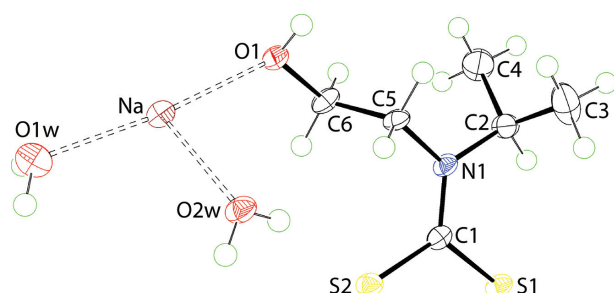


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Crystal structure of *catena*{di-aqua-sodium-[*N*-(hydroxyethyl), *N*-isopropyl-dithiocarbamato]}_n, [C₆H₁₆NNaO₂S₂]_n



$V = 1127.68(5) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0287$, $wR_{\text{ref}}(F^2) = 0.0788$, $T = 100(2) \text{ K}$.

CCDC no.: 2015506

A part of the molecular structure is 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:	$0.10 \times 0.06 \times 0.03 \text{ mm}$
Wavelength:	Cu $K\alpha$ radiation (1.54184 \AA)
μ :	4.51 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13616, 2016, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1839
$N(\text{param})_{\text{refined}}$:	135
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The dithiocarbamate ligand was prepared in situ (methanol) from the reaction of CS₂ (Merck, 0.06 mL, 1 mmol) with 2-(isopropylamino)ethanol (Sigma-Aldrich; 0.12 mL, 1 mmol) and NaOH (Merck, 0.08 mL, 1 mmol, 50% w/v); CS₂ was added dropwise into the methanol solution (10 mL). The resulting mixture was kept at 273 K for 2 h. The filtrate was evaporated until a white precipitate was obtained. The precipitate was recrystallised from acetone-methanol (1:1 v/v) by slow evaporation to yield colourless crystals.

Yield: 0.88 g (59%). **M.pt** (Mel-temp II digital melting point apparatus): 431–432 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{−1}): 1448 (s) $\nu(\text{C}=\text{N})$, 1008 (s) $\nu(\text{C}=\text{S})$, 958 (m) $\nu(\text{C}=\text{S})$. **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me₄Si, DMSO-*d*₆ solution; ppm): δ 1.03 (s, 6H, CH₃), 3.58–3.65 (m, 2H, NCH₂), 3.86–3.94 (m, 1H, CH), 4.88–4.95 (m, 2H, CH₂O); OH not observed. **¹³C{¹H} NMR** (as for ¹H NMR): δ 20.7 (CH₃), 48.3 (NC(H)), 50.5 (NCH₂), 61.5 (CH₂O), 215.0 (C=S).

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Abstract

C₆H₁₆NNaO₂S₂, monoclinic, $P2_1/c$ (no. 14), $a = 13.2126(4) \text{ \AA}$, $b = 5.9418(1) \text{ \AA}$, $c = 14.6038(3) \text{ \AA}$, $\beta = 100.395(3)^\circ$,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Na	0.43822(5)	0.24084(10)	0.45827(4)	0.01495(18)
S1	0.80588(3)	0.14666(7)	0.13337(3)	0.01472(14)
S2	0.62824(3)	0.00557(7)	0.21976(3)	0.01411(13)
O1	0.60676(9)	0.4000(2)	0.47018(8)	0.0150(3)
H1O	0.6549(13)	0.379(4)	0.5147(11)	0.022 [*]
O1W	0.26567(10)	0.1508(2)	0.44843(9)	0.0208(3)
H1W	0.2402(18)	0.036(3)	0.4195(16)	0.031 [*]
H2W	0.2405(18)	0.260(3)	0.4160(15)	0.031 [*]
O2W	0.50115(9)	−0.0797(2)	0.39079(8)	0.0164(3)
H3W	0.4649(16)	−0.179(3)	0.3602(14)	0.025 [*]
H4W	0.5419(14)	−0.044(4)	0.3553(13)	0.025 [*]
N1	0.78458(11)	0.2565(2)	0.30604(10)	0.0129(3)
C1	0.74353(13)	0.1481(3)	0.22787(11)	0.0124(3)
C2	0.88734(13)	0.3689(3)	0.31796(12)	0.0168(4)
H2	0.905425	0.383906	0.254637	0.020 [*]
C3	0.96896(15)	0.2212(3)	0.37517(16)	0.0291(5)
H3A	0.954913	0.206787	0.438545	0.044 [*]
H3B	1.036851	0.289583	0.377375	0.044 [*]
H3C	0.967781	0.071873	0.346495	0.044 [*]
C4	0.88495(15)	0.6047(3)	0.35762(15)	0.0254(4)
H4A	0.830649	0.692357	0.318830	0.038 [*]
H4B	0.951575	0.677853	0.358411	0.038 [*]
H4C	0.871086	0.596003	0.421226	0.038 [*]
C5	0.73687(13)	0.2468(3)	0.38939(11)	0.0133(3)
H5A	0.790832	0.267261	0.445317	0.016 [*]
H5B	0.706084	0.095977	0.393328	0.016 [*]
C6	0.65375(13)	0.4253(3)	0.38934(11)	0.0157(4)
H6A	0.684651	0.577094	0.389236	0.019 [*]
H6B	0.600775	0.410049	0.332373	0.019 [*]

