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Crystal and Molecular Structure of Tetrabutylammonium Bis(1,4-dithiin-2,3-dithiolato)nickelate(III), $(Bu^n{}_4N)[Ni(ddt)_2]$

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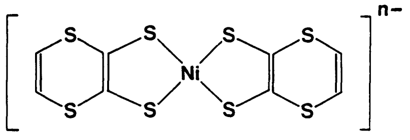
The crystal structure of tetrabutylammonium salt of a new multi-sulfur 1,3-dithiolene complex, $(Bu^n{}_4N)[Ni(ddt)_2]$ (ddt=1,4-dithiin-2,3-dithiolato) has been determined by the single-crystal X-ray diffraction technique. Crystals are monoclinic, space group $C2/c$, a=66.107(40), b=9.182(5), c=19.119(12) Å, β=147.29(3)°, V=6271(1) Å^3, and Z=8. The structure was solved by the heavy atom method, and refined by a block-diagonal least-squares method to R=0.070. There are two crystallographically independent molecules of $Ni(ddt)_2$, molecule-A and molecule-B. Molecule-B forms segregated uniform stacks along the b-axis. The $(Bu^n{}_4N)^+$ cations are located between two molecular planes of molecule-A. The $Ni(ddt)_2$ molecules are almost planar except two terminal vinylene moieties, which are folded to opposite side each other and the folding angles of molecule-A and molecule-B are 28° and 39°, respectively.

The intermolecular transverse interaction between multi-chalcogen π-donor and/or π-acceptor molecules is essential to enhance the dimensionality of the molecular metals, which is useful for the suppression of the Peierls instability which is the characteristic of the quasi-one-dimensional molecular metals. The structure of BEDT-TTF (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene) complexes clearly showed the way to introduce the transverse interactions and therefore to obtain 2-dimensional (2D) molecular conductors.[1] The superconductors, θ- and κ-(BEDT-TTF)$_2$I$_3$ are the most successful examples.[2,3] Recently, the 1D molecular metals without metal instabilities became to be noticed. In these systems, "multi-Fermi surface" nature of the molecular metals has been found to be important for supressing the Peierls instability and stabilizing the metallic state down to low temperature.[4,5] Two superconductors of metal 1,3-dithiolene complex (TTF)[Ni(dmit)$_2$]$_2$,[4] and [(CH$_3$)$_4$N][Ni(dmit)$_2$]$_2$[6] (dmit=2-thioxo-1,3-dithiolene-4,5-dithiolato) have been reported to be the examples of multi-Fermi surface systems. The stable metallic state of (DMe-DCNQI)$_2$Cu has been proposed to be originated from the same reason.[5]

Although a considerable number of studies have been made on the physical properties of the M(mnt)$_2$ (mnt=1,2-dicyano-1,2-ethylnendithiolato) and M(dmit)$_2$ compounds (M=Ni, Pd, Pt), reports on the syntheses of a new type of metal dithiolene complex are very few. A new multi-sulfur dithiolene complexes (Ni and Pd complexes of ddt; ddt=1,4-dithiin-2,3-dithiolato), which are expected to be a possible candidate to give highly conducting organic complexes, have been synthesized recently.[7] In this paper, the crystal structure of tetrabutylammonium salt of Ni(ddt)$_2$, $(Bu^n{}_4N)[Ni(ddt)_2]$ will be reported.



$[Ni(ddt)_2]^{n-}$

Experimental

Brown needle-type crystals of $(Bu^n{}_4N)[Ni(ddt)_2]$ were prepared by the method reported previously.[7] The unit cell parameters were determined by a least-squares fit of 2θ angles for 20 reflections ($17°<2\theta<30°$) measured with Mo $K\alpha$ radiation on an automated Rigaku AFC-6 four-circle diffractometer.

Details of the crystal data and experimental parameters along with data collection are summarized in Table 1. Three standard reflections were monitored every 100 reflections and their intensities showed random variation of ±0.6% throughout the data collection. The intensity data were corrected for Lorentz and polarization factors but not for absorption because of the small size of the crystal (<0.25 mm).

