Crystal structure of bis[{acetonitrile-*N*-3,6′-bis(methylbenzo)-18-crown-6}potassium]bis(1,1-dicyanoethene-2,2-dithiolato-*S*,*S*′)nickel(II), $[\{K(C_{22}H_{28}O_6)(CH_3CN)\}_2\{Ni(C_4N_2S_2)\}_2]$

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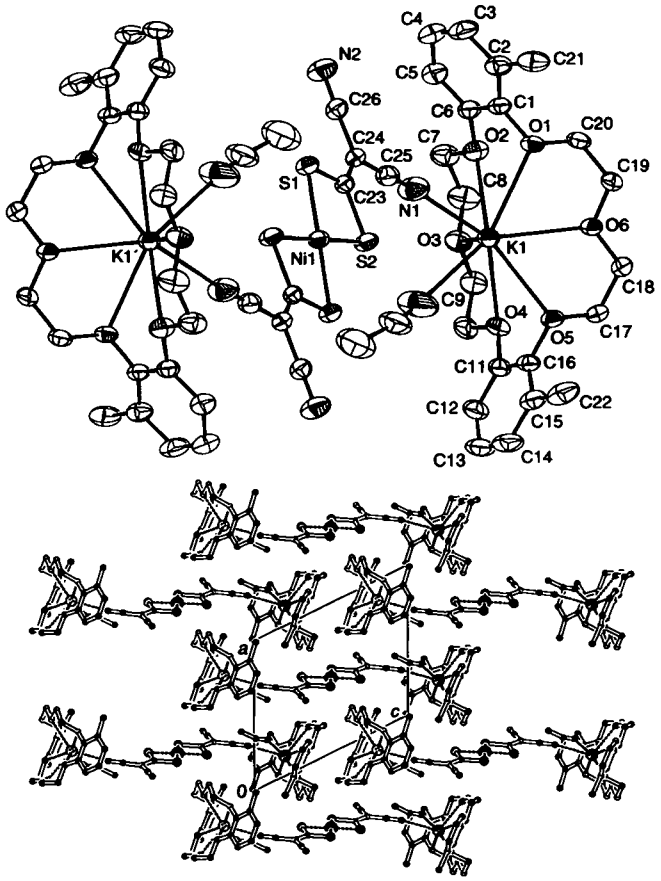

Abstract

$C_{56}H_{62}K_2N_6NiO_{12}S_4$, triclinic, $P\bar{1}$ (no. 2), a = 12.241(7) Å, b = 12.583(8) Å, c = 12.585(8) Å, α = 88.711(9)°, β = 65.351(9)°, γ = 65.629(9)°, V = 1578.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.073, $wR_{ref}(F^2)$ = 0.205, T = 293 K.

Source of material

To a solution of 0.50 mmol 3,6′-dimethyl dibenzo-18-crown-6 (dmdb18-cr-6) in 10 ml 1,2-dichloroethane was added 10 ml aqueous mixture of 0.125 mmol $NiCl_2$ and 0.25 mmol K_2(i-mnt) (i-mnt = 1,1-dicyanoethene-2,2-dithiolate, synonym isomaleonitriledithiolate). The reaction mixture was stirred for 4 hours at RT and then filtered. The precipitate was dissolved in the mixture of CH_3CN and CH_3COCH_3 (1:1 *v*/*v*). The single crystal was obtained by slowly evaporating the solution (yield 0.12 g, 85 % based on Ni, m.p. 271-273 °C).

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Elemental analysis: found – C, 52.47 %; H, 4.85 %; N, 6.47 %; calc. for $C_{56}H_{62}K_2N_6NiO_{12}S_4$ – C, 52.70 %; H, 4.90 %; N, 6.59 %. Selected FT-IR and ^{1}H NMR data are available in the CIF file.

Discussion

Among the cyclic polyethers, the ones with six oxygen atoms such as 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6 and dicyclohexano-18-crown-6 are known to form stable complexes with alkali metal, alkali earth metal and transition metal ions [1-3]. However, the solid structures of 3,6′-dimethyldibenzo-18-crown-6 complexes have not been studied.

