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CRYSTAL STRUCTURE AND ELECTRICAL CONDUCTIVITY OF $(Et_4N)_{0.5}[Ni(dmit)_2]$

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The crystal of $(Et_4N)_{0.5}[Ni(dmit)_2]$ belongs to triclinic system (dmit: isotrithionedithiolate). In the crystal, face-to-face stacking and side-by-side arrangement of $Ni(dmit)_2$ molecules form the two-dimensional S···S networks, which are weakly connected in the third direction by thioketone sulfur atoms in the isotrithione ring. The electrical conductivity measurements show that $(Et_4N)_{0.5}[Ni(dmit)_2]$ is a semiconductor with small anisotropy.

Recently the highly conducting mixed valence complex $[(n\text{-}Bu)_4N]_{0.29}[Ni(dmit)_2]$ (dmit: isotrithionedithiolate) has been reported.$^{1)}$ The crystals of partially oxidized 1,2-dithiolene complexes have the conduction pathway based on the ligand-centered π-system (predominantly sulfur orbitals), while partially occupied Pt-dz^2 electron energy band is responsible for the high conductivity of inorganic one-dimensional metals containing tetracyanoplatinate and bis(oxalato)-platinate anions.$^{2)}$ $[(n\text{-}Bu)_4N]_{0.29}[Ni(dmit)_2]$ having two-dimensional S···S network in the crystal is the first example of a conducting metal complex in which two-dimensionality is a key feature. In order to study the influence of the counter cation upon electrical conduction properties, we have chosen smaller tetraalkylammonium ion (Me_4N^+, Et_4N^+, and $(n\text{-}Pro)_4N^+$) than $(n\text{-}Bu)_4N^+$. We now report structure determination and electrical conductivity study of $(Et_4N)_{0.5}[Ni(dmit)_2]$.

The electrochemical oxidation (at a constant current of ca. 2 μA) of a solution containing $Et_4N[Ni(dmit)_2]$ (10^{-3}M) and Et_4ClO_4 (0.1 M) in acetone-acetonitrile (1:1) at room temperature gave black elongated plates. Elemental analysis (C, H, N) shows that the degree of partial oxidation is 0.5. The crystal data are: triclinic, space group $P\bar{1}$, a=20.109(2), b=7.316(1), c=6.432(1) Å, α=103.92(1), β=98.67(1), γ=80.62(1)°, V=900.0 Å^3, Z=2.$^{3)}$

The planar $Ni(dmit)_2$ molecules are stacked along the b-axis (Fig.1). There are two independent S···S contacts between the molecules A and B', slightly shorter than the van der Waals distance (3.7 Å) , but there is no short intermolecular S···S contact between the molecules A and B. The inter-planar distances are 3.437 Å (between A and B') and 3.759 Å (between A and B). Thus, $Ni(dmit)_2$

columns are considered to be composed of the weakly coupled Ni(dmit)$_2$ dimers. Many short S···S contacts are observed between the stacks. The side-by-side arrangement of Ni(dmit)$_2$ molecules along the c-axis (A-A'' and B-B'', Fig. 1) is very similar to the case of cation radical salts of BEDT-TTF(bis-ethylenedithio)-tetrathiafulvalene) in which the TTF moiety is extended by incorporating six-membered hetero-rings.$^{4)}$ There exist some short S···S contacts between the Ni(dmit)$_2$ molecules arranged along the [011] direction (A-B'', in Fig. 1). Thus, the crystal has two-dimensional S···S networks parallel to the bc plane. The shortest interstack S···S distance 3.499 Å is observed between sulfur atoms in the dithiolene part ("inner sulfur"), whereas the mutual contacts between sulfur atoms in the heterocyclic extension ("outer sulfur") are longer than the van der Waals distance. In the crystal of (Et$_4$N)$_{0.5}$[Ni(dmit)$_2$], the "inner sulfur" atoms play an important role in interstack S···S contacts.

