metal-organic papers

mer-Bis(diethylenetriamine)zinc(II) dichloride

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At 93 K, in the title compound, $[Zn(C_4H_{13}N_3)_2]Cl_2$, the Zn^{II} atom is coordinated by six N atoms from two diethylenetriamine ligands in a distorted octahedral geometry. In contrast to the previously determined chloride and bromide monohydrates, this compound is anhydrous. There is extensive hydrogen bonding between the amine H atoms in the cation and the chloride anions.

Comment

The structures of several bis(diethylenetriamine)zinc(II) cations have previously been determined (Hodgson, & Penfold, 1974; Liu *et al.*, 2005; Murphy *et al.*, 1980; Zocchi *et al.*, 1972; Johns & Abdul Malik, 2002; Razak *et al.*, 2000). In all cases there is extensive hydrogen bonding between the amine H atoms and the anions and solvent molecules (where appropriate), which has noticeable effects on the metrical parameters of the ZnN_6 chromophore. The structures of both $[Zn(dien)_2]Cl_2 \cdot H_2O$ (Liu *et al.*, 2005) and $[Zn(dien)_2]Br_2 \cdot H_2O$ (Hodgson & Penfold, 1974) are the most relevant to the title compound, $Zn(dien)_2]Cl_2$, (I), which, however, was synthesized under anhydrous conditions. Thus in (I) all the hydrogen-bonding interactions are between the amine H atoms and the chloride anions (see Table 2). A comparison between the metrical parameters of the three compounds reveals differences that show up most clearly in distortions in the N—Zn—N angles. Thus the *trans* chelate bite angles for N1A—Zn—N3A and N1B—Zn—N3B [157.55 (5) and 156.61 (5)°, respectively] are the smallest among those observed, while N2A—Zn—N2B is only 170.36 (5)°. While the usual pattern of longer Zn—$N_{primary}$ and shorter Zn—$N_{secondary}$ distances is observed, there are also some minor distortions in the Zn—N distances.

(I)
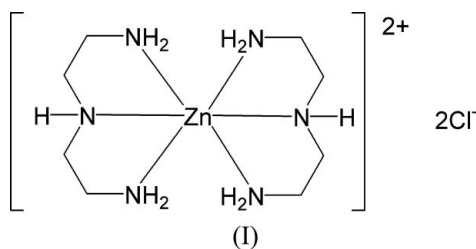
As indicated above, there is extensive hydrogen bonding between the amine H atoms and chloride anions. The two anions, Cl1 and Cl2, make four and six acceptor hydrogen bonds, respectively, to the amine H atoms, with N···Cl distances ranging from 3.2865 (13) to 3.4468 (13) Å.
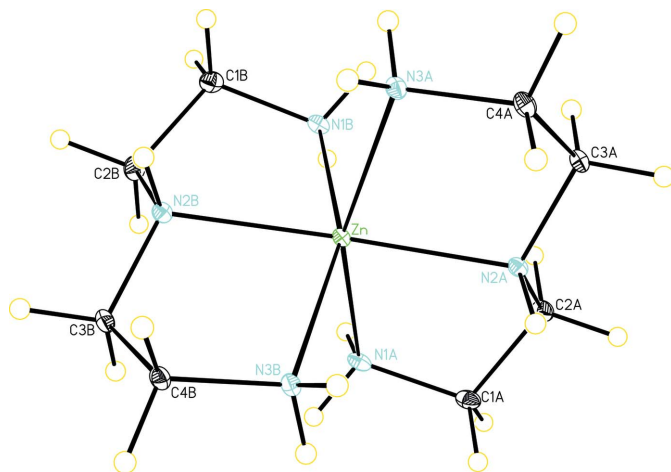
Figure 1
View of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size.
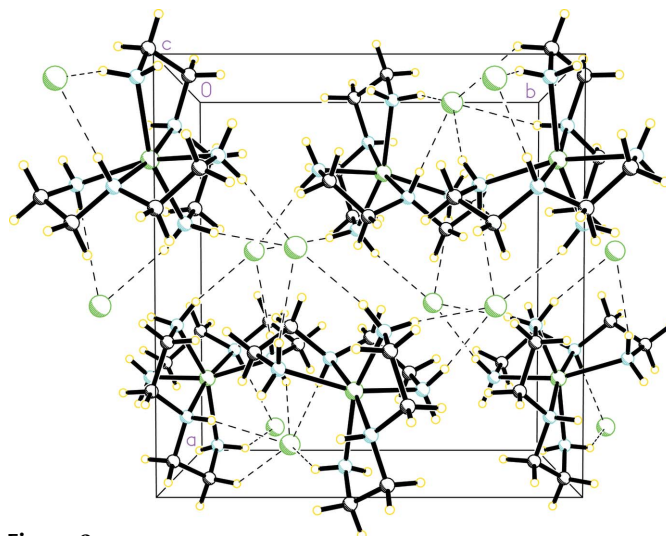

Figure 2
The molecular packing of (I), viewed down the c axis, with hydrogen bonds drawn as dashed lines.

