Hartl, H. & Mahdjour-Hassan-Abadi, F. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 772–773.
Hu, G. & Holt, E. M. (1994). *Acta Cryst.* C**50**, 1578–1580.
Nurtaeva, A. K. & Holt, E. M. (1998). *Acta Cryst.* C**54**, 594-597.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1990). *XP. Interactive Molecular Graphics Program.* Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1991). *XSCANS Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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A Tetrahedral Zinc(II) Complex of Tris(2-pyridylethyl)amine

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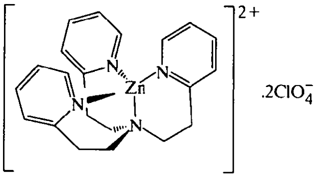
Abstract

The zinc ion in the title complex, [*N*,*N*′-bis(2-pyridylethyl)-2-(2-pyridyl)ethylamine-κ^4*N*]zinc(II) diperchlorate, $[Zn(C_{21}H_{24}N_4)](ClO_4)_2$, displays a distorted tetrahedral configuration. The Zn—N$_{py}$ distances range from 1.979 (5) to 1.999 (5) Å, while the Zn—N$_{amine}$ distance is 2.028 (5) Å. The N$_{py}$—Zn—N$_{py}$ and N$_{py}$—Zn—N$_{amine}$ angles range from 111.9 (2) to 119.6 (2)° and from 102.3 (2) to 103.4 (2)°, respectively. This behavior contrasts with the five-coordinate geometry normally observed in tripodal ligands of similar structure, and can be ascribed to the presence of weakly-coordinating anions and the ligand–metal chelate-ring size.

Comment

The title compound, (I), was isolated in the course of our studies into the design and synthesis of coordination complexes for molecular recognition (Allen *et al.*, 1995; Canary *et al.*, 1995; Chuang *et al.*, 1995). The general plan is to use coordination complexes as scaffolding to which organic functional groups can be attached for the development of synthetic receptors and enzyme mimics. Structural data on representative coordination complexes are critical for the design of such compounds. The goal of the present study was to determine coordinates that could be used for the design and modeling of supramolecular receptors.



(I)

The present structure is surprising in that previous studies of zinc(II) complexes of the closely related tripodal ligand tris(2-pyridylmethyl)amine (TPA) show them to be five-coordinate complexes, the cationic portions of which are typically very similar in structure to the analogous Cu^{II} complexes. In the present case, the structure of $[Zn(tepa)]^{2+}$ [tepa is tris(2-pyridylethyl)amine] is nearly isomorphous with the Cu^{I} complex $[Cu(tepa)]^+$ (Karlin *et al.*, 1982; Zubieta *et al.*, 1983). In the $[Cu(tepa)]^+$ complex, the Cu—N$_{py}$ distances range from 2.012 (5) to 2.022 (5) Å, with a Cu—N$_{amine}$ distance of 2.192 (6) Å. The N$_{py}$—Cu—N$_{py}$ and N$_{py}$—Cu—N$_{amine}$ angles range from 111.9 (2) to 121.2 (2)° and from 97.4 (2) to 99.8 (2)°, respectively. The three six-membered chelate rings formed in the tepa complex allow little room for anion coordination, as observed in the five-membered-chelate-ring tepa complexes.

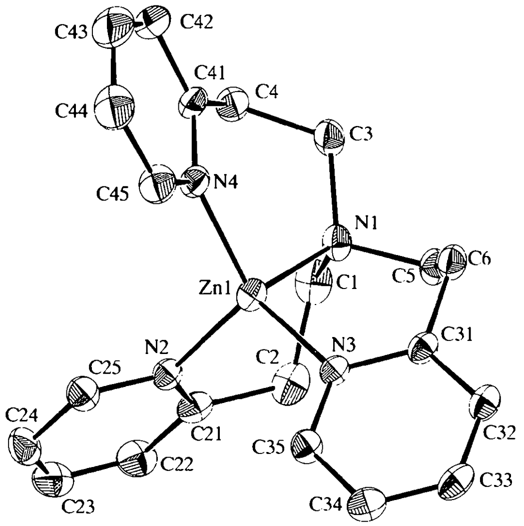


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

Tepa was prepared according to Karlin *et al.* (1982). Synthesis of the complexes was carried out by the slow addition of a 10 ml solution of tepa (0.69 g, 2.1 mmol) in methanol to a 10 ml solution of $Zn(ClO_4)_2.6H_2O$ (0.78 g, 2.1 mmol) dissolved in water. The resulting solution was heated for 30 min. A white precipitate formed upon cooling. The white powder was recrystallized from ethanol and water to give bright colorless crystals, m.p. 570–573 K. Analysis: calculated (mass %) for $C_{21}H_{24}Cl_2N_4O_8Zn$: C 42.30, H 4.05, N 9.33; found: C 42.12, H 4.26, N 9.33.

