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$[\mathrm{Ni(dmit)_2}]$ salts with supramolecular cation structure

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Contents

Abstract

The dithiolate complex, $[\mathrm{Ni(dmit)_2}]$ (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) is an organic π-molecule which gives highly conducting salts with closed shell cations or organic donors. We have found that crown ether macrocycles can be incorporated into the salts in which the crown ethers include alkali metal cations forming supramolecular cation (SC) structures. The SC structural diversity was observed to depend on the size of the crown ether and cation. Three kinds of crown ethers, 12-crown-4, 15-crown-5 and 18-crown-6 in addition to an acyclic polyether analog of pentaetyleneglycol were incorporated in the conducting

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[Ni(dmit)$_2$] crystals. The structure of these crystals will be described with emphasis on both the structures of SC and Ni(dmit)$_2$ conducting layers. In one example, the crown ether forms a channel in which the cation has a translational freedom. The cation, otherwise merely forms a periodic Coulomb potential in the crystal, can influence the electrical conduction through the motion in the channel. The monovalent [Ni(dmit)$_2$] salts, which are possible candidates for molecular magnets will be described on a salt having SC structure.

Keywords: Supramolecular cation; [Ni(dmit)$_2$] complex; Crystal structure; Electrical conductivity; Crown ether

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1. Introduction

The utilization of the self-organizing ability of molecules is one of the promising ways for the construction of complex molecular systems [1]. Such a ‘bottom up’ approach, that is the construction of the molecular systems from a single molecule through the molecular assemblies, is considered to be key to realizing future molecular electronic devices. The ‘bottom-up’ approach shows a sharp contrast with the ‘top-down’ methodology in the present silicon based device technology, although the fabrication of even a prototype of molecular devices by the former method is still a formidable task [2,3].

Away from the practical application, quite a number of complex molecular systems with electronic functions have been reported. These range from isolated molecular assemblies such as molecular shuttles [4] and molecular rectifiers [5] to the multi-component thin films of electroluminecent devices based on ion-conducting polymers [6]. Among others, the molecular systems in the solid state are interesting because they are often in single crystal form and it is easy to examine the structure–function relationship. In this paper, we will present self-assembled molecular systems in which self-assembled supramolecular cations are incorporated in the single crystals of [Ni(dmit)$_2$] (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) molecular conductors [7].

It is well known that the crown ethers can include alkali metal ions according to its cavity size [8]. The potassium cation, for example, best fits in the 18-crown-6 cavity. We have introduced crown ethers and acyclic polyethers into the crystals of [Ni(dmit)$_2$]. In the crystal, the polyethers and cations form novel supramolecular cation (SC) structures. In this paper, we will describe the structure and the electrical properties of 12-crown-4 [9], 15-crown-5 [10] and 18-crown-6 [11] in addition to a acyclic polyether, pentaethyleneglycol [12] containing [Ni(dmit)$_2$] salts as typical examples of SC containing salts. All of the conducting salts were prepared by the standard electrocrystallization method. The [Ni(dmit)$_2$] monovalent salts, which are not conducting but are interesting from the viewpoint of molecular magnetism [13] will also be presented adopting (NH_4^+)(15-crown-5)$_2$[Ni(dmit)$_2$] as an example [14]. However, before discussing these salts in detail, we will briefly summarize the common structural feature of [Ni(dmit)$_2$] conducting crystals.

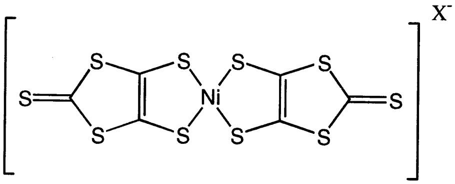
2. Common structural features of conducting [Ni(dmit)$_2$] salts

The metal dithiolate complex of [Ni(dmit)$_2$] is a well-known electron acceptor in the field of molecular conductors. The chemical structure is shown in Scheme 1. The divalent and monovalent anions are stable in solution. The monovalent form is further oxidized to a partially charged state forming conducting crystals with a variety of closed-shell cations or open-shell organic donors. The complexes of (Me$_4$N)[Ni(dmit)$_2$]$_2$ and the (TTF)[Ni(dmit)$_2$] are typical examples which show superconducting transitions [15,16].

The [Ni(dmit)$_2$] molecules form stacks by overlapping of π-electrons between adjacent molecules, through which the electronic conduction is observed. The electronic conduction is usually achieved by the LUMO band of [Ni(dmit)$_2$] and the tight binding approximation is applied for the calculation of the band structure [17]. If the conduction electron per molecule is less than unity, a significant energy gain is expected by band formation. This is one of the main reasons why conducting [Ni(dmit)$_2$] salts have columnar structure, which is a suitable molecular arrangement for band formation. On the other hand, if the LUMO orbital has one electron (i.e. monovalent salt), the energy gain can not be expected and the crystal no longer forms a stacking structure. This structural feature of monovalent salts will be discussed further in Section 4.

The [Ni(dmit)$_2$] stacks often form two-dimensional sheets through the side-by-side interactions in the crystal. The side-by-side interactions are essential to form two-dimensional band structures and thus to obtain superconductors in BEDT-TTF (bisethylenedithio-tetrathiafulvalene) salts by suppressing the Peierls instability at low temperature. However, in [Ni(dmit)$_2$] salts, the transfer integrals through the side-by-side interaction are small due to the symmetry of LUMO (b_{1u}, in the case of the HOMO band of BEDO-TTF, the symmetry is b_{zu}). Consequently, [Ni(dmit)$_2$] salts have highly one-dimensional electronic character even though they have two-dimensional sheet structures in the crystal.

