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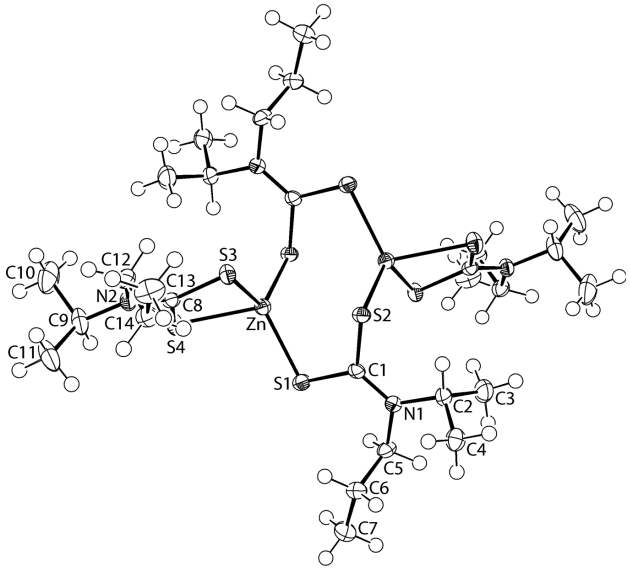
Crystal structure of bis(μ-*N*-*i*-propyl-*N*-*n*-propyldithiocarbamato-κ²*S*:*S*′) bis(*N*-*i*-propyl-*N*-*n*-propyldithiocarbamato-κ²*S*,*S*′)dizinc(II), $C_{28}H_{56}N_4S_8Zn_2$



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Abstract

$C_{28}H_{56}N_4S_8Zn_2$, monoclinic, $P2_1/n$ (no. 14), $a = 9.4123(2)$ Å, $b = 19.2708(4)$ Å, $c = 11.5228(3)$ Å, $\beta = 107.202(2)°$, $V = 1996.54(8)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0254$, $wR_{ref}(F^2) = 0.0572$, $T = 100(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The compound was obtained from reacting a 1:2 mixture of $ZnCl_2$ (Acros Organic) and Na[S_2CN(i-Pr)n-Pr] [prepared from the 1:1:1 reaction of CS_2 (Panreac), HN(i-Pr)n-Pr (Alfa Aesar) and NaOH (Merck) in acetone solution] in water which resulted in an immediate white precipitate. This was extracted with CH_2Cl_2 and filtered. The filtrate was allow to stand for slow evaporation under ambient conditions. Colourless crystals formed after a few days. **M.p.:** 384.2–384.4 K. **IR** (cm^{-1}): ν(C—S) 1189 (s, sh), 971 (s), ν(C—N) 1454 (s).

Table 1: Data collection and handling.

Crystal:	Prism, colourless
Size:	0.22 × 0.15 × 0.12 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.64 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, φ and ω-scans
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25064, 4077, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3556
$N(param)_{refined}$:	196
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

Experimental details

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

Discussion

On-going interest in the structural chemistry of zinc dithiocarbamates ($^-S_2CNRR'$) is reflected by the observation that there are approaching 250 "hits" for these derivatives in the Cambridge Structural Database (CSD) [5]. The motivations for continuing investigations broadly relate to crystal engineering [6–8] and biological considerations [9, 10]. In was in the former context that the centrosymmetric binuclear title compound, {Zn[S_2CN(i-Pr)n-Pr]$_2$}$_2$, with disparate R substituents, was studied.

As seen from the figure (70% displacement ellipsoids), the molecular structure comprises equals numbers of bidentate bridging and chelating dithiocarbamate ligands. The Zn—S bond lengths span a relatively narrow range of 2.3335(5) Å [for Zn—S1] to 2.4332(5) Å [Zn—S4]. The coordination geometry at Zn(II) approximates a tetrahedron with angles ranging from a narrow 76.289(17)° (chelate angle) to

