metal-organic papers

A cationic zinc(II) complex of a new ligand based on N,N,N′,N′-tetramethylstreptamine 2,4,6-orthoformate as the chloride salt

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In the title compound, rac-bis[μ-(1R,2S,12R,13s,15s,17S,18r)-14,16,19-trioxa-3,7,11-triazatetracyclo[13.3.1.0^{2,13}.0^{12,17}]nona-decan-18-olato-1κ^3N^3,N^7,N^{11}:2κ^2O^{18}]dizinc(II) dichloride, [Zn$_2$(C$_{13}$H$_{22}$N$_3$O$_4$)$_2$]Cl$_2$, the cation displays crystallographic inversion symmetry. The geometry at zinc is trigonal bipyramidal. Three hydrogen bonds N—H···Cl$^-$ lead to the formation of layers parallel to (101).

Comment

Many hydrolytic enzymes, particularly those that catalyse phosphoryl transfer reactions, use metal ions as cofactors (Bertini & Luchinat, 1994). The metal ion most commonly found in the active site of hydrolytic enzymes is Zn^{2+} (Vallee & Auld, 1993). The cations generally act as Lewis acid or electrophilic catalysts, withdrawing electron density from the coordinated substrate or stabilizing the negative charge that usually develops on the 'leaving group' in hydrolytic reactions. However, the binding of metal ions to anionic, even bidentate, substrate groups such as carboxylates or phosphates is not strong in aqueous solution (Fraústo da Silva & Williams, 1991) and enzyme structures have evolved to bind the cation in close and productive proximity to the substrate. We report the structure of a model system, designed to achieve this aim.
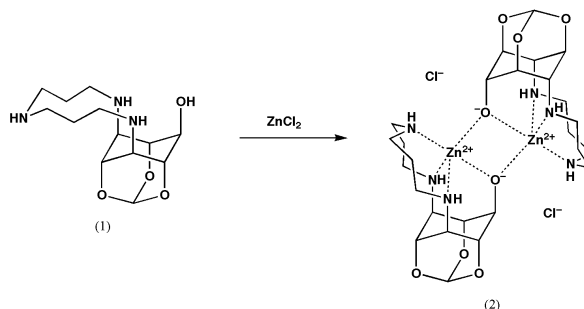
Enzyme model systems can only be expected to shed light on enzyme reaction mechanisms if they themselves are properly understood. If the model system features metal ion complexation, the structure and stability of the complex formed are fundamental to this understanding. We report here the structure of the zinc complex, (2), of the deprotonated triaminoalcohol ligand [(1), LOH], designed as a potential leaving group from phosphate mono- and diesters when a metal cation is bound.

The zinc cation (Fig. 1) is coordinated, as designed, by the alcohol O atom (which has lost its proton) and also by the three N atoms of the ligand (LO$^-$). The coordination number of the metal ion is made up to five by the formation of an inversion-symmetric dimer {[Zn$_2$(LO)$_2$]$_2^{2+}$}, with the alkoxide
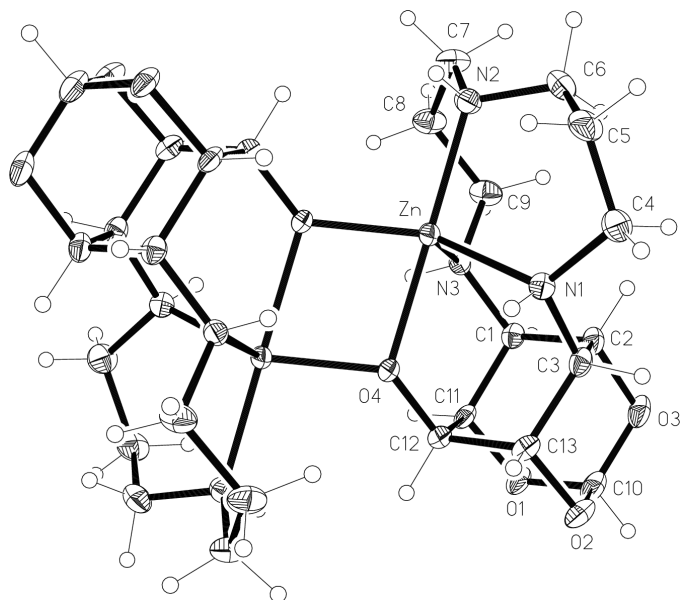
Figure 1
The cation of the title compound in the crystal. Ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.
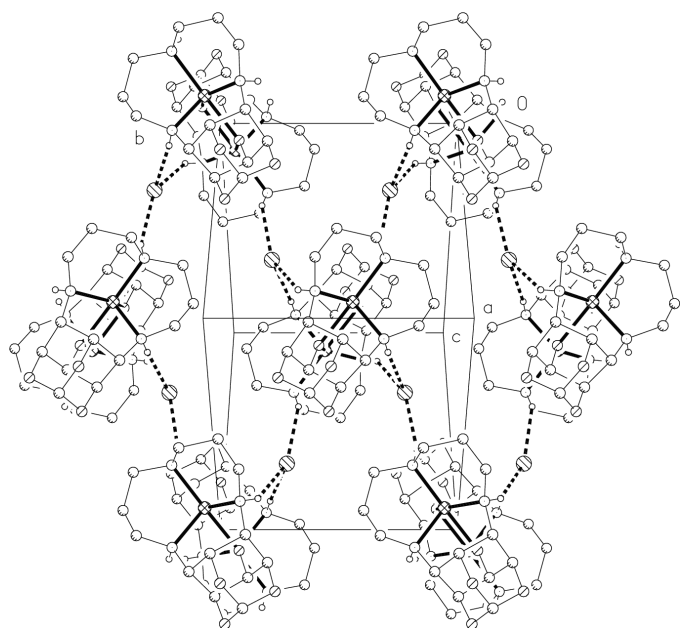

Figure 2
Packing diagram of the title compound, viewed perpendicular to (10$\bar{1}$). Hydrogen bonds are indicated by dashed lines. H atoms not involved in classical hydrogen bonds have been omitted.