To equalize the negative charge of the conduction electrons the counter cations locate between the [Ni(dmit)$_2$] stacks. The shape of the cation also affects the structure of the [Ni(dmit)$_2$] assembly even in the charged state, although the prediction of the crystal structure of each salt is almost impossible at present. One feature so far reported is the relationship between the cation size and the charge on [Ni(dmit)$_2$]. Usually the larger the counter cation, the smaller the charge on each



Scheme 1.

[Ni(dmit)$_2$] becomes. However, the generalization of this rule seems premature. We introduced SCs in the [Ni(dmit)$_2$] conducting salts through including alkali metal cations by the polyether macrocycles in the crystal. By changing the size of the macrocycles, we can change the size of the SC. But by introducing SCs, we had much larger diversity than expected in the crystal structures, or in the assembly patterns of the supramolecular cations and [Ni(dmit)$_2$]. In the following section, we will show the typical examples of these structures.

From the viewpoints of electronic functions, the counter cations usually form a periodic Coulomb potential and do not take part positively in the functions. However, by introducing SC structure, we can provide the cations a motional freedom in the crystal. Since the conduction electrons in the [Ni(dmit)$_2$] stacks and the cations in the SC structure are strongly correlated through Coulomb interactions, the dynamical change in the cation part strongly affect the conducting behavior. It is well known that the ordering of the tetrahedral anion in TMTSF (tetramethyltetraselenafulvalene) salts induces surperconducting transitions at low temperature [18]. By controlling the motional freedom or even the translational freedom of cations in the SC structure we should be able to provide the drastic change in the electrical conductivity of molecular conductors. An example where the cation motions indeed affect the electronic functions will be discussed in Section 3.2.

3. Conducting Ni[dmit]$_2$ salts with supramolecular cation structures

3.1. (Li$^+$)$_2$(12-crown-4)$_3$[Ni(dmit)$_2$]$_7$(acetone)$_2$ salt

This salt has a quite unique SC structure. Fig. 1 shows the unit cell viewed along the *b*-axis. The crystal is composed of the [Ni(dmit)$_2$] layers separated by the SC of

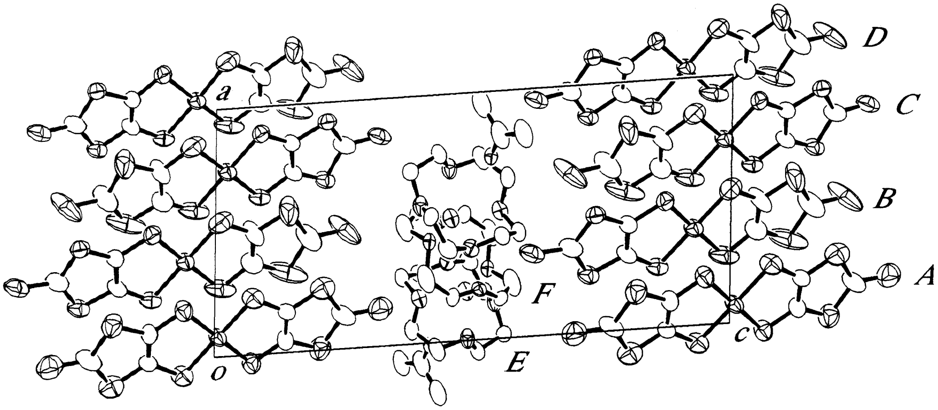


Fig. 1. Unit cell of (Li$^+$)$_2$(12-crown-4)$_3$[Ni(dmit)$_2$]$_7$(acetone)$_2$ viewed along the *b*-axis. The crystallographically identical [Ni(dmit)$_2$] molecules are labeled as A–D and those of 12-crown-4, E–F.

$(Li^+)_2$(12-crown-4)$_3$. In the [Ni(dmit)$_2$] layer, the segregated stack locates parallel to the $2a-b$ direction. The column is composed of tightly bound trimers (B-A-B′) and loosely interacting C and D molecules in A-B-C-D-D′-C′-B′-A arrangement (prime symbol indicates the molecule generated by inversion, not shown).

Although the [Ni(dmit)$_2$] part stacks as an ordinary conducting salt, the SC part has an intriguing structure as shown in Fig. 2(a). The Li^+ ion is coordinated by four basal oxygen atoms of 12-crown-4 (E) and axially by one oxygen atom of 12-crown-4 (F), resulting in a dimeric pentacoordinated unit. The Li^+ ions are tightly bound through the short interatomic Li^+–O distances, and all of these distances are shorter than the sum of the van der Waals radius of oxygen and ion radius of Li^+.

Fig. 2(b) shows the molecular arrangements of the supramolecular cation unit within the *ab*-layer viewed along the *c*-axis. The long axis of the dimeric penta-coordinated unit $(Li^+)_2$(12-crown-4)$_3$ is elongated to the $2a+b$ direction. Since each [Ni(dmit)$_2$] stack is along the $2a-b$ direction, the long axis of $(Li^+)_2$(12-crown-4)$_3$ is orthogonal to the high-electrical-conductivity direction. No interatomic contact shorter than the sum of van der Waals radii exists between these supramolecular cation units.

