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Key indicators

Single-crystal X-ray study
 T = 303 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.036
 wR factor = 0.077
 Data-to-parameter ratio = 14.5

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

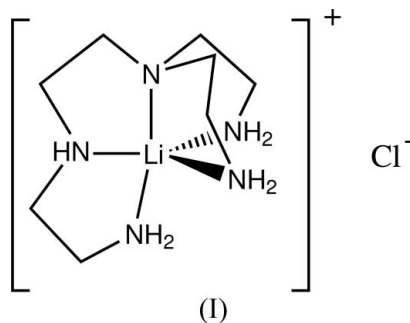
[4-(2-Aminoethyl)-1,4,7,10-tetraazadecane]-lithium chloride: a bilayered structure displaying the rare TRENEN ligand

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The pentadentate ligand TRENEN [4-(2-aminoethyl)-1,4,7,10-tetraazadecane] is not readily available in the pure state, but is present as a major impurity in commercial tetraethylene pentamine. Therefore, only four structures containing TRENEN have been reported previously. We report here the crystal structure of the title compound, $[\text{Li}(\text{trenen})]\text{Cl}$ or $[\text{Li}(\text{C}_8\text{H}_{23}\text{N}_5)]\text{Cl}$. The Li atom has a distorted trigonal-bipyramidal coordination geometry. The $[\text{Li}(\text{trenen})]^+$ cation is chiral since one of the N atoms is a chirogenic centre. A second type of chirality arises as a consequence of the chelating conformations. In the racemic crystal structure, molecules assemble into bilayers *via* $\text{N}-\text{H}\cdots\text{Cl}$ interactions.

Comment

The pentadentate ligand TRENEN [4-(2-aminoethyl)-1,4,7,10-tetraazadecane] has been described as a ‘new and interesting’ ligand (Maxwell, 1971). Nevertheless, only four crystal structures containing TRENEN are found in the Cambridge Structural Database (CSD; Version 5.27, November 2005; Allen, 2002), namely $[\text{CoN}_3(\text{trenen})]\text{NO}_3\cdot\text{H}_2\text{O}$ (Buckingham *et al.*, 1969; Maxwell, 1971), $[\text{CoCl}(\text{trenen})]\text{Cl}(\text{ClO}_4)\cdot\text{H}_2\text{O}$ (Gatehouse *et al.*, 1992), $[\{\text{Co}(\text{trenen})\}_2\text{O}_2](\text{ClO}_4)_4$ (Gatehouse *et al.*, 1991), $[\text{Cu}(\text{trenen})]\text{Br}_2$ (Cannas *et al.*, 1976). The rare occurrence of TRENEN complexes can be explained by the fact that the amine itself is not readily available in the pure state, but is present as a contaminant in commercial tetraethylene pentamine (Bergstedt *et al.*, 1970). In this paper, we report a new complex with the TRENEN ligand, $[\text{Li}(\text{trenen})]\text{Cl}$, (I), obtained from a chloride-containing organolithium solution and commercial tetraethylene pentamine.



The cation of (I) exhibits a distorted trigonal-bipyramidal geometry around the lithium ion, with atoms N1 and N3 in axial positions (Fig. 1). In this respect, it is analogous to $[\text{Cu}(\text{trenen})]\text{Br}_2$, the only five-coordinate TRENEN complex in the CSD. Given the TB-5 geometry around the central atom, the TRENEN ligand may give rise to three different

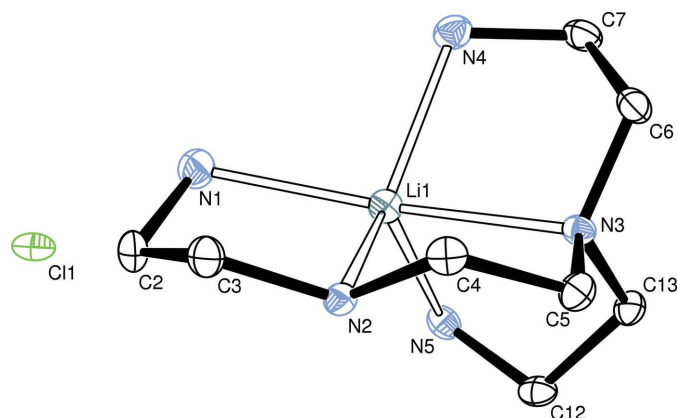


Figure 1

The asymmetric unit of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted.

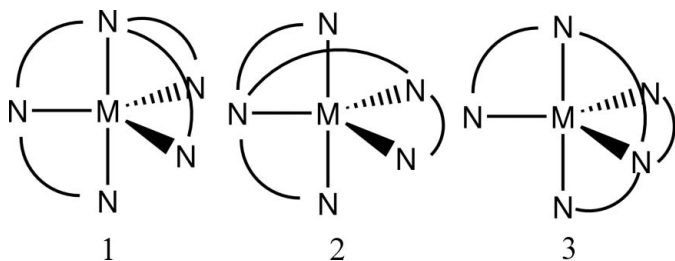


Figure 2

The TRENEN ligand may give rise to three different geometric isomers, given TB-5 coordination geometry around the central atom. Ignoring chelate-ring conformations, complexes of type 1 are achiral, whereas complexes of types 2 and 3 are present in two enantiomeric forms. The title compound is of type 1, and is chiral only due to the chelate-ring conformation.

