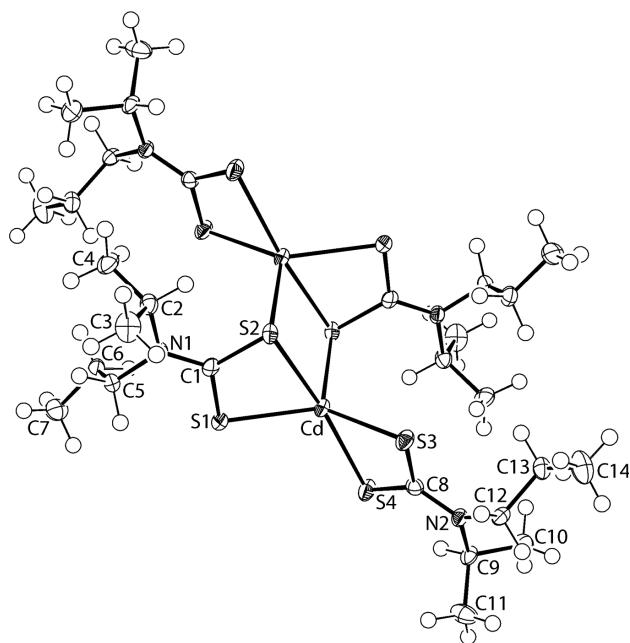


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Crystal structure of bis(μ -*N*-*i*-propyl-*N*-*n*-propyldithiocarbamato- κ^3 S,S')S)bis(*N*-*i*-propyl-*N*-*n*-propyldithiocarbamato- κ^2 S,S')dicadmium(II), $C_{28}H_{56}Cd_2N_4S_8$



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Abstract

$C_{28}H_{56}Cd_2N_4S_8$, monoclinic, $P2_1/n$ (no. 14), $a = 9.9003(3)$ Å, $b = 11.7373(3)$ Å, $c = 17.4539(5)$ Å, $\beta = 102.999(3)^\circ$, $V = 1976.22(10)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0243$, $wR_{ref}(F^2) = 0.0582$, $T = 100$ K.

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

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Table 1: Data collection and handling.

Crystal:	Block, pale-yellow
Size:	0.16 × 0.14 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.52 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω -scans
θ_{max} , completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	26079, 4038, 0.065
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3607
$N(param)_{refined}$:	196
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinXG and ORTEP [4]

Source of material

The compound was obtained from reacting a 1:2 mixture of $CdCl_2$ (Acros Organic) and $Na[S_2CN(i-Pr)n-Pr]$ [prepared from the 1:1:1 reaction of CS_2 (Panreac), $N(i-Pr)n-Pr$ (Alfa Aesar) and $NaOH$ (Merck) in acetone solution] in water which resulted in a white precipitate. This was extracted with CH_2Cl_2 and filtered. The filtrate was allowed to stand for slow evaporation under ambient conditions. Colourless crystals formed after a few days. **M.p.:** 467.5–468.4 K. **IR** (cm⁻¹): $\nu(C-S)$ 1188 (s, sh), 955 (s, br), $\nu(C-N)$ 1455 (s).

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

Until 2013, the structural chemistry of the binary cadmium dithiocarbamates, $Cd(S_2CNRR')_2$, was dominated by a single structural motif comprising a binuclear complex with equal numbers of μ_2 -bridging and chelating dithiocarbamate ligands leading to five-coordinate cadmium centres [5, 6]. Very recently, a new motif was discovered featuring μ_2 -bridging dithiocarbamate ligands exclusively, resulting in linear coordination polymers and six-coordinate cadmium centres [7, 8]. It was during such crystal engineering studies that the title compound, $\{Cd[S_2CN(i-Pr)n-Pr]_2\}_2$, with disparate R substituents, was characterised.

The molecular structure is shown in the figure (70% displacement ellipsoids) and the centrosymmetric binuclear

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}
Cd	0.02772(2)	0.36417(2)	0.06330(2)	0.01411(6)
S1	0.27314(5)	0.44245(4)	0.10583(3)	0.01487(12)
S2	0.03054(5)	0.59879(5)	0.08886(3)	0.01340(11)
S3	-0.15957(5)	0.29769(4)	0.13250(3)	0.01586(12)
S4	0.03365(5)	0.14132(5)	0.07563(4)	0.01705(12)
N1	0.29772(17)	0.66637(15)	0.12506(10)	0.0121(4)
N2	-0.18128(17)	0.07113(15)	0.13327(10)	0.0122(4)
C1	0.2107(2)	0.57904(18)	0.10730(12)	0.0116(4)
C2	0.2493(2)	0.78571(18)	0.13086(13)	0.0147(4)
H2	0.1468	0.7873	0.1092	0.018*
C3	0.2764(3)	0.8221(2)	0.21631(14)	0.0241(5)
H3A	0.2322	0.7681	0.2458	0.036*
H3B	0.2380	0.8984	0.2198	0.036*
H3C	0.3765	0.8234	0.2386	0.036*
C4	0.3159(2)	0.86568(18)	0.08149(14)	0.0189(5)
H4A	0.4152	0.8724	0.1051	0.028*
H4B	0.2724	0.9410	0.0795	0.028*
H4C	0.3030	0.8352	0.0281	0.028*
C5	0.4488(2)	0.64609(18)	0.14605(13)	0.0146(4)
H5A	0.4674	0.5781	0.1803	0.017*
H5B	0.4943	0.7120	0.1768	0.017*
C6	0.5139(2)	0.62823(18)	0.07590(13)	0.0150(4)
H6A	0.5152	0.7012	0.0477	0.018*
H6B	0.4580	0.5730	0.0391	0.018*
C7	0.6613(2)	0.5836(2)	0.10356(14)	0.0200(5)
H7A	0.7159	0.6379	0.1407	0.030*
H7B	0.7035	0.5745	0.0582	0.030*
H7C	0.6594	0.5098	0.1295	0.030*
C8	-0.1089(2)	0.15970(18)	0.11565(12)	0.0128(4)
C9	-0.1435(2)	-0.04848(17)	0.11873(13)	0.0140(4)
H9	-0.0692	-0.0456	0.0883	0.017*
C10	-0.2661(2)	-0.11282(19)	0.06898(15)	0.0207(5)
H10A	-0.3361	-0.1256	0.0998	0.031*
H10B	-0.2344	-0.1863	0.0530	0.031*
H10C	-0.3067	-0.0679	0.0221	0.031*
C11	-0.0847(3)	-0.1106(2)	0.19514(14)	0.0225(5)
H11A	-0.0052	-0.0681	0.2254	0.034*
H11B	-0.0549	-0.1870	0.1836	0.034*
H11C	-0.1561	-0.1166	0.2258	0.034*
C12	-0.2993(2)	0.08886(18)	0.17089(12)	0.0133(4)
H12A	-0.2748	0.1502	0.2105	0.016*
H12B	-0.3136	0.0183	0.1991	0.016*
C13	-0.4356(2)	0.12018(18)	0.11438(13)	0.0159(5)
H13A	-0.4216	0.1880	0.0833	0.019*
H13B	-0.4662	0.0564	0.0774	0.019*
C14	-0.5466(2)	0.1453(2)	0.15960(16)	0.0259(6)
H14A	-0.5578	0.0792	0.1919	0.039*
H14B	-0.6346	0.1614	0.1225	0.039*
H14C	-0.5190	0.2117	0.1936	0.039*

