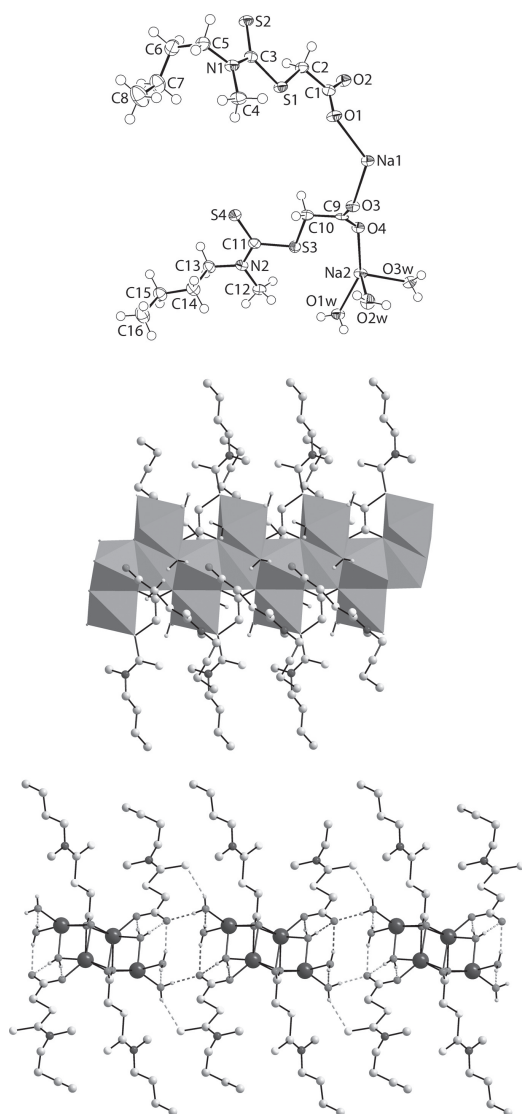


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Crystal structure of *catena*-{[tri-aqua-di-sodium bis(2-[[*n*-butyl(methyl)carbamothioyl]sulfanyl] acetate)]}_n, [C₁₆H₃₄N₂Na₂O₇S₄]_n



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Abstract

[C₁₆H₃₄N₂Na₂O₇S₄]_n, triclinic, $P\bar{1}$ (no. 2), $a = 5.3734(1)$ Å, $b = 11.0473(2)$ Å, $c = 22.2264(5)$ Å, $\alpha = 102.075(2)^\circ$, $\beta = 96.202(2)^\circ$, $\gamma = 97.383(2)^\circ$, $V = 1267.06(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0335$, $wR_{\text{ref}}(F^2) = 0.0941$, $T = 100(2)$ K.

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The constituents of the asymmetric unit 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 plate
Size:	0.17 × 0.04 × 0.02 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ :	4.12 mm ^{−1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	30669, 4523, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4210
$N(\text{param})_{\text{refined}}$:	302
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm^{−1}. The ¹H and ¹³C{¹H} NMR spectra were recorded at room temperature in CDCl₃ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

The dithiocarbamate ligand was prepared *in situ* (acetone) from the reaction of CS₂ (Merck, 0.25 mmol) with *n*-butylmethylamine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% w/v); CS₂ was added dropwise into the methanol solution

