

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, $K[\text{Ni}(\text{C}_3\text{S}_5)_2] \cdot \text{C}_{20}\text{H}_{24}\text{O}_6 \cdot \text{C}_3\text{H}_6\text{O}$, 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 $[\text{K}^+(\text{DB18c6})[(\text{CH}_3)_2\text{CO}]]$ 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. $[\text{Ni}(\text{dmit})_2]^-$ anions are also aligned along the a axis through side-by-side $\text{S} \cdots \text{S}$ interactions.

Comment

$[\text{Ni}(\text{dmit})_2]^-$ is a planar π -conjugated anion and has an open-shell electronic structure with $S = \frac{1}{2}$ spin. $[\text{Ni}(\text{dmit})_2]^-$ 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 $[\text{Ni}(\text{dmit})_2]^-$ 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 $[\text{Ni}(\text{dmit})_2]^-$ in order to control the spin arrangements of $[\text{Ni}(\text{dmit})_2]^-$. 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 $\text{Ca}^{2+}(\text{15-crown-5})_2$, in which Ca^{2+} 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-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 $[\text{Ni}(\text{dmit})_2]^-$ crystal using DB18c6 as a building block for the SC^+ structure. In the present study, we report the crystal structure of $\text{K}[\text{Ni}(\text{dmit})_2] \cdot \text{DB18c6} \cdot (\text{CH}_3)_2\text{CO}$, (I), in which DB18c6 forms a one-dimensional array through π - π interactions of the dibenzo moieties.

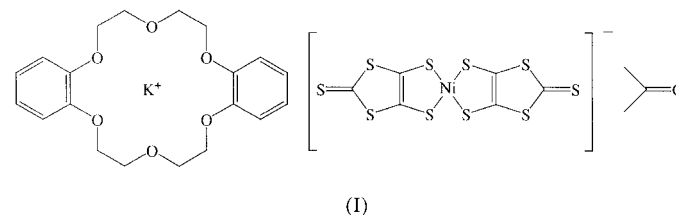


Fig. 1 represents an *ORTEP*III (Burnett & Johnson, 1996) view of salt (I). The six O atoms of the DB18c6 unit are coplanar, as reported in the literature (Bright & Truter, 1970), and K^+ is incorporated at the center of the DB18c6 cavity. The six $\text{K}-\text{O}$ distances are in the range 2.691 (3)–2.794 (3) Å. In addition, the propanone O atom is coordinated to K^+ with a $\text{K}-\text{O}$ 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 $\text{K}-\text{O}$ coordination.

The $[\text{Ni}(\text{dmit})_2]^-$ complex anion is planar in the crystal, as is usually reported (Pullen & Olk, 1999). The maximum deviation from the least-squares plane of $[\text{Ni}(\text{dmit})_2]^-$ is 0.105 Å for S7. Within the crystal, $[\text{Ni}(\text{dmit})_2]^-$ anions are arranged along the a axis and the direction of the molecular long axis alternately turns toward $[012]$ and $[0\bar{1}2]$, as shown in Fig. 2. The angles between the long axes of adjacent $[\text{Ni}(\text{dmit})_2]^-$ anions are 57.26 and 57.48° . The short $\text{S} \cdots \text{S}$ contact distances observed for side-by-side $\text{S} \cdots \text{S}$ interactions between neighboring molecules are nearly equal to or less than the van der Waals $\text{S} \cdots \text{S}$ contact distance of 3.60 Å (Bondi, 1964). $\text{S} \cdots \text{S}$ contacts less than 3.70 Å are summarized in Table 1. The side-

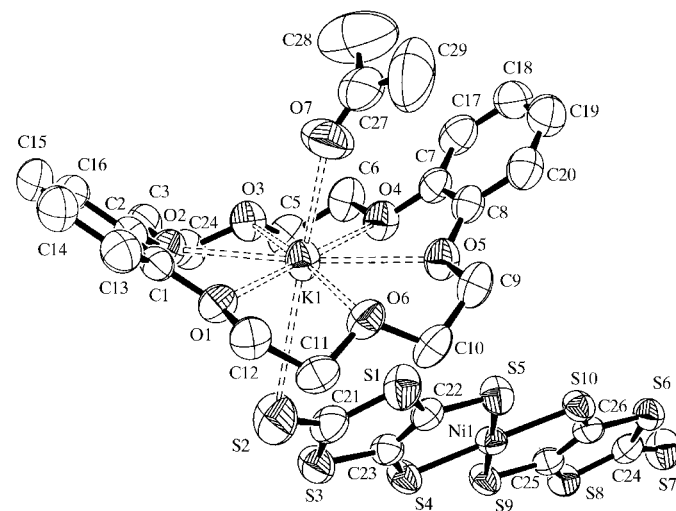


Figure 1

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

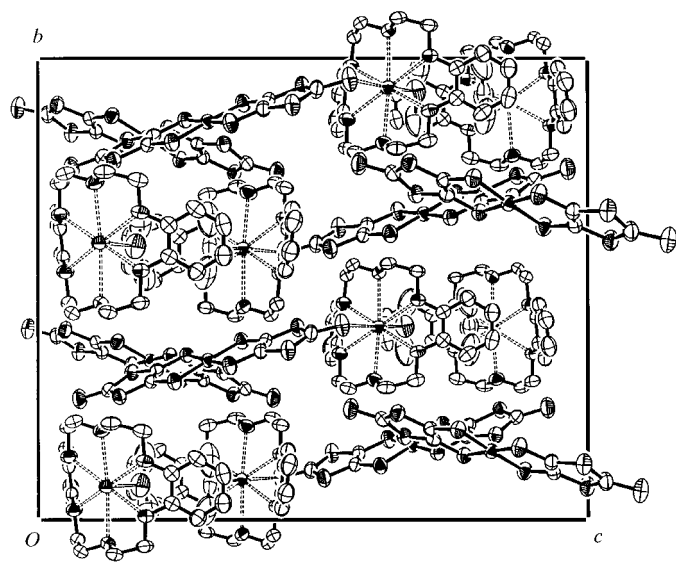


Figure 2
Packing diagram of (I) viewed along the a axis. The $[\text{Ni}(\text{dmit})_2]^-$ anions are arranged almost along the $[012]$ and $[0\bar{1}2]$ directions.