complex features μ_2 -bridging and chelating dithiocarbamate ligands, as is normal for these compounds [5, 6]. Thus, one ligand chelates one cadmium atom and simultaneously bridges the second centrosymmetrically-related cadmium atom.

The bridging S2 atom forms the longest of the Cd–S bond lengths in the structure at 2.6241(6) Å, for the bridging bond (symmetry operation: $-x, 1-y, -z$), and 2.7888(6) Å. The shortest bond length of 2.5471(5) Å is found for the Cd–S1 bond. The other ligand is chelating with Cd–S bond lengths intermediate to those formed by the S1 and S2 atoms. The S₅ donor set is highly distorted and based on the value of τ of 0.51, cf. the extreme values of 0.0 and 1.0 for ideal square-pyramidal and trigonal-bipyramidal geometries [9], respectively, the coordination geometry is intermediate between these extremes.

The aforementioned crystal chemistry studies on Cd[S₂CN(iPr)CH₂CH₂OH]₂ [6, 7] revealed the presence of supramolecular isomers for one-dimensional coordination polymers, i.e. {Cd[S₂CN(iPr)CH₂CH₂OH]₂-solvent}_n for solvent = acetonitrile [6] and ethanol [7]. This came about as all dithiocarbamate ligands in the polymers are μ_2 -bridging. Solvent-mediated structural transformations were also observed between the polymers and the anticipated binuclear molecules, i.e. {Cd[S₂CN(iPr)CH₂CH₂OH]₂-solvent}. The conclusion of these studies was that the polymers were kinetic outcomes of crystallisation and that the dimers were the thermodynamic products. The title structure is very similar to the zinc analogue, {Zn[S₂CN(i-Pr)n-Pr]₂} [10] except that the transannular interaction is not as significant so the coordination geometry for the zinc atom is best described as being distorted tetrahedral. This difference in structure relates to the different sizes of the zinc and cadmium atoms.

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References

1. Rigaku/Oxford Diffraction: CrysAlisPro. Rigaku Corporation, The Woodlands, TX, USA (2017).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45** (2012) 849–854.
5. Tiekink, E. R. T.: Molecular architecture and supramolecular association in the zinc-triad 1,1-dithiolates. Steric control as a design element in crystal engineering? *CrystEngComm* **5** (2003) 101–113.
6. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C.: The Cambridge structural database. *Acta Crystallogr. B* **72** (2016) 171–179.
7. Tan, Y. S.; Sudlow, A. L.; Molloy, K. C.; Morishima, Y.; Fujisawa, K.; Jackson, W. J.; Henderson, W.; Halim, S. N. Bt. A.; Ng, S. W.; Tiekink, E. R. T.: Supramolecular isomerism in a

- cadmium bis(*N*-hydroxyethyl, *N*-isopropylthiocarbamate) compound: physicochemical characterization of ball ($n = 2$) and chain ($n = \infty$) forms of $\{Cd[S_2CN(iPr)CH_2CH_2OH]_2\text{solvent}\}_n$. *Cryst. Growth Des.* **13** (2013) 3046–3056.
8. Tan, Y. S.; Halim, S. N. A.; Tiekink, E. R. T.: Exploring the crystallization landscape of cadmium bis(*N*-hydroxyethyl, *N*-isopropyl-dithiocarbamate), $Cd[S_2CN(iPr)CH_2CH_2OH]_2$. *Z. Kristallogr.* **231** (2016) 113–126.
 9. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C.: Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]-copper(II) perchlorate. *Dalton Trans.* (1984) 1349–1356.
 10. Tan, Y. S.; Tiekink, E. R. T.: Crystal structure of bis(μ -*N*-*i*-propyl-*N*-*n*-propylthiocarbamato- $\kappa^2S:S'$) bis(*N*-*i*-propyl-*N*-*n*-propylthiocarbamato- κ^2S,S')dizinc(II), $C_{28}H_{56}N_4S_8Zn_2$. *Z. Kristallogr. –NCS* **233** (2018) 477–479.