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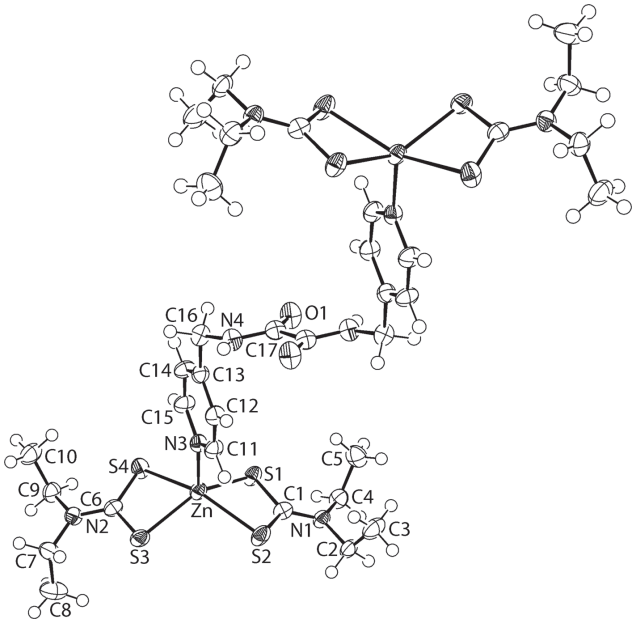
Crystal structure of (μ_2-*N*,*N*′-bis((pyridin-4-yl)methyl)ethanediamide-κ^2*N*:*N*′)-tetrakis(diethylcarbamodithioato-κ^2*S*,*S*′)dizinc(II), $C_{34}H_{54}N_8O_2S_8Zn_2$



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Abstract

$C_{34}H_{54}N_8O_2S_8Zn_2$, monoclinic, *C*2/*c* (no. 15), $a = 20.192(7)$ Å, $b = 16.448(5)$ Å, $c = 14.150(5)$ Å, $\beta = 102.368(8)°$, $V = 4590(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.052$, $wR_{ref}(F^2) = 0.123$, $T = 98$ K.

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The molecular structure of the title compound is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.30 × 0.17 × 0.08 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	14.5 cm^{-1}
Diffractometer, scan mode:	AFC12K/SATURN724, ω scans
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16452, 5264, 0.062
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4749
$N(param)_{refined}$:	251
Programs:	Rigaku programs [1, 2], SHELX [3, 4], ORTEP [5]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn	0.21031(2)	0.20249(2)	0.73375(3)	0.01958(11)
O1	0.52122(12)	0.43816(14)	0.91005(18)	0.0298(5)
S1	0.28223(4)	0.08693(5)	0.73415(6)	0.02308(18)
S2	0.22879(5)	0.14223(5)	0.90076(6)	0.02747(19)
S3	0.09406(4)	0.24463(5)	0.70649(6)	0.02297(17)
S4	0.16676(4)	0.20584(5)	0.55226(6)	0.02545(19)
N1	0.30869(13)	0.01153(15)	0.90478(19)	0.0208(5)
N2	0.03936(13)	0.26094(15)	0.51813(19)	0.0210(5)
N3	0.27190(13)	0.30336(15)	0.75524(19)	0.0191(5)
N4	0.43457(14)	0.52858(16)	0.8992(2)	0.0236(6)
H4N	0.4174(18)	0.5658(17)	0.931(2)	0.028*
C1	0.27747(16)	0.07369(18)	0.8533(2)	0.0215(6)
C2	0.30565(17)	−0.00001(19)	1.0066(2)	0.0247(7)
H2A	0.3110	−0.0586	1.0227	0.030*
H2B	0.2605	0.0172	1.0158	0.030*
C3	0.3597(2)	0.0473(2)	1.0755(3)	0.0343(8)
H3A	0.4046	0.0304	1.0670	0.051*
H3B	0.3558	0.0367	1.1422	0.051*
H3C	0.3536	0.1056	1.0617	0.051*
C4	0.34887(17)	−0.04722(19)	0.8627(3)	0.0255(7)
H4A	0.3256	−0.0580	0.7949	0.031*
H4B	0.3508	−0.0991	0.8988	0.031*
C5	0.42110(18)	−0.0190(2)	0.8643(3)	0.0327(8)
H5A	0.4199	0.0350	0.8347	0.049*
H5B	0.4430	−0.0576	0.8279	0.049*
H5C	0.4468	−0.0163	0.9314	0.049*
C6	0.09407(16)	0.23985(17)	0.5843(2)	0.0205(6)
C7	−0.02380(17)	0.2883(2)	0.5439(3)	0.0273(7)
H7A	−0.0466	0.3284	0.4956	0.033*
H7B	−0.0130	0.3155	0.6078	0.033*
C8	−0.0714(2)	0.2176(2)	0.5477(3)	0.0378(9)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
H8A	−0.0782	0.1870	0.4869	0.057*
H8B	−0.1151	0.2383	0.5567	0.057*
H8C	−0.0517	0.1818	0.6018	0.057*
C9	0.03756(17)	0.2543(2)	0.4136(2)	0.0257(7)
H9A	−0.0096	0.2441	0.3785	0.031*
H9B	0.0656	0.2075	0.4021	0.031*
C10	0.0637(2)	0.3312(2)	0.3743(3)	0.0338(8)
H10A	0.0366	0.3778	0.3869	0.051*
H10B	0.0602	0.3255	0.3045	0.051*
H10C	0.1113	0.3397	0.4064	0.051*
C11	0.28589(16)	0.34213(19)	0.8404(2)	0.0225(6)
H11	0.2660	0.3229	0.8913	0.027*
C12	0.32830(16)	0.40935(19)	0.8573(2)	0.0220(6)
H12	0.3364	0.4357	0.9184	0.026*
C13	0.35884(15)	0.43817(18)	0.7848(2)	0.0203(6)
C14	0.34439(17)	0.39753(19)	0.6969(2)	0.0233(6)
H14	0.3640	0.4153	0.6451	0.028*
C15	0.30149(17)	0.3313(2)	0.6848(2)	0.0244(7)
H15	0.2924	0.3041	0.6241	0.029*
C16	0.40502(17)	0.51158(18)	0.7985(2)	0.0238(6)
H16A	0.4419	0.5025	0.7635	0.029*
H16B	0.3789	0.5596	0.7694	0.029*
C17	0.48952(16)	0.48855(18)	0.9465(2)	0.0221(6)