The salt is semiconducting with a semiconductor–semiconductor transition at around 250 K (Fig. 3). The conductivity at room temperature (σ_{RT}) was relatively high (30 S cm^{-1}). Since the Li^+ ions are tightly bound in the SC structure, the transition may not be related to the ionic motion in the SC unit in this case. By the application of pressure, a conductivity jump was also observed at 5.8 kbar. The temperature-dependent conductivity at 10.2 kbar showed no deviation from an Arrhenius plot over the whole measuring range.

3.2. $Li_{0.6}$(15-crown-5)H_2O[Ni(dmit)$_2$]$_2$ salt

By replacing 12-crown-4 to 15-crown-5, we obtained a crystal with a completely different structure. This salt is considered to be an ion–electron correlation system. The crystal has the composition $Li_{0.6}$(15-crown-5)H_2O[Ni(dmit)$_2$]$_2$. A schematic view of the structure is presented in Fig. 4 in which the stack of macrocyclic molecules form an ion channel between the stacks of [Ni(dmit)$_2$]. Both stacks extend along the *a*-axis of the crystal so that the electron flow is parallel to the ion channel direction. The electron-conducting part is composed of a pair of one-dimensional [Ni(dmit)$_2$] columns and is surrounded by four ion channels of 15-crown-5 macrocycles.

Fig. 5 shows the crystal structure viewed along the *a*-axis. The stack of [Ni(dmit)$_2$] molecules is regular implying a metallic conductivity of the one-dimensional stack (see below). The face-to-face distance between the adjacent [Ni(dmit)$_2$] within a column is 3.70 Å which is somewhat longer than that observed in the superconductor (Me_4N)[Ni(dmit)$_2$]$_2$ [15]. The intracolumn overlap integral ($t_1 = 13.67$) is much larger than that of intercolumn ($t_2 = 1.41$ and $t_3 = 0.55$). The pairs of the [Ni(dmit)$_2$] columns are separated from each other by the macrocyclic molecules (Fig. 4), which prevent the formation of short sulfur–sulfur contacts ($t_4 = 0.72$) between the adjacent pairs of [Ni(dmit)$_2$]. Consequently, the pair of

[Ni(dmit)$_2$]stacks can be regarded as a spin-ladder. The magnetic measurements, however, showed no evidence of the spin gap.

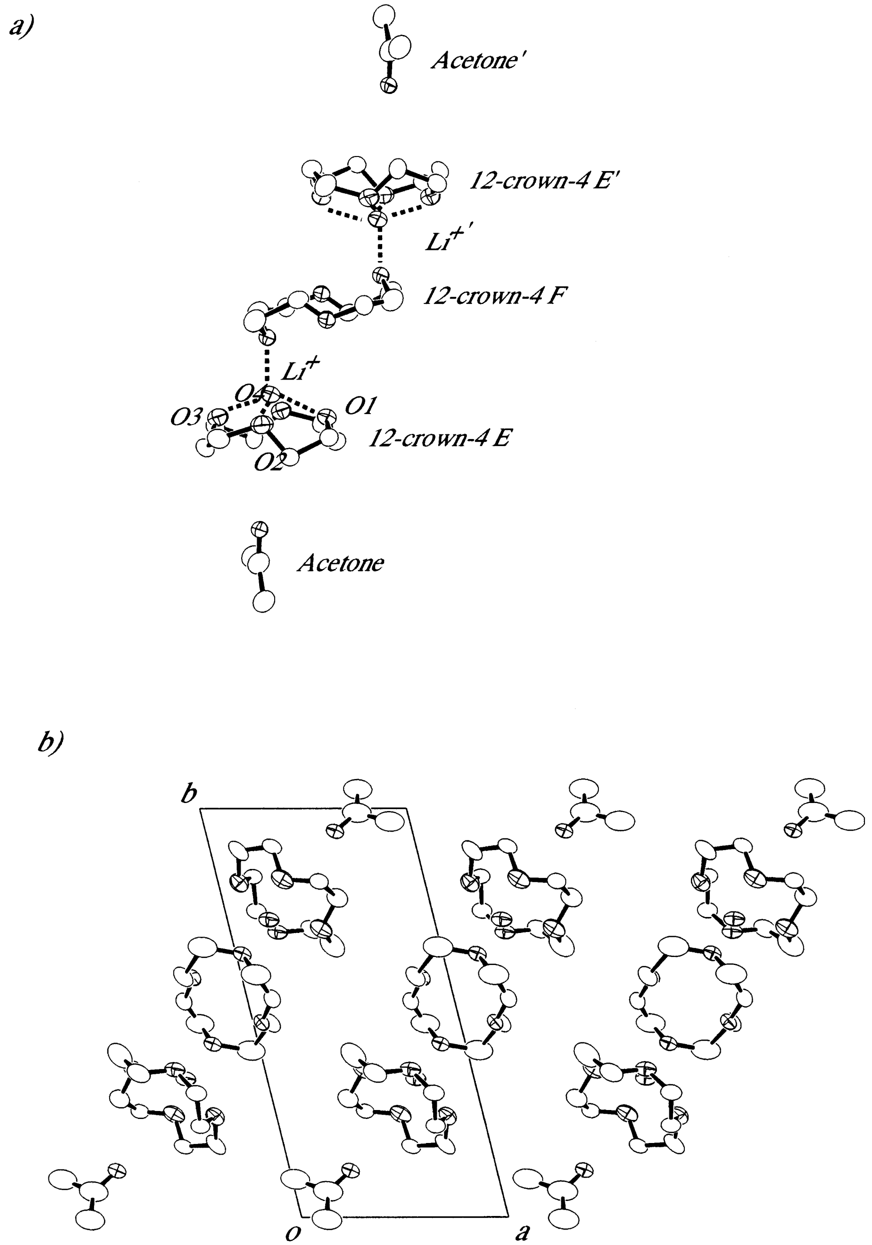


Fig. 2. (a) Dimeric penta-coordinated Li$^+$ ion in the SC unit. (b) The SC unit within the $a-b$ plane viewed along the c-axis.

