

sealed in a thin-walled glass capillary for the crystal structure determination.

Crystal data

[LiPrBr(C₉H₁₃)₃(C₄H₈O)₃]

$M_r = 807.68$

Triclinic

$P\bar{1}$

$a = 11.905(4) \text{ \AA}$

$b = 12.337(3) \text{ \AA}$

$c = 14.218(4) \text{ \AA}$

$\alpha = 88.17(2)^\circ$

$\beta = 80.50(3)^\circ$

$\gamma = 84.52(2)^\circ$

$V = 2049.9(3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.308 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Rigaku AFC-7R diffractometer

ω -2 θ scans

Absorption correction:

empirical ΔF (Walker & Stuart, 1983)

$T_{\min} = 0.569$, $T_{\max} = 0.645$

4993 measured reflections

4717 independent reflections

Refinement

Refinement on F^2

$R(F) = 0.039$

$wR(F^2) = 0.086$

$S = 1.067$

4706 reflections

496 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 4.6185P]$

where $P = (F_o^2 + 2F_c^2)/3$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 20 reflections

$\theta = 18.52$ – 21.67°

$\mu = 2.194 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prismatic

$0.30 \times 0.20 \times 0.20 \text{ mm}$

Yellow

3252 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\text{max}} = 21.5^\circ$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 0$

$l = -14 \rightarrow 14$

3 standard reflections

every 200 reflections

intensity decay: 1.73%

$(\Delta/\sigma)_{\text{max}} = 0.009$

$\Delta\rho_{\text{max}} = 0.603 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.388 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray*

Crystallography (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pr1—Br1	2.995 (1)	Br1—Li1	2.495 (15)
Pr1—Cp1	2.602 (7)	Li1—O2	1.918 (13)
Pr1—Cp2	2.585 (8)	Li1—O3	1.924 (13)
Pr1—Cp3	2.589 (7)	Li1—O1	1.929 (14)
Br1—Pr1—Cp1	102.4 (3)	Cp1—Pr1—Cp3	117.5 (3)
Br1—Pr1—Cp2	102.1 (4)	Cp2—Pr1—Cp3	116.9 (4)
Br1—Pr1—Cp3	97.8 (4)	Li1—Br1—Pr1	137.3 (3)
Cp1—Pr1—Cp2	115.3 (3)		

The structure was solved by the heavy-atom Patterson method and refined by least-squares calculations. H atoms were included but not refined. The quality of the crystals and disorder prevented collection of intensity data to greater than $\theta = 21.5^\circ$.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1291). Services for accessing these data are described at the back of the journal.

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Chloro(1,4,8,12-tetraazacyclopentadecane- κ^4N)zinc(II) Perchlorate

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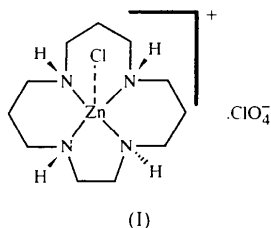
Abstract

The Zn^{II} ion in [ZnCl(C₁₁H₂₆N₄)]ClO₄ has a distorted trigonal-bipyramidal geometry, with the tetradentate macrocyclic ligand and the Cl⁻ ion constituting the

coordination sphere. The Zn—Cl and average Zn—N bond lengths are 2.284 (1) and 2.159 (4) Å, respectively. The three six-membered and one five-membered chelate rings are in chair, chair, skew and *gauche* conformations, respectively.

Comment

The stereochemistry of Zn^{II} complexes varies from linear to dodecahedral with the coordination numbers 2 to 8, respectively (Melnik *et al.*, 1995). Since there is no ligand-field stabilization effect in the Zn^{II} ion because of the completed *d* shell, the stereochemistry is determined solely by considerations of size, electrostatic forces and covalent bonding forces with the ligands. Crystallographic studies of [Zn([15]aneN₄)(NCS)₂] and [$\{Zn([15]aneN_4)\}_3(O_2COCH_3)_2\}(ClO_4)_4$] ([15]aneN₄ is 1,4,8,12-tetraazacyclopentadecane) have been published (Ito *et al.*, 1984a; Kato & Ito, 1985). Structural data show different coordination geometries around Zn^{II} in these two complexes. In the present paper, we report the crystal structure of [Zn([15]aneN₄)Cl]ClO₄, (I), determined by X-ray analysis.



