Crystal Structure and Molecular Structure of Neutral Nickel Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolate), Ni(dddt)$_2$

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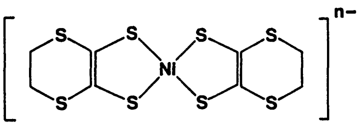
Synopsis. Neutral species of multi-sulfur 1,2-dithiolene complex, Ni(dddt)$_2$ (dddt=5,6-dihydro-1,4-dithiin-2,3-dithiolate), was synthesized and the crystal structure has been determined. Crystals are monoclinic, space group $P2_1/c$, with $Z=4$, $a=18.350(10)$, $b=4.672(1)$, $c=20.326(12)$ Å, $\beta=125.56(3)°$, $V=1417(1)$ Å^3. The structure was solved by the Patterson method, and refined by a block-diagonal least-squares method to $R=0.081$ for 1316 unique reflections. Two independent molecules of Ni(dddt)$_2$ are stacked along the b-axis separately, with interplanar distances of 3.76 Å and 3.74 Å, respectively.

Recent discoveries of the molecular conductors containing metal 1,2-dithiolene complexes have promoted to synthesize new inorganic conductors. In these compounds, the conduction pathways are formed by the overlapping of the ligand-centered π-system (predominantly the sulfur orbitals) and not principally of the metal orbitals.[1] The transverse intermolecular S‥S contacts in the metal-dmit complex (dmit=2-thioxo-1,3-dithiole-4,5-dithiolate) suggest the probability of the multi-dimensional molecular conductors.[2]

Recently, we have synthesized M(dddt)$_2$, which is a multi-sulfur 1,2-dithiolene complex as M(dmit)$_2$ and also has ethylene moieties in the outer sides of the ligand as well-known BEDT-TTF (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene; In M(dddt)$_2$, the central C=C double bond of BEDT-TTF is replaced by the transition metal). Unlike the case of planar M(dmit)$_2$, steric effect of the ethylene groups of M(dddt)$_2$ will prevent the face-to-face overlapping of the molecules and will enhance the two-dimensional (2-D) molecular contacts to produce the 2-D conductors similar to the BEDT-TTF compounds.

In this paper, we report the molecular and crystal structure of neutral Ni(dddt)$_2$ determined by X-ray analysis.



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

Experimental

(n-Bu$_4$N)[Ni(dddt)$_2$] was prepared following the method discribed by Kato et al.[3] The black powder of neutral Ni(dddt)$_2$ was prepared by I$_2$-oxidation of (n-Bu$_4$N)[Ni(dddt)$_2$]. Black, needle-type single crystal was obtained during the process of recrystallization from benzene.

Crystal data are as follows: Ni(dddt)$_2$, NiC$_8$H$_8$S$_8$, F.W.=419.39, monoclinic, $P2_1/c$, $a=18.350(10)$, $b=4.672(1)$, $c=20.326(12)$ Å, $\beta=125.56(3)°$, $V=1417(1)$ Å^3, $Z=4$, $d_c=1.97$ g cm^{-3}, μ(Mo $K\alpha$)=24.8 cm^{-1}, crystal dimension=0.5 mm×0.08 mm×0.03 mm. X-Ray diffraction data were collected on a Rigaku AFC-6 automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) and by the 2θ-ω scan technique. The three standard reflections were monitored every 100 reflections, and their intensities showed a good stability. A total of 3713 reflections in the range of $2\theta<50°$ were collected. The intensity data were made for Lorentz and polarization corrections and not for absorption. The 1316 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for structure analysis. The structure was solved by the heavy atom method and refined by a block-diagonal least-squares method. The hydrogen coordinates were calculated and were included in the final cycles. The weighting scheme $w=(0.001+0.0045|F_o|^2)^{-1}$ for $|F_o|<15.0$ and $(\sigma(|F_o|)^2+0.0045|F_o|^2)^{-1}$ for $|F_o|\geqq 15.0$ was employed. Anisotropic thermal parameters were adopted for Ni, S, and C atoms, and the isotropic temperature factors of H atoms were fixed to 4.0 Å^2. The final R and R_w values are 0.081 and 0.108, respectively. The atomic scattering factors were adopted from International Tables for X-Ray Crystallography.[4] All the calculations were performed on HITAC M-680H computer at the Computer Center of the University of Tokyo, using the program UNICS III.[5]

