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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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Acta Crystallographica Section C
Crystal Structure Communications
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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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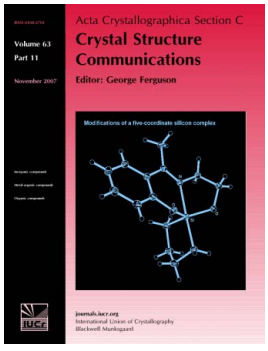

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Potassium bis(4,5-dimercapto-1,3-dithiole-2-thionato)nickelate 1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzocyclooctadeca-2,11-diene propanone solvate

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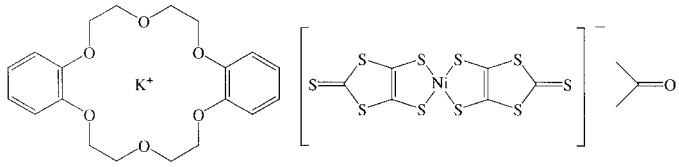
In the title compound, $K[Ni(C_3S_5)_2]\cdot C_{20}H_{24}O_6\cdot C_3H_6O$, K^+ is incorporated in the cavity of the 1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzocyclooctadeca-2,11-diene (DB18c6) molecule and is coordinated by the six DB18c6 O atoms and the propanone O atom. Two $\{K^+(DB18c6)[(CH_3)_2CO]\}$ 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 $S = \frac{1}{2}$ 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 $Ca^{2+}(15\text{-crown-}5)_2$, 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 $[Ni(dmit)_2]^-$ crystal using DB18c6 as a building block for the SC^+ structure. In the present study, we report the crystal structure of $K[Ni(dmit)_2]\cdot DB18c6\cdot\cdot(CH_3)_2CO$, (I), in which DB18c6 forms a one-dimensional array through π–π interactions of the dibenzo moieties.



(I)

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 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 [0$\bar{1}$2], 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-

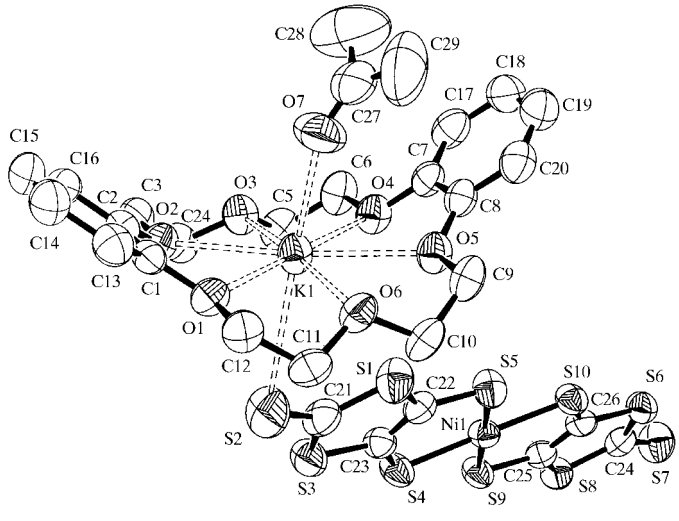


Figure 1
The molecular structure of (I), with displacement ellipsoids at the 50% probablity level and H atoms omitted for clarity.

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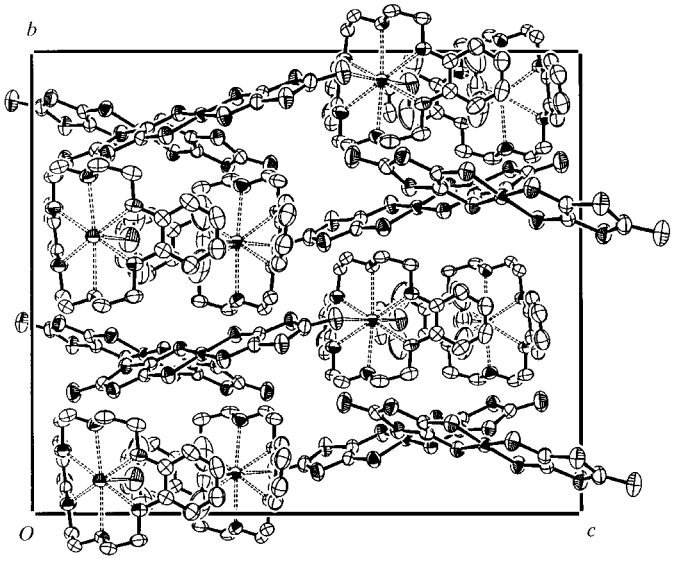

