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A zinc–lithium complex of 4,7-bis(2-aminoethyl)-1,4,7-triazacyclononane-1-acetate

Alexander J. Blake,* Lorenzo Tei, Claire Wilson and Martin Schröder

School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England
Correspondence e-mail: a.j.blake@nottingham.ac.uk

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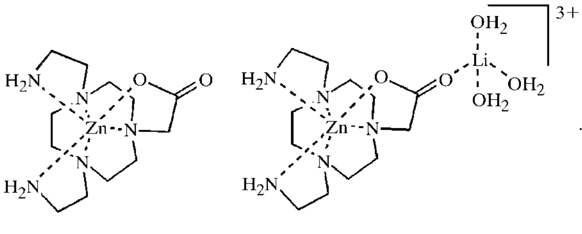
The asymmetric unit of {[4,7-bis(2-aminoethyl)-1,4,7-triazacyclononan-1-yl]acetato}zinc(II) triaqua{μ-[4,7-bis(2-aminoethyl)-1,4,7-triazacyclononan-1-yl]acetato}lithium(I)zinc(II) chloride diperchlorate, $[Zn(C_{12}H_{26}N_5O_2)][LiZn(C_{12}H_{26}N_5O_2)(H_2O)_3]Cl(ClO_4)_2$, obtained from the reaction between the lithium salt of 4,7-bis(2-aminoethyl)-1,4,7-triazacyclononane-1-acetate and $Zn(ClO_4)_2$, contains two Zn^{II} complexes in which each Zn^{II} ion is six-coordinated by five N-atom donors and one O-atom donor from the ligand. One carboxylate O-atom donor is not involved in coordination to a Zn^{II} atom, but coordinates to an Li^+ ion, the tetrahedral geometry of Li^+ being completed by three water molecules. The two complexes are linked *via* a hydrogen bond between a primary amine N—H group and the carboxylate-O atom not involved in coordination to a metal.

Comment

The synthesis of novel polyazamacrocyclic ligands containing functional pendant arms has received much attention because of the effects exerted by these functional groups on the coordination geometry and chemical properties of the resultant complexes (Bernhardt & Lawrence, 1990; Wainwright, 1997, 2001; Haines, 2001; Costamagna *et al.*, 2000). Among the metal complexes with polyazamacrocycles, those with the small tridentate macrocycle 1,4,7-triazacyclononane ([9]ane-N_3) have been widely studied, for example, for the mimicry of metalloenzymes (Chaudhuri & Wieghardt, 1987; Wieghardt, 1989; Tolman, 1997) and for the catalysis of oxidative organic transformations (De Vos *et al.*, 1999; Bolm *et al.*, 2000; Grenz *et al.*, 2001). Many derivatives of [9]aneN_3 containing four, five or six donor atoms have been synthesized and studies of their coordination chemistry with a wide range of transition metal ions in different oxidation states have been reported (Bernhardt & Lawrence, 1990; Wainwright, 1997, 2001; Haines, 2001; Costamagna *et al.*, 2000). Less work has been reported on the synthesis of [9]aneN_3 derivatives having different pendant donor groups, reflecting the increased synthetic difficulty encountered for these types of ligands. However, they are of major interest because they can be used for the construction of multifunctional materials such as dendrimers (Beer & De Gao, 2000), and their complexes exhibit useful chemical properties (Stockheim *et al.*, 1996; Di Vaira *et al.*, 1998) and have practical applications, including radio-labelling (André *et al.*, 1998) and selective cation binding (Huskens & Sherry, 1996).

Recently, we reported a new synthetic route to the asymmetric functionalization of [9]aneN_3, the synthesis of the Mn^{II} complexes of these new ligands and the trigonal prismatic crystal structures of two of them (Tei *et al.*, 2002). In an attempt to explore further the reactivity of one of these new ligands, namely 4,7-bis(2-aminoethyl)-1,4,7-triazacyclononane-1-acetate (H*L*), its lithium salt, Li(*L*), was reacted with one molar equivalent of $Zn(ClO_4)_2$ in MeOH. Diffraction quality colourless crystals of the title compound, (I), were obtained by slow diffusion of Et_2O vapour into an MeCN solution of the complex. A single-crystal X-ray structural determination shows two Zn^{II} complexes in the asymmetric unit, in both of which the Zn^{II} ion is coordinated by one O-atom and five N-atom donors from the ligand (Fig. 1). No major difference has been detected between the coordination environment in the two independent Zn^{II} complexes, as can be seen from the data in Table 1. The only difference between the two complexes is that in one of them an Li^+ ion is bound by the O atom (O3*C*) of the carboxylate group not involved in coordination of the metal, and by three water molecules, giving a tetrahedral geometry [Li—O = 1.921 (9)–1.978 (9) Å and O—Li—O = 102.5 (4)–117.6 (4)°]. A hydrogen bond between a primary amine N—H (N3*B*) group in this complex and the carboxylate-O atom (O3*C*′) not involved in coordination to the other metal connects the two complex cations (H···O = 2.13 Å and N—H···O = 174°; see Fig. 1). In contrast to the Mn^{II} complex with Li(*L*), where the geometry around the metal centre is a rather regular trigonal prism (Tei *et al.*, 2002), $[Zn(L)]^+$ does not adopt a specific ideal geometry around the Zn^{II} centre in either of the complex cations; twist angles between the triangular faces defined by the macrocyclic-N donors and the pendant arm donors are 37.0 and 36.6°, which are intermediate between those of an octahedron and a trigonal prism. This absence of a specific coordination polyhedron at the Zn^{II} ion is not surprising considering that a d^{10} metal ion does not have any electronically preferred geometry and therefore the disposition of the donor atoms is regulated by steric factors only. While the Zn—O bond lengths