The structure was solved by Patterson method, and refined by a block-diagonal least-squares method. From the sharpened Patterson map, the positions of the nickel atoms were determined. A total of 33 non-hydrogen atoms were identified in the Fourier map calculated from the structure factors phased with heavy atoms. All the coordinates of the hydrogen atoms were calculated and were included in the final refinement cycles. Anisotropic thermal parameters were adopted for non-hydrogen atoms and the hydrogen atoms were refined isotropically. The weighting scheme $w=(1.0+0.004|F_o|^2)^{-1}$ for $|F_o|<12.0$ and $(\sigma(|F_o|)^2+0.004|F_o|^2)^{-1}$ for $|F_o|\geqq 12.0$ was employed. The atomic scattering factors were taken from International Tables for X-ray Crystallography.[8] All the calculations were performed on HITAC M-680H computer at the Computer Centre of the University of Tokyo, using the program UNICS III.[9]

Table 1. Crystal Data and Experimental Parameters for the X-Ray Diffraction Study of $(Bu^n{}_4N)[Ni(ddt)_2]$

Formula	$C_{24}H_{44}NS_8Ni$
Formula weight	657.1
Crystal system	Monoclinic
Space group	$C2/c$
Cell constant	
a/Å	66.107(40)
b/Å	9.182(5)
c/Å	19.119(12)
β/°	147.29(3)
V/Å^3	6271(1)
Z	8
X-Ray	Mo $K\alpha$ vadiation (λ=0.71069Å)
Monochromator	Graphite
$d_{cal.}$/g cm^{-1}	1.39
μ(Mo $K\alpha$)/cm^{-1}	11.5
Crystal size/mm^3	0.13×0.025×0.025
Scan technique	$2\theta-\omega$ scan
Scan rate/° min^{-1}	2
Scan width (ω)	$1.23+0.5\tan\theta$
Scan range	$2\theta \leqq 50°$
Number of reflections measured	5258
Number of reflections used in the calculation ($\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$)	1494
R value$^{a)}$	0.070
R_2 value$^{b)}$	0.087
Goodness of fit (g.o.f.)$^{c)}$	1.09

a) $R=\sum\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. b) $R_2=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum\lvert F_o\rvert^2]^{1/2}$. c) g.o.f.$=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(N-M)]^{1/2}$, where N=number of reflections, M=number of parameters.

Results and Discussion

The atomic coordinates are listed in Table 2.** The bond distances and angles are shown in Fig. 1. The crystal structure is shown in Fig. 2.

There are two types of $Ni(ddt)_2$ molecules (A and B) which are crystallographically independent. Both of them are located on the centers of the symmetry. The monoclinic unit cell contains eight $Ni(ddt)_2$ molecules (four molecule-As and four molecule-Bs), and eight $(Bu^n{}_4N)^+$ cations. The averaged Ni–S distances are 2.148 Å in molecule-A and 2.137 Å in molecule-B, which are close to those of other monoanionic dithiolato-nickelate.[10] The $Ni(ddt)_2$ molecules are almost planar except the terminal vinylene moieties while the VT molecules in usual cases are not planar (bis(vinylenedithio)tetrathiafulvalene, BVDT-TTF, is abbreviated as VT; in $Ni(ddt)_2$, the central C=C double bond of VT is replaced by the Ni atom). The planarity of $Ni(ddt)_2$ molecules is better than that of the $VT^{+1/2}$ molecules in VT_2PF_6 which is better than that of VT^0 molecules in neutral VT.[11] The two terminal vinylene groups of the each side of a $Ni(ddt)_2$ molecule are folded to opposite side each other, and the folding angles of molecule-A and molecule-B are 28° and 39°, respectively. The shapes of $Ni(ddt)_2$) molecules (A and B) and the folding angles are shown in Fig. 1.

The molecule-B forms the independent uniform stacks along the b-axis on the position of x/a=0, 1/2. The interplanar distances within the stacks of molecule-B are 4.03 Å. $(Bu^n{}_4N)^+$ cations are located between two molecular planes of molecule-A. There is

