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A triclinic polymorph of bis(μ -*N,N*-bis(2-hydroxyethyl)dithiocarbamato- κ^3 S,S':S') bis(*N,N*-bis(2-hydroxyethyl)dithiocarbamato- κ^2 S:S')zinc(II), $C_{20}H_{40}N_4O_8S_8Zn_2$

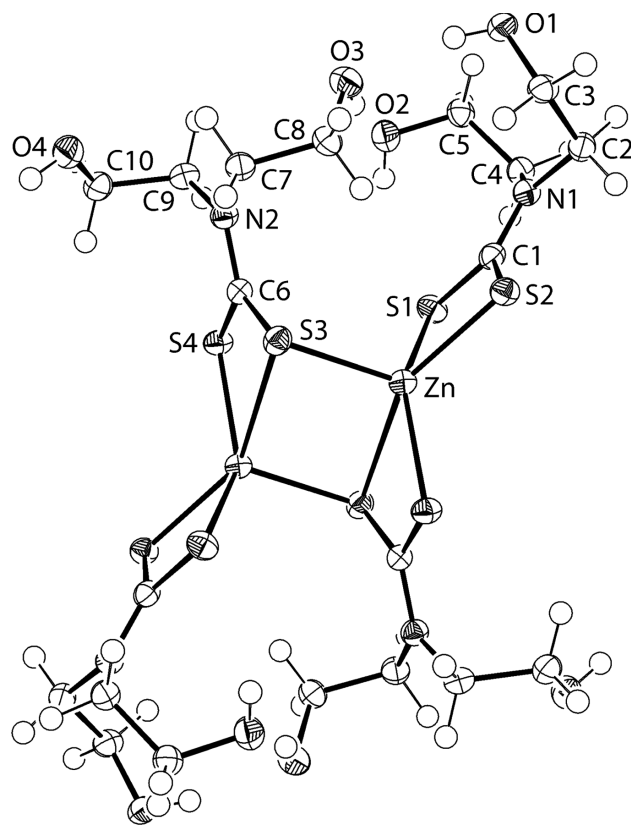


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.10 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	20.7 cm ⁻¹
Diffractometer, scan mode:	AFC12K/SATURN724, ω scans
$2\theta_{\max}$, completeness:	81.6°, 85.8%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13476, 8923, 0.037
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7374
$N(\text{param})_{\text{refined}}$:	202
Programs:	Rigaku programs [1, 2], SHELX [3, 4], ORTEP [5]

of the atoms including atomic coordinates and displacement parameters.

Source of materials

Crystals of the title compound were prepared in accord with the literature procedure [6]. Recrystallisation succeeded by layering an ethanol solution of the compound with diethyl ether. The harvested crystals were analysed directly and found to exhibit unit cell parameters that differed from literature precedents [6, 7].

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.99 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O-bound H-atoms were located in difference Fourier maps, but were refined with a distance restraint of O–H = 0.84 + –0.01 Å, and with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$. The maximum and minimum residual electron density peaks are located 1.07 and 0.63 Å from the Zn atom.

Discussion

There are two distinct structural motifs for the binary zinc(II) dithiocarbamates of the general formula $Zn(S_2CNRR')_2$ [8]. When the steric bulk of R/R' is relatively great, monomeric species with tetrahedral zinc coordination geometries are found. The majority of the structures are binuclear, owing to the presence of equal numbers of both chelating and μ_2 -bridging dithiocarbamate ligands.

As seen from the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation: $-x, -y, 1-z$). The title complex is binuclear and features

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Abstract

$C_{20}H_{40}N_4O_8S_8Zn_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.0675(10)$ Å, $b = 9.9000(10)$ Å, $c = 12.9252(17)$ Å, $\alpha = 106.813(10)^\circ$, $\beta = 93.741(9)^\circ$, $\gamma = 109.863(8)^\circ$, $V = 800.65(18)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.069$, $wR_{\text{ref}}(F^2) = 0.176$, $T = 98(2)$ K.

