metal-organic papers

Redetermination of dichloro(N,N,N′,N′-tetramethyl-ethylenediamine)zinc(II)

Di-Mei Chen,[a] Xin-Jü Ma,[b] Bing Tu,[b] Wen-Jie Feng[b] and Zhi-Min Jin[b]*

[a]School of Chemistry and Materials Engineering, Wenzhou University, Zhejiang, Wenzhou 325027, People's Republic of China, and [b]College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

Correspondence e-mail: zimichem@sina.com

The crystal structure determination of the title compound, [ZnCl$_2$(C$_6$H$_{16}$N$_2$)], has been reported previously and converged with an $R(F)$ value of 0.067 [Htoon & Ladd (1973). *J. Cryst. Mol. Struct.* **3**, 95–102]. The present redetermination [$R(F)$ = 0.025] confirms the previous study, but with higher precision and with smaller ranges of N—C bond lengths and Zn—N—C(methyl) angles.

Comment

The crystal structure of the title compound, (I), has been determined previously by Htoon & Ladd (1973) with a reliability factor $R(F)$ = 0.067 [$P2_1/c$, a = 7.716 (3), b = 13.335 (9), c = 11.545 (5) Å, β = 105.59 (6)°] (CSD refcode TMENZN; Cambridge Structural Database, Version 5.26; Allen, 2002). In addition, some other N,N,N',N'-tetramethylethylenediamine (TMEDA) metal complexes have been subject to single-crystal X-ray diffraction, such as lead(II)–TMEDA (Kokozay & Sienkiewicz, 1995), alkoxopalladium–TMEDA (Kim *et al.*, 1995), (TMEDA)nickel bis(acetylacetonate) (Zeller *et al.*, 2001) and (TMEDA)copper tropolonate (Camard *et al.*, 2005). The present redetermination of (I) converges with a better reliability factor [$R(F)$ = 0.025] and confirms the previous study by Htoon & Ladd (1973), but with significant changes in the N—C bond lengths and Zn—N—C(methyl) bond angles.

(I)
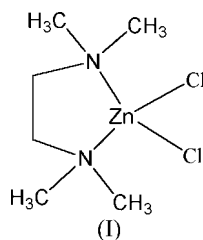
As shown in Fig. 1, in (I) zinc is chelated by two N atoms from the TMEDA ligand, and the geometry around the Zn atom is distorted tetrahedral. The Zn—N bond lengths (Table 1) are close to those observed in the previous study [2.107 (8) and 2.057 (9) Å]. The N—C bond lengths range from 1.481 (2) to 1.488 (2) Å, and deviate significantly from those of the previous study [1.416 (1)–1.583 (4) Å], but are similar to those in (TMEDA)copper tropolonate [1.483 (2)–1.503 (2) Å; Camard *et al.*, 2005]. The Zn—N—C bond angles [102.71 (9) and 103.99 (10)°] in the Zn/N1/C3/C4/N2 ring deviate somewhat from those of the previous determination [100.2 (6) and 105.5 (7)°]. In the present study, the Zn—N—C(methyl) bond angles, ranging from 110.92 (10) to 114.61 (10)°, are comparable to one another, whereas in the previous study the two Zn—N—C(methyl) bond angles
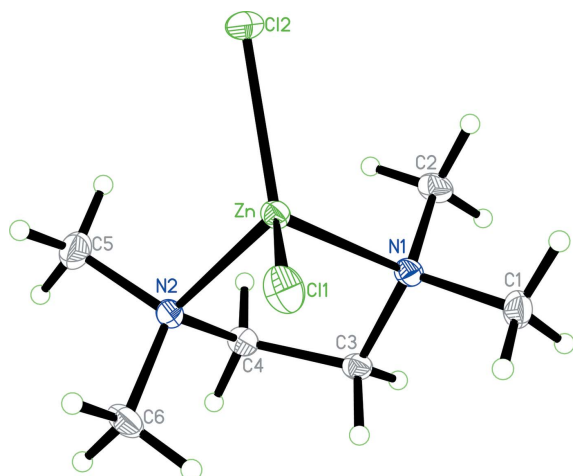
Figure 1
A view of the molecular structure of (I) with displacement ellipsoids drawn at the 40% probability level.
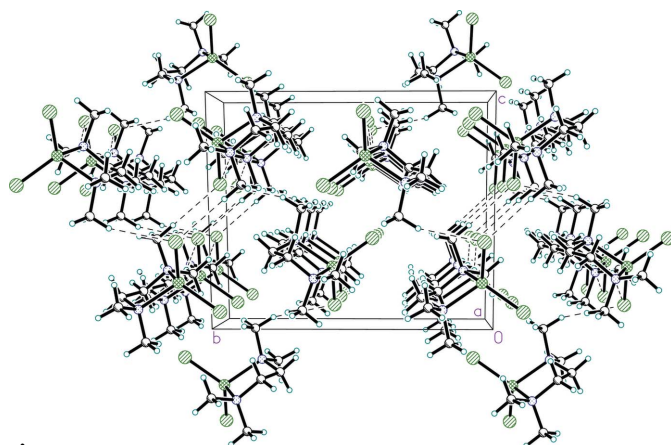

