Crystal structure of *catena*-poly[(μ_2-chlorido)-bis(*N*-ethyl,*N*-hydroxyethylcarbamodithioato-κ^2*S*,*S*′)bismuth(III) monohydrate], $C_{10}H_{22}BiClN_2O_3S_4$

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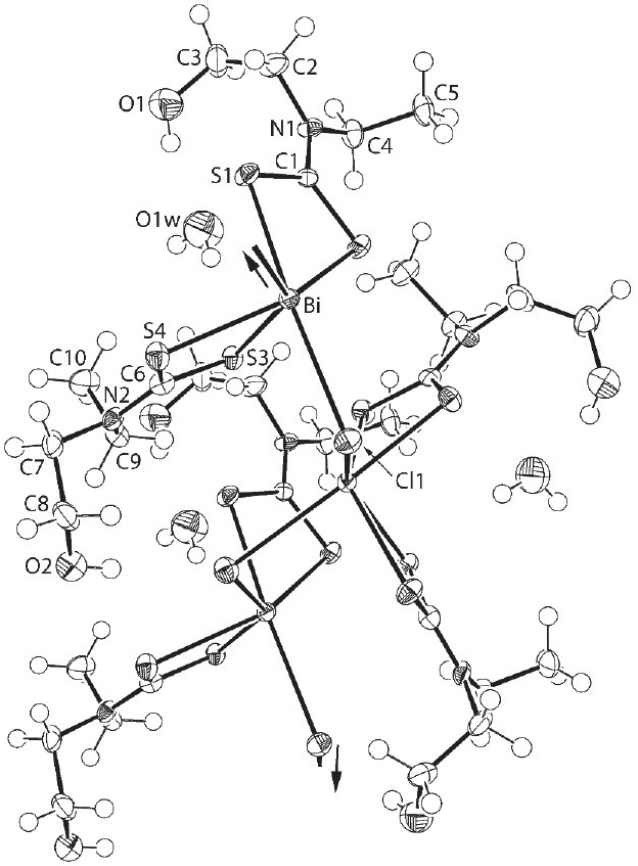

Abstract

$C_{10}H_{22}BiClN_2O_3S_4$, orthorhombic, $Pca2_1$ (no. 29), a = 8.1121(4) Å, b = 10.8634(5) Å, c = 20.7900(9) Å, V = 1832.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.0278, $wR_{ref}(F^2)$ = 0.0574, T = 100 K.

Source of material

Carbon disulfide (0.015 mol) was added drop-wise to an ethanol solution (20 ml) of *N*-ethyl-*N*-ethanolamine (0.015 mol). The solution was kept at 277 K for 2 h. Bismuth trichloride (0.005 mol) dissolved in ethanol (20 ml) was added to give a white precipitate. This raw product was collected and recrystallized from a methanol/dichloromethane (1:2 *v*/*v*) mixture. Yield: 85%. **m. p.**: 401-403 K. **Elemental Analysis** % anal. (calcd.): C, 22.25 (20.96); H, 3.63 (3.52); N, 4.88 (4.89); S, 20.23 (22.39); Bi, 35.1 1(36.47). **^{1}H NMR** (DMSO-d_6, ppm): 1.34 *t* (CH_3CH$_2$-; J = 7.20 Hz), 3.91 *q* (CH$_3$CH_2-; J = 4.80 Hz), 3.95 *t* (-CH_2CH$_2$OH; J = 6.60 Hz), 4.76 *s* (-CH_2OH). **^{13}C{^{1}H} NMR** (DMSO-d_6, ppm): 11.46 (*C*H$_3$CH$_2$-), 50.59 (CH$_3$*C*H$_2$-); 55.29 (-*C*H$_2$CH$_2$OH), 59.02 (-*C*H$_2$OH); 201.78 (*C*S$_2$). **IR** (KBr, cm^{-1}): 3294 ν(O–H), 1480 ν(C–N), 980 ν(CS$_2$), 1177 ν(C–N), 354 ν(Bi–S). UV–Vis (EtOH, nm): 361 (n-π* transition for NCS$_2$), 260 (π-π* transition for NCS$_2$).