Table 2. Fractional Atomic Coordinates (×10^4) with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	B_{eq}/Å$^{2\,a)}$	Atom	x/a	y/b	z/c	B_{eq}/Å$^{2\,a)}$
Ni1	2500	2500	5000	5.9	N	1510(3)	−980(11)	3250(10)	4.0
Ni2	5000	5000	5000	7.1	C(N)1	1575(5)	−2315(16)	3908(16)	5.4
S1	2125(2)	2129(5)	3050(5)	6.7	C(N)2	1779(4)	−937(15)	3422(13)	4.3
S2	2068(2)	3584(5)	4328(5)	6.8	C(N)3	1590(4)	412(16)	3909(13)	4.9
S3	1326(2)	2561(7)	425(5)	8.5	C(N)4	1103(4)	−1027(15)	1835(13)	4.6
S4	1269(2)	4146(5)	1849(6)	8.1	C(N)5	1968(4)	−2596(17)	5318(14)	5.5
S5	5203(2)	3640(6)	6408(5)	8.6	C(N)6	1772(4)	−2310(16)	2941(15)	5.4
S6	4575(1)	3454(6)	3490(5)	8.1	C(N)7	1342(5)	605(20)	3845(17)	6.9
S7	4964(2)	933(7)	6397(7)	11.3	C(N)8	976(5)	259(18)	1025(18)	7.9
S8	4308(2)	642(6)	3298(7)	10.3	C(N)9	2012(5)	−3979(16)	5837(17)	6.2
C1	1697(5)	2794(14)	2091(17)	6.1	C(N)10	2047(5)	−2104(14)	3116(16)	5.6
C2	1682(5)	3445(16)	2698(17)	5.9	C(N)11	1433(6)	2128(25)	4437(19)	9.5
C3	1030(5)	3882(24)	−196(21)	9.9	C(N)12	589(5)	−98(28)	−392(20)	13.4
C4	993(6)	4538(19)	309(22)	9.9	C(N)13	2410(5)	−4291(22)	7172(16)	8.3
C5	4893(5)	2171(20)	5489(19)	8.4	C(N)14	2084(5)	−3524(16)	2811(16)	6.0
C6	4619(4)	2130(24)	4237(19)	9.8	C(N)15	1204(6)	2458(32)	4407(22)	13.0
C7	4845(7)	−631(21)	5653(23)	10.6	C(N)16	443(9)	968(48)	−1174(36)	23.1
C8	4575(5)	−802(21)	4377(21)	9.7					

a) $B_{eq}=(4/3)(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$.

** The coordinates of the hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms and the F_o—F_c tables have been deposited as a Document No. 8806 at the Office of the Editor of Bull. Chem. Soc. Jpn.

no short intermolecular S···S (<3.70 Å) contacts within the $Ni(ddt)_2$ molecules.

The amplitudes of LUMO (lowest unoccupied molecular orbital) of $[Ni(ddt)_2]^-$ anion were calculated on the basis of extended Hückel approximation (Fig. 3). The LUMO of $[Ni(ddt)_2]^-$ has the same symmetry as those of $[Ni(dmit)_2]^-$, the well-known metal 1,3-dithiolene complex, and $[Ni(dddt)_2]^-$.[12] In the case of $[Ni(dmit)_2]^-$, shown in Table 3, the amplitudes of LUMO of the "outer sulfur atoms" (a_o) are one-fifth as small as those of the "inner sulfur atoms" (a_i) therefore the side-by-side interactions of the $Ni(dmit)_2$ molecules are not so strong.[4] In the case of $[Ni(dddt)_2]^-$, which have ethylene moieties instead of thioxo group of $Ni(dmit)_2$ in the outer side of the molecule, the ratio of a_o, to a_i are one-half. Consequently, compared with $[Ni(dmit)_2]^-$, $[Ni(dddt)_2]^-$ is considered to be liable to form the 2D molecular conductor. In the case of $[Ni(ddt)_2]^-$, the

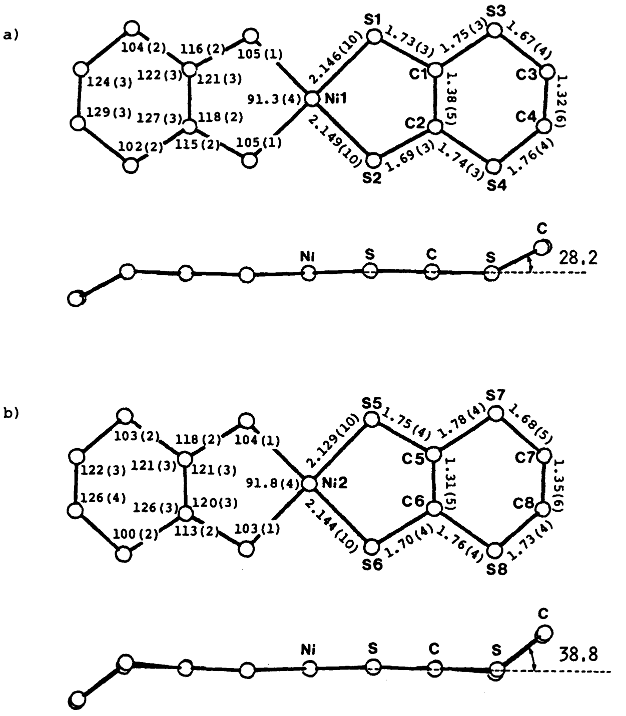


Fig. 1. Molecular structure, bond distances (l/Å), bond angles (ϕ/°), and folding angles (ϕ/°) of a) molecule-A and b) molecule-B of $Ni(ddt)_2$.

