

Data collection

Enraf–Nonius CAD-4 diffractometer	6163 reflections with $I > 3\sigma(I)$
ω - 2θ scans	$R_{int} = 0.043$
Absorption correction: empirical ψ scan (North <i>et al.</i> , 1968)	$\theta_{max} = 25.0^\circ$
$T_{min} = 0.803$, $T_{max} = 0.875$	$h = 0 \rightarrow 12$
8062 measured reflections	$k = -14 \rightarrow 14$
8050 independent reflections	$l = -21 \rightarrow 21$
	3 standard reflections every 250 reflections
	intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.04$
$R = 0.052$	$\Delta\rho_{max} = 1.12 \text{ e } \text{\AA}^{-3}$
$wR = 0.059$	$\Delta\rho_{min} = -0.88 \text{ e } \text{\AA}^{-3}$
$S = 1.44$	Extinction correction: none
6163 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
485 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o) + 0.01(F_o^2) + 1.0]$	

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

Cu(1)—S(1)	2.4188 (17)	P(1)—C(31)	1.825 (6)
Cu(1)—S(2)	2.4265 (15)	P(2)—C(41)	1.835 (6)
Cu(1)—P(1)	2.2672 (17)	P(2)—C(51)	1.845 (6)
Cu(1)—P(2)	2.289 (2)	P(2)—C(61)	1.827 (6)
S(1)—C(1)	1.719 (5)	N(1)—C(3)	1.171 (8)
S(2)—C(1)	1.713 (5)	N(2)—C(4)	1.158 (8)
P(1)—C(11)	1.826 (6)	C(1)—C(2)	1.405 (8)
P(1)—C(21)	1.829 (6)	C(2)—C(4)	1.408 (9)
S(1)—Cu(1)—S(2)	74.5 (5)	C(11)—P(1)—C(31)	101.1 (3)
S(1)—Cu(1)—P(1)	108.61 (6)	C(21)—P(1)—C(31)	107.5 (3)
S(1)—Cu(1)—P(2)	113.60 (6)	Cu(1)—P(2)—C(51)	115.2 (2)
S(2)—Cu(1)—P(1)	118.32 (6)	Cu(1)—P(2)—C(61)	115.1 (2)
S(2)—Cu(1)—P(2)	107.65 (6)	C(51)—P(2)—C(61)	100.8 (2)
P(1)—Cu(1)—P(2)	123.74 (6)	S(1)—C(1)—S(2)	117.5 (3)
Cu(1)—S(1)—C(1)	82.6 (2)	S(1)—C(1)—C(2)	120.0 (4)
Cu(1)—S(2)—C(1)	82.5 (2)	S(2)—C(1)—C(2)	122.3 (4)
C(11)—P(1)—C(21)	102.0 (3)		

The structure was solved by direct methods. All non-H atoms were refined with anisotropic displacement parameters. The positions of all H atoms were generated geometrically ($C-H = 0.96 \text{ \AA}$) and assigned isotropic displacement parameters; they were not refined but included in R -value calculations. All calculations were performed on an HP586/75 computer.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *MolEN* (Fair, 1990) and *CAD-4 SDP/VAX* (Enraf–Nonius, 1989). Data reduction: *CAD-4 SDP/VAX*. Program(s) used to solve structure: *MULTAN11/82* (Main *et al.*, 1982). Program(s) used to refine structure: *LSFM* (B. A. Frenz & Associates Inc., 1985) in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

This work was supported by the National Natural Scientific Foundation of China and Natural Scientific Foundation of Fujian Province.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1018). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 338–340

Chloro(*N,N',N''*-trimethyl-1,5,9-triazacyclododecane- κ^3N)zinc(II) Hexafluorophosphate

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(Received 1 October 1997; accepted 3 November 1997)

Abstract

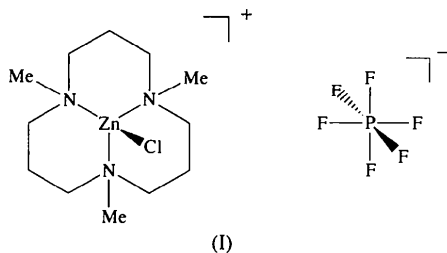
The preparation and crystal structure of $[ZnCl(C_{12}H_{27}N_3)]PF_6$ are described. The Zn atom has a tetrahedral environment, coordinated to three N atoms of the triaza macrocyclic ligand and to one Cl^- ion. The Zn—N distances are in the range 2.037 (1)–2.048 (1) \AA , with Zn—Cl 2.2010 (4) \AA .

