOMO band and 1-dimensional LUMO band) [2]. The space group is C2/c and the unit cell contains two "solid-crossing" columns that are related by a glide plane. Each of these columns consists of strongly dimerized Pd(dmit)₂ units with very short Pd...Pd contact. These columns form conducting layers which are separated from each other by a cation sheet.

At ambient pressure, the conduction band is formed by the half-filled HOMO band as a result of a small HOMO-LUMO gap and a strong dimerization (Notice that in ordinary molecular conductors based on the acceptor the conduction band is a LUMO band). This HOMO band is narrow and the system is a Mott insulator. In the Me_4Sb and $\text{Et}_2\text{Me}_2\text{P}$ salts, an application of the pressure changes a low-temperature ground state as non-metal \rightarrow superconductor \rightarrow metal \rightarrow non-metal. This pressure effect is quite sensitive to the choice of cation. The cation effect can be correlated to a difference in the dimensionality of the electronic structure. The counter cation affects intermolecular spacings and overlapping modes of Pd(dmit)₂ molecules and tunes anisotropy of intermolecular interactions. We have proposed that the pressure and cation effects are described by two parameters, "overlap of HOMO- and LUMO-bands" and "dimensionality of the electronic structure near the Fermi level" [2].

With the aim of extending the range of metallic and superconducting materials based on the Pd(dmit)₂ complex, we are interested in a series of trialkylsulfonium cations $\text{Me}_x\text{Et}_{3-x}\text{S}'$ ($x = 1, 2, 3$) with the pyramidal coordination geometry. This series of anion radical salts shows various crystal and electronic structures depending on the cation. Table 1 shows crystal data for this series of anion radical salts. Structural and conducting properties for the anion radical salt with $x=1$ has already been reported by the French group [3].

All these salts have a unit cell with the space group of $\text{P}\bar{1}$ and contain strongly dimerized columns of Pd(dmit)₂ units. The number of columns and arrangement of columns in the unit cell depend on the cation. The simplest system (one column / unit cell) is the EtMe_2S salt. Other salts

TABLE 1 Crystal data of $\text{Me}_x\text{Et}_{3-x}\text{S}[\text{Pd}(\text{dmit})_2]_2$ ($x = 1, 2, 3$)

Cation	Me_3S	EtMe_2S	Et_3MeS
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	11.697(2)	7.673(1)	7.804(4)
$b / \text{\AA}$	18.019(3)	18.341(2)	36.171(18)
$c / \text{\AA}$	7.7230(8)	6.2520(7)	6.284(2)
α / degree	94.884(9)	98.031(8)	91.68(2)
β / degree	91.930(9)	110.539(8)	112.08(4)
γ / degree	75.492(8)	84.665(6)	88.79(5)
$V / \text{\AA}^3$	1570.0(4)	814.9(2)	1643(1)
Z	2	1	2
ref.	This work	This work	[3]

contain two columns in the unit cell.

The EtMe_2S salt is isostructural with the high-pressure superconductor $\text{Et}_2\text{Me}_2\text{N}[\text{Pd}(\text{dmit})_2]_2$ (Figure 1). The unit cell contains two strongly dimerized $\text{Pd}(\text{dmit})_2$ units. Cations are disordered around the inversion centers. This structure is similar to the first organic superconductor $(\text{TMTSF})_2\text{PF}_6$ and its isostructural series. In the TMTSF salts, however, the conducting part comes from cation radicals and the counter part is formed by closed-shell anions. That is, the EtMe_2S salt has a stoichiometry which is the "charge reversal" image of the TMTSF salts. This salt is a semiconductor at ambient pressure (Figure 1), as is the case of high-pressure $\text{Pd}(\text{dmit})_2$ superconductors. The resistivity measurement under high pressure is in progress.