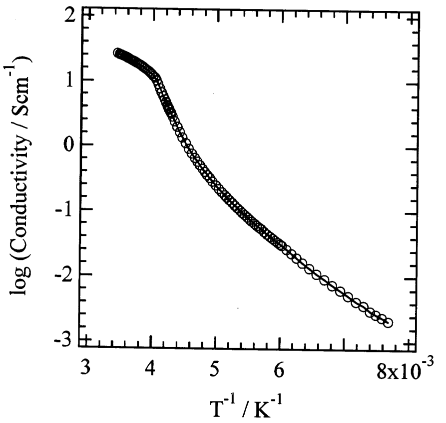


Fig. 3. The temperature dependence of the conductivity of $(Li^+)_2$(12-crown-4)$_3$[Ni(dmit)$_2$]$_7$(acetone)$_2$ single crystal.

The most striking feature of this salt is that the crown ether macrocycle regularly stacks forming an ion channel structure parallel to the [Ni(dmit)$_2$] columns. The crown ether molecules are disordered, possessing two orientations related to the point symmetry around the center of gravity of the molecule. One water molecule occupies a position at the mid-point of two adjacent crown ether molecules. The lithium cations are located at positions just above and below the center of the

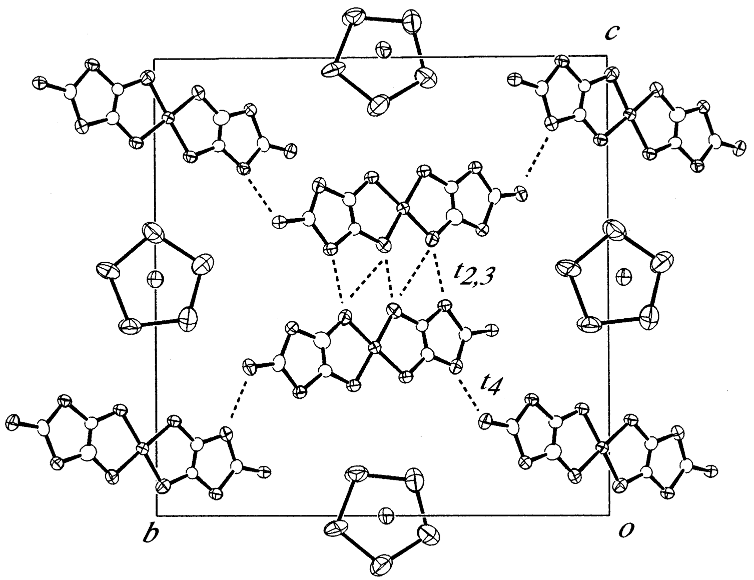


Fig. 4. The crystal structure of $Li_{0.6}$(15-crown-5)H_2O[Ni(dmit)$_2$]$_2$ viewed along the *a*-axis.

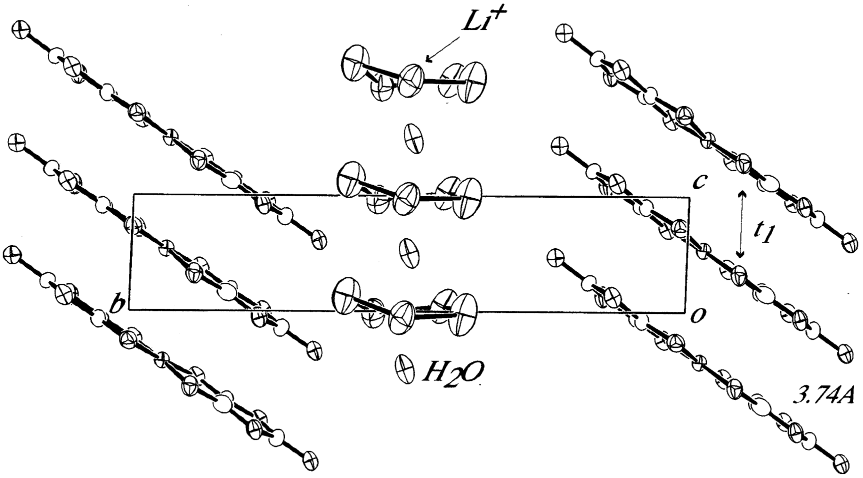


Fig. 5. A packing motif of the regular stack of [Ni(dmit)$_2$] and 15-crown-5 viewed along the *a*-axis.

crown-ether plane, thus forming a mixed chain with the water molecule in the ion channel. Since the amount of the lithium atom was determined to be 0.6 per one crown ether molecule, nearly four sites are available for one Li^+ ion. This suggests the possibility of band-filling control because the number of Li^+ ions corresponds to that of the conduction electrons in the [Ni(dmit)$_2$] LUMO band. The larger amount of Li^+ ions is included in the crystal when the [Ni(dmit)$_2$] anions are at a lower oxidation level. However, we have not obtained evidence for the variation of the amount of lithium in this salt.