Results and Discussion

The atomic coordinates are listed in Table 1. The bond distances and angles are shown in Fig. 1. The crystal structure is shown in Fig. 2. The molecules of Ni(dddt)$_2$ are on the center of symmetry. The unit cell contains four Ni(dddt)$_2$ molecules, and the half of

Table 1. Atomic Coordinates (×10^4)

Atom	x	y	z	B_{eq}
Ni1	0	0	0	2.8
Ni2	5000	5000	5000	2.6
S1	1340(3)	1158(12)	482(3)	3.4
S2	−475(3)	2423(12)	−1057(3)	3.0
S3	2319(3)	4461(13)	51(3)	3.7
S4	249(3)	5974(13)	−1726(3)	3.5
S5	6307(3)	6718(12)	4182(3)	3.3
S6	4535(3)	7084(12)	4383(3)	3.0
S7	7251(3)	10297(14)	2759(3)	3.8
S8	5226(3)	10768(11)	2992(3)	3.0
C1	1266(11)	3299(42)	−222(11)	2.9
C2	455(11)	3817(43)	−910(11)	2.9
C3	2056(13)	6696(44)	−768(13)	3.8
C4	1335(11)	5684(54)	−1575(12)	4.0
C5	6230(11)	8760(39)	3521(9)	2.4
C6	5419(10)	8873(38)	3598(9)	2.4
C7	6943(13)	12615(47)	2244(11)	3.6
C8	6367(13)	11132(47)	2057(11)	3.5

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

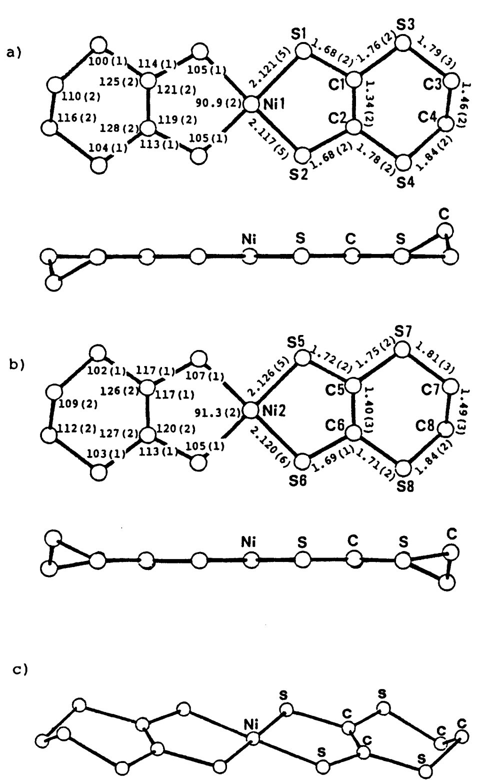


Fig. 1. Molecular structure, bond distances (*l*/Å) and bond angles (*ϕ*/°) of Ni(dddt)$_2$; a) molecule-A, b) molecule-B, and c) the conformation of terminal ethylene groups.

