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{*N*-[Bis(2-pyridyl)methyl]-*N*,*N*-bis(2-pyridyl)methylamine-κ^5N}chlorozinc(II) perchlorate monohydrate

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Key indicators

Single-crystal X-ray study
T = 113 K
Mean σ(C–C) = 0.005 Å
R factor = 0.056
wR factor = 0.163
Data-to-parameter ratio = 15.3

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

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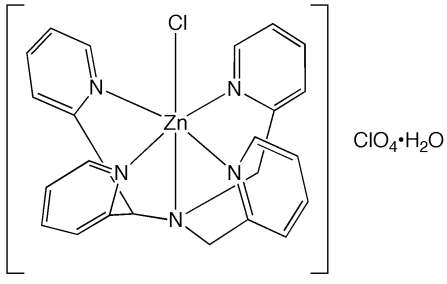
The structure of the title compound, $[ZnCl(C_{23}H_{21}N_5)]ClO_4\cdot H_2O$, has been determined at 113 K, revealing a discrete mononuclear six-coordinate Zn^{II} structure with a fairly large displacement [0.502 (2) Å] of Zn^{II} from the equatorial plane of N atoms.

Comment

Zinc(II) ions usually form four- and five-coordinate complexes in tetrahedral and trigonal–bipyramidal or square-pyramidal geometries (Cotton & Wilkinson, 1980). A six-coordinate octahedral structure is also common, and can be found in polymeric complexes (Angeloff *et al.*, 2001), parts of polyoxometallates (Lei *et al.*, 2004), and bis-chelate complexes of tridentate ligands (Parkin, 2004, and references therein). Many kinds of multidentate ligands have been applied to the preparation of Zn^{II} complexes, however, to date no example has been reported that demonstrates reliable stability of six-coordinate Zn^{II} complexes with a potentially active site at the metal center in solution. This limitation prevents investigation of the reactivity of Zn^{II} complexes from the extension of their structural variety and reactivity. In addition, Zn complexes are recognized to be flexible in terms of their solution structures. This structural flexibility is due to the d^{10} configuration of the Zn^{II} ion, which results in weak interactions with ligands.



(I)

The labile character of Zn^{II} complexes requires very careful characterization and scrutiny of the reaction mechanisms relating to hydrolysis, *etc*. However, a pentadentate ligand could give rise to a rigid structure that restricts the reactive site on the Zn^{II} center and stabilizes the structure. If such rigidity could be achieved, we would be in a position to establish the reaction mechanism and to construct catalytic systems by introducing appropriate functional groups on the ligand. On the basis of this concept, the utilization of a pentadentate pyridylamine ligand, *N*-[bis(2-pyridyl)methyl]-*N*,*N*-bis(2-pyridylmethyl)amine (N_4py) (Lubben *et al.*, 1995; Roelfes *et al.*, 1997), allowed us to access a novel discrete six-coordinate Zn^{II} complex, (I), with one potentially reactive site.

An *ORTEP* drawing of (I) is depicted in Fig. 1, showing the atom-numbering scheme, and selected bond lengths and angles are given in Table 1. The Zn^{II} center in (I) shows a distorted octahedral geometry with a displacement of 0.502 (2) Å toward the chloride ligand from the basal least-squares plane consisting of N2–N5. Hydrogen bonding between the perchlorate anion and the water molecule of crystallization provides an interatomic distance of 2.852 (4) Å for O2···O5.

Experimental

The title complex, (I), was prepared by the reaction of $Zn(ClO_4)_2{\cdot}6H_2O$ (48 mg, 1.3×10^{-4} mol) with $N_4py{\cdot}4HClO_4$ (100 mg, 1.3×10^{-4} mol) in methanol (5 ml) in the presence of triethylamine (90 µl) with stirring at room temperature. Following the addition of an aqueous solution of NaCl (8.6 mg in 0.3 ml of H_2O), the product was afforded in almost quantitative yield. A single-crystal suitable for X-ray crystallographic analysis was obtained by the recrystallization of the crude product from methanol.