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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}
S1	1.14745(10)	0.13521(5)	0.31092(3)	0.01677(13)
S2	1.20238(10)	−0.12848(5)	0.24774(3)	0.01810(14)
S3	−0.09303(11)	0.55782(5)	0.30283(3)	0.01951(14)
S4	0.07497(11)	0.40808(5)	0.18787(3)	0.01860(14)
O1	0.8756(3)	0.23449(14)	0.40388(8)	0.0185(3)
O2	0.6459(3)	0.06077(15)	0.41707(8)	0.0195(3)
O3	0.4094(3)	0.51778(14)	0.42949(7)	0.0163(3)
O4	0.0078(3)	0.54681(14)	0.43245(7)	0.0158(3)
N1	1.4657(4)	0.08311(18)	0.23274(9)	0.0171(4)
N2	−0.2638(4)	0.56527(18)	0.19006(9)	0.0175(4)
C1	0.8092(4)	0.1187(2)	0.39188(11)	0.0158(4)
C2	0.9367(4)	0.0355(2)	0.34436(11)	0.0173(5)
H2A	0.8070	−0.0189	0.3114	0.021 [*]
H2B	1.0333	−0.0188	0.3649	0.021 [*]
C3	1.2883(4)	0.0276(2)	0.26040(10)	0.0156(4)
C4	1.5381(4)	0.2203(2)	0.24791(12)	0.0197(5)
H4A	1.3916	0.2592	0.2363	0.030 [*]
H4B	1.6758	0.2432	0.2249	0.030 [*]
H4C	1.5950	0.2497	0.2926	0.030 [*]
C5	1.5901(4)	0.0086(2)	0.18504(11)	0.0204(5)
H5A	1.6369	−0.0653	0.1995	0.024 [*]
H5B	1.7481	0.0599	0.1799	0.024 [*]
C6	1.4227(5)	−0.0357(2)	0.12220(12)	0.0250(5)
H6A	1.2690	−0.0904	0.1273	0.030 [*]
H6B	1.5155	−0.0871	0.0930	0.030 [*]
C7	1.3407(5)	0.0692(3)	0.09316(12)	0.0287(6)
H7A	1.2108	0.0320	0.0566	0.034 [*]
H7B	1.2616	0.1255	0.1237	0.034 [*]
C8	1.5590(6)	0.1466(3)	0.07287(14)	0.0369(7)
H8A	1.6828	0.1887	0.1093	0.055 [*]
H8B	1.4935	0.2095	0.0530	0.055 [*]
H8C	1.6409	0.0914	0.0433	0.055 [*]
C9	0.1897(4)	0.51760(19)	0.40392(10)	0.0131(4)
C10	0.1442(4)	0.4765(2)	0.33315(11)	0.0163(4)
H10A	0.0865	0.3849	0.3204	0.020 [*]
H10B	0.3040	0.4956	0.3162	0.020 [*]
C11	−0.1018(4)	0.5105(2)	0.22109(11)	0.0166(5)
C12	−0.4020(4)	0.6599(2)	0.22157(11)	0.0194(5)
H12A	−0.5205	0.6213	0.2452	0.029 [*]
H12B	−0.4964	0.6946	0.1907	0.029 [*]
H12C	−0.2818	0.7273	0.2499	0.029 [*]
C13	−0.3042(4)	0.5392(2)	0.12204(11)	0.0197(5)
H13A	−0.4853	0.5384	0.1075	0.024 [*]
H13B	−0.2621	0.4552	0.1052	0.024 [*]
C14	−0.1418(5)	0.6370(2)	0.09735(11)	0.0223(5)
H14A	−0.1658	0.7218	0.1189	0.027 [*]
H14B	0.0391	0.6295	0.1070	0.027 [*]
C15	−0.2070(5)	0.6224(2)	0.02784(11)	0.0229(5)
H15A	−0.3840	0.6364	0.0186	0.028 [*]
H15B	−0.1959	0.5355	0.0065	0.028 [*]
C16	−0.0323(5)	0.7133(3)	0.00220(13)	0.0309(6)
H16A	−0.0551	0.7994	0.0200	0.046 [*]
H16B	−0.0737	0.6956	−0.0431	0.046 [*]
H16C	0.1442	0.7032	0.0132	0.046 [*]
Na1	0.70753(15)	0.40096(8)	0.46389(4)	0.01489(19)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Na2	−0.26699(16)	0.69607(8)	0.43202(4)	0.0169(2)
O1W	−0.5177(3)	0.81183(15)	0.38060(8)	0.0201(3)
H1W	−0.587(5)	0.800(3)	0.3438(6)	0.030 [*]
H2W	−0.450(5)	0.8867(13)	0.3939(12)	0.030 [*]
O2W	0.0821(3)	0.85602(17)	0.45241(8)	0.0247(4)
H3W	0.135(5)	0.891(3)	0.4898(6)	0.037 [*]
H4W	0.206(4)	0.839(3)	0.4337(12)	0.037 [*]
O3W	−0.3720(3)	0.75892(15)	0.53094(8)	0.0184(3)
H5W	−0.247(4)	0.755(3)	0.5561(10)	0.028 [*]
H6W	−0.447(5)	0.817(2)	0.5469(12)	0.028 [*]