Comment

Macrocyclic triamine complexes of zinc(II) have been studied as model structures of the zinc-containing active

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sites of hydrolytic metalloenzymes (*e.g.* carbonic anhydrase and carboxypeptidase) (Kodama & Kimura, 1978; Kimura *et al.*, 1990). It has been found that the 12-membered triamine, 1,5,9-triazacyclododecane or [12]aneN₃, is the most appropriate ligand to mimic the zinc coordination environment in carbonic anhydrase. The ligand in the title complex, (I), is a trimethyl deriva-



tive of [12]aneN₃ that might also be effective in this role. Complexes of 12-membered cyclic triamines with zinc exhibit several types of coordination environment (Kimura *et al.*, 1988; Alcock *et al.*, 1991). In reported structures of zinc complexes with the unsubstituted [12]aneN₃ ligand, the metal geometry is tetrahedral (Schaber *et al.*, 1988; Kimura *et al.*, 1990). The title compound belongs to the same family and might also be expected to contain a tetrahedral Zn atom, as indeed has been found in this study (Fig. 1). The crystal consists of an ordered 1:1 array of [Zn(Me₃[12]aneN₃)Cl]⁺ cations and hexafluorophosphate anions. The Zn atom has a slightly distorted tetrahedral coordination environment. The Cl—Zn—N angles are rather larger than the N—Zn—N angles, though both are slightly uneven, in the ranges 113.13(4)–117.37(4) and 102.41(5)–104.76(5)°, respectively. The Zn—Cl bond length of 2.2009(4) Å is shorter than the Zn^{II}—Br bond length of 2.36 Å in the previously reported [Zn([12]aneN₃)Br]Br complex (Schaber *et al.*, 1988). The Zn—N distances

are close to those for complexes with the unmethylated ligand. Thus, the presence of the methyl group seems to have no steric effect on the zinc geometry. Two chelate six-membered rings of the tridentate ligand adopt chair conformations, but the third has a twist conformation. All the methyl groups are oriented to the same side of the ring as the Zn—Cl bond.

The crystal structure aids interpretation of the ¹H NMR spectrum of the complex. The spectrum of the free ligand shows three peaks, a singlet from nine methyl protons, a quintet due to the six protons on the three middle C atoms in the propyl bridge and a triplet corresponding to the twelve protons on the C atoms next to the N atoms. In the spectrum of the zinc complex, the singlet of protons from the —CH₃ groups is shifted downfield, but its appearance is the same as for the free ligand. The peaks corresponding to the protons on the triazamacrocyclic ring are more interesting. Instead of two, there are now four multiplet peaks. In order to assign these and interpret their splitting patterns, the ring conformations have to be taken into account. The chair conformation of the chelate rings differentiates the equatorial and axial protons, with the protons in equatorial positions usually having higher chemical shifts, resulting from the shielding of the C—C bond. Thus, the change in the spectrum arises from the appearance of rings with two different conformations.

Experimental

Unsubstituted triazacyclododecane, [12]aneN₃, was synthesized by the Richmann–Atkins procedure (Richmann & Atkins, 1974). The ligand Me₃[12]aneN₃ was prepared by methylation of [12]aneN₃.3HBr with formaldehyde in formic acid. The resulting ligand salt was passed through a neutral alumina column and the free base eluted with a CHCl₃–MeOH (9:1) mixture. The ligand was characterized by ¹H NMR spectroscopy using a CDCl₃ solution: δ 1.5 (*m*, 6H), 2.13 (*s*, 9H), 2.35 (*t*, 12H). The title compound was synthesized when a methanolic solution of ZnCl₂ was added to a freshly prepared solution of the ligand in methanol. An acetonitrile solution of NH₄PF₆ was then added to the solution. This reaction mixture gave good quality colorless crystals of the title complex on standing. ¹H NMR (in D₂O): δ 2 and 2.1 (*m*, 3H; *m*, 3H), 2.5 (*s*, 9H), 2.75 and 3.03 (*m*, 6H; *m*, 6H).

