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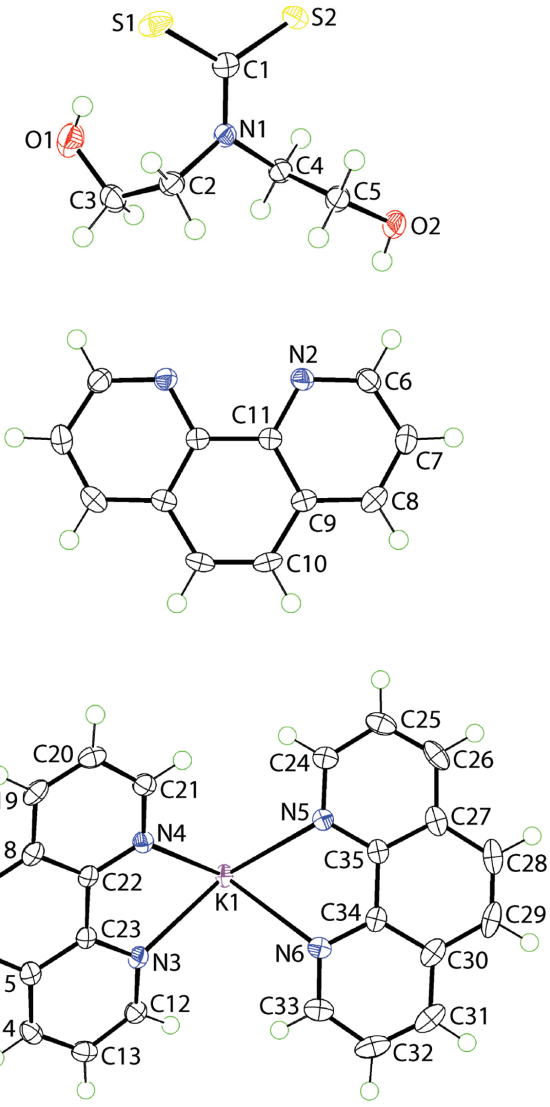
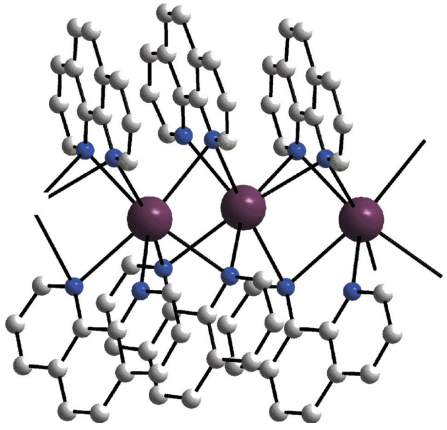
Crystal structure of *catena*{(μ_2-1,10-phenanthroline-κ^4*N*,*N*,*N*′,*N*′)-(μ_2-1,10-phenanthroline-κ^3*N*,*N*,*N*′)potassium(I) {[bis(2-hydroxyethyl)iminiumyl](sulfanidyl)methyl}sulfanide hemi(1,10-phenanthroline)}, {$C_{24}H_{16}KN_4$, 0.5($C_{12}H_8N_2$), $C_5H_{10}NO_2S_2$}





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Abstract

$C_{35}H_{30}KN_6O_2S_2$, monoclinic, *C*2/*c* (no. 15), $a = 32.8001(4)$ Å, $b = 7.1562(1)$ Å, $c = 26.0400(3)$ Å, $\beta = 94.385(1)°$, $V = 6094.32(13)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0315$, $wR_{ref}(F^2) = 0.0911$, $T = 100(2)$ K.