Crystal data

$[ZnCl(C_{23}H_{21}N_5)]ClO_4{\cdot}H_2O$
$M_r = 585.75$
Monoclinic, $P2_1/n$
$a = 14.635$ (7) Å
$b = 12.476$ (5) Å
$c = 15.314$ (7) Å
$\beta = 115.726$ (5)°
$V = 2519$ (2) Å^3
$Z = 4$
$D_x = 1.544$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8514 reflections
$\theta = 4.5$–27.5°
$\mu = 1.23$ mm^{-1}
$T = 113$ K
Prism, colorless
0.60 × 0.40 × 0.20 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{min} = 0.466$, $T_{max} = 0.780$
19298 measured reflections
5808 independent reflections
4985 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.057$
$\theta_{max} = 27.5°$
$h = -18 \rightarrow 18$
$k = -9 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.163$
$S = 1.51$
4985 reflections
325 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.075(\mathrm{Max}(F_o^2,0) + 2F_c^2)/3)^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.78$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl1	2.2546 (8)	Zn1—N3	2.143 (3)
Zn1—N1	2.264 (2)	Zn1—N4	2.233 (3)
Zn1—N2	2.169 (3)	Zn1—N5	2.178 (3)
Cl1—Zn1—N1	177.85 (7)	N1—Zn1—N5	75.87 (9)
Cl1—Zn1—N2	104.47 (7)	N2—Zn1—N3	86.66 (10)
Cl1—Zn1—N3	102.92 (7)	N2—Zn1—N4	152.68 (10)
Cl1—Zn1—N4	102.76 (7)	N2—Zn1—N5	90.12 (10)
Cl1—Zn1—N5	103.04 (7)	N3—Zn1—N4	89.41 (10)
N1—Zn1—N2	77.44 (9)	N3—Zn1—N5	153.82 (9)
N1—Zn1—N3	78.07 (9)	N4—Zn1—N5	81.65 (9)
N1—Zn1—N4	75.30 (9)		

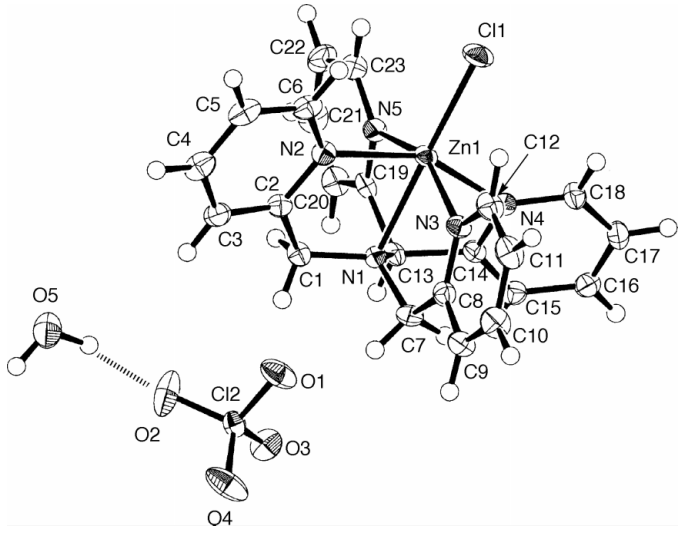


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by small spheres, and the H bond by a dashed line.

H atoms were included but were not refined. All H atoms were located on the basis of a differential Fourier map. The maximum residual peak is near the Zn atom.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear* and *TEXSAN* (Version 1.11; Molecular Structure Corporation and Rigaku, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN* (Version 1.10; Molecular Structure Corporation, 1999); molecular graphics: *ORTEP* in *TEXSAN* (Version 1.11); software used to prepare material for publication: *TEXSAN* (Version 1.11).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Angeloff, A., Daran, J.-C., Bernadou, J. & Meunier, B. (2001). *J. Organomet. Chem.* **624**, 58–62.
Cotton, F. A. & Wilkinson, G. (1980). *Advanced Inorganic Chemistry*, 4th ed., p. 589. New York: John Wiley and Sons.
Lei, C., Mao, J.-G., Sun, Y.-Q. & Song, J.-L. (2004). *Inorg. Chem.* **43**, 1964–1968.
Lubben, M., Meetsma, A., Wilkinson, E. C., Feringa, B. L. & Que, L. Jr (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1512–1514.
Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation and Rigaku (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, Tokyo, Japan.
Parkin, G. (2004). *Chem. Rev.* **104**, 699–767.
Rigaku (2000). *CrystalClear*. Version l.3. Rigaku Corporation, Tokyo, Japan.
Roelfes, G., Lubben, M., Leppard, S. W., Schudde, E. P., Hermant, R. M., Hage, R., Wilkinson, E. C., Que, L., Jr & Feringa, B. L. (1997). *J. Mol. Cat. A*, **117**, 223–227.