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

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


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1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzocyclooctadeca-2,11-diene
propanone solvate

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In the title compound, K[Ni(C5S2)2]2C10H12O6C3H6O, K+ is incorporated in the cavity of the 1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzocyclooctadeca-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 (Takamatsumi et al., 2000; Akutagawa et al., 2001).

1,4,7,10,13,16-Hexaoxa-2,3:11,12-dibenzocyclooctadeca-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 [Ni(dmit)2]−DB18c6-(CH3)2CO, (I), in which DB18c6 forms a one-dimensional array through π–π interactions of the dibenzo moiety.

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 [012], 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-chain

Figure 1
The molecular structure of (I), with displacement ellipsoids at the 50% probability level and H atoms omitted for clarity.
metal-organic compounds

Figure 2
Packing diagram of (I) viewed along the a axis. The [Ni(dmit)₂]⁻ anions are arranged almost along the [012] and [0T2] directions.

by-side S···S contacts arrange the [Ni(dmit)₂]⁻ anions in a one-dimensional manner.

As shown in Fig. 3, SC⁺ is aligned along the a axis, forming a one-dimensional structure. Two [K⁺(DB18c6)][(CH₃)₂CO] units form a dimer related by C₂ 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)BF₄⁻ 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 π···π interactions and hydrogen bonding between the host and guest molecules (Lämsä et al., 1998; Talanova et al., 1999). In the present case, intermolecular π···π interactions between the benzene rings of the host molecules form a one-dimensional [K⁺(DB18c6)(CH₃)₂CO]₂ dimer array.

Experimental

The title crystal was prepared by slow evaporation of a propanone solution of ([Bu₄N][Ni(dmit)₂]), DB18c6 and KClO₄. Shiny black plate-like crystals were obtained.

Crystal data
K[Ni(C₃H₃S)₂]·C₆H₆·H₂O·C₆H₄O
M_r = 908.95
Monoclinic, C2/c
a = 12.8232 (5) Å
b = 22.4666 (8) Å
c = 26.612 (1) Å
β = 90.201 (2)°
V = 7666.6 (5) Å³
Z = 8

Data collection
Rigaku R-AXIS RAPID Imaging Plate diffractometer
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_min = 0.699, T_max = 0.887
36 400 measured reflections

Refinement
Refinement on F²
H-atom parameters not refined
w = 1/[σ²(F²) + 0.05(max(F²,0)) + 2F²/3]²
Δρ_max = 0.32 e Å⁻³
Δρ_min = -0.24 e Å⁻³
4422 reflections
433 parameters

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).

<table>
<thead>
<tr>
<th></th>
<th>S4···S6</th>
<th>C1···C13</th>
<th>S3···S4</th>
<th>C2···C23</th>
<th>S9···S9</th>
<th>C1···C14</th>
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<tbody>
<tr>
<td></td>
<td>3.637 (2)</td>
<td>3.524 (6)</td>
<td>3.549 (2)</td>
<td>3.479 (7)</td>
<td>3.534 (2)</td>
<td>3.509 (6)</td>
</tr>
<tr>
<td>C1···C14</td>
<td>3.486 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Symmetry codes: (i) −x, y, 1/2 − z; (ii) 1 − x, y, 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.

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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