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The binuclear title structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
Zn	0.23737(5)	0.14200(3)	0.53126(2)	0.01532(7)
S1	0.13149(9)	0.34543(7)	0.54439(5)	0.01650(11)
S2	0.54637(9)	0.36534(7)	0.61693(5)	0.01532(10)
S3	0.11104(9)	0.03366(7)	0.66564(5)	0.01575(10)
S4	−0.30278(9)	0.03922(7)	0.60522(5)	0.01529(10)
O1	0.5937(3)	0.7703(2)	0.91005(16)	0.0187(3)
H1O	0.497(5)	0.700(4)	0.920(4)	0.028*
O2	0.0516(3)	0.5759(2)	0.76005(17)	0.0196(3)
H2O	−0.016(6)	0.524(5)	0.6966(17)	0.029*
O3	0.2588(3)	0.5172(2)	0.91301(17)	0.0200(3)
H3O	0.183(6)	0.521(5)	0.862(3)	0.030*
O4	−0.2827(3)	0.0897(2)	0.96370(18)	0.0221(4)
H4O	−0.326(7)	−0.0027(18)	0.958(4)	0.033*
N1	0.4359(3)	0.6076(2)	0.66298(17)	0.0141(3)
N2	−0.0661(3)	0.1915(2)	0.80190(17)	0.0147(3)
C1	0.3797(4)	0.4582(3)	0.61427(19)	0.0143(3)
C2	0.6492(4)	0.7035(3)	0.7191(2)	0.0158(4)
H2A	0.6754	0.8097	0.7228	0.019*
H2B	0.7424	0.6686	0.6740	0.019*
C3	0.7014(4)	0.7020(3)	0.8353(2)	0.0169(4)
H3A	0.6674	0.5954	0.8330	0.020*
H3B	0.8504	0.7573	0.8625	0.020*
C4	0.2959(4)	0.6859(3)	0.6498(2)	0.0160(4)
H4A	0.1962	0.6246	0.5805	0.019*
H4B	0.3764	0.7855	0.6428	0.019*
C5	0.1787(4)	0.7128(3)	0.7435(2)	0.0167(4)
H5A	0.2779	0.7791	0.8122	0.020*
H5B	0.0920	0.7676	0.7284	0.020*
C6	−0.0825(4)	0.1006(3)	0.7005(2)	0.0142(3)
C7	0.1169(4)	0.2430(3)	0.8866(2)	0.0167(4)
H7A	0.1626	0.1573	0.8801	0.020*
H7B	0.0801	0.2726	0.9601	0.020*
C8	0.2929(4)	0.3772(3)	0.8772(2)	0.0174(4)
H8A	0.4203	0.3891	0.9220	0.021*
H8B	0.3119	0.3554	0.7997	0.021*
C9	−0.2359(4)	0.2348(3)	0.8400(2)	0.0166(4)
H9A	−0.3088	0.2523	0.7801	0.020*
H9B	−0.1804	0.3311	0.9029	0.020*
C10	−0.3850(4)	0.1117(3)	0.8746(2)	0.0184(4)
H10A	−0.5000	0.1417	0.8975	0.022*
H10B	−0.4416	0.0153	0.8117	0.022*

a symmetry independent chelating dithiocarbamate ligand which forms disparate Zn—S1, S2 bond lengths of 2.3426(7) and 2.4230(8) Å. The second dithiocarbamate ligand is bridging, forming an almost symmetric bridge, with Zn—S3, S4ⁱ bond lengths of 2.3650(7) and 2.3202(7) Å, while at the same time forming a somewhat weaker transannular Zn—S3ⁱ bond length of 3.0458(9) Å. The resultant S₅ donor set is a square pyramid as judged from the value of $\tau = 0.16$ cf. 0.0 and 1.0 for ideal square-pyramidal and trigonal-bipyramidal geometries, respectively [9]. In this description the S1, S2, S3ⁱ, S4ⁱ atoms define the basal plane with a r.m.s. deviation of 0.0009 Å. The

zinc atom lies 0.7400(5) Å above this plane in the direction of the S3 atom. Overall, the conformation of the Zn₂S₄ core is that of a chair or step-ladder.

Significant hydrogen bonding is present in the crystal. Thus, hydroxyl-O—H...O(hydroxyl) hydrogen bonding involving three of the hydroxyl groups is found [O1—H1o...O3: 1.98(4) Å and 169(5)°; O3—H3o...O2: 1.87(4) Å and 167(4)°; and O4—H4o...O1ⁱ: 2.01(3) Å and 166(4)° for symmetry operation *i*: −1 + *x*, −1 + *y*, *z*]. Two of these interactions are intramolecular while one is intermolecular. The fourth hydroxyl group forms an intramolecular hydroxyl-O—H...S(dithiocarbamate) hydrogen bond [O2—H2o...S1: 2.76(4) Å and 121(4)°]. Such hydroxyl-O—H...S(dithiocarbamate) hydrogen bonds are not unusual for dithiocarbamate ligands functionalised with hydroxyethyl groups [10]. The result of the hydrogen bonding is a supramolecular chain parallel to [1 1 0].

There are two known polymorphs for {Zn[S₂CN(CH₂CH₂OH)₂]}₂. The first report was of a monoclinic (*C2/c*) form [7] and the second of an orthorhombic (*Pbcn*) one [6]. The common feature of all polymorphs is the centrosymmetric, binuclear structure and chair conformation of the Zn₂S₄ core. The differences between the polymorphs relate primarily to the supramolecular patterns. Thus, in both of the known polymorphs, only hydroxyl-O—H...O (hydroxyl) hydrogen bonding is observed. In the *C2/c* form [7], flat supramolecular layers are formed while in the *Pbcn* form [6], layers are undulating.

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