Crystal data

$[Zn(C_{21}H_{24}N_4)](ClO_4)_2$
$M_r = 596.72$
Monoclinic
$P2_1/c$
$a = 13.398\,(3)$ Å
$b = 13.988\,(3)$ Å
$c = 13.674\,(3)$ Å
$\beta = 104.24\,(2)°$
$V = 2483.8\,(9)$ Å^3
$Z = 4$
$D_x = 1.596$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 16.72–17.47°$
$\mu = 3.88$ mm^{-1}
$T = 293\,(2)$ K
Block
0.25 × 0.20 × 0.20 mm
Colorless

Data collection

Rigaku AFC-6*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.396$, $T_{\max} = 0.460$
4001 measured reflections
3819 independent reflections

2850 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 59.49°$
$h = -10 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 14$
3 standard reflections every 500 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.184$
$S = 1.142$
3819 reflections
326 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 7.3791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.75$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0015 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn1—N4	1.979 (5)	N1—C3	1.516 (9)
Zn1—N3	1.999 (5)	C34—C33	1.355 (11)
Zn1—N2	1.999 (5)	C34—C35	1.393 (9)
Zn1—N1	2.028 (5)	C5—C6	1.529 (10)
N3—C35	1.327 (8)	C33—C32	1.355 (11)
N3—C31	1.336 (8)	C32—C31	1.390 (9)
N1—C1	1.494 (9)	C31—C6	1.498 (10)
N1—C5	1.503 (8)		
N4—Zn1—N3	119.6 (2)	C5—N1—C3	107.9 (5)
N4—Zn1—N2	114.4 (2)	C33—C34—C35	118.5 (7)
N3—Zn1—N2	111.9 (2)	N1—C5—C6	112.6 (5)
N4—Zn1—N1	102.3 (2)	C32—C33—C34	119.9 (7)
N3—Zn1—N1	102.5 (2)	C33—C32—C31	119.8 (7)
N2—Zn1—N1	103.4 (2)	N3—C31—C32	120.4 (7)
C35—N3—C31	119.6 (5)	N3—C31—C6	118.2 (5)
C35—N3—Zn1	121.8 (4)	C32—C31—C6	121.4 (7)
C31—N3—Zn1	118.2 (4)	N3—C35—C34	121.8 (7)
C1—N1—C5	109.6 (6)	C31—C6—C5	112.7 (6)
C1—N1—C3	109.3 (6)		

H atoms were placed in idealized positions and allowed to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2\,U_{\rm eq}({\rm C})$, and C—H = 0.93 and 0.97 Å.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1069). Services for accessing these data are described at the back of the journal.

References

Allen, C. S., Chuang, C.-L., Cornebise, M. & Canary, J. W. (1995). *Inorg. Chim. Acta*, **239**, 29–37.
Canary, J. W., Allen, C. S., Castagnetto, J. M. & Wang, Y. (1995). *J. Am. Chem. Soc.* **117**, 8484–8485.
Chuang, C.-L., Lim, K., Chen, Q., Zubieta, J. & Canary, J. W. (1995). *Inorg. Chem.* **34**, 2562–2568.
Karlin, K. D., Hayes, J. C., Hutchinson, J. P., Hyde, J. R. & Zubieta, J. (1982). *Inorg. Chim. Acta*, **64**, L219.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Zubieta, J., Karlin, K. D. & Hayes, J. C. (1983). *Structural Systematics of Cu(I) and Cu(II) Derivatives of Tripod Ligands. Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, pp. 97–108. New York: Adenine Press.

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A Dinuclear Indium(III) Complex with Two Pyrazolate Bridging Ligands

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Abstract

The crystal structure of bis[μ-3-(2-pyridyl)-1*H*-pyrazolato]-1κ^2N',N^2:2κN^1;1κN^1:2$\kappa N'$,N^2-bis[dichloro(dimethylformamide-*O*)indium]–dimethylformamide (1/2), $[In_2Cl_4L_2(dmf)_2]$.2dmf [where H*L* is 3-(2-pyridyl)-pyrazole, $C_8H_7N_3$, and dmf is dimethylformamide,