Since the stack of [Ni(dmit)$_2$] in the crystal is regular, a high and metallic electrical conductivity is expected. The temperature dependence of the conductivity (σ) is shown in Fig. 6. The salt showed a very high room-temperature conductivity (around 240 S cm^{-1}) and a metallic temperature dependence at around room temperature. On the other hand, the crystal becomes semiconducting at lower temperatures. The semiconducting behavior was not suppressed by applying pressure up to 7.5 kbar. These phenomena are explained as follows. Since the Li^+ ions are nonstoichiometric in the crystal, they can essentially form random potentials. The electrons in the highly one-dimensional π-band are easily pinned through these potentials and the electronic system becomes semiconducting. This is the situation at lower temperatures. However, the ions are mobile in the channel at higher temperatures, which had been confirmed by the ion-conductivity measurements [10]. Consequently, they no longer form a random potential for localizing conduction electrons. The conduction electrons are on the regular [Ni(dmit)$_2$] stacks and can exhibit a metallic conductivity.

In summary, ionic motion in the channel strongly affects the electronic system and causes a metal–insulator transition at low temperature.

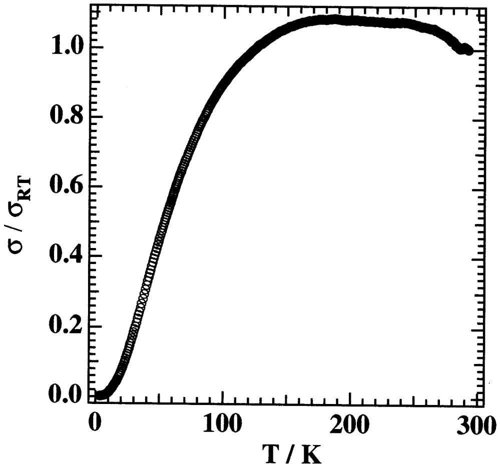


Fig. 6. The temperature dependence of the electrical conductivity of the single crystal of $Li_{0.6}$(15-crown-5)$H_2O[Ni(dmit)_2]_2$.

3.3. (NH_4^+)(18-crown-6)$[Ni(dmit)_2]_3$ salt

This salt has a SC structure ‘typical’ for crown-ether inclusion compounds. Fig. 7 shows the unit cell of the crystal of (NH_4^+)(18-crown-6)$[Ni(dmit)_2]_3$. The $[Ni(dmit)_2]$ layers are separated from each other by SC units in which the NH_4^+ ion is fully included in the cavity of the 18-crown-6 molecule. The SC of (NH_4^+)(18-

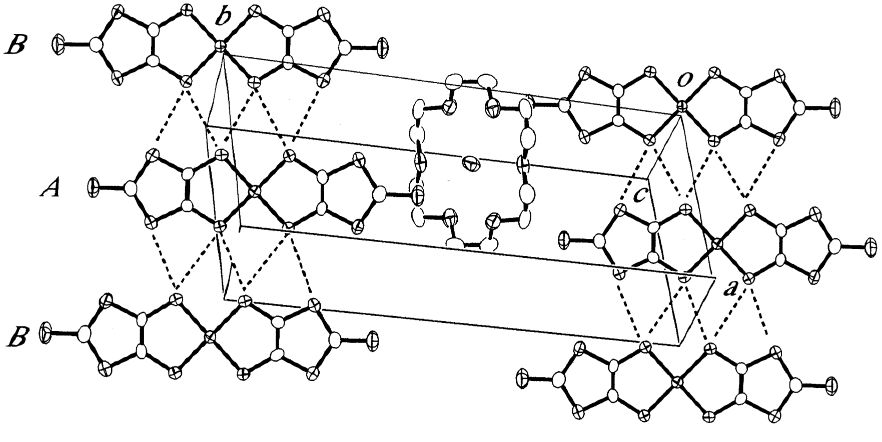


Fig. 7. Crystal structure of (NH_4^+)(18-crown-6)$[Ni(dmit)_2]_3$. Unit-cell structure viewed perpendicular to the $[Ni(dmit)_2]$ plane.

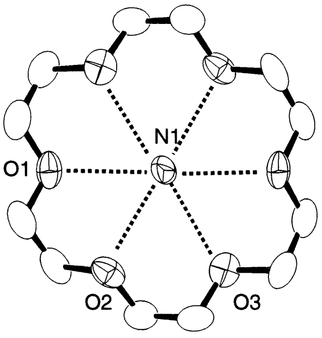


Fig. 8. The SC unit of (NH_4^+)(18-crown-6) viewed from the top and the side of 18-crown-6 plane.

crown-6) acts as a large disc-shaped cation in the crystal. In the $[Ni(dmit)_2]$ layer, the molecule forms a trimer unit (B-A-B′) and stacks along the $a + c$ direction. The strength of trimerization is weaker compared with that of $(Li^+)_2$(12-crown-4)$_3$-$[Ni(dmit)_2]_7$(acetone)$_2$.