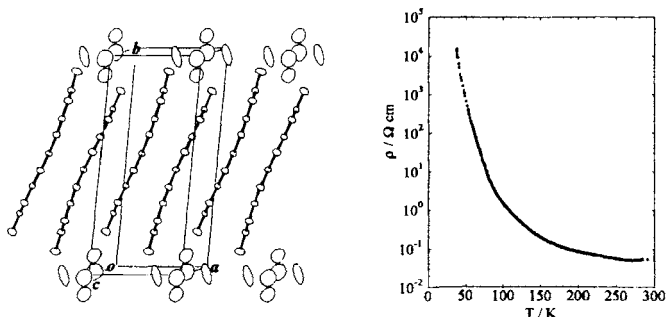


FIGURE 1 Crystal structure and electrical resistivity (at ambient pressure) of $\text{EtMe}_2\text{S}[\text{Pd}(\text{dmit})_2]_2$

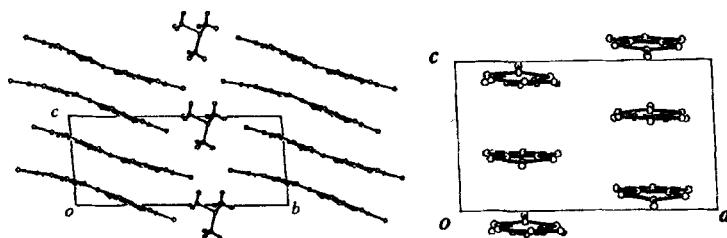


FIGURE 2 Crystal structure of $\text{Me}_3\text{S}[\text{Pd}(\text{dmit})_2]_2$

The unit cell of the Et_2MeS salt contains two columns. An interesting point is that these two columns are crystallographically independent and there are two types of conduction layers which are separated by a cation layer. It is possible for each band to take different band dispersion and filling and therefore different Fermi surfaces. This situation is very similar to that of the organic superconductor $(\text{TMET-STF})_2\text{BF}_4$ ($T_c = 4.1 \text{ K}$) [4].

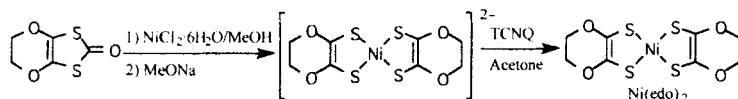
In the Me_3S salt, the unit cell contains two $\text{Pd}(\text{dmit})$ columns interrelated by the inversion symmetry to each other (Figure 2). In contrast to the Et_2MeS salt, these two crystallographically equivalent columns are arranged along the direction parallel the short molecular axis and there is only one conduction layer in the unit cell. The tight-binding band calculation indicates that this new type of molecular arrangement gives a two-dimensional Fermi surface. As is shown in other $\text{Pd}(\text{dmit})_2$ salts, the conduction band is a narrow and half-filled HOMO band. Therefore, this system is considered a Mott insulator. Indeed, this system is non-metallic at ambient pressure and the application of pressure extends the highly-conducting region. But, in the higher pressure region, the insulating behavior is enhanced. Unfortunately, we could not find superconductivity in the Me_3S salt.

Systematic understanding of factors which governs the electronic state of this series of anion radical salts is in progress.

NEW DONOR-TYPE DITHIOLENE COMPLEXES, $\text{Ni}(\text{edo})_2$ AND ITS UNSYMMETRICAL DERIVATIVES

The donor-type metal dithiolene complex, a system where the central C=C bond in the TTF-type organic donor is replaced by the transition metal, is one of promising components for molecular conductors. The number of this kind of molecular conductor, however, is still limited. This is partly because poor-solubility of known complexes gives a difficult obstacle in the preparation of the cation radical salt. In order to expand the materials chemistry of the donor type metal-dithiolene complex, we have directed our attention to metal complexes with edo ligands as an analog of the organic donor BEDO-TTF [bis(ethylenedioxy)tetrathiafulvalene]. The donor molecule BEDO-TTF is soluble in various organic solvents and is known to form superconducting cation radical salts [5].

We have failed to effect the metal complex formation by the conventional procedure, the ring opening of the corresponding ketone with alkali [NaOMe or K_2CO_3] followed by the addition of $NiCl_2$ in MeOH. We have found that the addition of $NiCl_2$ *ahead* of the ring opening reaction affords violet $[Ni(edo)_2]^{n-}$ (probably $n=2$) which can be oxidized to the deep blue neutral species by air or TCNQ.