Figure 2
The molecular packing of (I), viewed along the *a* axis. Hydrogen bonds are indicated by dashed lines. Atom code: Zn checkered green spheres, Cl hatched green spheres, N blue dotted spheres, C black spheres, H grey-blue spheres.

around the same N atom [116.0 (8) and 108.3 (8)°, 115.3 (8) and 108.8 (6)°] differ greatly from each other.

In the crystal structure, molecules are linked together by weak C—H···Cl interactions (Fig. 2 and Table 2).

Experimental

N,N,N′,N′-tetramethylethylenediamine and zinc chloride were mixed in an equimolar ratio in water and heated until a clear solution resulted. Colourless block-shaped single crystals of (I) were obtained from the solution by slow evaporation at room temperature over a period of 5 d.

Crystal data

$[ZnCl_2(C_6H_{16}N_2)]$	$Z = 4$
$M_r = 252.50$	$D_x = 1.512$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.6017$ (2) Å	$\mu = 2.65$ mm^{-1}
$b = 13.2521$ (4) Å	$T = 273$ (2) K
$c = 11.3396$ (3) Å	Block, colourless
$\beta = 103.873$ (1)°	$0.50 \times 0.45 \times 0.43$ mm
$V = 1109.01$ (5) Å^3	

Data collection

Siemens P4 diffractometer	2549 independent reflections
ω scans	2424 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.031$
(*SHELXTL*; Bruker, 1998)	$\theta_{max} = 27.5°$
$T_{min} = 0.351$, $T_{max} = 0.396$	3 standard reflections
(expected range = 0.285–0.321)	every 97 reflections
10612 measured reflections	intensity decay: 1.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$+ 0.6052P]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
2549 reflections	$\Delta\rho_{max} = 0.56$ e Å^{-3}
105 parameters	$\Delta\rho_{min} = -0.61$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0239 (13)

Table 1
Selected geometric parameters (Å, °).

Zn—N2	2.0876 (14)	N1—C2	1.4861 (19)
Zn—N1	2.0968 (13)	N1—C3	1.487 (2)
Zn—Cl1	2.2116 (5)	N2—C5	1.481 (2)
Zn—Cl2	2.2173 (4)	N2—C6	1.485 (2)
N1—C1	1.481 (2)	N2—C4	1.488 (2)
N2—Zn—N1	87.68 (5)	C1—N1—Zn	114.61 (10)
N2—Zn—Cl1	110.75 (4)	C2—N1—Zn	110.92 (10)
N1—Zn—Cl1	112.60 (4)	C3—N1—Zn	102.71 (9)
N2—Zn—Cl2	111.70 (4)	C5—N2—Zn	112.59 (11)
N1—Zn—Cl2	110.85 (4)	C6—N2—Zn	111.54 (11)
Cl1—Zn—Cl2	119.001 (19)	C4—N2—Zn	103.99 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5A···Cl1[i]	0.98	2.83	3.676 (2)	144
C6—H6A···Cl1[ii]	0.98	2.84	3.7534 (18)	156

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y + 1, -z$.

The H atoms were placed in calculated positions and allowed to ride on their parent atoms at distances of 0.98 and 0.99 Å, with U_{iso}(H) values of $1.2U_{eq}$ of the parent atoms.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998).

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