(10 mL). The resulting mixture solution was kept at 273 K for 1 h. Sodium chloroacetate (Merck, 0.03 g, 0.25 mmol) was added into the solution. The filtrate was evaporated slowly until a white precipitate was formed. The precipitate was washed with *n*-hexane and recrystallized from a methanol-acetone solution. Colourless crystals of the title salt were obtained from the slow evaporation of the solvent. Yield: 0.027 g (20.0%). **M.pt:** >623 K. IR (cm^{−1}) 1570 (s) ν(C=O), 1486 (s) ν(C=N), 1382 (s) ν(C=N), 1117 (m) ν(C=O), 1012 (m) ν(C=S), 980 (m) ν(C=S). **¹H NMR** (CDCl₃, p.p.m.): δ 0.93 (s, 3H, CH₃), 1.20–1.44 (m, 4H, CH₂CH₂), 2.80–2.82 (m, 2H, CH₂), 2.87–2.90 (m, 6H, water-OH), 3.44 (s, 3H, NCH₃), 4.00–4.04 (m, 4H, NCH₂). **¹³C{¹H} NMR** (CDCl₃, p.p.m.): 13.9 (CH₃), 20.0, 28.5 (CH₂CH₂), 40.0 (SCH₂), 43.6 (NCH₃), 57.0 (NCH₂), 175.2 (CO), 197.2 (CS₂).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98–0.99 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C). The O-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint O–H = 0.84 ± 0.01 Å, and with *U*_{iso}(H) set to 1.5*U*_{eq}(O). A number of reflections were omitted from the final cycles of refinement owing to poor agreement; details are given in the CIF.

Comment

The title sodium salt of a hybrid dithiocarbamate ester of a carboxylic acid, isolated as a trihydrate, was investigated as a part of on-going studies of the structural chemistry of these molecules [5] and their organotin derivatives [6]. The motivation for these studies is to ultimately investigate the biological potential of the organotin derivatives, as both organotin carboxylates [7] and organotin dithiocarbamates [8] are known to exhibit a range of pharmaceutical potential. Indeed, a very recent publication highlighted the potential anti-tumour activity of several organotin species containing

these molecules [9]. The structure of the substituted tribenzyl tin complex comprising the same dithiocarbamate anion reported in this publication has also been reported in the literature [10].

The constituents comprising the asymmetric unit of the title salt hydrate are shown in the upper view of the figure (70% displacement ellipsoids) and comprise two independent sodium cations, two *n*-Bu(Me)NC(=S)SCH₂CO₂ anions and three water molecules of crystallization. The pattern in C–S bond lengths, with C3–S3 [1.682(2) Å] being significantly shorter than C3–S1 [1.762(2) Å] and C2–S1 [1.804(2) Å] match those involving the S3 and S4 atoms [1.675(2), 1.776(2) and 1.802(2) Å, respectively. Further, they follow the pattern established in another dithiocarbamate ester, i.e. recently determined MeSC(=S)N(Me)Ph [11], with equivalent values being 1.6590(18), 1.7662(17) and 1.789(2) Å. Further, the pattern in the angles about the C3 atom, with the wider angles subtended by the S2 atom [S1–C3–S2 = 122.81(13)° and S2–C3–N1 = 124.12(17)° cf. S1–C3–N1 = 113.06(16)°] is consistent with the presence of a C3=S2 and C11=S4 thione bonds, as the equivalent angles about the C11 atom follow the same trends [S3–C11–S4 = 122.93(14)°, S4–C11–N2 = 124.66(18)° and S3–C11–N2 = 112.41(17)°]. Further, in a recently authenticated dithiocarbamate anion, [−]S₂CN(CH₂CH₂)₂NPh [12], the angles about the quaternary-carbon atom spanned a very narrow range 119.45(8) to 120.57(10)°, consistent with significant delocalization of π -electron density over the CS₂ chromophore, clearly absent in the anions of the title compound. The above descriptors are consistent with the presence of carboxylate groups in the anions. However, the C–O bond lengths are not equivalent [C1–O1, O2 = 1.247(3) and 1.267(3) Å; C9–O3, O4 = 1.253(3) and 1.261(3) Å]. As discussed below, these variations are related to the different interactions the carboxylate-O atoms have with the sodium cations and in the supramolecular assembly. There is a significant difference in the conformations of the carboxylate ligands. While the CO₂ and CS₂ residues are close to co-planar in the O1-carboxylate anion, with the CO₂/CS₂ dihedral angle being 4.5(5)°, these are inclined in the O3-carboxylate anion with the CO₂/CS₂ dihedral angle being 32.55(16)°. This conformational difference arises from variable twists about the O1–C1–C2–S1 [−5.0(3)°] and O3–C9–C10–S3 torsion angles [−148.67(16)°]. The other conformational difference in the carboxylate anions relates to the *n*-butyl groups. Thus, in the O1-carboxylate anion, the N1–C5–C6–C7 [60.2(3)°] and C5–C6–C7–C8 [68.2(3)°] torsion angles are indicative of + *syn*-clinal conformation whereas the equivalent N2–C13–C14–C15 [−172.0(2)°] and C13–C14–C15–C16 [−175.6(2)°] torsion angles indicate an − anti-periplanar conformation.