Neutral $Ni(edo)_2$ is soluble in various organic solvents and easily purified by column chromatography (silica gel, CH_2Cl_2). Unsymmetrical complexes were easily obtained by the ligand exchange reaction in dichloroethane followed by the column chromatography (silica gel, CS_2 : CH_2Cl_2 = 2 : 1 or 1 : 1). They show much improved solubility in usual organic solvents.

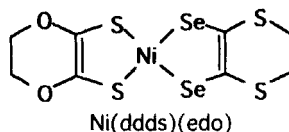
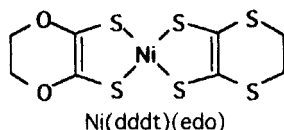
Table 2 shows the electrochemical data for $Ni(edo)_2$ and its unsymmetrical derivatives. Compared with $Ni(dddt)_2$, $Ni(edo)_2$ shows negative shifts of redox potentials. This indicates that $Ni(edo)_2$ has stronger donor ability than $Ni(dddt)_2$. The same relation is observed between BEDT-TTF and BEDO-TTF. The electrochemical data of mixed-ligand complexes suggests that each redox potential shows the mean value of those for the corresponding symmetrical species except for E_3 of $Ni(ddds)(edo)$. Such a tendency is also observed in unsymmetrical organic donor molecules.

TABLE 2 Cyclic voltammetric data

Complexes	E_1 (-2 / -1)*	E_2 (-1 / 0)*	E_3 (0 / +1)**
Ni(edo) ₂	-1.55	-0.86	0.11
Ni(dddt)(edo)	-1.46	-0.73	0.19
Ni(dddt) ₂	-1.34	-0.59	0.28
Ni(ddds)(edo)	-1.46	-0.72	0.15
Ni(ddds) ₂	-1.27	-0.51	-0.08

Measured at a Pt electrode in benzonitrile, 0.1M Buⁿ₄NClO₄ (V vs. 0.01M Ag / AgNO₃); at room temperature; Scanned between -1.90 and 0.50 V with scan rate of 100 mV / s.

* Reversible ** Irreversible wave



Crystal structure of the neutral Ni(edo)₂ was investigated by X-ray diffraction method (Crystal data: triclinic, space group P1, $a = 9.557(6)$, $b = 15.26(1)$, $c = 4.451(5)$ Å, $\alpha = 90.29(4)$, $\beta = 97.90(6)$, $\gamma = 86.77(5)^\circ$, $V = 641.9(8)$ Å³, $Z = 2$). The unit cell contains two Ni(edo)₂ molecules, each of which lies on the inversion center and is repeated uniformly along the c -axis. These crystallographically independent Ni(edo)₂ molecules are planar except for the terminal ethylene groups, as is the case of the neutral Ni(dddt)₂ molecule [6]. It should be noted that the corresponding organic donor BEDT-TTF and BEDO-TTF are non-planar in the neutral state. The averaged bond lengths of Ni-S, S-C and C=C are 2.15, 1.68 and 1.41 Å, respectively. The Ni...S bond length in the neutral Ni(edo)₂ is longer than that in Ni(dddt)₂ (2.12 Å).

The donor-type dithiolene complexes containing the edo ligand(s) form cation radical salts with novel crystal structures which have never been observed. For example, the cation radical salt, [Ni(edo)₂]₃(PF₆)₂ shows an interesting donor arrangement (Crystal data: monoclinic, space group P2₁/c, $a = 16.760(1)$, $b = 12.292(1)$, $c = 10.8640(7)$ Å, $\beta = 104.073(5)^\circ$, $V = 2171.0(2)$ Å³, $Z = 2$). The unit cell contains six Ni(edo)₂ molecules (Figure 3). The Ni(edo)₂ molecules form trimers. These trimers lie on the inversion centers and one and half Ni(edo)₂ units are crystallographically independent. These trimers are packed almost perpendicularly to each other. This structural feature reminds us of the

