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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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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In the title compound, K[Ni(C5S2)3]·C2H5H2O6·C3H8O, 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 (Takamatsu et al., 2000; Akutagawa et al., 2001).

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.

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 [0T2], 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).

Figure 1
The molecular structure of (I), with displacement ellipsoids at the 50% probability level and H atoms omitted for clarity.
by-side S···S contacts arrange the \([\text{Ni(dmit)}_2]^-\) anions in a one-dimensional manner.

As shown in Fig. 3, SC\(^+\) is aligned along the \(a\) axis, forming a one-dimensional structure. Two \([K'(\text{DB18c6})(\text{CH}_3)_2\text{CO}])\) 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 \(\text{C}=\text{O}\) bonds are opposite to each other. Intermolecular distances between carbonyl groups are 3.276 (9) \((\text{C}27\cdots\text{C}27)\) and 3.385 (6) \(\text{Å}\) \((\text{C}27\cdots\text{O}7)\), and these distances are close to the van der Waals C···O contact distance of 3.22 \(\text{Å}\) (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 \(\text{Å}\), which is nearly equal to the van der Waals contact distances of aromatic hydrocarbon atoms, \(ca\) 3.4 \(\text{Å}\). Selected intermolecular distances less than 3.6 \(\text{Å}\) between two benzene rings are summarized in Table 1. A one-dimensional supramolecular array of \((\text{pyridinium})^+\)-(DB18c6)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 (Lämsä et al., 1998; Talanova et al., 1999). In the present case, intermolecular \(\pi\)–\(\pi\) interactions between the benzene rings of the host molecules form a one-dimensional \([K'(\text{DB18c6})(\text{CH}_3)_2\text{CO}])_2\) dimer array.

**Experimental**

The title crystal was prepared by slow evaporation of a propanone solution of \("\text{Bu}_4\text{N}[\text{Ni(dmit)}_2]\), DB18c6 and KClO_4. Shiny black plate-like crystals were obtained.

**Crystal data**

\[
\begin{align*}
\text{K}[\text{Ni(C}_2\text{S}_4)_2]\cdot\text{C}_8\text{H}_8\text{O}_2\cdot\text{C}_6\text{H}_6\text{O} & \quad D_s = 1.575 \text{ Mg m}^{-3} \\
M_r & = 908.95 \\
\text{Monoclinic, } C2/c & \quad \text{Mo } K\alpha \text{ radiation} \\
\alpha & = 12.8233 \text{ (5) } \text{Å} & \quad \text{Cell parameters from 18 032} \\
b & = 22.4666 \text{ (8) } \text{Å} & \quad \text{reflections} \\
c & = 26.6162 \text{ (1) } \text{Å} & \quad \theta = 2.4–27.5^\circ \\
\beta & = 90.201 \text{ (2)} & \quad \mu = 1.20 \text{ mm}^{-1} \\
V & = 7666.6 \text{ (5) } \text{Å}^3 & \quad T = 296.2 \text{ K} \\
Z & = 8 & \quad \text{Plate, black} \\
\end{align*}
\]

\[
\begin{align*}
\text{Data collection} & \quad 8776 \text{ independent reflections} \\
\text{Rigaku R-AXIS RAPID Imaging} & \quad 4422 \text{ reflections with } F^2 > 2\sigma(F^2) \\
\text{Plate diffractometer} & \quad R_{int} = 0.050 \\
\text{\(\omega\) scans} & \quad \varphi_{max} = 27.5^\circ \\
\text{Absorption correction: multi-scan} & \quad \psi = 0 \rightarrow 16 \\
\text{(ABSCOR; Higashi, 1995)} & \quad k = 0 \rightarrow 29 \\
\text{\(T_{min} = 0.699\), } T_{max} = 0.887 & \quad \varphi = -34 \rightarrow 34 \\
36400 \text{ measured reflections} & \\
\end{align*}
\]

**Refinement**

\[
\begin{align*}
\text{Refinement on } F^2 & \quad \text{H-atom parameters not refined} \\
R(F) = 0.035 & \quad w = 1/\sigma^2(F^2) + [0.05 \max(F^2,0)] \\
wR(F^2) = 0.088 & \quad + 2F^2/[S(3)] \\
S = 1.05 & \quad (\Delta/\sigma)_{max} < 0.001 \\
4422 \text{ reflections} & \quad \Delta \rho_{max} = 0.32 \text{ e } \text{Å}^{-3} \\
433 \text{ parameters} & \quad \Delta \rho_{min} = -0.24 \text{ e } \text{Å}^{-3} \\
\end{align*}
\]

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 \(\text{Å}\).
Table 1
Selected intermolecular S - S and benzene-benzene contact distances (Å).

<table>
<thead>
<tr>
<th>Distance</th>
<th>Value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4 - S9'</td>
<td>3.637 (2)</td>
</tr>
<tr>
<td>S6 - S10'</td>
<td>3.549 (2)</td>
</tr>
<tr>
<td>S9 - S9'</td>
<td>3.534 (2)</td>
</tr>
<tr>
<td>C1 - C1'</td>
<td>3.486 (7)</td>
</tr>
</tbody>
</table>

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.

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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