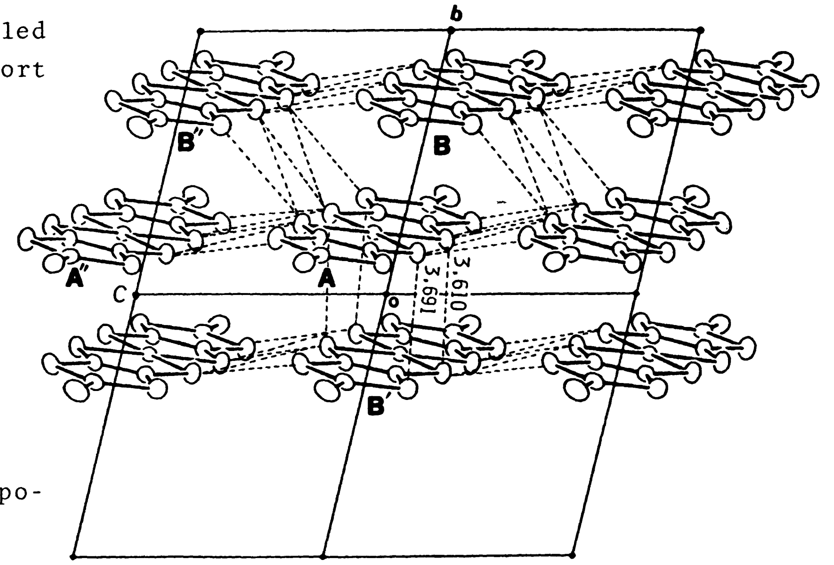


Fig. 1a. Crystal structure viewed along the a*-axis. For clarity, the Et$_4$N cations are omitted.

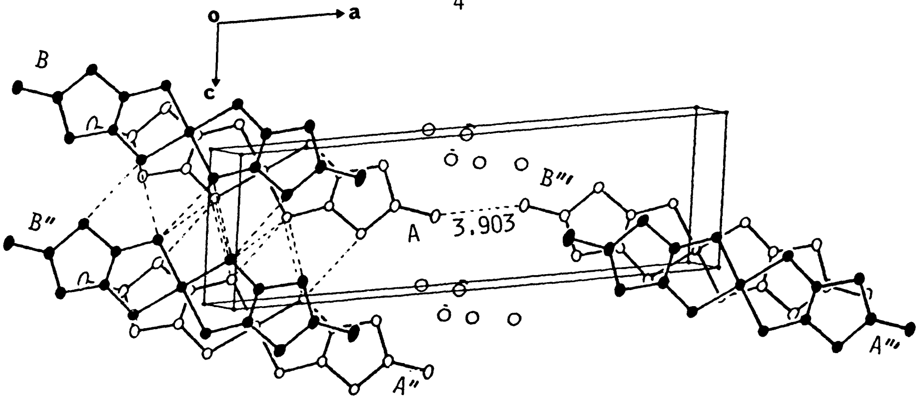


Fig. 1b. Molecules A''' and B''' are related to A by symmetry operations, (1+x,y,1+z) and (1-x,-y,1-z). The disordered Et$_4$N cations are located at the center of the ab plane.

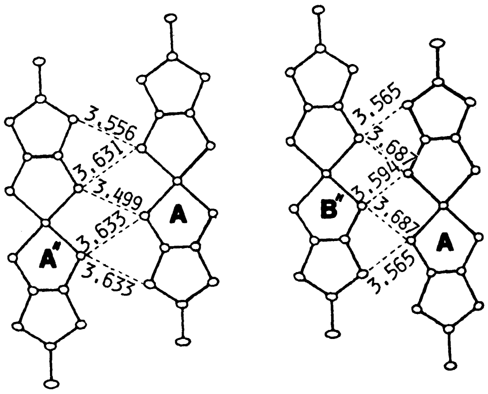


Fig. 1c. Interstack S···S contacts.

In the crystal of [(n-Bu)$_4$N]$_{0.29}$[Ni(dmit)$_2$], the two-dimensional S···S networks parallel to the ab plane are separated by layers of bulky (n-Bu)$_4$N cations.$^{1)}$ As shown in Fig. 1b, in the crystal of (Et$_4$N)$_{0.5}$[Ni(dmit)$_2$], Et$_4$N cations are located at the center of the ab plane and highly disordered. The weak S···S interaction (between A and B''', 3.903 Å) along the a-axis which

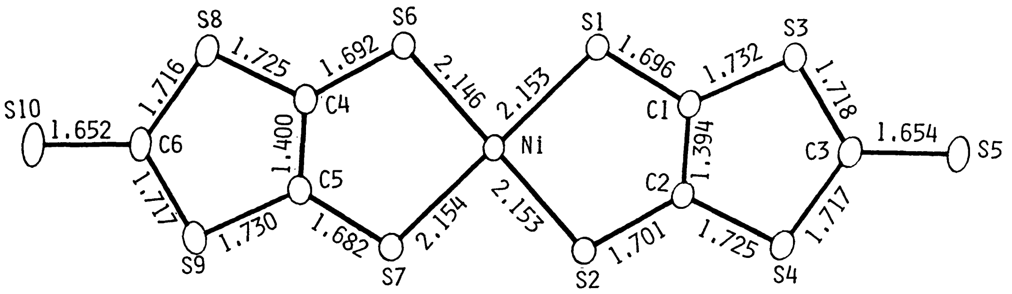


Fig. 2. Molecular structure of $Ni(dmit)_2$. The standard deviations are 0.003-0.011 Å.

cannot be neglected are observed between thioketone sulfur atoms.