The structure consists of two $[K(3,6'\text{-dmdb18-cr-6})(CH_3CN)]^+$ complex cations and one $[Ni(i\text{-mnt})_2]^{2-}$ complex anion (figure, top). The Ni atom is located on an inversion centre and does not bond directly to the O atoms of the crown ether. In the $[Ni(i\text{-mnt})_2]^{2-}$ complex anion, Ni atom is coordinated by four S atoms from i-mnt ligand. Bond angles of S1–Ni–S1′ and S2–Ni–S2′ are both 180°, indicating that the NiS_4 group is square planar. The plane of the i-mnt ligand is slightly tilted at an angle of about 11° with respect to the NiS_4 metal square plane, indicating the coplanar feature of the $[Ni(i\text{-mnt})_2]^{2-}$ complex anion. The S1–C23–S2 bond angles of 108.4° – 110.6° are much smaller than that of Na_2(i-mnt) [5] with 122.8° [4] and K_2(i-mnt) with 121.3°, implying a chelating coordination nature of the i-mnt ligand. The averaged bond lengths of Ni—S, S—C, C—N and C—C are 2.201 Å, 1.712 Å, 1.138 Å and 1.425 Å, respectively, which is consistent with the corresponding values in the structure of $[Na(b15\text{-cr-}5)]_2[Ni(i\text{-mnt})_2] \cdot CH_2Cl_2$ [6].

In the $[K(3,6'\text{-dmdb18-cr-6})(CH_3CN)]^+$ complex cation, the potassium ion lies within the crown ether and is bonded by six ether oxygen atoms. The equatorial K—O (ether) distances fall in the range from 2.800(4) Å to 2.895(3) Å (average 2.851 Å), which is slightly longer than the corresponding value in the complex $[K(naphto18\text{-cr-}6)]_2[Ni(i\text{-mnt})_2]$ (average 2.741 Å) [7] and shorter than the sum (3.17 Å) of effective ionic radii of eight-coordinated K^+ ion [8] and the van der Waals radii of O atom [9]. K^+ ion is also coordinated by N1 atom from i-mnt ligand of $[Ni(i\text{-mnt})_2]^{2-}$ complex anion and the distance of K1—N1 is 2.893(6) Å, which is consistent with the corresponding values in complex $[K(naphto18\text{-cr-}6)]_2[Ni(i\text{-mnt})_2]$ (2.889(6) Å) [7]. The remainder of its coordinating sphere is occupied by one nitrogen atom from CH_3CN molecule and the distance of K1—N3 is 2.753(8) Å, the bond angle of N3–K1–N1′ is 69.7(2)°, indicating that the CH_3CN molecule is at the same side with the i-mnt ligand of $[Ni(i\text{-mnt})_2]^{2-}$ complex anion. The crystal packing (figure, bottom) is characterised by alternate stacking of the formular units interlinked via C–H···O, C–H···N and C–H···S interactions.

Table 1. Data collection and handling.

Crystal:	crimson prism, size 0.21 × 0.28 × 0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.33 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8349, 5491
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3356
$N(param)_{refined}$:	367
Programs:	SHELXS-97 [10], SHELXL-97 [11]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	2*i*	0.7670	0.2863	1.0788	0.103
H(4)	2*i*	0.6074	0.3437	1.0110	0.118
H(5)	2*i*	0.6147	0.4596	0.8656	0.096
H(7A)	2*i*	0.6149	0.6284	0.7725	0.094
H(7B)	2*i*	0.6935	0.5034	0.6894	0.094
H(8A)	2*i*	0.8395	0.5704	0.5502	0.100
H(8B)	2*i*	0.6911	0.6461	0.5703	0.100
H(9A)	2*i*	0.7335	0.8052	0.5094	0.086
H(9B)	2*i*	0.8836	0.7348	0.4866	0.086
H(10A)	2*i*	0.8066	0.9419	0.5238	0.083
H(10B)	2*i*	0.7027	0.9462	0.6527	0.083
H(12)	2*i*	0.7934	1.0943	0.6146	0.093
H(13)	2*i*	0.8441	1.2306	0.6773	0.115
H(14)	2*i*	0.9908	1.1757	0.7584	0.112
H(17A)	2*i*	1.2373	0.7602	0.5769	0.072
H(17B)	2*i*	1.1398	0.7251	0.5516	0.072
H(18A)	2*i*	1.3155	0.5568	0.5670	0.074
H(18B)	2*i*	1.2575	0.6133	0.7005	0.074
H(19A)	2*i*	1.2079	0.4568	0.7720	0.071
H(19B)	2*i*	1.2748	0.3933	0.6394	0.071
H(20A)	2*i*	1.0648	0.4007	0.6737	0.074
H(20B)	2*i*	1.1275	0.3195	0.7498	0.074
H(21A)	2*i*	1.0690	0.2720	0.9440	0.127
H(21B)	2*i*	0.9680	0.2770	1.0750	0.127
H(21C)	2*i*	0.9930	0.3870	1.0410	0.127
H(22A)	2*i*	1.1388	1.0319	0.8207	0.150
H(22B)	2*i*	1.2154	0.9054	0.7421	0.150
H(22C)	2*i*	1.0953	0.9324	0.8681	0.150
H(28A)	2*i*	0.6126	1.1418	1.1158	0.273
H(28B)	2*i*	0.5006	1.1001	1.1444	0.273
H(28C)	2*i*	0.5188	1.1858	1.0531	0.273