molecule-A and the half of molecule-B are crystallographically independent. The Ni-S bond distance of Ni(dddt)$_2$ is 2.119(5) Å in molecule-A and 2.123(6) Å in molecule-B, which are shorter than 2.148(2) Å in [Ni(dddt)$_2$]$^{-1}$ anion[6] and are very close to those of other monoanionic nickel dithiolene complexes. Except the terminal ethylene groups, the planarity of molecule-A is better than that of molecule-B. The deviations of atoms from the least-squares planes calculated from all the atoms except the terminal ethylene groups are within 0.01 Å (molecule-A) and 0.04 Å (molecule-B). The equations of the least-squares planes and the deviations of all the atoms are listed in Table 2. Neutral molecule of Ni(dddt)$_2$, as well as [Ni(dddt)$_2$]$^{-1}$ anion of (Et$_4$N)[Ni(dddt)$_2$],[6] has an inversion center, and the conformation of terminal ethylene groups of each side of a molecule is different from that of BEDT-TTF molecules which have pseudo-D$_{2h}$ symmetry. The conformation of terminal ethylene groups of neutral Ni(dddt)$_2$ is shown in Fig. 1.

The molecule-A and molecule-B are arranged separately to form the independent uniform stacks along the b-axis. As for the crystal of neutral BEDT-TTF, we found a dimer structure composed by two neutral BEDT-TTF molecules.[7] But in both cases of neutral Ni(dddt)$_2$ and neutral Ni(dmit)$_2$,[8] they form uniform stacks. Within the stacks of Ni(dddt)$_2$, the Ni-Ni distance is given by the lattice constant of the b-axis, 4.672 Å. The interplanar distances are 3.76 Å in the stacks of molecule-A, and 3.74 Å in those of molecule-B. There is no short intermolecular S···S contact (<3.70 Å) within a stack, and between molecules of adjacent stacks along the c-axis.

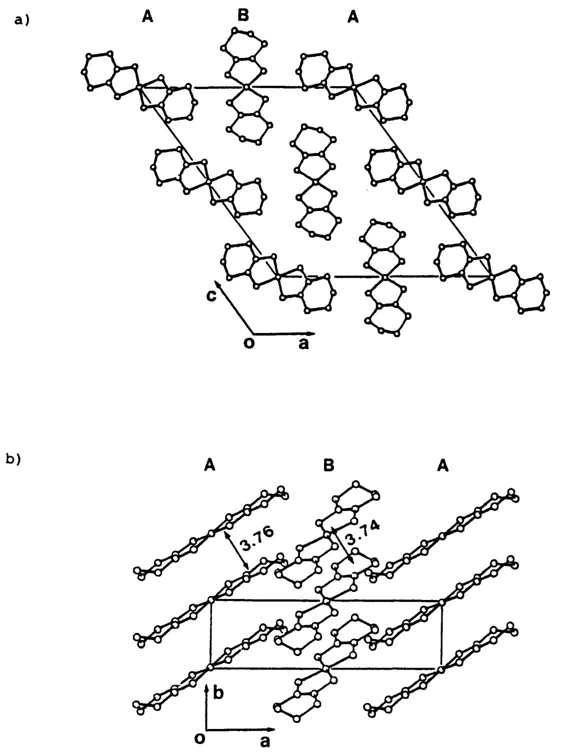


Fig. 2. Crystal structure of Ni(dddt)$_2$; a) projection along the b-axis, b) projection along the c-axis and the interplanar distances (*l*/Å).

Table 2. The Equations of the NiC$_2$S$_4$ Least-Squares Planes and the Deviations (*l*/Å)

Molecule-A $-0.41068X+0.80422Y+0.42961Z+0.0=0$
Molecule-B $-0.11165X-0.80227Y+0.58643Z+8.40681=0$

Molecule-A		Molecule-B	
Ni1	0.0	Ni2	0.0
S1	0.001	S5	0.010
S2	0.005	S6	0.006
S3	−0.010	S7	−0.021
S4	−0.007	S8	−0.004
C1	0.020	C5	0.033
C2	0.002	C6	0.004
C3	0.047	C7	0.215
C4	−0.753	C8	−0.667