Crystal data

[ZnCl(C₁₂H₂₇N₃)]PF₆
M_r = 459.16
 Orthorhombic
*Pna*2₁
a = 15.896(2) Å
b = 11.1691(5) Å
c = 10.365(1) Å
V = 1840.3(2) Å³
Z = 4
D_x = 1.657 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 8192 reflections
 θ = 3–20°
 μ = 1.624 mm⁻¹
T = 180(2) K
 Block
 0.50 × 0.38 × 0.38 mm
 Colorless

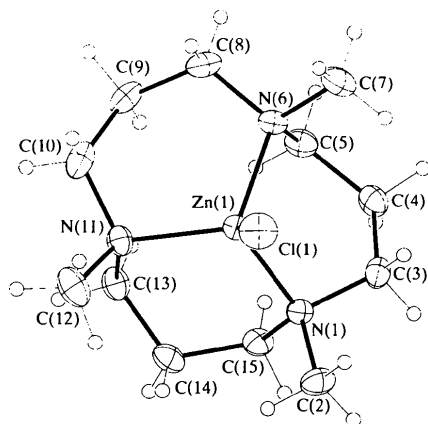


Fig. 1. View of the cation of the title compound showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

Data collection

Siemens SMART diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.476$, $T_{\max} = 0.539$
 10 628 measured reflections
 4186 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.043$
 $S = 1.03$
 4186 reflections
 222 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0253P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.006$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$

Extinction correction: SHELXL97
 Extinction coefficient: 0.0092 (3)
 Scattering factors from International Tables for Crystallography (Vol. C)
 Original structure: Flack (1983)
 Flack parameter = 0.580 (6)

Table 1. Selected geometric parameters (Å, °)

Zn(1)—N(11)	2.0363 (13)	Zn(1)—N(6)	2.0484 (13)
Zn(1)—N(1)	2.0429 (13)	Zn(1)—Cl(1)	2.2010 (4)
N(11)—Zn(1)—N(1)	104.76 (5)	N(11)—Zn(1)—Cl(1)	117.37 (4)
N(11)—Zn(1)—N(6)	104.45 (5)	N(1)—Zn(1)—Cl(1)	113.21 (4)
N(1)—Zn(1)—N(6)	102.41 (5)	N(6)—Zn(1)—Cl(1)	113.13 (4)

H atoms were added at calculated positions and refined using a riding model (including free rotation about C—C bonds for methyl groups). Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2U_{eq} (or 1.5U_{eq} for methyl H atoms) of the carrier atom.

Data collection: SMART (Siemens, 1994). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTL/PC (Sheldrick, 1995). Software used to prepare material for publication: SHELXTL/PC.

These studies were made possible by funding from the Monsanto Company whose support is greatly appreciated. EPSRC and Siemens plc generously supported the purchase of the SMART diffractometer. We wish to acknowledge the use of the EPSRC's Chemical Database Service at the Daresbury Laboratory, Cheshire, England (Fletcher *et al.*, 1996), for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1373). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 340–342

The Monomeric Form of a Cobalt(III) Complex of a Tetraaza Macrocyclic Ligand with a Dangling Carboxylate Arm

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(Received 1 October 1997; accepted 3 November 1997)

Abstract

The monomeric structure of *cis*-dichloro[3-(1,4,7,10-tetraazacyclododecan-1-yl)toluic acid- κ^4N]cobalt(III) chloride monohydrate, [CoCl₂(C₁₆H₂₆N₄O₂)]Cl·H₂O, has been determined. Previous work has only yielded crystals of the dinuclear complex or the monomeric complex in powdered form. Crystallization was effected from concentrated hydrochloric acid which contributed to the retention of the chlorides coordinated to the cobalt as well as providing the chloride counter-anion. Hydrogen bonding of the hydroxyl group of the carboxylic acid function to the chloride counter-anion played a significant role in the formation of crystals of this species.