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	1*f*	½	0	½	0.0541(5)	0.0463(5)	0.0551(6)	−0.0287(4)	−0.0242(4)	0.0136(4)
K(1)	2*i*	0.8672(1)	0.71364(9)	0.80173(9)	0.0632(7)	0.0460(6)	0.0500(6)	−0.0267(5)	−0.0203(5)	0.0110(5)
N(1)	2*i*	0.3203(7)	0.2759(5)	0.9588(5)	0.136(5)	0.087(4)	0.066(4)	−0.061(4)	−0.015(4)	0.011(3)
N(2)	2*i*	0.5687(6)	0.3869(5)	0.6648(5)	0.112(4)	0.094(4)	0.083(4)	−0.075(4)	−0.034(3)	0.017(3)
N(3)	2*i*	0.704(1)	0.9459(7)	0.9164(9)	0.29(1)	0.078(5)	0.173(9)	−0.058(7)	0.124(9)	−0.022(6)
O(1)	2*i*	0.9755(3)	0.4730(3)	0.8430(3)	0.075(2)	0.040(2)	0.046(2)	−0.032(2)	−0.024(2)	0.008(2)
O(2)	2*i*	0.7974(4)	0.5360(3)	0.7583(3)	0.078(2)	0.067(2)	0.077(3)	−0.044(2)	−0.044(2)	0.029(2)
O(3)	2*i*	0.7533(4)	0.7299(3)	0.6447(3)	0.090(3)	0.059(2)	0.066(2)	−0.035(2)	−0.046(2)	0.018(2)
O(4)	2*i*	0.8908(3)	0.8662(3)	0.6268(3)	0.072(2)	0.043(2)	0.069(2)	−0.024(2)	−0.038(2)	0.022(2)
O(5)	2*i*	1.0626(3)	0.8041(3)	0.7180(3)	0.067(2)	0.050(2)	0.048(2)	−0.033(2)	−0.019(2)	0.017(2)
O(6)	2*i*	1.1402(3)	0.5601(3)	0.6708(3)	0.057(2)	0.045(2)	0.067(2)	−0.026(2)	−0.029(2)	0.025(2)
S(1)	2*i*	0.5558(1)	0.1448(1)	0.5042(1)	0.0661(8)	0.0576(8)	0.0512(7)	−0.0389(7)	−0.0209(6)	0.0145(6)
S(2)	2*i*	0.3953(1)	0.0733(1)	0.6912(1)	0.0711(9)	0.0611(8)	0.0585(8)	−0.0449(7)	−0.0204(7)	0.0151(6)
C(1)	2*i*	0.8759(5)	0.4347(4)	0.8867(4)	0.069(3)	0.045(3)	0.047(3)	−0.035(3)	−0.019(3)	0.009(2)
C(2)	2*i*	0.8767(6)	0.3629(5)	0.9725(5)	0.095(4)	0.060(3)	0.052(3)	−0.047(3)	−0.027(3)	0.010(3)
C(3)	2*i*	0.7723(7)	0.3317(6)	1.0192(6)	0.114(5)	0.081(4)	0.077(4)	−0.067(4)	−0.032(4)	0.037(4)
C(4)	2*i*	0.6759(7)	0.3668(6)	0.9791(7)	0.095(5)	0.083(4)	0.119(6)	−0.062(4)	−0.026(5)	0.034(4)
C(5)	2*i*	0.6800(6)	0.4357(5)	0.8925(6)	0.078(4)	0.071(4)	0.102(5)	−0.045(3)	−0.038(4)	0.022(4)
C(6)	2*i*	0.7824(5)	0.4685(4)	0.8464(5)	0.067(3)	0.048(3)	0.057(3)	−0.033(3)	−0.020(3)	0.010(2)
C(7)	2*i*	0.7019(6)	0.5715(5)	0.7126(6)	0.097(4)	0.069(4)	0.101(5)	−0.048(3)	−0.061(4)	0.026(4)
C(8)	2*i*	0.7503(7)	0.6262(5)	0.6078(6)	0.124(5)	0.077(4)	0.093(5)	−0.055(4)	−0.075(5)	0.021(4)