O atoms acting as bridging ligands in the central four-membered ring (which is exactly planar by symmetry). The coordination geometry of Zn^{2+} (for exact values and s.u.'s, see Table 1) is that of a distorted trigonal bipyramid; the axial angle N2—Zn—O4$_{ax}$ is 178.5° and the sum of the three equatorial angles at Zn is ca 351°. The three Zn—N distances are similar (between 2.06 and 2.11 Å), but the axial Zn—O4 distance (2.16 Å) is markedly longer than that to the bridging equatorial O atom (Zn—O4^i = 1.95 Å). The six-membered ring Zn—N3—C1—C11—C12—O4 displays a chair conformation, whereas Zn—N1—C3—C2—C1—N3 is a chair flat-

tened around zinc, and Zn—N1—C4—C5—C6—N2 a distorted half-chair.

The overall 2+ charge of the dimer unit is balanced by two chloride anions. These participate in three classical hydrogen bonds N—H···Cl⁻ (Table 2), the net effect of which is to form layers of anions and cations parallel to (101) (Fig. 2). There is also a Zn···Cl^i contact (not shown in Fig. 2) of 3.6628 (7) Å.

The following paper (Jones et al., 2003) reports the structure of another compound containing the same cation.

Experimental

The title complex, (2), precipitated as a microcrystalline solid upon addition of a solution of zinc chloride in ether to a solution of (1) (Beckmann, 1998) and the strong base 1,8-diazabicyclo[5.4.0]undec-7-ene in acetonitrile. A single crystal was obtained by slow evaporation of a solution in acetonitrile. The stoichiometric composition of (2) can be described as [(1) + ZnCl₂ − HCl]₂.

Crystal data

[Zn₂(C₁₃H₂₂N₃O₄)₂]Cl₂	$D_x = 1.720$ Mg m⁻³
$M_r = 770.31$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 56
$a = 12.706$ (2) Å	reflections
$b = 9.2379$ (16) Å	$\theta = 10–11.5°$
$c = 13.050$ (2) Å	$\mu = 1.85$ mm⁻¹
$\beta = 103.849$ (12)°	$T = 143$ (2) K
$V = 1487.3$ (4) Å³	Tablet, colourless
$Z = 2$	$0.60 \times 0.50 \times 0.25$ mm

Data collection

Stoe Stadi-4 diffractometer	$R_{int} = 0.017$
ω/θ scans	$\theta_{max} = 27.6°$
Absorption correction: ψ scans	$h = 0 \rightarrow 16$
(XEMP; Siemens, 1994)	$k = -12 \rightarrow 1$
$T_{min} = 0.611$, $T_{max} = 0.988$	$l = -16 \rightarrow 16$
3862 measured reflections	3 standard reflections
3416 independent reflections	frequency: 60 min
3146 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 1.1834P]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3416 reflections	$\Delta\rho_{max} = 0.42$ e Å⁻³
211 parameters	$\Delta\rho_{min} = -0.44$ e Å⁻³
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Zn—O4^i	1.9480 (13)	Zn—N2	2.1128 (16)
Zn—N3	2.0603 (16)	Zn—O4	2.1629 (13)
Zn—N1	2.1074 (16)		
O4^i—Zn—N3	107.23 (6)	C12—O4—Zn	123.92 (11)
O4^i—Zn—N1	143.00 (6)	Zn^i—O4—Zn	100.91 (5)
N3—Zn—N1	101.68 (6)	C3—N1—C4	110.97 (16)
O4^i—Zn—N2	100.39 (6)	C3—N1—Zn	112.49 (11)
N3—Zn—N2	97.90 (6)	C4—N1—Zn	122.06 (12)
N1—Zn—N2	97.94 (6)	C6—N2—C7	110.89 (16)
O4^i—Zn—O4	79.09 (5)	C6—N2—Zn	112.54 (12)
N3—Zn—O4	83.57 (6)	C7—N2—Zn	115.45 (12)
N1—Zn—O4	81.77 (6)	C1—N3—C9	113.97 (14)
N2—Zn—O4	178.53 (6)	C1—N3—Zn	113.58 (11)
C12—O4—Zn^i	130.20 (11)	C9—N3—Zn	114.45 (11)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H01$\cdots$Cl^i	0.855 (17)	2.445 (18)	3.2017 (17)	147.8 (18)
N2—H02$\cdots$Cl^{ii}	0.860 (18)	2.48 (2)	3.2382 (18)	148 (2)
N3—H03$\cdots$Cl	0.862 (17)	2.407 (18)	3.2622 (16)	172 (2)
C10—H10$\cdots$O1^{iii}	1.00	2.66	3.331 (2)	125
C9—H9$B\cdots$O3^{iv}	0.99	2.53	3.350 (2)	140
C8—H8$B\cdots$Cl^v	0.99	2.95	3.634 (2)	127
C5—H5$B\cdots$Cl^i	0.99	3.00	3.751 (2)	133
C11—H11$\cdots$Cl	1.00	2.83	3.6770 (19)	143

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $2-x, 1-y, 1-z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $1-x, -y, 1-z$.

H atoms of NH groups were identified in difference syntheses and refined freely, but with a common N—H distance restraint. Other H atoms were included using a riding model with fixed C—H bond lengths of 1.00 (CH) or 0.99 Å (CH$_2$); U_{iso}(H) values were fixed at 1.2U_{eq} of the parent atom.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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