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2$ – $1.5U_{\text{eq}}(\text{C})$. The O-bound H atoms were refined with O–H = 0.84 ± 0.01 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Comment

During the course of structural investigations related to crystal engineering considerations [5, 6] and putative biological activities of metal dithiocarbamates (S_2CNR_2), e.g. anti-tumour [7] and anti-bacterial [8], occasionally, crystals of alkali metal salts of the dithiocarbamate anions have been isolated and characterised by X-ray crystallography [9, 10]. In continuation of a long-term interest in such structural chemistry [11], in particular for dithiocarbamate anions carrying hydrogen bonding functionality, herein the crystal and molecular structures of the title salt dihydrate, $\text{Na}[\text{S}_2\text{CN}(\text{i-Pr})\text{CH}_2\text{CH}_2\text{OH}] \cdot 2\text{H}_2\text{O}$, (I), are described.

The molecular structures of the constituents of (I) are shown in the figure (upper view: 70% displacement ellipsoids). The asymmetric unit comprises a Na^+ cation, a $\text{S}_2\text{CN}(\text{i-Pr})\text{CH}_2\text{CH}_2\text{OH}$ anion and two water molecules of crystallisation. The anion exhibits the expected features in that the C1–S1 [1.7301(17) Å] and C1–S2 [1.7282(17) Å] bond lengths are equal within experimental error, and the C1–N1 bond length [1.337(2) Å] is short, consistent with a major contribution of the dithiolate canonical form, i.e. $^{(2-)}\text{S}_2\text{C}=\text{N}^{(+)}$ (i-Pr) $\text{CH}_2\text{CH}_2\text{OH}$, to the electronic structure of the anion.

The O1w water molecule is bound terminally to the Na^+ cation [$\text{Na} \cdots \text{O1w} = 2.3208(15)$ Å]; in contrast, the O2w molecule is bridging [$\text{Na} \cdots \text{O2w} = 2.3632(14)$ Å and $\text{Na} \cdots \text{O2w}^{\text{i}} = 2.4043(14)$ Å for symmetry operation (i) $1 - x, -y, 1 - z$]. In the same way, the hydroxyl-O1 is bridging [$\text{Na} \cdots \text{O1} = 2.3966(13)$ Å and $\text{Na} \cdots \text{O1}^{\text{ii}} = 2.4946(13)$ Å for (ii) $1 - x, 1 - y, 1 - z$]. The sixth position in the distorted octahedral geometry for the Na^+ cation is occupied by a symmetry-related S2 atom [$\text{Na} \cdots \text{S2}^{\text{iii}} = 3.0300(7)$ Å for (iii) $1 - x, 1/2 + y, 1/2 - z$]. In this description, one of the octahedral faces is occupied by three oxygen atoms derived from three water molecules, and the second face is occupied by two hydroxyl-O atoms and the S2 atom. The aforementioned links between the asymmetric units results in helical chains of NaO_5 polyhedra along the *b*-axis. The connections between translationally-related chains to form a layer in the *bc*-plane are mediated by $\text{Na} \cdots \text{O}(\text{hydroxyl})\text{CH}_2\text{CH}_2\text{NCS} \cdots \text{Na}$ links. A view of the layer is shown in the lower view of the figure. Additional stability to the layer is afforded by $\text{O} \cdots \text{H} \cdots \text{S}$ hydrogen bonding, as described next.

Within layers, the S1 atom accepts hydrogen bonding interactions from hydroxyl-O1 and water-O1w ($\times 2$) residues [$\text{O1} \cdots \text{H1o} \cdots \text{S1}$: $\text{H1o} \cdots \text{S1} = 2.400(17)$ Å, $\text{O1} \cdots \text{S1} = 3.2273(13)$ Å with angle at $\text{H1o} = 172.6(17)^\circ$; $\text{O1w} \cdots \text{H1w} \cdots \text{S1}^{\text{iv}}$: $\text{H1w} \cdots \text{S1}^{\text{iv}} = 2.480(19)$ Å, $\text{O1w} \cdots \text{S1}^{\text{iv}} = 3.2994(13)$ Å with angle at $\text{H1w} = 165.4(19)^\circ$ and $\text{O1w} \cdots \text{H2w} \cdots \text{S1}^{\text{iii}}$: $\text{H2w} \cdots \text{S1}^{\text{iii}} = 2.452(19)$ Å, $\text{O1w} \cdots \text{S1}^{\text{iii}} = 3.2548(13)$ Å with angle at $\text{H2w} = 161.1(18)^\circ$ for (iv) $1 - x, -1/2 + y, 1/2 - z$] and the S2 atom accepts two distinct hydrogen bonds from symmetry related O2w-water molecules [$\text{O2w} \cdots \text{H3w} \cdots \text{S2}^{\text{iv}}$: $\text{H3w} \cdots \text{S2}^{\text{iv}} = 2.423(19)$ Å, $\text{O2w} \cdots \text{S2}^{\text{iv}} = 3.2566(13)$ Å with angle at $\text{H3w} = 174.2(16)^\circ$ and $\text{O2w} \cdots \text{H4w} \cdots \text{S2}$: $\text{H4w} \cdots \text{S2} = 2.474(19)$ Å, $\text{O2w} \cdots \text{S2} = 3.2906(13)$ Å with angle at $\text{H4w} = 164.6(19)^\circ$]. The layers stack along the *a*-direction without directional interactions between them.

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