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The molecular structures are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.13 × 0.10 × 0.04 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	3.17 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	68443, 5436, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5312
$N(param)_{refined}$:	421
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
K1	0.24739(2)	0.76681(6)	0.23559(2)	0.01307(11)
S1	0.42721(2)	0.79102(7)	0.47775(2)	0.02119(13)
S2	0.34084(2)	0.67345(7)	0.44974(2)	0.01543(12)
O1	0.46034(5)	0.5084(2)	0.56831(6)	0.0249(3)
H1O	0.4555(9)	0.600(3)	0.5486(9)	0.037*
O2	0.33745(4)	0.0814(2)	0.40190(6)	0.0219(3)
H2O	0.3440(8)	−0.018(2)	0.4173(9)	0.033*
N1	0.40170(5)	0.4369(2)	0.47346(6)	0.0130(3)
C1	0.39106(6)	0.6185(3)	0.46721(7)	0.0141(4)
C2	0.44452(6)	0.3738(3)	0.48204(7)	0.0158(4)
H2A	0.462567	0.468502	0.467832	0.019*
H2B	0.447805	0.255876	0.462907	0.019*
C3	0.45809(6)	0.3421(3)	0.53821(8)	0.0188(4)
H3A	0.438763	0.254670	0.553029	0.023*
H3B	0.485345	0.281948	0.540525	0.023*
C4	0.37211(6)	0.2836(3)	0.46627(7)	0.0141(4)
H4A	0.344818	0.327875	0.474692	0.017*
H4B	0.380370	0.180066	0.490056	0.017*
C5	0.36966(6)	0.2123(3)	0.41091(7)	0.0168(4)
H5A	0.365144	0.319009	0.386961	0.020*
H5B	0.395910	0.152553	0.404022	0.020*
N2	0.50532(5)	0.1491(2)	0.69801(6)	0.0150(3)
C6	0.51018(6)	0.1454(3)	0.64784(8)	0.0180(4)
H6	0.512114	0.261391	0.630458	0.022*
C7	0.51264(6)	−0.0195(3)	0.61884(7)	0.0194(4)
H7	0.516025	−0.014036	0.582962	0.023*
C8	0.51006(6)	−0.1875(3)	0.64326(8)	0.0170(4)
H8	0.511446	−0.300914	0.624509	0.020*
C9	0.50532(5)	−0.1907(3)	0.69672(7)	0.0130(4)
C10	0.50252(6)	−0.3631(3)	0.72436(8)	0.0151(4)
H10	0.504203	−0.478451	0.706594	0.018*
C11	0.50272(5)	−0.0175(3)	0.72246(7)	0.0120(4)
N3	0.26891(5)	0.9293(2)	0.14466(6)	0.0136(3)
N4	0.31818(5)	1.0166(2)	0.23208(6)	0.0129(3)
C12	0.24521(6)	0.8937(3)	0.10232(7)	0.0155(4)
H12	0.218137	0.851359	0.106007	0.019*
C13	0.25778(6)	0.9149(3)	0.05220(7)	0.0171(4)
H13	0.239283	0.892092	0.022999	0.020*
C14	0.29719(6)	0.9690(3)	0.04629(7)	0.0164(4)
H14	0.306640	0.980893	0.012856	0.020*
C15	0.32366(6)	1.0069(3)	0.09044(7)	0.0137(4)
C16	0.36502(6)	1.0677(3)	0.08658(7)	0.0157(4)
H16	0.375465	1.079126	0.053690	0.019*
C17	0.38925(6)	1.1090(3)	0.12955(8)	0.0159(4)
H17	0.416607	1.148462	0.126466	0.019*
C18	0.37417(6)	1.0939(3)	0.17964(7)	0.0136(4)
C19	0.39851(6)	1.1421(3)	0.22464(8)	0.0157(4)
H19	0.425566	1.186986	0.222363	0.019*
C20	0.38287(6)	1.1237(3)	0.27171(8)	0.0170(4)
H20	0.398974	1.153480	0.302499	0.020*
C21	0.34261(6)	1.0600(3)	0.27339(7)	0.0150(4)
H21	0.332105	1.047055	0.306207	0.018*
C22	0.33386(6)	1.0330(2)	0.18511(7)	0.0115(4)
C23	0.30788(6)	0.9878(3)	0.13905(7)	0.0120(4)
N5	0.22844(5)	0.9509(2)	0.32469(6)	0.0126(3)
N6	0.18191(5)	1.0397(2)	0.23553(6)	0.0138(3)
C24	0.25027(6)	0.9062(3)	0.36800(7)	0.0154(4)
H24	0.277986	0.870670	0.365833	0.018*
C25	0.23483(6)	0.9085(3)	0.41668(7)	0.0191(4)
H25	0.251693	0.875056	0.446560	0.023*
C26	0.19502(7)	0.9597(3)	0.42030(8)	0.0198(4)
H26	0.183850	0.961794	0.452900	0.024*
C27	0.17062(6)	1.0093(3)	0.37552(8)	0.0169(4)
C28	0.12854(6)	1.0623(3)	0.37680(8)	0.0213(4)
H28	0.116573	1.066655	0.408864	0.026*
C29	0.10569(6)	1.1061(3)	0.33317(9)	0.0217(4)
H29	0.077899	1.141047	0.334987	0.026*
C30	0.12274(6)	1.1005(3)	0.28405(8)	0.0171(4)
C31	0.09965(6)	1.1444(3)	0.23768(9)	0.0219(4)
H31	0.071785	1.180103	0.238081	0.026*
C32	0.11782(7)	1.1350(3)	0.19199(9)	0.0226(5)
H32	0.102702	1.163273	0.160369	0.027*
C33	0.15903(6)	1.0830(3)	0.19276(8)	0.0180(4)
H33	0.171362	1.078298	0.160941	0.022*
C34	0.16408(6)	1.0480(3)	0.28096(7)	0.0132(4)
C35	0.18864(6)	1.0015(3)	0.32802(7)	0.0123(4)