The NH_4^+ ion is hexa-coordinated from the 18-crown-6 molecule in the SC structure (Fig. 8) and is tightly bound within the cavity of 18-crown-6 molecule through short N–O interactions. Although such a structure is seen in K^+-18-crown-6 salts and considered to be typical for crown-ether inclusion compounds, the NH_4^+ ion is not usually completely enclosed in the cavity of 18-crown-6. For example, the NH_4^+ ion exists 1.00 Å above the mean oxygen plane of the 18-crown-6 in the (NH_4^+)(18-crown-6)(Br^-) crystal [19]. The coordination observed in the present crystal is the first example, to our knowledge, of the fully enclosed NH_4^+ ion in the 18-crown-6 cavity forming a disk-shaped supramolecular cation.

The interesting thing is that the terminal sulfur of $[Ni(dmit)_2]$ is coordinated axially to the NH_4^+ ion. By replacing the NH_4^+ with the magnetic cation, we can expect localized spin-conduction electron interactions in the crystal if the crystal remains isostructural. The crystal showed typical semiconducting behavior with $\sigma_{RT} = 0.4$ S cm^{-1}, as expected from the trimer structure observed in the $[Ni(dmit)_2]$ stack.

3.4. *K^+(pentaethyleneglycol)$[Ni(dmit)_2]_3$ salt*

Polyethyleneoxides (PEO) are acyclic analogs of crown ethers and are extensively used as non-crystalline polymeric ion-conducting materials [20]. However, reports of the detailed structures of PEO, especially those of the ion-moving environment are limited so far [21]. Clarifying the nature of the coordination in PEO-ion moieties will be helpful in designing organic crystalline ionic conductors. We introduced an acyclic polyether, pentaethyleneglycol (PEG) to the potassium cation to form $K^+(PEG)[Ni(dmit)_2]_3$. The crystal structure is shown in Fig. 9. The arrangement in the $[Ni(dmit)_2]$ layer is similar to that observed in (NH_4^+)(18-crown-6)$[Ni(dmit)_2]_3$, although the details in the stacking manner are somewhat different.

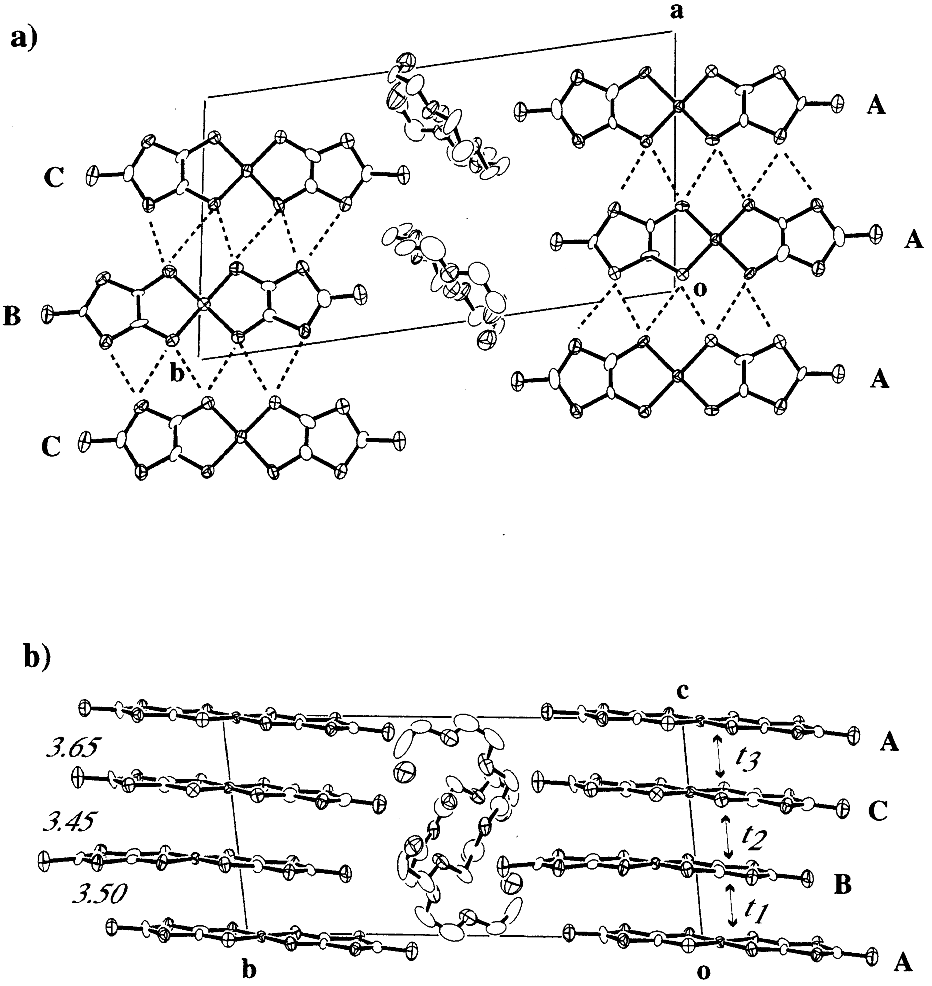


Fig. 9. Crystal structure of $K^+(PEG)[Ni(dmit)_2]_3$, viewed along the *c*-axis (a) and along the *a*-axis (b).