(I)

involving atoms O4*C* and O4*C*′ are 2.098 (3) and 2.102 (3) Å, respectively, the Zn—N(primary amine) bond lengths lie in the range 2.116 (4)–2.145 (4) Å, shorter than the Zn—N(tertiary amine) bonds which are in the range 2.180 (4)–2.231 (4) Å. These differences in Zn—N bond lengths are expected and are due to the increased steric repulsion at the tertiary amines and the lower donor ability of tertiary amine groups compared with primary amine groups. Of the numerous [9]aneN$_3$ pendant arms functionalized ligands, Mani and co-workers have reported (Di Vaira *et al.*, 1998) a comparable Zn^{II} complex with the [9]aneN$_3$ derivative containing one carboxylate and two imidazole pendant coordinating groups where the bond lengths between the metal and the macrocyclic N-atom donors are quite long [2.224 (2)–2.339 (2) Å] with the Zn^{II} ion shifted towards the N- and O-atom donors of the pendant arms [range 2.074 (3)–2.081 (2) Å] within a distorted trigonal prismatic geometry.

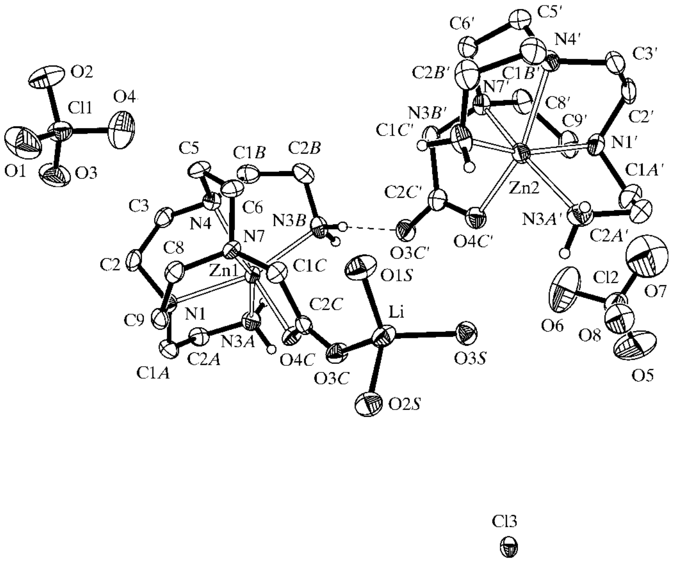


Figure 1

The structure of the title compound showing the atom-numbering scheme adopted. Only the H atoms of primary amine groups are shown. Displacement ellipsoids are drawn at the 50% probability level and only the major disorder components of atoms C2*A*′ and O8 are shown.

Experimental

Zn(ClO$_4$)$_2$·6H$_2$O (34.6 mg, 0.093 mmol) in MeOH (10 ml) was added to a solution of Li(*L*) (26.0 mg, 0.093 mmol) in MeOH (10 ml). The resulting solution was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and the residue dissolved in MeCN. Single crystals suitable for X-ray structural analysis were obtained by diffusion of Et$_2$O vapour into the MeCN solution of the complex (35.0 mg, 0.074 mmol, 79.3% yield). Mass spectrum (electrospray): m/z = 336 (M^+ [Zn(*L*)]$^+$). Elemental analysis, found (calculated for C$_{24}$H$_{58}$Cl$_3$LiN$_{10}$O$_{15}$Zn$_2$): C 30.12 (29.69), H 6.47 (6.02), N 14.58% (14.43%). IR spectrum (KBr disc) (ν/cm^{-1}): 3293 (*s*), 3161 (*m*), 2966 (*w*), 2919 (*w*), 2858 (*w*), 1609 (s), 1474 (*w*), 1400 (*w*), 1325 (*w*), 1121 (*s*), 1051 (*m*), 1006 (*m*), 799 (*w*), 634 (*m*).