The sodium cations have quite distinct donor sets and coordination geometries. The Na1 cation is coordinated by six oxygen atoms, five of which are carboxylate-O and the sixth being a water-O atom. The Na1–O bond lengths range from 2.3443(18) Å, for Na1–O3, to 2.5370(18) Å for Na1–O4ⁱ [symmetry operation (i) 1 − *x*, 1 − *y*, 1 − *z*]. The O₆ donor set defines a distorted trigonal prismatic geometry. By contrast, the Na2 cation is coordinated within a O₅S donor set defined by two carboxylate-O, three water-O and thioester-S atoms. The Na2–O bonds range from 2.3161(19) Å, for Na2–O3w, to 2.4410(18) Å, for Na2–O3ⁱⁱ [(ii) −1 + *x*, *y*, *z*] and define a square-pyramidal geometry. The S3 atom occupies the sixth site [Na2–S3 = 3.2502(11) Å] leading to a distorted octahedral geometry. As seen in the middle view of the figure, the aforementioned connections give rise to a one-dimensional chain along the *a* axis with edge-shared coordination polyhedra. The inner polyhedra encompass the Na1-cations and the outer polyhedra contain the Na2-cations. Additional stability to the one-dimensional coordination polymer arises from hydrogen bonding interactions of the type water-O–H⋯O(carboxylate, water) [O2w–H3w⋯O2ⁱ: H3w⋯O2ⁱ = 2.192(16) Å, O2w⋯O2ⁱ = 3.003(2) Å with angle at H3w = 162(3)°; O2w–H4w⋯O1wⁱⁱⁱ: H4w⋯O1wⁱⁱⁱ = 2.01(2) Å, O2w⋯O1wⁱⁱⁱ = 2.845(2) Å, with angle at H4w = 172(3)°; O3w–H5w⋯O1ⁱ: H5w⋯O1ⁱ = 2.07(2) Å, O3w⋯O1ⁱ = 2.879(2) Å with angle at H5w = 161(2)° and O3w–H6w⋯O2^{iv}: H6w⋯O2^{iv} = 1.93(3) Å, O3w⋯O2^{iv} = 2.762(2) Å with angle at H6w = 175(3)° for (iii) 1 + *x*, *y*, *z* and (iv) −*x*, 1 − *y*, 1 − *z*]. The connections between the chains along the *b* axis to form a supramolecular layer are of the type water-O–H⋯S(thione) and water-O–H⋯O(carboxylate) O1w–H1w⋯S2^v: H1w⋯S2^v = 2.62(2) Å, O1w⋯S2^v = 3.3952(18) Å with angle at H1w = 154(3)° and O1w–H2w⋯O2^{vi}: H2w⋯O2^{vi} = 1.872(17) Å, O1w⋯O2^{vi} = 2.699(2) Å with angle at H2w = 170(3)° for (v) −2 + *x*, 1 + *y*, *z* and (vi) −1 + *x*, 1 + *y*, *z*]. The layers stack along the *c* axis direction without directional interactions between them.

Further analysis of the molecular packing was performed using Crystal Explorer 17 [13] to calculate the Hirshfeld surfaces (including the full and delineated two-dimensional fingerprint plots) for the specified asymmetric unit (see figure), following standard procedures [14]. Reflecting, to a large extent, the hydrophobic contacts along the *c* axis, H⋯H contacts make the greatest contribution to the overall Hirshfeld surface, at 52.5%. The next most significant contribution to the surface contacts are S⋯H/H⋯S at 17.1% followed closely by O⋯H/H⋯H [14.6%], then Na⋯O/O⋯Na [7.7%] and C⋯H/H⋯C [3.9%] contacts. An accompanying structural report of a closely related sodium

salt, Na[S₂CN(Me)_n-Bu]·H₂O [15], also adopts a layer structure with the layers separated by hydrophobic interactions. The percentage contribution by H···H contacts to the Hirshfeld surface also computes to 52.5% in this crystal [15].

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