Fig. 10 shows the SC unit viewed along the orthogonal (Fig. 10(a)) and parallel (Fig. 10(b)) directions to the molecular plane. The SC unit of $K_2^+(PEG)_2$ is composed of two $K^+(PEG)$ units connected through two axial $K^+\cdots O1'$ interactions (solid lines in Fig. 10(b)). The K^+ is coordinated by six PEG oxygen atoms (dashed lines) and by an axial oxygen of another PEG unit (solid lines). The average $K^+\cdots O$ distance within the PEG unit is in the same range as the sum of the van der Waals radius of oxygen and the ion radius of K^+. The coordination is much looser compared to those observed in $(NH_4^+)(18\text{-crown-}6)[Ni(dmit)_2]_3$. The weaker cation binding is probably due to the lack of the macrocyclic effect [22], and it may be more appropriate to realize the ionic motion in the solid. A weak

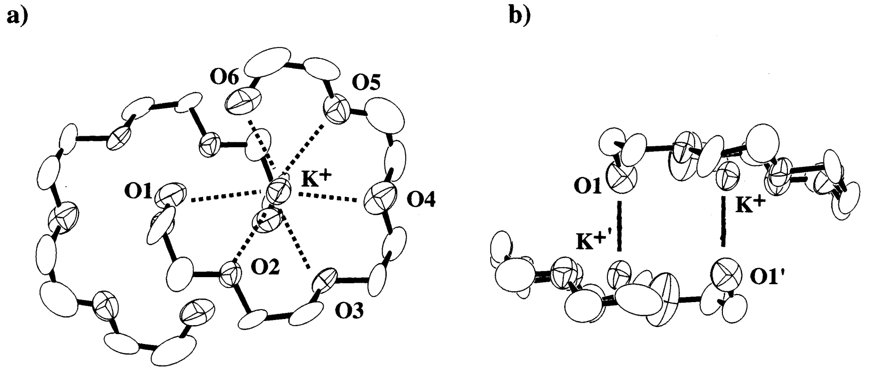


Fig. 10. (a) The SC unit of $K_2^+(PEG)_2$, viewed along the perpendicular direction to the $K^+(PEG)$ plane with the numbering schemes of oxygen atoms. (b) The side view of $K^+(PEG)$ dimer.

interatomic contact is also found between the terminal sulfur of $[Ni(dmit)_2]$ and K^+ as in the case of (NH_4^+)(18-crown-6)$[Ni(dmit)_2)_3$.

The $K^+(PEG)[Ni(dmit)_2]_3$ salt showed a room temperature conductivity of $\sigma_{RT} = 10^{-3}$ S cm^{-1} and a semiconducting behavior, which is consistent with the non-uniform dimerized stack of $[Ni(dmit)_2]$.

4. Monovalent Ni[dmit]$_2$ salts with supramolecular cations

As mentioned before, the $[Ni(dmit)_2]$ molecules do not necessarily form stacking structures in the monovalent salts. Thus, a large structural diversity in $[Ni(dmit)_2]$ arrangements in these crystals is expected. The assemblies of 1/2 spins (one unpaired electron on every $[Ni(dmit)_2]$) in the crystal are also interesting from the view points of molecular magnets. In fact, a spin-ladder system has been reported in the $[Ni(dmit)_2]$ monovalent salt [23]. According to the diversity in SC structure, a variety of the arrangements of $[Ni(dmit)_2]$ is expected in the $SC^+[Ni(dmit)_2]$ salts. We will describe here an example, a $SC^+[Ni(dmit)_2]$ salt in which 15-crown-5 forms a barrel-like SC structure and $[Ni(dmit)_2]$ forms a unique dimer array [15].

The composition of the crystal is (NH_4^+)(15-crown-5)$_2[Ni(dmit)_2]$, which is formed through cation exchange from tetrabutylammonium to the supramolecular unit, (NH_4^+)(15-crown-5)$_2$. The unit cell viewed along the *b*-axis is shown in Fig. 11(a) in which the molecules in the plane around (010) are depicted. Fig. 11(b) shows the $[Ni(dmit)_2]$ layer and supramolecular cation unit viewed along the *a*-axis. A zigzag arrangement of $[Ni(dmit)_2]$ lies along the *c*-axis. Since the $[Ni(dmit)_2]$ forms a dimer, the spins of $[Ni(dmit)_2]$ most probably form singlet pairs.

The SC structure composed of two sandwich units forming a barrel-like structure. Within the sandwich unit, the NH_4^+ ion is loosely coordinated through the NH_4^+–O contacts from 15-crown-5 molecules. All NH_4^+–O distances are longer than the typical NH_4^+–O hydrogen-bond distance [24]. Although the $[Ni(dmit)_2]$