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.10×0.20×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	102.33 cm^{-1}
Diffractometer, scan mode:	SuperNova Dual with Atlas detector, ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5837, 3272
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3094
$N(param)_{refined}$:	204
Programs:	CrysAlisPRO, ORTEP-3, SHELXL [4–6]

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) = 1.2-1.5U_{eq}(C). The O-bound H-atoms was located in a difference Fourier map and were refined with an O–H restraint of 0.84±0.01 Å, and with U_{iso}(H) =1.5U_{eq}(O). A number of reflections, *i.e.* (4 8 $\overline{11}$), (4 7 $\overline{10}$), (2 9 $\overline{10}$), (2 3 $\overline{16}$), (0 9 2), (2 4 $\overline{17}$), (3 9 $\overline{11}$) and (2 5 $\overline{1}$), were omitted from the final refinement owing to their very poor agreement (too low or even negative integrated intensities). The maximum and minimum residual electron density peaks of 1.20 and 1.55 eÅ^{-3}, respectively, were located 0.83 and 1.75 Å from the Bi atom. The absolute structure was determined based on differences in Friedel pairs included in the data set [7].

Discussion

Biological activity [1, 2] and utility as synthetic precursors for the generation of Bi_2S_3 nanoparticles [3] motivated many studies on bismuth dithiocarbamates, including those of the general formula $Bi(S_2CNR_2)_2Cl$, *i.e.* analogues. The bismuth atom in the crystal structure is chelated by two dithiocarbamate ligands, which show disparate Bi–S1, S2 [2.628(2) and 2.799(2) Å] and Bi–S3, S4 [2.661(2) and 2.757(2) Å] distances. The chlorido bridges two bismuth centres. The bridge is almost symmetric with Bi–Cl1, Cl1^i = 2.990(2) and 2.929(2) Å for *i*: ½+*x*, 1–*y*, *z*. The resulting one-dimensional coordination polymer, has a zig-zag topology and is aligned along the *a* axis. Within the chain, there are also further Bi···S3^i contacts [3.351(2) Å] and additional stability is afforded by hydrogen bonding interactions. Thus, the hydroxy-O1–H group connects to a water molecule [O1···O1w = 2.746(11) Å], which in turn forms a hydrogen bond to the dithiocarbamate-S3 atom [O1w···S3 = 3.479(9) Å]. The hydroxy-O2–H group forms a hydrogen bond with Cl1^{ii} [O2···Cl1^{ii} = 3.195(8) Å, for *ii*:

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–½+*x*, 1–*y*, *z*]. Neighbouring chains are connected *via* hydrogen bonds into a two-dimensional array parallel to (0 0 1). Thus, the water molecule forms a hydrogen bond with a hydroxy-O1^{iii} atom [O1w···O1^{iii} = 2.752(11) Å, *iii*: –½+*x*, –*y*, *z*]. There are two analogous structures available in the crystallographic literature, namely $\{Bi[S_2CN(CH_2)_4]_2Cl\}_n$ [3] and $[Bi(S_2CNMe_2)_2Cl]_n$ [2] which feature essentially the same one-dimensional chain structures having helical and zig-zag topologies, respectively.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1O)	4*a*	1.177(4)	0.07(1)	0.085(6)	0.049
H(2O)	4*a*	0.50(1)	0.215(7)	0.411(4)	0.045
H(2A)	4*a*	1.4892	0.2304	0.0958	0.024
H(2B)	4*a*	1.4968	0.2767	0.0229	0.024
H(3A)	4*a*	1.2872	0.1297	–0.0034	0.030
H(3B)	4*a*	1.4569	0.0681	0.0188	0.030
H(4A)	4*a*	1.0931	0.3967	0.0235	0.020
H(4B)	4*a*	1.2133	0.3194	–0.0222	0.020
H(5A)	4*a*	1.2263	0.5347	–0.0459	0.030
H(5B)	4*a*	1.4032	0.4838	–0.0247	0.030
H(9C)	4*a*	1.2932	0.5602	0.0252	0.030

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7A)	4*a*	0.8995	0.0647	0.4000	0.022
H(7B)	4*a*	0.7276	0.0009	0.3819	0.022
H(8A)	4*a*	0.7255	0.1121	0.4835	0.026
H(8B)	4*a*	0.7431	0.2368	0.4432	0.026
H(9A)	4*a*	0.6096	0.2011	0.2609	0.017
H(9B)	4*a*	0.5396	0.1032	0.3117	0.017
H(10A)	4*a*	0.5775	0.0072	0.2112	0.034
H(10B)	4*a*	0.7000	–0.0532	0.2627	0.034
H(10C)	4*a*	0.7683	0.0447	0.2117	0.034
H(1W)	4*a*	0.90(1)	0.097(8)	0.098(5)	0.062
H(2W)	4*a*	0.96(1)	0.193(9)	0.136(3)	0.062