Source of material

Diethanolamine (Merck, 0.29 mL, 3 mmol) was slowly added dropwise into a solution of carbon disulfide (Merck, 0.18 mL, 3 mmol) and potassium hydroxide (Merck, 0.17 g, 3 mmol) in methanol (5 mL) at 0 °C. Then, the mixture was stirred for 2 h. Next, europium(III) nitrate pentahydrate (Sigma-Aldrich, 0.43 g, 1 mmol) and 1,10-phenanthroline (Merck, 0.18 g, 1 mmol) in water (5 mL) was added to the mixture followed by stirring for 4 h. Upon standing at room temperature for 3 days, the white precipitate formed was filtered and dried in air. It was recrystallised from methanol/DMSO (1:1). The title compound was a side-product obtained from the reaction. Yield: 0.15 g (7.5%). **M.pt** (Stuart SMP30 digital melting point apparatus): >573 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 3361 (b) ν(OH), 1540(m) ν(CN), 1504(m) ν(CC), 1410(m) ν(CO), 1077 (m) ν(CS). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me_4Si, DMSO-d_6 solution, p.p.m.): 2.81–2.99 (m, 4H, NCH_2), 4.40–4.51 (m, 4H, OCH_2), 7.74–8.10, 8.45–8.58, 9.01–9.12 (m, 24H, Ar-H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 52.9, (NCH_2), 60.3 (OCH_2), 123.8, 127.2, 128.9, 136.8, 145.9, 150.5 (Ar-C), 197.6 (CS).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The O-bound H atoms were refined with

O—H = 0.84 ± 0.01 Å, and with U_{iso}(H) = 1.5U_{eq}(O). Owing to poor agreement, five reflections, i.e. (−13 1 16), (−22 2 2), (1 3 14), (−13 5 15) and (−22 0 2), were removed from the final cycles of refinement.