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

As shown in Fig. 3, SC^+ is aligned along the a axis, forming a one-dimensional structure. Two $\{\text{K}^+(\text{DB18c6})[(\text{CH}_3)_2\text{CO}]\}$ 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

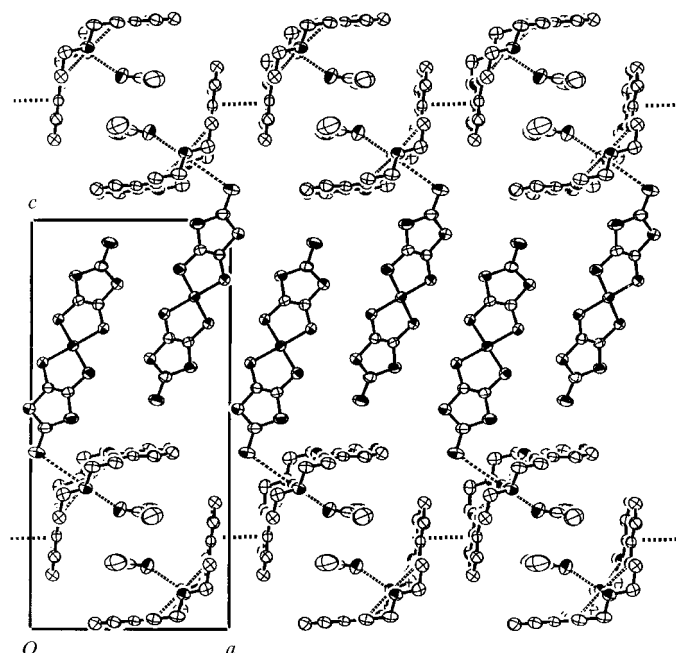


Figure 3
The arrangements of SC^+ viewed along the b axis. The dimers are aligned along the a axis.

distances between carbonyl groups are 3.276 (9) ($\text{C27}\cdots\text{C27}$) and 3.385 (6) Å ($\text{C27}\cdots\text{O7}$), and these distances are close to the van der Waals $\text{C}\cdots\text{O}$ 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) 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 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 $[\text{K}^+(\text{DB18c6})(\text{CH}_3)_2\text{CO}]_2$ dimer array.

Experimental

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

Crystal data

$\text{K}[\text{Ni}(\text{C}_3\text{S}_5)_2]\cdot\text{C}_{20}\text{H}_{24}\text{O}_6\cdot\text{C}_3\text{H}_6\text{O}$
 $M_r = 908.95$
 Monoclinic, $C2/c$
 $a = 12.8232$ (5) Å
 $b = 22.4666$ (8) Å
 $c = 26.612$ (1) Å
 $\beta = 90.201$ (2)°
 $V = 7666.6$ (5) Å³
 $Z = 8$

$D_x = 1.575$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 18 032 reflections
 $\theta = 2.4$ – 27.5°
 $\mu = 1.20$ mm⁻¹
 $T = 296.2$ K
 Plate, black
 $0.35 \times 0.35 \times 0.10$ mm

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

8776 independent reflections
 4422 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 27.5^\circ$
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 29$
 $l = -34 \rightarrow 34$

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
 $w = 1/[\sigma^2(F_o^2) + \{0.05[\max(F_o^2, 0) + 2F_c^2]/3\}^2]$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

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).

S4...S9 ⁱ	3.637 (2)	C1...C13 ⁱⁱ	3.524 (6)
S6...S10 ⁱⁱ	3.549 (2)	C2...C2 ⁱⁱ	3.479 (7)
S9...S9 ⁱ	3.534 (2)	C2...C16 ⁱⁱ	3.509 (6)
C1...C1 ⁱⁱ	3.486 (7)		

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

- Akutagawa, T., Takamatsu, N., Shitagami, K., Hasegawa, T., Nakamura, T., Inabe, T., Fujita, W. & Awaga, K. (2001). *J. Mater. Chem.* In the press.
- Altomare, A., Casciarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bright, D. & Truter, M. R. (1970). *J. Chem. Soc. B*, pp. 1544–1550.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Imai, H., Otuska, T., Naito, T., Awaga, K. & Inabe, T. (1999). *J. Am. Chem. Soc.* **121**, 8098–8103.
- Lämsä, M., Huuskonen, J., Rissanen, K. & Purisianen, J. (1998). *Chem. Eur. J.* **4**, 84–92.
- Molecular Structure Corporation & Rigaku (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
- Pullen, A. E. & Olk, R.-M. (1999). *Coord. Chem. Rev.* **188**, 211–262.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Takamatsu, N., Akutagawa, T., Hasegawa, T., Nakamura, T., Inabe, T., Fujita, W. & Awaga, K. (2000). *Inorg. Chem.* **39**, 870–871.
- Talanova, G. G., Elkarim, N. S. A., Talanov, V. S., Hanes, R. E. Jr, Hwang, H.-S., Bartsch, R. A. & Rogers, R. (1999). *J. Am. Chem. Soc.* **121**, 11281–11290.