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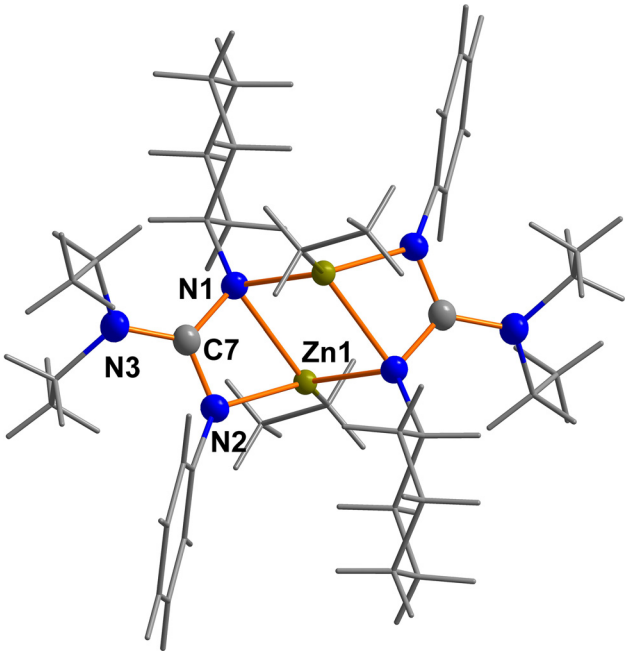
Crystal structure of bis{[(cyclohexylimino)(phenylimino)-l5-(methyl)diethylazane-$\kappa^2N:N'$]-(ethyl)-zinc(II)]}, $C_{38}H_{62}N_6Zn_2$



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Abstract

$C_{38}H_{62}N_6Zn_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.5907(4) Å, b = 10.6743(4) Å, c = 11.2593(4) Å, α = 107.6980(10)°, β = 113.5840(10)°, γ = 97.2290(10)°, V = 965.12(6) Å^3, Z = 1, $R_{gt}(F)$ = 0.0232, w$R_{ref}(F^2)$ = 0.0577, T = 200(2) K.

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A part of the title coordination compound is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.35 × 0.33 × 0.30 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.28 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	25.1°, 97 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7251, 3331, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3149
N(param)$_{refined}$:	211
Programs:	SHELX [1], BRUKER [2, 3], DIAMOND [4]

1 Source of materials

All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques. Solvents were dried with appropriate drying agents, degassed, and stored over a potassium mirror or activated molecular sieves prior to use. $ZnEt_2$ (1.0 M solution in hexane; Alfa Aesar) was obtained commercially and used as received. Et_2NH (Aldrich) was dried over KOH and redistilled before use. Carbodiimine CyN=C=NC_6H_5 was prepared according to the literature procedures [5]. To a stirred solution of diethylamine (0.20 mL, 2.0 mmol) in hexane (15 mL), diethylzinc (2.00 mL of a 1.0 M solution in hexane, 2.0 mmol) was slowly dropped into the above solution at ambient temperature. The mixture was heated to 60 °C for 12 h and then cooled to room temperature. Carbodiimine CyN=C=NC_6H_5 (0.401 g, 2.0 mmol) was added. The mixture was stirred for 8 h to afford a cloudy solution, which was filtered. The filtrate was concentrated to ca. 5 mL in *vacuo* and stored at −10 °C, yielding colorless crystals (0.36 g, 74.6 %). section

2 Experimental details

2.1 Comment

N,N-Bidentate ligands generated by the deprotonation of guanidines can provide a wide range of patterns by adjusting