The amplitudes of LUMO (lowest unoccupied molecular orbital) were calculated as to [Ni(dddt)$_2$]$^{-1}$ anion by means of the extended Hückel approximation, with the parameters adopted from Ref. 9, and are shown in Fig. 3. In [Ni(dmit)$_2$]$^{-1}$, the amplitudes of the "outer sulfur atoms" in the five-membered heteroring are about one-fifth as small as those of the "inner sulfur atoms,"[1] but in [Ni(dddt)$_2$]$^{-1}$ half as small as those of the "inner sulfur atoms." In M(dmit)$_2$, the side-by-side interactions are not so strong owing to the small amplitude on the "outer sulfur atoms" and the symmetry of LUMO. In BEDT-TTF, the amplitudes of HOMO (highest occupied molecular orbital) on the

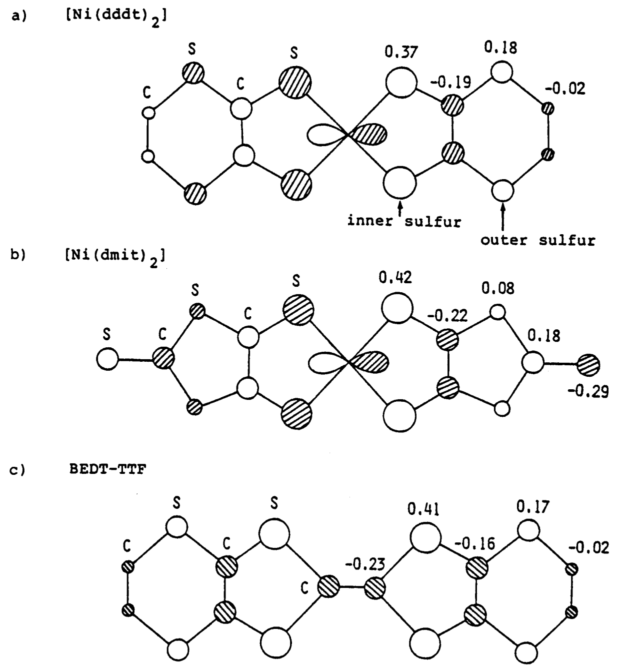


Fig. 3. Schematic drawing of a) LUMO of Ni(dddt)$_2$, b) LUMO of Ni(dmit)$_2$[1] and c) HOMO of BEDT-TTF.[10]

"outer sulfur atoms" are about 40% of those of the "inner sulfur atoms" (Fig. 3). Thus the side-by-side arrangement of M(dddt)$_2$ will be supposed to be sufficient for the realization of the 2-D molecular interaction similar in BEDT-TTF.

Both BEDT-TTF and M(dddt)$_2$ are approximately the same size and both of the molecules seem to have a tendency to form a 2-D layered type structure with close S ·· S contacts. As mentioned above, however, as for M(dmit)$_2$, we found that the side-by-side interactions by S atoms were weaker than those expected at first, and M(dmit)$_2$ had a tendency to form 1-D system.[1] This discrepancy is originated from the difference in the symmetries of HOMO of BEDT-TTF and LUMO of M(dmit)$_2$, from which the conduction bands are formed. Further, both M(dddt)$_2$ and M(dmit)$_2$ contain tetrathio-substituted ethylene moieties, and have the same type of delocalized π-MO. So that M(dddt)$_2$ is considered to be an intermediate between M(dmit)$_2$ and BEDT-TTF from the electronic and molecular structural points of view. At the same time, it should be recalled that the redox behavior is a very important factor in the systhesis of the molecular conductors. The most prominent difference between $[\mathrm{Ni(dddt)_2}]^{-1}$ and $[\mathrm{Ni(dmit)_2}]^{-1}$ is their redox behavior. $[\mathrm{Ni(dmit)_2}]^{-1}$ is much more easily reduced to the dianion than $[\mathrm{Ni(dddt)_2}]^{-1}$.[3] Therefore, further careful works will be required to examine the ability of formation of conducting complex of [Ni(dddt)$_2$].

The coordinates of the hydrogen atoms, the anisotropic thermal parameters of the Ni, S, and C atoms, and the F_o—F_c tables have been deposited as a Document No. 8783 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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