The crystal structures of [Cu([15]aneN₄)(ClO₄)₂] (Fabbrizzi *et al.*, 1979), [Ni([15]aneN₄)(NCS)₂] (Ito *et al.*, 1984b), [Ni([15]aneN₄)Cl₂] (Ito *et al.*, 1984b) and [Zn([15]aneN₄)(NCS)₂] (Ito *et al.*, 1984a) reveal distorted octahedral geometry around the metal ion. The structure of [$\{Zn([15]aneN_4)\}_3(O_2COCH_3)_2\}^{4+}$] contains a [Zn([15]aneN₄)]²⁺ trimer bridged by (CH₃OCO₂)⁺, where the central Zn^{II} segment has tetragonally-distorted octahedral geometry and the two terminal Zn^{II} segments have trigonal-bipyramidal geometries. The coordination about the Zn^{II} ion in [Zn([15]aneN₄)Cl]⁺ in the present structure is five-coordinate in a distorted trigonal bipyramid and the tetradentate macrocyclic ligand coordinates in a folded fashion. The trigonal plane is formed by atoms N1, N3 and C11. The axial bonds, Zn1—N2 [2.174 (4) Å] and Zn1—N4 [2.197 (4) Å], are longer than the in-plane bonds, Zn1—N1 [2.149 (4) Å] and Zn1—N3 [2.115 (4) Å]. The three six-membered and one five-membered chelate rings are in chair, chair, skew and *gauche* conformations, respectively. Similar conformations were reported for [Ni([15]aneN₄)(NCS)₂] and [Zn([15]aneN₄)(NCS)₂]. However, in [Cu([15]aneN₄)(ClO₄)₂], [Ni([15]aneN₄)Cl₂] and [$\{Zn([15]aneN_4)\}_3(O_2COCH_3)_2\}(ClO_4)_4$], the corresponding con-

formations have been reported as chair, skew, chair and *gauche*.

All bond lengths and angles in the ligand moiety are normal. The Zn—Cl bond length is 2.284 (1) Å, which is shorter than that in [Zn(1,4,8,11-tetraazacyclopentadecane)Cl]⁺ [2.730 (4) Å; Alcock *et al.*, 1992], but longer than that in [Zn(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclopentadecane)Cl]⁺ [2.265 (4) Å; Alcock *et al.*, 1978]. The geometry of the perchlorate ion is normal and, while it is not coordinated to the metal ion, two of the perchlorate O atoms (O3 and O4) are hydrogen bonded to two of the three *cis*-H atoms of the complex (as shown in Fig. 1). The perchlorate O2 atom is 2.62 Å from the H atom on N3, too long a separation for this to be considered an effective N—H···O hydrogen bond. The remaining perchlorate O atom (O1) takes part in an N—H···O hydrogen bond to a symmetry-related molecule to give rise to hydrogen-bonded chains which extend in the [101] direction; details are in Table 2.

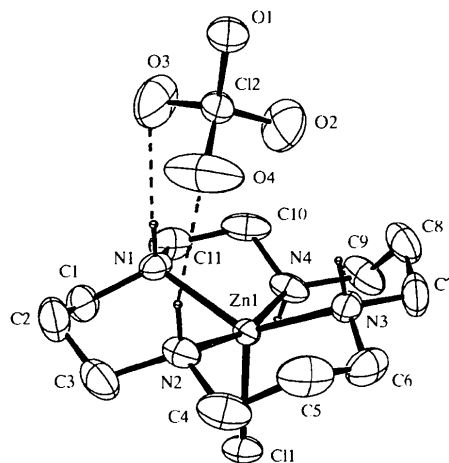


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms have been excluded, except for the H atoms of the amido groups. The dotted lines represent N—H···O hydrogen bonds.