Crystal data

[Zn(C$_{12}$H$_{26}$N$_5$O$_2$)][LiZn(C$_{12}$H$_{26}$N$_5$O$_2$)(H$_2$O)$_3$]Cl(ClO$_4$)$_2$
M_r = 970.85
Monoclinic, $P2_1/c$
a = 15.6382 (12) Å
b = 8.8403 (7) Å
c = 29.595 (2) Å
β = 103.672 (2)°
V = 3975.5 (5) Å^3
Z = 4

D_x = 1.612 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4413 reflections
θ = 2.4–25.4°
μ = 1.48 mm^{-1}
T = 150 (2) K
Column, colourless
0.26 × 0.08 × 0.08 mm

Data collection

Bruker SMART1000 CCD area detector with an Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min}$ = 0.722, $T_{\max}$ = 0.888

24884 measured reflections
9917 independent reflections
5504 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.063
$\theta_{\max}$ = 29.0°
$h = -21 \rightarrow 13$
$k = -12 \rightarrow 11$
$l = -37 \rightarrow 40$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.139
S = 1.00
9356 reflections
498 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.008
$\Delta\rho_{\max}$ = 0.88 e Å^{-3}
$\Delta\rho_{\min}$ = −1.01 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Zn1—N1	2.212 (4)	Zn2—N7′	2.231 (4)
Zn1—N4	2.180 (4)	Zn2—N3*A*′	2.127 (4)
Zn1—N7	2.203 (4)	Zn2—N3*B*′	2.116 (4)
Zn1—N3*A*	2.145 (4)	Zn2—O4*C*′	2.102 (3)
Zn1—N3*B*	2.126 (4)	Li—O3*C*	1.932 (9)
Zn1—O4*C*	2.098 (3)	Li—O1*S*	1.939 (9)
Zn2—N1′	2.199 (4)	Li—O2*S*	1.921 (9)
Zn2—N4′	2.210 (4)	Li—O3*S*	1.978 (9)
N1—Zn1—N4	80.61 (14)	N1′—Zn2—N3*B*′	160.40 (16)
N1—Zn1—N7	80.85 (13)	N1′—Zn2—O4*C*′	99.39 (14)
N1—Zn1—N3*A*	80.29 (14)	N4′—Zn2—N7′	79.41 (14)
N1—Zn1—N3*B*	160.89 (15)	N4′—Zn2—N3*A*′	108.47 (16)
N1—Zn1—O4*C*	100.67 (13)	N4′—Zn2—N3*B*′	81.44 (15)
N4—Zn1—N7	80.68 (14)	N4′—Zn2—O4*C*′	157.52 (14)
N4—Zn1—N3*A*	108.39 (15)	N7′—Zn2—N3*A*′	157.84 (16)
N4—Zn1—N3*B*	81.27 (15)	N7′—Zn2—N3*B*′	104.28 (15)
N4—Zn1—O4*C*	159.28 (13)	N7′—Zn2—O4*C*′	78.46 (13)
N7—Zn1—N3*A*	157.34 (15)	N3*A*′—Zn2—N3*B*′	97.44 (17)
N7—Zn1—N3*B*	102.12 (15)	N3*A*′—Zn2—O4*C*′	93.63 (15)
N7—Zn1—O4*C*	79.13 (13)	N3*B*′—Zn2—O4*C*′	100.20 (14)
N3*A*—Zn1—N3*B*	99.82 (15)	O3*C*—Li—O1*S*	117.6 (4)
N3*A*—Zn1—O4*C*	92.13 (14)	O3*C*—Li—O2*S*	102.5 (4)
N3*B*—Zn1—O4*C*	98.42 (14)	O3*C*—Li—O3*S*	109.5 (4)
N1′—Zn2—N4′	80.74 (15)	O1*S*—Li—O2*S*	103.2 (4)
N1′—Zn2—N7′	80.37 (14)	O1*S*—Li—O3*S*	112.4 (4)
N1′—Zn2—N3*A*′	80.57 (16)	O2*S*—Li—O3*S*	110.9 (4)

One C atom (C2*A*′) of one pendant arm and one perchlorate O atom (O8) were found to be disordered. The disorder was modelled by a partial occupancy model over two sites for C2*A*′/C2*A*″, with occupancy factors of 0.85/0.15, respectively, and over three sites for O8, with occupancy factors of 0.50/0.30/0.20 for O8/O8′/O8″. Appropriate restraints were applied to all bond distances and angles involving the disordered atoms.

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Methylene and amine H atoms, after location from ΔF syntheses, were placed geometrically and refined with a riding model for which the C—H and N—H distances were constrained to be 0.99 and 0.92 Å, respectively, and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C, N})$. Attempts to locate the water H atoms were unsuccessful and they were therefore not included in the refinement model, but they were accounted for in the chemical formula. Possible O—H···O hydrogen bonds can be identified from short O···O distances.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1237). Services for accessing these data are described at the back of the journal.

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