Comment

The crystal and molecular structures described herein of the title salt co-crystal, $[K(phen)_2][S_2CN(CH_2CH_2OH)_2](phen)_{0.5}$, (I), represents a rare report of an alkali metal salt of phen and a dithiocarbamate anion; phen is 1,10-phenanthroline. Indeed, the sole example of a crystallographically determined structure related to (I) is that of $Na(phen)_2(S_2CNEt_2)$ whereby the Na^+ cation is chelated by two phen molecules as well as by the dithiocarbamate anion [5]. In continuation of investigations into the structures of alkali metal salts of dithiocarbamate anions [6–8], herein details for (I) described.

Referring to the figure (70% displacement ellipsoids), the crystallographic asymmetric unit of (I) comprises a dithiocarbamate anion, half a phen molecule (disposed about a 2-fold axis of symmetry with unlabelled atoms related by the symmetry operation 1 − x, y, 3/2 − z) and a $K[(phen)_2]^+$ cation; the later represents the repeat unit of a coordination polymer, as discussed below.

The dithiocarbamate anion exhibits the expected features with experimentally equivalent C—S bond lengths [C1—S1 = 1.719(2) Å and C1—S2 = 1.7205(19) Å] and a short C—N bond [C1—N1 = 1.353(3) Å], the latter being consistent with a significant contribution of the $^{(2-)}S_2C{=}N^{(+)}$ canonical form to the electronic structure of the anion. An intramolecular hydroxyl-O—H···S hydrogen bond is noted [O1—H1o···S1: H1o···S1 = 2.42(2) Å, O1···S1 = 3.2312(16) Å with angle at H1o = 162(2)°]. As mentioned above, there is a 2-fold symmetric phen molecule in the crystal. Finally, the third component of the asymmetric unit, i.e. a $K[(phen)_2]^+$ cation, assembles into a helical chain (2_1 symmetry) along the b-axis, as shown in the right-hand view of the figure. Within the asymmetric unit, the K1···N3–N6 bond lengths are 2.7773(16), 2.9373(16), 2.7795(16) and 2.9025(16) Å, respectively. The repeat units are connected by three additional K1···$N4^i$–$N6^i$ contacts, i.e. 2.9692(16), 2.8973(16) and 2.8843(16) Å, respectively; symmetry operation (i) 1/2 − x, −1/2 + y, 1/2 − z. The N_7 donor set about the K1 ion is, to a first approximation, based on a cube with one position vacant. The K1···$N3^i$ separation is 4.0123(16) Å, a separation which correlates with the K1—N3 contact being the shortest of all K···N contacts.

Globally, the molecular packing of (I) comprises columns of cations, parallel to the b-axis assembled into rows in the ab-plane with the neutral phen molecules between neighbouring columns. The connections between the chains are of the type chain-phen-C—H···π(phen) [shortest contact C19—H19···Cg($C9^{ii}$—$C11^{ii}$,$C9^{iii}$—$C11^{iii}$) = 2.49 Å with angle at H19 = 152° for (ii) 1 − x, 1 − y, 1 − z and (iii) x, 1 − y, −1/2 + z] so that supramolecular layers are formed. Interspersed between layers are the dithiocarbamate anions which form hydroxyl-O—H···S(dithiocarbamate) hydrogen bonds [O2—H2o···$S2^{iv}$: H2o···$S2^{iv}$ = 2.369(16) Å, O2···$S2^{iv}$ = 3.1727(15) Å with angle at H2o = 161(2)° for (iv) x, −1 + y, z] which serve to connect anions along the b-axis. The dithiocarbamate anions also link phen molecules, coordinated and non-coordinated, via phen-C—H···O(hydroxyl) [shortest contact: C21—H21···$O2^v$: H21···$O2^v$ = 2.50 Å, C21···$O2^v$ = 3.367(2) Å with angle at H21 = 152° for (v) x, 1 + y, z] and phen-C—H···S(dithiocarbamate) [C16—H16···$S1^{vi}$: H16···$S1^{vi}$ = 2.86 Å, C16···$S1^{vi}$ = 3.755(2) Å with angle at H16 = 158° for (vi) x, 2 − y, −1/2 + z] contacts to consolidate the three-dimensional architecture.

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