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Dichloro(*N*,*N*,*N*′-trimethylethylenediamine)-zinc(II)

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Key indicators

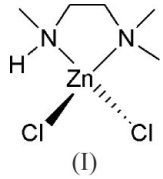
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.098
Data-to-parameter ratio = 27.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[ZnCl_2(CH_3NHCH_2CH_2NHCH_3)]$, crystallizes as tetrahedral monomers. The complex is chiral but forms racemic crystals. Molecules which have the (*R*)-configuration at nitrogen have a δ-conformation of the five-membered chelate ring, and those with (*S*)-configuration have λ-conformation. Intermolecular N—H···Cl hydrogen bonds [H···Cl = 2.56 (4) Å] form infinite chains.

Comment

The title compound, $[ZnCl_2$(trimeda)] (trimeda = *N*,*N*,*N*′-trimethylethylenediamine), (I), was prepared from optically inactive starting materials but generated a stereogenic N atom, which makes the complex chiral. Since $[ZnCl_2$(trimeda)] is stereochemically labile and racemizes in solution, it may be possible to obtain an enantiopure product by total spontaneous resolution if the complex crystallizes as a conglomerate, even though it is most likely that the complex will form racemic crystals. Interestingly, $[TiCl_4$(trimeda)] (Drake *et al.*, 1994), does crystallize as a conglomerate (in $P2_1$), but no information regarding the absolute structure or enantiopurity of the product has been reported. In our search for a conglomerate of $[ZnCl_2$(trimeda)], we have so far only been able to isolate a racemic phase, which crystallizes in the centrosymmetric space group *Pbca*. The molecular structure of the complex is shown in Fig. 1. Apart from the stereogenic N atom, the complex also displays another element of chirality: the five-membered trimeda-zinc chelate ring is conformationally chiral. Molecules which have the (*R*)-configuration at nitrogen have a δ-conformation of the five-membered chelate ring, and those with (*S*)-configuration have λ-conformation. In $[TiCl_4$(trimeda)], the (*R*)-configuration is also accompanied by a δ-conformation of the chelate ring. As can be seen in Fig. 2, intermolecular N—H···Cl hydrogen bonds [H···Cl = 2.56 (4) Å] form infinite chains.



(I)

Several tmeda (tmeda = *N*,*N*,*N*′*N*′-tetramethylethylenediamine) complexes with divalent zinc, *viz*. zinc chloride (Sen Gupta *et al.*, 1982), zinc bromide (Citeau *et al.*, 2001) and zinc iodide (Htoon & Ladd, 1974), as well as dialkyl zinc (Yasuda *et al.*, 1980, Andrews *et al.*, 1998), have been reported. However, the only crystal structures of zinc complexes with the trimeda ligand in the Cambridge Structural Database (CSD; Version

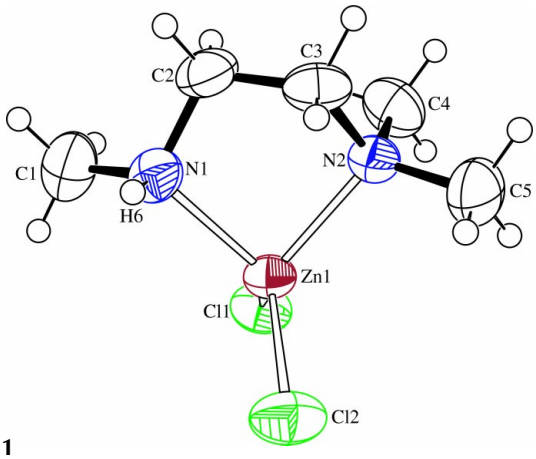


Figure 1
*ORTEP*III (Farrugia, 1997) plot of [$ZnCl_2$(trimeda)], with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

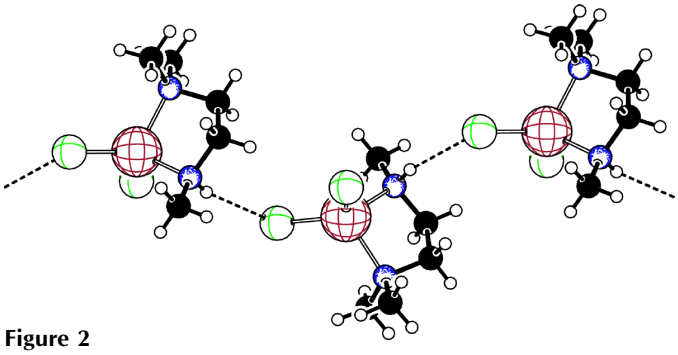


Figure 2
PLUTON (Spek, 2003) plot, showing an infinite chain formed by intermolecular hydrogen bonds (dashed lines).