Source of materials

The compound was isolated from the 2:1 reaction of $Zn(S_2CNEt_2)_2$ and (*4*-NC_5H_4)$CH_2N(H)C(=O)-C(=O)N(H)CH_2$-($C_5H_4N$-*4*) following standard procedures [6, 7]. Colourless crystals were obtained by the diffusion of ethyl ether into a dimethylformamide solution of the compound. **M.p.**: >553 K but, turns opaque at 513 K. **IR** (cm^{-1}): *ν*(C–S) 1065 (s, sh), *ν*(C–N) 1484 (s).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95 − 0.99 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The N-bound H-atoms were located in difference Fourier maps, and refined with a distance restraint of N—H = 0.88(1) Å, and with $U_{iso}(H)$ set to $1.2U_{eq}(N)$. Owing to poor agreement, two low order reflections, *i.e.* (2 0 0) and (−1 1 1), were omitted from the final cycles of refinement. The maximum and minimum residual electron density peaks of 0.48 and 1.02 e $Å^{-3}$, respectively, were located 1.37 and 0.81 Å from the Zn atom.

Comment

The isomeric molecules of general formula (*n*-NC_5H_4)$CH_2N(H)C(=O)-C(=O)N(H)CH_2$-($C_5H_4N$-*n*), for *n* = 2, 3 and 4, abbreviated as $^nLH_2$, are bifunctional in the sense that they contain a central di-amide moiety as well as pyridyl-N donors. With metals, the situation may be envisaged whereby the pyridyl-N atoms bridge metal centres and the diamide forms supramolecular tapes *via* amide-N—H···O(amide) hydrogen bonding. As a continuation of investigations coordinating $^nLH_2$ with zinc dithiocarbamates, *i.e.* $Zn(S_2CNRR')_2$ for R, R′ = alkyl [6, 7], the title compound, $[Zn[S_2CNEt_2]_2\}_2{}^4LH_2$, was studied.

The binuclear complex is disposed about a centre of inversion with the unlabelled atoms in the Figure related by the symmetry operation $1 - x$, $1 - y$, $2 - z$. The Zn atom is coordinated by two dithiocarbamate ligands forming Zn–S bonds that span the relatively narrow range 2.3913(10) to 2.5306(12) Å, and the pyridyl-N atom. The resulting NS_4 coordination approximates a square pyramid, with the N atom in the apical position, as judged by the value of $\tau = 0.20$, *cf.* $\tau = 0.0$ for an ideal square pyramid and 1.0 for an ideal trigonal bipyramid [8]. In these respects, the structure resembles literature precedents [6, 7]. Interestingly, the molecular packing does not feature conventional hydrogen bonding interactions. Instead, the three-dimensional architecture features methylene-C—H···O(amide) and pyridyl-C–H···S interactions. This observation contradicts binuclear $\{Zn[S_2CN(Me)CH_2CH_2OH]_2\}_2{}^3LH_2$ [6], where supramolecular chains were formed as a result of hydroxy-O—H···(hydroxy) hydrogen bonding. The diamide fuctionality come into play to connect centrosymmetrically related chains into double chains *via* hydroxy-O—H···O(amide) hydrogen bonding. The situation changed somewhat when the dithiocarbamate ligand carry residues incapable of forming hydrogen bonding interactions. Thus, in binuclear $\{Zn[S_2CN(n\text{-}Pr)_2]_2\}_2{}^3LH_2$ the diamide groups form amide-N—H···O(amide) hydrogen bonds to form supramolecular tapes [7].

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