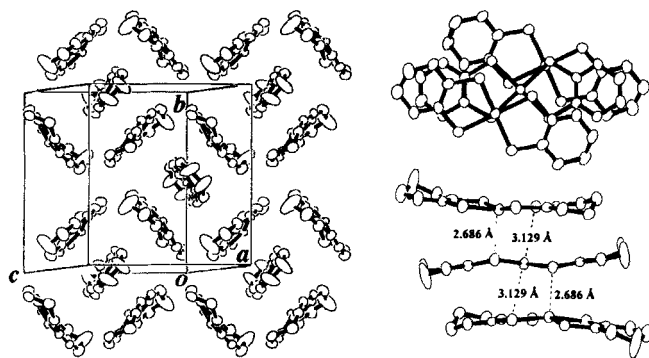


FIGURE 3 Donor arrangement (left), and top and side views of the trimer (right) in $[\text{Ni}(\text{edo})_2]_3(\text{PF}_6)_2$

κ -type arrangement which is frequently observed in the BEDT-TTF superconductors with high T_c . The κ -type BEDT-TTF salt is composed of orthogonally packed “dimer”s, and thus we describe this structural type of $[\text{Ni}(\text{edo})_2]_3(\text{PF}_6)_2$ as a “trimeric κ -type”. The PF_6^- anions lie between the donor layers.

Side and top views of the trimer are shown in Figure 3. The point is that the central molecule spans top and bottom molecules, which are displaced from each other along the direction of the short molecular axis. This novel overlapping mode enlarges the width of the trimer to fit the inter-planar spacing of the adjacent trimer and enables the κ -type packing of the trimer. The central molecule takes chair-conformation, while the top and bottom molecules take boat-conformation. Such a difference in the conformation and the bond lengths examination suggest disproportionation of the formal charge between the central and terminal (top and bottom) molecules. The present data, however, are not enough for more detailed analysis. The Ni atom in the central molecule exhibits an elongated octahedral coordination and the Ni atoms in the top and bottom molecules is penta-coordinated (Figure 3). Similar coordination geometries are also observed in $\text{Ni}(\text{dddt})_2$ salts [7]. In the trimer, $\text{S}\cdots\text{S}$ distances (3.313(2) Å) shorter than the van der Waals distance are observed, and there is no short inter-trimer $\text{O}\cdots\text{O}$, $\text{S}\cdots\text{S}$ and $\text{O}\cdots\text{S}$ distances.

Calculations of overlap integrals between frontier orbitals based on

the extended Hückel approximation indicate an isotropic inter-trimer interaction which would lead to two-dimensional electronic structures with appropriate band filling. Unfortunately, the tight-binding band calculation with the present valence state predicts that this compound is a semiconductor with an energy gap. Indeed, $[\text{Ni}(\text{edo})_2]_3(\text{PF}_6)_2$ shows semiconductive behavior in electrical resistivity ($\rho_{\text{rt}} = 1.1 \times 10^8 \Omega\text{cm}$, $E_g = 0.2 \text{ eV}$).

In conclusion, we have described two types of metal-dithiolene complexes as building blocks of molecular conductors. They exhibit unique structural and conducting properties which were never observed in conventional organic conductors. We hope to take advantage of these properties in development of new molecular materials.

Acknowledgements

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References

- [1] (a) A. Kobayashi and H. Kobayashi, *Handbook of Organic Conductive Molecules and Polymers*. Vol. 1, Ed by H. S. Nalwa. John Wiley & Sons Ltd., p249 (1997); (b) P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, **110**, 115 (1991).
- [2] R. Kato, Y-L. Liu, Y. Hosokoshi, S. Aonuma, and H. Sawa, *Mol. Cryst. Liq. Cryst.*, **296**, 217 (1997).
- [3] C. Faulmann, A. Errami, B. Donnadiou, I. Malfant, J-P. Legros, P. Cassoux, C. Rovira, and E. Canadell, *Inorg. Chem.*, **35**, 3856 (1996).
- [4] R. Kato, K. Yamamoto, Y. Okano, H. Tajima, and H. Sawa, *Chem. Commun.*, **1997**, 947.
- [5] T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann and F. Wudl, *J. Am. Chem. Soc.*, **111**, 3108 (1989).
- [6] H. Kim, A. Kobayashi, Y. Sasaki, R. Kato and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **61**, 579 (1988).
- [7] E. B. Yagubskii, A. I. Kotov, E. E. Laukhina, A. A. Ignatiev, L. I. Buravov and A. G. Khomenko, *Synth. Met.*, **41-43**, 2515 (1991).