Potassium bis(4,5-dimercapto-1,3-dithiole-2-thionato)nickelate 1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzocyclooctadeca-2,11-diene propanone solvate

Kozo Shitagami, Tomoyuki Akutagawa, Tatsuo Hasegawa, Takayoshi Nakamura and Neil Robertson


Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see http://journals.iucr.org/services/authorrights.html

Acta Crystallographica Section C: Crystal Structure Communications specializes in the rapid dissemination of high-quality studies of crystal and molecular structures of interest in fields such as chemistry, biochemistry, mineralogy, pharmacology, physics and materials science. The numerical and text descriptions of each structure are submitted to the journal electronically as a Crystallographic Information File (CIF) and are checked and typeset automatically prior to peer review. The journal is well known for its high standards of structural reliability and presentation. Section C publishes approximately 1000 structures per year; readers have access to an archive that includes high-quality structural data for over 10000 compounds.

Crystallography Journals Online is available from journals.iucr.org
Potassium bis(4,5-dimercapto-1,3-dithiole-2-thionato)nickelate 1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzo cyclooctadeca-2,11-diene propanone solvate

Kozo Shitagami, a Tomoyuki Akutagawa, a,b,c Tatsuo Hasegawa, a,b Takayoshi Nakamura a,b,s and Neil Robertson d

aGraduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan, bResearch Institute for Electronic Science, Hokkaido University, Sapporo 060-0812, Japan, cPRESTO, JST, Japan, and dDepartment of Chemistry, University of Edinburgh, Edinburgh EH9 3J, Scotland

Received 22 June 2001
Accepted 17 August 2001

In the title compound, K[Ni(C15S3)2]·C20H25O6·C3H8O, K+ is incorporated in the cavity of the 1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzo cyclooctadeca-2,11-diene (DB18c6) molecule and is coordinated by the six DB18c6 O atoms and the propanone O atom. Two [K+(DB18c6)(CH3)2CO] units form a dimer which is aligned in a one-dimensional manner along the a axis through a face-to-face interaction between the benzene rings of neighboring DB18c6 molecules. [Ni(dmit)2]− anions are also aligned along the a axis through side-by-side S···S interactions.

Comment

[Ni(dmit)2]− is a planar π-conjugated anion and has an open-shell electronic structure with S = 1/2 spin. [Ni(dmit)2]− salts with various counter-cations have been reported and some possess interesting magnetic properties, such as the spin-ladder system (Imai et al., 1999). Counter-cations for [Ni(dmit)2]− salts are necessary to neutralize the total charge in the crystal and they affect the whole crystal structure. We have introduced supramolecular cation (SC+) structures composed of metal cations and crown ethers as the counter-cation for [Ni(dmit)2]− in order to control the spin arrangements of [Ni(dmit)2]−. In the crystal, SC+ shows a variety of structures, such as the typical disc-shaped structure, in which K+ is completely included at the center of the crown-ether cavity, and the sandwich-type Ca2+(15-crown-5), in which Ca2+ is located at the midpoint between two crown-ether molecules (Takamatsu et al., 2000; Akutagawa et al., 2001).

1,4,7,10,13,16-Hexaoxa-2,3:11,12-dibenzo cyclooctadeca-2,11-diene (DB18c6) is a typical crown ether having two phenyl rings. A novel SC+ assembly through π···π interaction is expected within the [Ni(dmit)2]− crystal using DB18c6 as a building block for the SC+ structure. In the present study, we report the crystal structure of K[Ni(dmit)2]·DB18c6-(CH3)2CO, (I), in which DB18c6 forms a one-dimensional array through π···π interactions of the dibenzo moieties.

Fig. 1 represents an ORTEPIII (Burnett & Johnson, 1996) view of salt (I). The six O atoms of the DB18c6 unit are coplanar, as reported in the literature (Bright & Truter, 1970), and K+ is incorporated at the center of the DB18c6 cavity. The six K−O distances are in the range 2.691 (3)–2.794 (3) Å. In addition, the propanone O atom is coordinated to K+ with a K−O distance of 2.611 (4) Å. The DB18c6 molecule has a V-shaped conformation, with a dihedral angle of 100.46° between the two benzene rings. One propanone molecule is enclosed by the V-shaped DB18c6 molecule and is fixed by a short K−O coordination.

The [Ni(dmit)2]− complex anion is planar in the crystal, as is usually reported (Pullen & Olk, 1999). The maximum deviation from the least-squares plane of [Ni(dmit)2]− is 0.105 Å for S7. Within the crystal, [Ni(dmit)2]− anions are arranged along the a axis and the direction of the molecular long axis alternately turns toward [012] and [021], as shown in Fig. 2. The angles between the long axes of adjacent [Ni(dmit)2]− anions are 57.26 and 57.48°. The short S···S contact distances observed for side-by-side S···S interactions between neighboring molecules are nearly equal to or less than the van der Waals S···S contact distance of 3.60 Å (Bondi, 1964). S···S contacts less than 3.70 Å are summarized in Table 1. The side-
metal-organic compounds

Figure 2
Packing diagram of (I) viewed along the a axis. The \([\text{Ni}^{2+}](\text{dmit})_2^{-}\) anions are arranged almost along the [012] and [0T2] directions.

by-side S···S contacts arrange the \([\text{Ni}^{2+}](\text{dmit})_2^{-}\) anions in a one-dimensional manner.