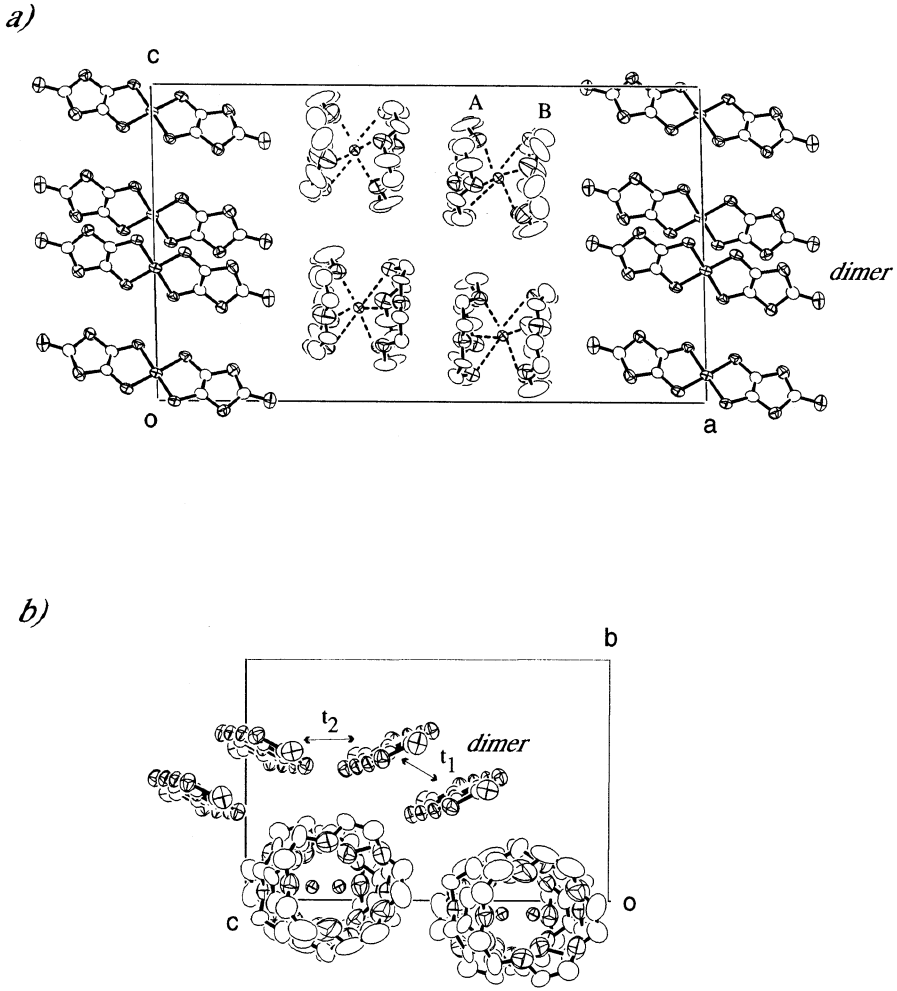


Fig. 11. Crystal structure of $(NH_4^+)(15\text{-crown-}5)_2[Ni(dmit)_2]$. (a) Unit cell viewed along the *b*-axis. (b) The structure viewed along the *a*-direction.

molecules form a one-dimensional chain in the crystal, the conductivity of the crystal was less than 10^{-6} S cm^{-1} due to the fully charge transferred state of the $[Ni(dmit)_2]$.

5. Conclusion

Thanks to the large stabilization energy due to the affinity of crown ethers (or acyclic polyethers) for alkali metal ions, the supramolecular structures were formed in the $[Ni(dmit)_2]$ crystals. In the crystal of $(Li^+)_2(12\text{-crown-}4)_3[Ni(dmit)_2]_7$-

(acetone)$_2$, the [Ni(dmit)$_2$] conducting layer is separated by $(Li^+)_2$(12-crown-4)$_3$ having a unique SC structure. The (NH_4^+)(18-crown-6)[Ni(dmit)$_2$]$_3$ crystal consists of a non-uniform trimerized stack of [Ni(dmit)$_2$] and a disk-shaped supramolecular ion of (NH_4^+)(18-crown-6). The NH_4^+ is completely enclosed in the cavity through the N–H···O hydrogen-bonding interactions. A similar SC unit of K^+(PEG) is incorporated in the electrically conducting [Ni(dmit)$_2$] salt by using an acyclic polyether analog. The coordinating ability of PEG to K^+ is smaller than that of 18-crown-6 due to the lack of a macrocyclic effect. Reflecting the non-uniform stack of [Ni(dmit)$_2$], these crystals are semiconducting.

Although the cations are fixed in these crystals, the SC structure of an ion channel in which the ions have a translational freedom was found in $Li_{0.6}$(15-crown-5)H_2O[Ni(dmit)$_2$]$_2$. The electrical conductivity measurements suggest that the control of the electrical conduction in the [Ni(dmit)$_2$] stacks is possible through ionic motion in the SC unit. The number of Li^+ ions in the ion-channel SC unit is non-stoichiometric. Since the number of the Li^+ ions corresponds to that of the conduction electrons, the filling control of the [Ni(dmit)$_2$] LUMO band may be possible through controlling the amount of Li^+ ions.

The crystal of (NH_4^+)(15-crown-5)$_2$[Ni(dmit)$_2$] was obtained by the cation exchange process of the monovalent salt. In the crystal, the strips formed by the weak side-by-side interactions of [Ni(dmit)$_2$] dimers are separated from each other by the barrel-like SC units of (NH_4^+)(15-crown-5)$_2$.

The SC structures as well as the [Ni(dmit)$_2$] arrangements are not limited to those reported here. We have already observed a variety of crystals with SC structures including those which have ion-channel structures besides the crystals reported here [25–27]. According to the diversity in the SC structure, the [Ni(dmit)$_2$] monovalent salts with SC also give a wide variety of [Ni(dmit)$_2$] arrangements in the crystal. The array of 1/2 spins thus obtained will be promising candidates for novel magnetic properties. We hope that novel electronic functions will emerge from these SC containing crystals in the near future.

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