$Ni(dmit)_2$ molecule is almost planar. The bond lengths are given in Fig. 2. It is well known that bond lengths in the dithiolene complexes vary with their oxidation state.$^{5)}$ The Ni-S and S-C distances increase and the "ethylenic" bond distances decrease as the overall charge increases, which can be related to the coefficients of the lowest unoccupied molecular orbital (LUMO) of the neutral molecule. As shown in Table 1, the bond lengths of $Ni(dmit)_2^{n-}$ (n=0.5,1,2) series also agree with this tendency. The variation of the bond lengths in the isotrithione ring is small, but the C=S bond lengths (C3-S5 and C6-S10) vary slightly.

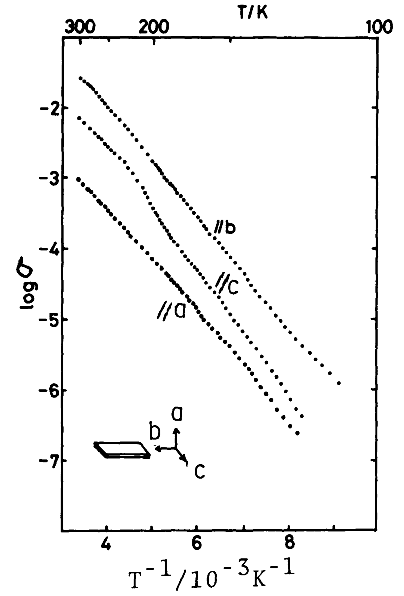
Table 1. Structural data for $Ni(dmit)_2^{n-}$.

n	Ni-S	C-S	C-C	C=S	Ref.
0.5	2.152	1.69	1.40	1.65	this work
1	2.156	1.73	1.35	1.63	6
2	2.216	1.75	1.39	1.68	7

The bond distances(Å) given are average values.

The electrical conductivities were measured along the a-, b-, and c-axes(σ_a, σ_b, σ_c; Fig. 3) by the two-probe method. $(Et_4N)_{0.5}[Ni(dmit)_2]$ is a semicondutor with small anisotropy. The maximum value of σ_b is 4.5×10^{-2} $(\Omega\ cm)^{-1}$ and the activation energies of σ_a, σ_b, and σ_c are 0.15, 0.16, and 0.16 eV, respectively. At room temperature, the anisotropy of the electrical conductivity is $\sigma_a : \sigma_b : \sigma_c = 1 : 50 : 8$, which is in contrast to $\sigma_a : \sigma_b : \sigma_c = 2 : 1 : 10^{-4}$ of $[(n\text{-}Bu)_4N]_{0.29}[Ni(dmit)_2]$.$^{1)}$ Although the relatively low conductivity of $(Et_4N)_{0.5}[Ni(dmit)_2]$ is considered to be responsible for the small anisotropy, the three-dimensional character of the structure also plays an important role; two-dimensional S···S networks parallel to the bc plane are weakly connected to each other along the a-axis by S···S contacts between thioketone sulfur atoms in the isotrithione ring.

Fig. 3.——>



We calculated the intermolecular overlap integrals (S) between the LUMO of the neutral $Ni(dmit)_2$ molecule obtained by means of extended Hückel method.$^{8)}$ As shown in in Table 2, the overlap integrals along face-to-face stacking (S(A-B), S(A-B')) are larger than the interstack overlap integrals (S(A-A"), S(A-B")), which is consistent with the highest value of σ_b. And the value of S(A-B"') indicates weak interaction along the a-axis through thioketone sulfur atoms.

Table 2. Overlap integrals (× 10^3) of the LUMO of the neutral $Ni(dmit)_2$ molecule illustrated in Fig. 1.

S(A-B')	S(A-B)	S(A-A")	S(A-B")	S(A-B"')
9.06	-2.06	1.17	0.89	0.27

The dmit-complex is characterized by the isotrithione ring incorporated into the 1,2-dithiolene moiety, which makes the multi-dimensional S···S interaction possible. Small cations will enhance this ability. $(Et_4N)_{0.5}[Ni(dmit)_2]$ is considered to be a precursor of the three-dimensional molecular metal.

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