As shown in Fig. 3, \(\text{SC}^+\) is aligned along the a axis, forming a one-dimensional structure. Two \([\text{K'}(\text{DB18c6})(\text{CH}_3\text{CO})]\) units form a dimer related by \(C_2\) symmetry; the dimer is a repeating unit. In the dimer, the molecular planes of the propanone molecule are parallel and the directions of the C—O bonds are opposite to each other. Intermolecular distances between carbonyl groups are 3.276 (9) (C27···C27) and 3.385 (6) Å (C27···O7), and these distances are close to the van der Waals C···O contact distance of 3.22 Å (Bondi, 1964). Since the propanone molecule has a strong dipole moment (2.88 D), dipole–dipole interactions between the carbonyl groups can contribute to the formation of the dimer structure.

The benzene rings of neighboring DB18c6 molecules have a face-to-face orientation and the mean interplanar distance between them is 3.421 Å, which is nearly equal to the van der Waals contact distances of aromatic hydrocarbon atoms, ca 3.4 Å. Selected intermolecular distances less than 3.6 Å between two benzene rings are summarized in Table 1. A one-dimensional supramolecular array of (pyridinium)\(^{-}\)-DB18c6\(^{+}\) \((\text{BF}_4)^{-}\) has been reported in which pyridinium and the V-shaped DB18c6 molecule stack alternately to form a one-dimensional column by utilizing intermolecular face-to-face \(\pi\)-\(\pi\) interactions and hydrogen bonding between the host and guest molecules (Låmså et al., 1998; Talanov et al., 1999).

In the present case, intermolecular \(\pi\)-\(\pi\) interactions between the benzene rings of the host molecules form a one-dimensional \([\text{K'}(\text{DB18c6})(\text{CH}_3\text{CO})_2]_2\) dimer array.

Experimental

The title crystal was prepared by slow evaporation of a propanone solution of \("\text{Bu},\text{N}[\text{Ni}(\text{dmit})_2]\). DB18c6 and \(\text{KClO}_4\). Shiny black plate-like crystals were obtained.

Crystal data

\[
\begin{align*}
\text{K}[\text{Ni}(\text{C}_3\text{S}_3)_2]\cdot\text{C}_8\text{H}_8\text{O}_2\cdot\text{C}_6\text{H}_9\text{O} & \quad D_t = 1.575 \text{ Mg m}^{-3} \\
M_r & = 908.95 \\
\text{Monoclinic, } C2/c & \quad \text{Cell parameters from 18 032 reflections} \\
a & = 12.8232 (5) \text{ Å} & \quad \theta = 2.4–27.5^\circ \\
b & = 22.4666 (8) \text{ Å} & \quad \mu = 1.20 \text{ mm}^{-1} \\
c & = 26.612 (1) \text{ Å} & \quad T = 296.2 \text{ K} \\
\beta & = 90.201 (2) & \quad \text{Plate, black} \\
V & = 7666.6 (5) \text{ Å}^3 & \quad 0.35 \times 0.35 \times 0.10 \text{ mm} \\
Z & = 8 & \\
\end{align*}
\]

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
\(\omega\) scans
Absorption correction: multi-scan
\(\text{ABSQCOR, Higashi, 1995}\)
\(T_{\text{max}} = 0.699, T_{\text{min}} = 0.887\)
36 400 measured reflections
8776 independent reflections
4422 reflections with \(F^2 > 2\sigma(F^2)\)
\(R_{\text{int}} = 0.050\)

Refinement

Refinement on \(F^2\)
\(R(F) = 0.035\)
\(wR(F^2) = 0.088\)
\(S = 1.05\)
4422 reflections
433 parameters

H-atom parameters not refined

The molecule of (I) crystallized in the monoclinic system; space group \(C2/c\) was assumed from the systematic absences. The propanone methyl groups undergo motion or are slightly disordered. H-atom positions were idealized and were refined with a riding model in which the C—H distance was constrained to 0.95 Å.
Table 1
Selected intermolecular S···S and benzene-benzene contact distances (Å).

\[ \begin{array}{ccc}
S4···S9^a & 3.637 (2) & C1···C13^a & 3.524 (6) \\
S6···S10^a & 3.549 (2) & C2···C2^a & 3.479 (7) \\
S9···S9^a & 3.534 (2) & C2···C16^a & 3.509 (6) \\
C1···C1^a & 3.486 (7) & & \\
\end{array} \]

Symmetry codes: (i) \(-x, y, \frac{1}{2} - z\); (ii) \(1 - x, y, \frac{1}{2} - z\).

Data collection: PROCESS-AUTO (Rigaku, 1998); cell refinement: PROCESS-AUTO; data reduction: PROCESS-AUTO; program(s) used to solve structure: SIR92 (Altomare et al., 1994); program(s) used to refine structure: TEXSAN (Molecular Structure Corporation and Rigaku, 1999); molecular graphics: ORTEPIII (Burnett & Johnson, 1996); software used to prepare material for publication: TEXSAN.

This work was partially supported by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by the Proposal-Based New Industry Creative Type Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) in Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1119). Services for accessing these data are described at the back of the journal.

References