5.25; Allen, 2002) are [$Zn(NCS)_2$(trimeda)] (Cameron *et al.*, 1998) and [$Zn(Q_T)_2$(trimeda)], where Q_T = bis(1-phenyl-3-methyl-4-(2,2-dimethylpropyl)carbonyl-pyrazol-5-onate (Marchetti *et al.*, 2000). The Zn—Cl and Zn—N bond distances in the title compound are similar to those found in [$ZnCl_2$(tmeda)]. It is common in tetrahedral MCl_2 complexes that the Cl—*M*—Cl angle increases with decreasing size of the metal; the Cl—Cd—Cl angle in dichlorobis(triphenylphosphine)cadmium is 113.9° and the S—Hg—S angle in dithiocyanoatobis(triphenylphosphine)mercury is 96.7° (Makhija *et al.*, 1973). The structure of the title compound is also consistent with this trend, the Cl—Zn—Cl angle being 115.61 (3)°. The N—Zn—N angle is 86.73 (9)°, and the N—Zn—Cl angles are 112.41 (6)–113.17 (6)°. A bite angle of 86° is within the normal range for the trimeda ligand; the mean value of N—Zn—N angles in tmeda/zinc complexes found in the CSD is 84.3±2.7°.

Experimental

All manipulations were carried out under nitrogen, using standard Schlenk techniques. Dichloromethane was distilled from CaH_2 and stored over 4 Å molecular sieves. Toluene was distilled from sodium/benzophenone prior to use and $ZnCl_2$ was dried by treatment with thionyl chloride (Pray, 1990). Anhydrous $ZnCl_2$ (0.35 g, 2.57 mmol) was suspended in dichloromethane (1 ml) and *N,N,N′*-trimethylethylenediamine (0.26 g, 2.57 mmol) was then added, yielding a colourless solution. The solution was stirred for a few minutes and then toluene (4 ml) was layered over the solution. Colourless single crystals, suitable for X-ray analysis, formed in 70% yield after 12 h at ambient temperature.

Crystal data

[$ZnCl_2(C_5H_{14}N_2)$]
M_r = 238.45
Orthorhombic, *Pbca*
a = 12.921 (2) Å
b = 11.882 (2) Å
c = 13.264 (2) Å
V = 2036.5 (6) Å^3
Z = 8
D_x = 1.555 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 16 870 reflections
θ = 2.8–29.0°
μ = 2.88 mm^{-1}
T = 293 (2) K
Block, colourless
0.4 × 0.2 × 0.2 mm

Data collection

Rigaku R-AXIS IIC image plate system diffractometer
φ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
T_{min} = 0.400, T_{max} = 0.561
16 870 measured reflections
2646 independent reflections
2322 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 29.0°
h = −17 → 17
k = −16 → 16
l = −17 → 18

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.098
S = 1.10
2646 reflections
95 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.5567P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.065 (2)	Zn1—Cl2	2.2074 (8)
Zn1—N2	2.081 (2)	Zn1—Cl1	2.2120 (7)
N1—Zn1—N2	86.73 (9)	N1—Zn1—Cl1	113.15 (7)
N1—Zn1—Cl2	112.41 (6)	N2—Zn1—Cl1	112.44 (6)
N2—Zn1—Cl2	113.17 (6)	Cl2—Zn1—Cl1	115.61 (3)

All H atoms except H6 were included in calculated positions (C—H = 0.96–0.97 Å) and refined using a riding model, with U_{iso} = 1.2 or 1.5(methyl)U_{eq}(parent atom). Atom H6 was located in a difference map and allowed to refine without constraints.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Farrugia, 1997) and *PLUTON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999); *SHELXL*97 (Sheldrick, 1997).

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