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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}
Zn1	0.60539 (2)	0.40972 (2)	0.51052 (2)	0.01920 (7)
N1	0.44183 (15)	0.46831 (13)	0.33300 (13)	0.0178 (3)
N2	0.39439 (15)	0.26901 (13)	0.35955 (13)	0.0196 (3)
N3	0.23948 (16)	0.27281 (14)	0.13577 (14)	0.0244 (3)
C1	0.48522 (18)	0.53042 (16)	0.24683 (16)	0.0199 (3)
H1	0.4233	0.4662	0.1458	0.024*
C2	0.4477 (2)	0.66790 (17)	0.26216 (18)	0.0254 (4)
H2A	0.4998	0.7290	0.3631	0.031*
H2B	0.3317	0.6526	0.2258	0.031*
C3	0.5038 (2)	0.73836 (19)	0.1827 (2)	0.0331 (4)
H3A	0.4438	0.6821	0.0804	0.040*
H3B	0.4824	0.8288	0.1995	0.040*
C4	0.6803 (2)	0.75754 (19)	0.2307 (2)	0.0365 (4)
H4A	0.7409	0.8206	0.3310	0.044*
H4B	0.7130	0.7993	0.1751	0.044*
C5	0.7179 (2)	0.6208 (2)	0.21221 (19)	0.0327 (4)
H5A	0.8337	0.6360	0.2481	0.039*
H5B	0.6651	0.5608	0.1109	0.039*
C6	0.6616 (2)	0.54984 (18)	0.29112 (18)	0.0266 (4)
H6A	0.6825	0.4592	0.2731	0.032*
H6B	0.7232	0.6053	0.3935	0.032*
C7	0.35327 (18)	0.33511 (15)	0.27347 (16)	0.0182 (3)
C8	0.28979 (18)	0.15661 (15)	0.34987 (15)	0.0195 (3)
C9	0.3447 (2)	0.04614 (17)	0.37047 (18)	0.0261 (4)
H9	0.4483	0.0444	0.3831	0.031*
C10	0.2494 (2)	−0.06100 (18)	0.3727 (2)	0.0316 (4)
H10	0.2886	−0.1354	0.3872	0.038*
C11	0.0981 (2)	−0.06112 (18)	0.35419 (19)	0.0310 (4)
H11	0.0330	−0.1351	0.3553	0.037*
C12	0.0425 (2)	0.04837 (17)	0.33387 (17)	0.0268 (4)
H12	−0.0613	0.0494	0.3213	0.032*
C13	0.13690 (19)	0.15602 (17)	0.33178 (17)	0.0230 (3)
H13	0.0973	0.2304	0.3179	0.028*
C14	0.1342 (2)	0.34620 (19)	0.06832 (19)	0.0327 (4)
H14A	0.1373	0.3382	−0.0205	0.039*
H14B	0.1743	0.4447	0.1309	0.039*
C15	−0.0364 (2)	0.2925 (2)	0.0362 (2)	0.0488 (5)
H15A	−0.0785	0.1961	−0.0290	0.073*
H15B	−0.1003	0.3463	−0.0068	0.073*
H15C	−0.0406	0.3004	0.1237	0.073*
C16	0.2077 (2)	0.12696 (18)	0.05327 (18)	0.0330 (4)
H16A	0.1322	0.1052	−0.0460	0.040*
H16B	0.1564	0.0714	0.0887	0.040*
C17	0.3547 (3)	0.0867 (2)	0.0590 (2)	0.0462 (5)
H17A	0.4088	0.1439	0.0279	0.069*
H17B	0.3249	−0.0099	−0.0029	0.069*
H17C	0.4260	0.0999	0.1558	0.069*
C18	0.8251 (2)	0.40070 (19)	0.5614 (2)	0.0302 (4)
H18A	0.8913	0.4925	0.5857	0.036*
H18B	0.8652	0.3804	0.6472	0.036*
C19	0.8492 (3)	0.2964 (2)	0.4505 (2)	0.0460 (5)
H19A	0.7856	0.2044	0.4259	0.069*
H19B	0.9616	0.2994	0.4875	0.069*
H19C	0.8158	0.3179	0.3664	0.069*

the type of the substituents on the conjugated N–C–N skeleton, and exhibit extensive utility in metal complexes [6]. Various types of metal guanidinate complexes and their properties have been reported, such as cobalt [7], titanium [8, 9], tungsten [10], cerium [11], platinum [12] and lutetium [13]. For zinc complex [14], several examples with guanidinate ligands have been studied [15], they exhibited good to excellent catalytic activity. With particular relevance to this work, the room temperature reaction between *N*-cyclohexyl-*N*-phenylmethanediimine and $ZnMe_2$ yielded the dinuclear Zn alkyl complex $[\{C_5H_{10}NC(NC_6H_{11})\ (NC_6H_5)\}ZnEt]_2$.

The title compound crystallised as the dimeric complex $[\{C_5H_{10}NC(NC_6H_{11})\ (NC_6H_5)\}ZnEt]_2$, in which the zinc centre is described as distorted tetrahedral with bond angles in the range 61.94 (5)°–130.37 (7)°, four sites are occupied by three N atoms from two different μ_2–guanidinato ligand and one C donor of the ethyl. The Zn1–N2 (2.0422(13) Å) and Zn1–N1^i (2.0968(12) Å) bond distances are shorter than Zn1–N1 (2.3119(12) Å) (symmetrycodes: (i) $-x + 1, -y + 1, -z + 1$). The Zn–N distance are comparable to those observed in the related literature [16]. The $\{C_5H_{10}NC(NC_6H_{11})(NC_6H_5)\}^{-1}$ anion coordinates two zinc centers in μ_2–η^2:η^1 coordination modes through nitrogen atoms to a centrosymmetric dimer with Zn–Zn distance of 2.9550(4) Å. The dimer has an *anti* arrangement of guanidines ligands about the central Zn_2N_2 metallacycle, a likely consequence of the different steric requirements of the ligands at the zinc centre. The Zn_2N_2 core of the molecule is perfectly planar and forms an angle of 74.84° to the essentially planar ZnN_2C metallacycle. In agreement with this postulate, the C(7)–N(3) bond length of ***1*** [1.369(2) Å] is intermediate between the value expected for C–N single and C=N double bonds. The C(7)–N(1) and C(7)–N(2) bond lengths (1.3613(19) and 1.369(2) Å, respectively) formed by guanidinato ligand are similar to those found in related CN bonds in the Zn complexes [17, 18]. Such bond lengths are consistent with the presence of a delocalized NCN ligand back bone.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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