Experimental

The ligand 1,4,8,12-tetraazacyclopentadecane was prepared according to the literature methods of Hay & Tarafder (1991) and Richman & Atkins (1974). Equimolar quantities of ZnCl₂ and the ligand were mixed in aqueous solution and allowed to react for 3 h at room temperature. The resulting solution was evaporated to dryness by rotary evaporation. Colorless crystals suitable for crystallographic analysis were obtained by recrystallization from a mixture of acetone and 2 *N* NaClO₄ at room temperature over a period of several days.

Crystal data

[ZnCl(C₁₁H₂₆N₄)]ClO₄
M_r = 414.63

Mo K α radiation
 λ = 0.71073 Å

Monoclinic

$P2_1/n$
 $a = 9.8504(7) \text{ \AA}$
 $b = 15.1177(10) \text{ \AA}$
 $c = 11.9574(8) \text{ \AA}$
 $\beta = 95.831(1)^\circ$
 $V = 1771.4(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.555 \text{ Mg m}^{-3}$
 D_m not measured

Cell parameters from 4254 reflections

$\theta = 5\text{--}25^\circ$
 $\mu = 1.709 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Pillar
 $0.30 \times 0.29 \times 0.20 \text{ mm}$
 Colorless

Data collection

Siemens SMART CCD diffractometer
 ω scan
 Absorption correction: multi-scan based on 4062 symmetry-equivalent reflections (Sheldrick, 1990b)
 $T_{\min} = 0.558, T_{\max} = 0.710$

10 962 measured reflections
 4222 independent reflections
 2648 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\text{max}} = 28.82^\circ$
 $h = -12 \rightarrow 11$
 $k = -19 \rightarrow 20$
 $l = -6 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.131$
 $S = 1.083$
 4222 reflections
 225 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 1.4143P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.024$
 $\Delta\rho_{\text{max}} = 0.535 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.339 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ($\text{\AA}, ^\circ$)

Zn1—N3	2.115(4)	Zn1—N4	2.197(4)
Zn1—N1	2.149(4)	Zn1—Cl1	2.284(1)
Zn1—N2	2.174(4)		
N3—Zn1—N1	132.3(1)	N2—Zn1—N4	164.8(2)
N3—Zn1—N2	89.6(2)	N3—Zn1—Cl1	113.7(1)
N1—Zn1—N2	86.4(2)	N1—Zn1—Cl1	114.0(1)
N3—Zn1—N4	94.0(2)	N2—Zn1—Cl1	97.2(1)
N1—Zn1—N4	80.2(2)	N4—Zn1—Cl1	94.9(1)

Table 2. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$)

$D\text{---}H\text{---}A$	$D\text{---}H$	$H\text{---}A$	$D\text{---}A$	$D\text{---}H\text{---}A$
N1—H1N1...O3	0.91	2.32	3.218(6)	170
N2—H1N2...O4	0.91	2.21	3.044(6)	153
N4—H1N4...O1'	0.91	2.29	3.100(6)	148

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Decay was monitored by repeating the initial frame at the end of data collection and analyzing the duplicate reflections; no decay was observed.

Data collection: SMART (Siemens, 1995). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: NRCVAX (Gabe *et al.*, 1989). Software used to prepare material for publication: SHELXL93.

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trans-Dichloro[(1RS,4RS,5SR,7RS,8SR,11SR,12RS,14SR)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane- κ^4N]-cobalt(III) Perchlorate

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Abstract

The crystal and molecular structure of the title compound, [CoCl₂(C₁₄H₃₂N₄)]ClO₄, has been determined. The Co^{III} ion is six-coordinate with a distorted octahedral geometry consisting of the four N atoms of the