C(9)	2*i*	0.7936(6)	0.7871(5)	0.5458(5)	0.089(4)	0.071(4)	0.066(4)	−0.037(3)	−0.045(3)	0.023(3)
C(10)	2*i*	0.7901(6)	0.8972(5)	0.5878(5)	0.071(4)	0.058(3)	0.072(4)	−0.019(3)	−0.036(3)	0.027(3)
C(11)	2*i*	0.9137(5)	0.9554(4)	0.6591(5)	0.069(3)	0.042(3)	0.054(3)	−0.024(3)	−0.012(3)	0.011(2)
C(12)	2*i*	0.8535(6)	1.0712(5)	0.6473(5)	0.088(4)	0.046(3)	0.079(4)	−0.023(3)	−0.026(3)	0.023(3)
C(13)	2*i*	0.8842(8)	1.1518(5)	0.6848(6)	0.124(6)	0.046(3)	0.088(5)	−0.045(4)	−0.016(4)	0.013(3)
C(14)	2*i*	0.9723(8)	1.1191(6)	0.7330(6)	0.135(6)	0.064(4)	0.079(5)	−0.068(4)	−0.022(5)	0.005(3)
C(15)	2*i*	1.0341(6)	1.0027(5)	0.7443(5)	0.093(4)	0.069(4)	0.060(3)	−0.055(3)	−0.016(3)	0.007(3)
C(16)	2*i*	1.0041(5)	0.9216(4)	0.7055(4)	0.074(3)	0.043(3)	0.044(3)	−0.032(3)	−0.017(3)	0.012(2)
C(17)	2*i*	1.1718(5)	0.7291(4)	0.6095(5)	0.061(3)	0.056(3)	0.065(3)	−0.036(3)	−0.020(3)	0.024(3)
C(18)	2*i*	1.2343(5)	0.6078(4)	0.6366(5)	0.052(3)	0.058(3)	0.074(4)	−0.028(3)	−0.025(3)	0.023(3)
C(19)	2*i*	1.1910(5)	0.4479(4)	0.7047(5)	0.059(3)	0.044(3)	0.063(3)	−0.018(2)	−0.024(3)	0.021(2)
C(20)	2*i*	1.0898(5)	0.4005(4)	0.7374(5)	0.079(4)	0.037(2)	0.062(3)	−0.028(3)	−0.023(3)	0.011(2)
C(21)	2*i*	0.9842(8)	0.3213(6)	1.0111(6)	0.133(6)	0.074(4)	0.069(4)	−0.060(4)	−0.052(4)	0.034(3)
C(22)	2*i*	1.1295(8)	0.9647(6)	0.7987(6)	0.133(6)	0.111(5)	0.085(5)	−0.093(5)	−0.036(5)	0.019(4)
C(23)	2*i*	0.4693(4)	0.1674(4)	0.6553(4)	0.043(3)	0.046(2)	0.055(3)	−0.022(2)	−0.024(2)	0.016(2)
C(24)	2*i*	0.4593(5)	0.2471(4)	0.7342(4)	0.050(3)	0.051(3)	0.053(3)	−0.027(2)	−0.014(2)	0.014(2)
C(25)	2*i*	0.3833(6)	0.2612(5)	0.8593(5)	0.075(4)	0.057(3)	0.058(4)	−0.032(3)	−0.022(3)	0.012(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(26)	2*i*	0.5209(5)	0.3236(5)	0.6952(5)	0.059(3)	0.062(3)	0.055(3)	–0.032(3)	–0.022(3)	0.008(3)
C(27)	2*i*	0.656(1)	1.0212(7)	0.9898(9)	0.172(9)	0.055(4)	0.128(8)	–0.033(5)	0.029(7)	0.005(5)
C(28)	2*i*	0.565(1)	1.1202(8)	1.083(1)	0.21(1)	0.096(7)	0.19(1)	–0.052(7)	–0.06(1)	0.030(7)

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