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}
Bi	4*a*	1.15624(3)	0.43209(2)	0.27150(2)	0.0099(1)	0.0097(1)	0.0138(1)	–0.0006(1)	0.0012(2)	–0.0009(2)
Cl(1)	4*a*	0.9513(3)	0.6037(2)	0.35052(9)	0.015(1)	0.017(1)	0.0175(9)	0.0018(9)	–0.0009(9)	–0.0009(9)
S(1)	4*a*	1.3345(3)	0.2924(2)	0.19526(9)	0.014(1)	0.015(1)	0.0139(9)	0.0056(9)	–0.0011(8)	0.0007(9)
S(2)	4*a*	1.1109(3)	0.4808(2)	0.1405(1)	0.015(1)	0.014(1)	0.019(1)	0.0052(9)	–0.0005(9)	0.0023(9)
S(3)	4*a*	0.8790(3)	0.3147(2)	0.24123(9)	0.013(1)	0.012(1)	0.0135(9)	–0.0014(9)	–0.0017(8)	0.0001(8)
S(4)	4*a*	1.0669(3)	0.2528(2)	0.3586(1)	0.013(1)	0.015(1)	0.0201(9)	–0.0028(9)	–0.0034(9)	0.0028(9)
O(1)	4*a*	1.279(1)	0.0526(7)	0.0810(3)	0.033(5)	0.031(4)	0.033(4)	0.000(4)	0.007(4)	–0.002(3)
O(2)	4*a*	0.5273(9)	0.1565(7)	0.4344(3)	0.032(4)	0.027(4)	0.031(4)	0.005(3)	0.008(3)	0.005(3)
N(1)	4*a*	1.2914(9)	0.3290(7)	0.0693(3)	0.008(4)	0.018(4)	0.014(3)	0.003(3)	–0.002(3)	0.000(3)
N(2)	4*a*	0.7794(9)	0.1497(6)	0.3280(3)	0.010(4)	0.008(3)	0.019(3)	–0.001(3)	–0.001(3)	–0.002(3)
C(1)	4*a*	1.249(1)	0.3649(8)	0.1280(4)	0.005(3)	0.013(4)	0.018(3)	0.000(3)	0.000(3)	0.002(3)
C(2)	4*a*	1.423(1)	0.2418(8)	0.0562(4)	0.022(5)	0.025(5)	0.014(4)	0.008(4)	0.003(4)	–0.001(4)
C(3)	4*a*	1.362(1)	0.1176(9)	0.0337(5)	0.037(6)	0.015(5)	0.024(5)	0.000(4)	0.005(4)	0.003(4)
C(4)	4*a*	1.210(1)	0.3806(8)	0.0131(4)	0.017(5)	0.016(4)	0.018(5)	–0.002(4)	–0.005(4)	0.004(4)
C(5)	4*a*	1.291(1)	0.5007(8)	–0.0102(4)	0.020(5)	0.018(5)	0.022(4)	–0.004(4)	–0.006(4)	0.009(4)
C(6)	4*a*	0.895(1)	0.2303(8)	0.3127(4)	0.012(4)	0.015(5)	0.011(4)	0.000(4)	–0.003(3)	–0.003(3)
C(7)	4*a*	0.784(1)	0.0811(8)	0.3879(4)	0.016(5)	0.011(4)	0.027(4)	–0.003(4)	0.001(4)	0.004(4)
C(8)	4*a*	0.699(1)	0.1518(9)	0.4419(4)	0.024(4)	0.020(4)	0.020(4)	–0.005(4)	0.005(3)	0.003(3)
C(9)	4*a*	0.637(1)	0.1255(8)	0.2853(4)	0.013(4)	0.015(4)	0.013(6)	–0.005(3)	–0.001(3)	–0.002(3)
C(10)	4*a*	0.674(1)	0.0219(9)	0.2386(4)	0.023(5)	0.019(5)	0.026(5)	–0.005(4)	0.003(4)	–0.010(4)
O(1W)	4*a*	0.972(1)	0.1518(8)	0.1018(4)	0.044(5)	0.039(5)	0.041(4)	–0.009(4)	0.004(4)	–0.013(4)

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