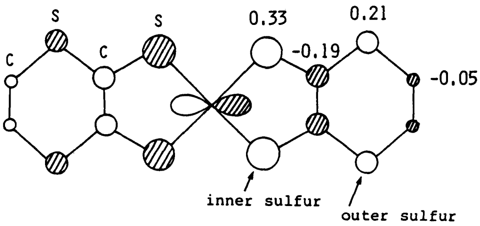
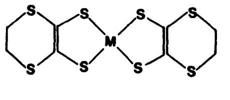


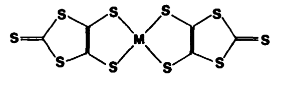
Fig. 3. Schematic drawing of LUMO of $[Ni(ddt)_2]^-$.

Table 3. Comparison of the a_i and a_o Values of the Monoanionic Dithiolatonickelates

	a_i	a_o	a_o/a_i
$[Ni(ddt)_2]^-$	0.33	0.21	64%
$[Ni(dddt)_2]^-$	0.37	0.18	49%
$[Ni(dmit)_2]^-$	0.42	0.08	19%



M(dddt)₂



M(dmit)₂

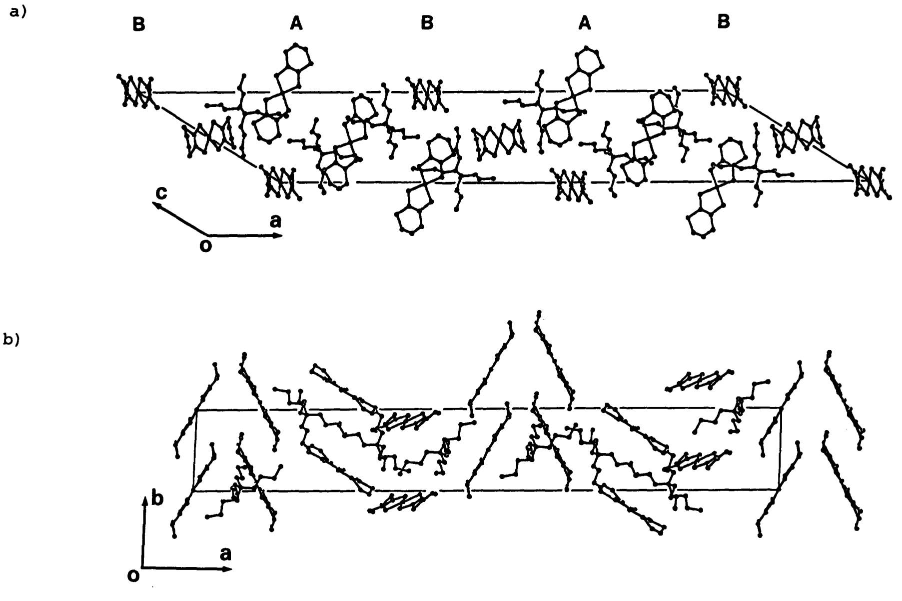


Fig. 2. Crystal structure of $(Bu^n{}_4N)[Ni(ddt)_2]$ projected along a) the b-axis and b) the c*-axis.

ratio of a_0 to a_i is three-fifth which is larger than that of $[Ni(dddt)_2]^-$. But in case of synthesizing the real molecular conductor, the electrochemical property of $Ni(ddt)_2$ molecule become an important factor. As reported by Nakamura et al.,[7] the $\Delta E(=E_1-E_2)$[13] value of $[Ni(ddt)_2]^-$, which is a measure of the on-site Coulomb repulsion, lies between that of $[Ni(dmit)_2]^-$ and that of $[Ni(dddt)_2]^-$.

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13) E_1 and E_2 are the redox potentials of $[ML_2]^{2-} \overset{E_1}{\rightleftharpoons} [ML_2]^- \overset{E_2}{\rightleftharpoons} [ML_2]^0$, where ML_2 is a metal 1,3-dithiolene complex.