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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}
Zn	0.37991(2)	0.01105(2)	0.84818(2)	0.01427(7)
S1	0.23765(5)	−0.07186(2)	0.91107(4)	0.01680(11)
S2	0.37630(5)	0.03187(2)	1.10103(4)	0.01369(10)
S3	0.33473(5)	0.12972(2)	0.81372(4)	0.01565(10)
S4	0.27001(6)	0.01889(2)	0.62911(4)	0.01789(11)
N1	0.22070(17)	−0.07957(8)	1.13595(14)	0.0141(3)
N2	0.17867(17)	0.15084(8)	0.58165(14)	0.0152(3)
C1	0.27372(19)	−0.04443(9)	1.05904(17)	0.0126(4)
C2	0.2486(2)	−0.05890(10)	1.26581(17)	0.0177(4)
H2	0.3058	−0.0144	1.2785	0.021*
C3	0.3434(2)	−0.11270(12)	1.35064(19)	0.0265(5)
H3A	0.4324	−0.1224	1.3259	0.040*
H3B	0.2859	−0.1555	1.3467	0.040*
H3C	0.3729	−0.0949	1.4340	0.040*
C4	0.1023(2)	−0.04519(10)	1.29285(18)	0.0200(4)
H4A	0.0467	−0.0091	1.2380	0.030*
H4B	0.1225	−0.0297	1.3772	0.030*
H4C	0.0433	−0.0880	1.2808	0.030*
C5	0.1321(2)	−0.14292(9)	1.09520(18)	0.0164(4)
H5A	0.1332	−0.1710	1.1674	0.020*
H5B	0.1801	−0.1707	1.0449	0.020*
C6	−0.0290(2)	−0.12934(10)	1.02204(18)	0.0192(4)
H6A	−0.0320	−0.0958	0.9563	0.023*
H6B	−0.0829	−0.1087	1.0755	0.023*
C7	−0.1051(3)	−0.19655(11)	0.9673(2)	0.0280(5)
H7A	−0.2087	−0.1869	0.9212	0.042*
H7B	−0.1027	−0.2296	1.0325	0.042*
H7C	−0.0530	−0.2164	0.9129	0.042*
C8	0.2525(2)	0.10501(9)	0.66396(17)	0.0136(4)
C9	0.1123(2)	0.13041(10)	0.45210(18)	0.0230(5)
H9	0.1032	0.0787	0.4497	0.028*
C10	0.2184(3)	0.15005(13)	0.3801(2)	0.0370(6)
H10A	0.3164	0.1296	0.4187	0.056*
H10B	0.2276	0.2007	0.3785	0.056*
H10C	0.1797	0.1325	0.2969	0.056*
C11	−0.0426(3)	0.15985(12)	0.3985(2)	0.0336(6)
H11A	−0.1057	0.1456	0.4484	0.050*
H11B	−0.0850	0.1424	0.3156	0.050*
H11C	−0.0374	0.2106	0.3970	0.050*
C12	0.1667(2)	0.22389(9)	0.61543(18)	0.0165(4)
H12A	0.1462	0.2531	0.5416	0.020*
H12B	0.2630	0.2389	0.6719	0.020*
C13	0.0444(2)	0.23543(10)	0.67548(19)	0.0191(4)
H13A	−0.0532	0.2245	0.6164	0.023*
H13B	0.0596	0.2033	0.7451	0.023*
C14	0.0422(2)	0.30923(10)	0.7197(2)	0.0271(5)
H14A	−0.0393	0.3146	0.7558	0.041*
H14B	0.0275	0.3413	0.6511	0.041*
H14C	0.1370	0.3196	0.7809	0.041*

129.055(19)° for S1—Zn—S3. This wide angle may be traced to the close approach of the transannular S2 atom which is separated from the zinc atom by 2.9512(5) Å.

In the most recent comprehensive review of the structural chemistry of the binary zinc-triad 1,1-dithiolates, of which dithiocarbamate is an exemplar, two structural motifs were described for molecules of the general formula $Zn(S_2CNRR')_2$ [11]. One was based on the dimeric structure just described, as exemplified by $[Zn(S_2CNMe_2)_2]_2$ [12], while the other was monomeric, with $Zn(S_2CNCy_2)_2$ being archetypal [13]. The adoption of one motif over the other is ascribed to steric effects with bulky substituents precluding dimerisation. Of the approximately 60 structures of $Zn(S_2CNRR')_2$ included in the CSD [5], the ratio of dimer to monomer is almost exactly 2:1. The fine balance between the adoption of either motif is seen in the structure for R = i-Bu [14]. Here, the crystal comprises equal numbers of each motif. Finally, the structure of the cadmium analogue of the title compound is described in the following paper [15]. Essentially, the same structural motif is observed except that the transannular Cd—S is considered bonding and therefore, the cadmium five-coordinate. This difference arises owing to the larger size of the cadmium atom.

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