Figure 2
Packing diagram of (I) viewed along the *a* axis. The $[Ni(dmit)_2]^-$ anions are arranged almost along the [012] and [0$\bar{1}$2] directions.

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 $\{K^+(DB18c6)[(CH_3)_2CO]\}$ 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 $(pyridinium)^+$-$(DB18c6)BF_4^-$ 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 $\{K^+(DB18c6)(CH_3)_2CO\}_2$ dimer array.

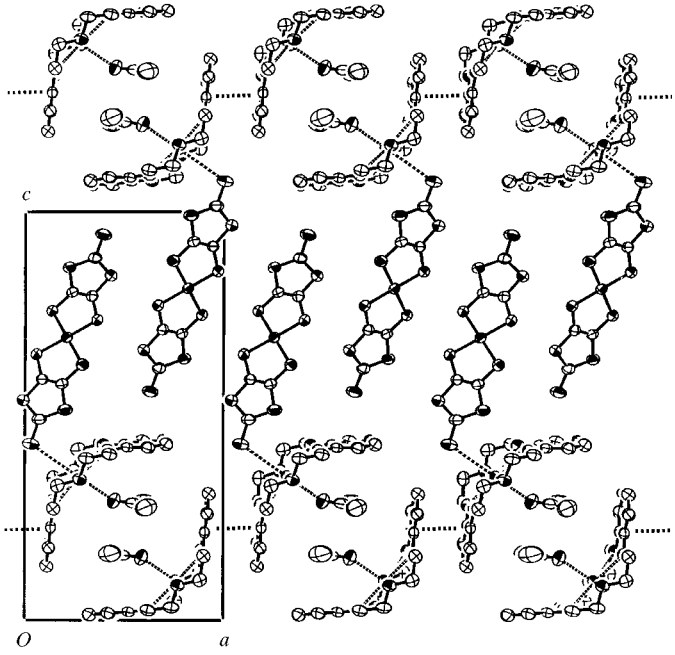

Figure 3
The arrangements of SC^+ viewed along the *b* axis. The dimers are aligned along the *a* axis.

Experimental

The title crystal was prepared by slow evaporation of a propanone solution of $(^nBu_4N)[Ni(dmit)_2]$, DB18c6 and $KClO_4$. Shiny black plate-like crystals were obtained.

Crystal data

$K[Ni(C_3S_5)_2]\cdot C_{20}H_{24}O_6\cdot C_3H_6O$	D_x = 1.575 Mg m^{-3}
M_r = 908.95	Mo $K\alpha$ radiation
Monoclinic, *C*2/*c*	Cell parameters from 18 032 reflections
a = 12.8232 (5) Å	θ = 2.4–27.5°
b = 22.4666 (8) Å	μ = 1.20 mm^{-1}
c = 26.612 (1) Å	*T* = 296.2 K
β = 90.201 (2)°	Plate, black
V = 7666.6 (5) Å^3	0.35 × 0.35 × 0.10 mm
Z = 8	

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer	8776 independent reflections
ω scans	4422 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	R_{int} = 0.050
T_{min} = 0.699, T_{max} = 0.887	θ_{max} = 27.5°
36 400 measured reflections	$h = 0 \rightarrow 16$
	$k = 0 \rightarrow 29$
	$l = -34 \rightarrow 34$

Refinement

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

The molecule of (I) crystallized in the monoclinic system; space group *C*2/*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.

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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: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation and Rigaku, 1999); molecular graphics: *ORTEP*III (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.

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