CRYSTAL STRUCTURE AND ELECTRICAL CONDUCTIVITY OF \((\text{Et}_4\text{N})_{0.5}[\text{Ni(dmit)}_2]\)

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The crystal of \((\text{Et}_4\text{N})_{0.5}[\text{Ni(dmit)}_2]\) belongs to triclinic system (dmit: isotriothionedithiolate). In the crystal, face-to-face stacking and side-by-side arrangement of \(\text{Ni(dmit)}_2\) molecules form the two-dimensional \(\cdots\text{S}\cdots\text{S}\) networks, which are weakly connected in the third direction by thioketone sulfur atoms in the isotriothione ring. The electrical conductivity measurements show that \((\text{Et}_4\text{N})_{0.5}[\text{Ni(dmit)}_2]\) is a semiconductor with small anisotropy.

Recently the highly conducting mixed valence complex \([\text{(n-Bu)}_4\text{N}]_{0.29}[\text{Ni(dmit)}_2]\) (dmit: isotriothionedithiolate) has been reported.\(^1\) The crystals of partially oxidized 1,2-dithiolen complexes have the conduction pathway based on the ligand-centered \(\pi\)-system (predominantly sulfur orbitals), while partially occupied \(\text{Pt-d}\) electron energy band is responsible for the high conductivity of inorganic one-dimensional metals containing tetracyanoplatinate and bis(oxalato)platinum anions.\(^2\) \([\text{(n-Bu)}_4\text{N}]_{0.29}[\text{Ni(dmit)}_2]\) having two-dimensional \(\cdots\text{S}\cdots\text{S}\) 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 (\(\text{Me}_4\text{N}^+\), \(\text{Et}_4\text{N}^+\), and \(\text{(n-Pro)}_4\text{N}^+\) than \(\text{(n-Bu)}_4\text{N}^+\). We now report structure determination and electrical conductivity study of \((\text{Et}_4\text{N})_{0.5}[\text{Ni(dmit)}_2]\).

The electrochemical oxidation (at a constant current of ca. 2 \(\mu\)A) of a solution containing \(\text{Et}_4\text{N}[\text{Ni(dmit)}_2]\) (10\(^{-3}\)M) and \(\text{Et}_4\text{ClO}_4\) (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 \(\text{P}\overline{1}\), \(a=20.109(2), b=7.316(1), c=6.432(1)\) \(\text{Å}\), \(\alpha=103.92(1),\) \(\beta=98.67(1),\) \(\gamma=80.62(1)\) \(\text{o}\), \(V=900.0\) \(\text{Å}^3\), \(Z=2.\)\(^3\)

The planar \(\text{Ni(dmit)}_2\) molecules are stacked along the b-axis (Fig.1). There are two independent \(\cdots\text{S}\cdots\text{S}\) contacts between the molecules A and B', slightly shorter than the van der Waals distance (3.7 \(\text{Å}\)), but there is no short intermolecular \(\cdots\text{S}\cdots\text{S}\) contact between the molecules A and B. The inter-planar distances are 3.437 \(\text{Å}\) (between A and B') and 3.759 \(\text{Å}\) (between A and B). Thus, \(\text{Ni(dmit)}_2\)
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 heteroring.$^4$ 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 is 3.499 Å observed between sulfur atoms in the dithiolenene 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.

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 isotrichione 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-}$.

<table>
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<tr>
<th>n</th>
<th>Ni-S</th>
<th>C-S</th>
<th>C-C</th>
<th>C=S</th>
<th>Ref.</th>
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<td>1.75</td>
<td>1.39</td>
<td>1.68</td>
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The bond distances (Å) given are average values.

The electrical conductivities were measured along the a, b, and c-axes ($\sigma_a$, $\sigma_b$, $\sigma_c$; Fig. 3) by the two-probe method. (Et$_4$N)$_{0.5}$[Ni(dmit)$_2$] is a semiconductor with small anisotropy. The maximum value of $\sigma_b$ is $4.5 \times 10^{-2}$ (Ω cm)$^{-1}$ and the activation energies of $\sigma_a$, $\sigma_b$, and $\sigma_c$ 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-Bu)$_4$N]$_{0.29}$[Ni(dmit)$_2$].$^{11}$ Although the relatively low conductivity of (Et$_4$N)$_{0.5}$[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 isotrichione 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. As shown 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 $\sigma_B$. And the value of S(A-B") indicates weak interaction along the a-axis through thioketone sulfur atoms.

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<td>1.17</td>
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Table 2. Overlap integrals ($\times 10^3$) of the LUMO of the neutral Ni(dmit)$_2$ molecule illustrated in Fig. 1.

The dmit-complex is characterized by the isotrithione ring incorporated into the 1,2-dithiole moiety, which makes the multi-dimensional S⋯S interaction possible. Small cations will enhance this ability. (Et$_4$N)$_{0.5}$[Ni(dmit)$_2$] is considered to be a precursor of the three-dimensional molecular metal.

References

3) The structure was determined using 4352 independent reflections measured with Mo Kα radiation for which |Fo|>3σ(|Fo|). The final R factor is 0.071.

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