Experimental

$ZnCl_2$ (0.0704 g), Se (0.0218 g), $AuCl_3$ (0.0316 g) and anhydrous diethylenetriamine (0.4 ml) were loaded into a 5 mm OD/3 mm ID quartz tube. This tube was cooled to 77 K and flame-sealed under vacuum at a length of 11.6 cm (57% fill). The tube was heated in a 418 K oil bath for 12 d, which resulted in a large number of clear, colorless crystals and Au flakes in the top half of the tube, and a clump of Au metal at the bottom. The crystals were washed with dry diethylenetriamine and diethyl ether in a drybox and immersed in Cargille #2 oil.

Crystal data

$[Zn(C_4H_{13}N_3)_2]Cl_2$	$Z = 4$
$M_r = 342.62$	$D_x = 1.492$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.2492$ (9) Å	$\mu = 1.95$ mm^{-1}
$b = 10.8810$ (9) Å	$T = 93$ (2) K
$c = 12.4813$ (10) Å	Irregular fragment, colorless
$\beta = 93.218$ (1)°	$0.68 \times 0.55 \times 0.35$ mm
$V = 1525.3$ (2) Å^3	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	11570 measured reflections
φ and ω scans	3697 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3416 reflections with $I > 2\sigma(I)$
$T_{min} = 0.746$, $T_{max} = 1.000$	$R_{int} = 0.023$
(expected range = 0.377–0.505)	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0265P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$+ 0.733P]$
$wR(F^2) = 0.057$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
3697 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
155 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
H-atom parameters constrained	Extinction correction: SHELXL97
	Extinction coefficient: 0.0022 (5)

Table 1
Selected geometric parameters (Å, °).

Zn—N2A	2.1332 (12)	N2A—C2A	1.4663 (19)
Zn—N2B	2.1566 (12)	N2A—C3A	1.4749 (18)
Zn—N1B	2.1943 (12)	N3A—C4A	1.4766 (18)
Zn—N3A	2.2356 (12)	N1B—C1B	1.478 (2)
Zn—N1A	2.2448 (12)	N2B—C2B	1.4673 (18)
Zn—N3B	2.2462 (12)	N2B—C3B	1.4694 (18)
N1A—C1A	1.477 (2)	N3B—C4B	1.4749 (18)
N2A—Zn—N2B	170.36 (5)	N1B—Zn—N1A	88.62 (4)
N2A—Zn—N1B	107.23 (5)	N3A—Zn—N1A	157.55 (5)
N2B—Zn—N1B	81.02 (5)	N2A—Zn—N3B	94.56 (4)
N2A—Zn—N3A	79.09 (4)	N2B—Zn—N3B	78.15 (4)
N2B—Zn—N3A	96.37 (5)	N1B—Zn—N3B	156.61 (5)
N1B—Zn—N3A	89.05 (4)	N3A—Zn—N3B	103.67 (5)
N2A—Zn—N1A	80.30 (5)	N1A—Zn—N3B	86.72 (4)
N2B—Zn—N1A	105.30 (5)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1A—H1AC$\cdots$Cl2^i	0.92	2.47	3.3410 (12)	158
N1A—H1AD$\cdots$Cl1^{ii}	0.92	2.39	3.3035 (12)	172
N2A—H2AC$\cdots$Cl2	0.93	2.36	3.2876 (12)	174
N3A—H3AC$\cdots$Cl1	0.92	2.63	3.4468 (13)	148
N3A—H3AD$\cdots$Cl2^{iii}	0.92	2.50	3.3480 (13)	153
N1B—H1BC$\cdots$Cl1	0.92	2.39	3.2865 (13)	164
N1B—H1BD$\cdots$Cl1^{ii}	0.92	2.44	3.3535 (13)	174
N2B—H2BC$\cdots$Cl2^{iii}	0.93	2.49	3.3635 (13)	156
N3B—H3BC$\cdots$Cl2^i	0.92	2.61	3.4432 (13)	151
N3B—H3BD$\cdots$Cl2	0.92	2.63	3.2919 (13)	130

Symmetry codes: (i) $-x + 2, -y, -z$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

All H atoms were initially located in a difference Fourier map. The positions of the amine H atoms were idealized at 0.92 Å (NH$_2$) or 0.93 Å (NH), with U_{iso}(H) = 1.2U_{eq}(N). Other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in of 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C).

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Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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