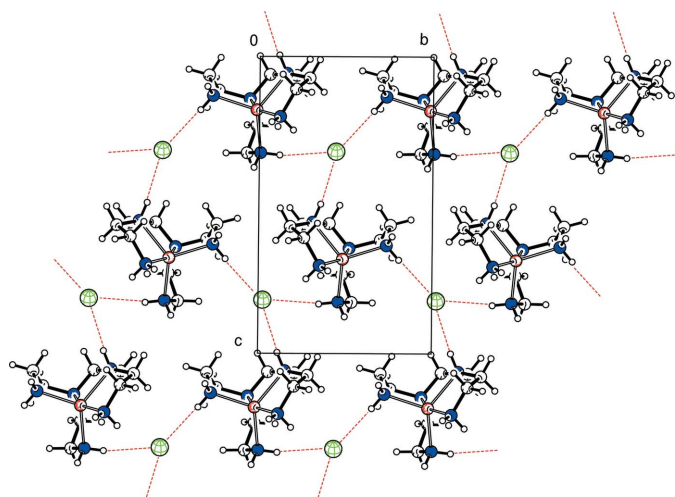


Figure 3

N—H...Cl interactions (dashed lines) in a monolayer.

geometric isomers (Fig. 2), and both (I) and [Cu(trenen)]Br₂ display the same coordination arrangement of the TRENEN ligand. Molecules of (I) are chiral due both to the chirogenic N2 atom and to the chelate-ring conformations, which are either λδδδ or δλλλ (von Zelewsky *et al.*, 1996), in the order of increasing C-atom number.

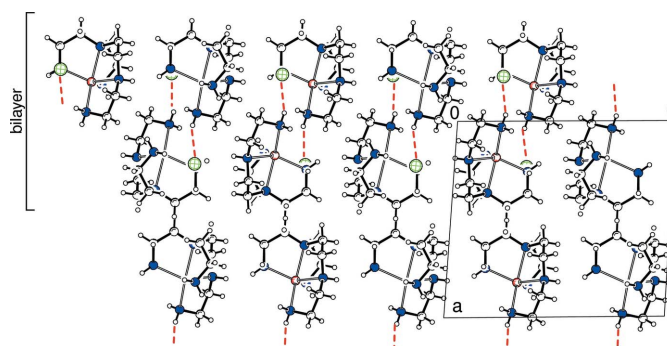


Figure 4

N—H...Cl interactions (dashed lines) giving rise to bilayers.

The crystal structure of (I) is built up by layers in the *bc* plane, held together by N—H...Cl interactions, each chloride ion being surrounded by three cations within the same layer (Fig. 3). The N—H...Cl distances are 2.59 (2) Å for Cl1—H14ⁱ [symmetry code: (i) $-x, \frac{1}{2} + y, \frac{3}{2} - z$], 2.61 (2) Å for Cl1—H13ⁱⁱ [symmetry code: (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$] and 2.55 (2) Å for Cl1—H11ⁱⁱⁱ [symmetry code: (iii) $-x, 1 - y, 1 - z$]. The layers formed in this way are polar, but are connected into bilayers through a fourth set of N—H...Cl interactions [Cl1...H9 = 2.56 (2) Å; Fig. 4]. The bilayers display two identical surfaces, and there are no interactions between adjacent bilayers within the sum of the van der Waals radii. Each chloride ion is surrounded by four cations in an enantiomeric ratio of 1:3, which means that the crystal structure consists of chiral structural motifs larger than the asymmetric unit.

Experimental

A few crystals of the title compound were isolated from a solution obtained by addition of commercial (Aldrich) tetraethylenepentamine to a solution of indenyl lithium in THF, containing traces of lithium chloride.

Crystal data

[Li(C₈H₂₃N₅)Cl]
M_r = 231.70
 Monoclinic, *P*2₁/*c*
a = 12.079 (9) Å
b = 7.914 (5) Å
c = 13.559 (10) Å
 β = 94.48 (3)°
V = 1292.2 (16) Å³

Z = 4
D_x = 1.191 Mg m⁻³
 Mo K α radiation
 μ = 0.27 mm⁻¹
T = 303 (2) K
 Prism, colourless
 0.15 × 0.10 × 0.10 mm

Data collection

Rigaku R-Axis IIC image-plate system diffractometer
 φ scans
 Absorption correction: none
 8324 measured reflections

2386 independent reflections
 2170 reflections with $I > 2\sigma(I)$
*R*_{int} = 0.034
 θ_{\max} = 25.5°

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.077$
S = 1.11
 2386 reflections
 164 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2 + 0.8724P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1—Li1	2.151 (3)	N4—Li1	2.139 (3)
N2—Li1	2.169 (3)	N5—Li1	2.096 (3)
N3—Li1	2.262 (3)		
N5—Li1—N4	112.66 (13)	N1—Li1—N2	82.59 (11)
N5—Li1—N1	117.13 (14)	N5—Li1—N3	82.48 (10)
N4—Li1—N1	99.87 (12)	N4—Li1—N3	80.32 (11)
N5—Li1—N2	111.84 (13)	N1—Li1—N3	157.70 (14)
N4—Li1—N2	127.89 (14)	N2—Li1—N3	79.97 (10)

All H atoms were included in calculated positions (C—H = 0.96–0.97 Å) and refined using a riding model, except for the amine H atoms which were refined without constraints. The refined N—H distances lie in the range 0.88 (2) to 0.91 (2) Å.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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