

A Schiff base lateral macrobicycle derived from 4,13-diaza-18-crown-6 in its protonated form

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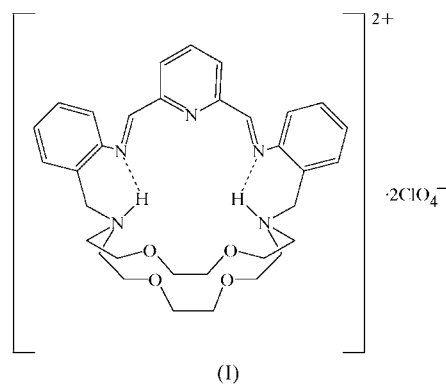
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In the structure of the title compound, 28,31,36,39-tetraoxa-9,17,42-triaza-1,25-diazoniapentacyclo[23.8.5.1^{11,15}.0^{3,8}.-0^{18,23}]nonatriaconta-3,5,7,9,11,13,15,16,18,20,22-undecene bis-(perchlorate), C₃₃H₄₃N₅O₄²⁺·2ClO₄⁻ or (H₂L)(ClO₄)₂, the cation and one of the two independent anions lie on crystallographic twofold axes, while the second perchlorate anion is disordered about a centre of inversion. The conformation of the macrobicycle *L* is conditioned by two strong intramolecular hydrogen-bonding interactions involving the pivot and imine N atoms, and is quite different from that observed when a metal ion is placed inside its cavity. The two imine groups are not coplanar with the pyridine moiety, and the deviation from planarity is considerably larger than that found in the corresponding Ba complex. Moreover, the fold of the macrobicycle in H₂L²⁺ causes a significant approach of the two pivot N atoms compared with their disposition in the Ba complex. This is the first X-ray crystal structure analysis of an uncoordinated Schiff base lateral macrobicycle.

Comment

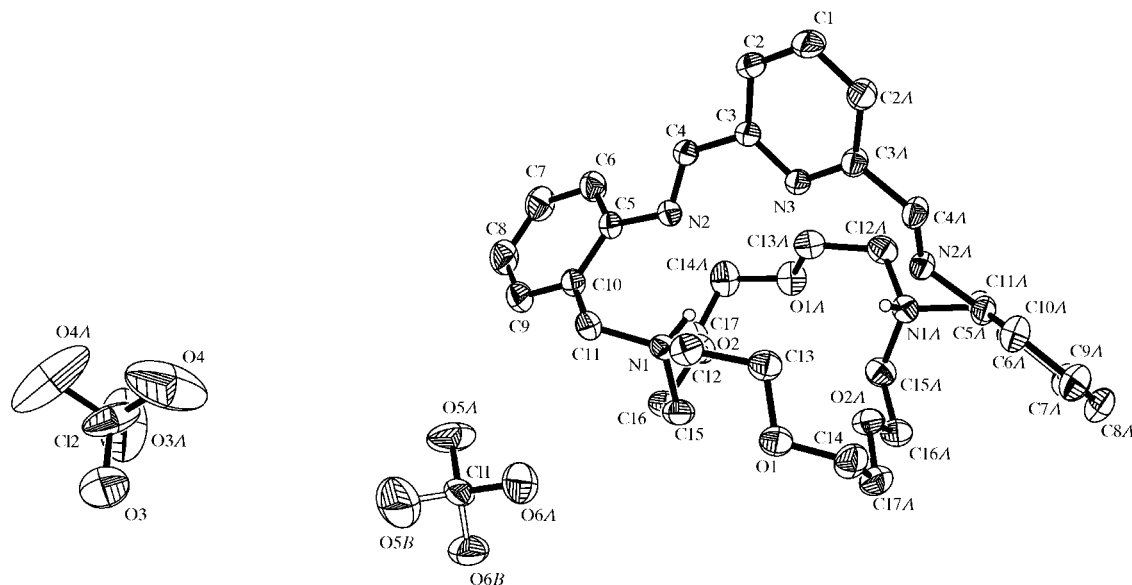
Macrocyclic compounds have been studied extensively from many different points of view, such as molecular recognition, artificial catalysis and supramolecular structure. Our current research interest in this field includes the design of novel macrobicyclic architectures. According to the number of connecting bridges used for their construction and the nature of the subunits used as building blocks, two different kinds of macrobicyclic structures may be envisaged, namely axial macrobicycles, which result from a coaxial arrangement of two tripodal subunits linked by three bridges, and lateral macrobicycles, which are dissymmetrical molecules structurally based on the combination of two different binding units, one chelating and one macrocyclic (Lehn, 1980). We have reported a novel family of Schiff base lateral macrobicycles containing

two different binding units, namely a rigid unsaturated N₂X set (*X* = N or O) and a flexible cyclic N₂O_{*n*} set linked by aromatic bridges (Esteban *et al.*, 1999). These macrobicycles are structurally derived from bibracchial lariat ethers incorporating pendant aniline moieties, and constitute the first examples of lateral macrobicycles containing imine groups. This type of Schiff base lateral macrobicyclic architecture cannot be prepared by direct reaction between the organic precursors. However, some metal ions can template the corresponding reactions, thereby allowing access to the desired macrobicycles in high yields (Platas-Iglesias *et al.*, 2003), although in all cases the metal ion acts as a permanent template, remaining trapped in the macrobicyclic cavity. Thus, to date, all the X-ray crystal structures described for this type of lateral macrobicycle correspond to the metal-coordinated form. We have found that the addition of perchloric acid to the Pb complex of *L* causes the demetallation of the complex, yielding the macrobicycle *L* in its protonated form, *viz.* (H₂L)(ClO₄)₂, (I). We describe here the structure of (I), which represents the first X-ray structure determination of an uncoordinated Schiff base lateral macrobicycle.



The asymmetric unit of (I) comprises a half-molecule of the cation H₂L²⁺ and half molecules of two crystallographically independent perchlorate anions. The cation and one of the anions (Cl2) are located on twofold axes, while the second perchlorate is situated on a centre of symmetry, with half-occupied disordered oxygen sites. Fig. 1 shows the structure of (I), while selected bond lengths and angles are given in Table 1 and do not show any significant deviation from expected values. The N2=C4 distance of 1.261 (3) Å is consistent with an imine group and the bond angle of 119.8 (2)° for C4–N2–C5 confirms the sp² character of atom N2.

The conformation of the macrobicycle *L* in (I) is conditioned by two strong intramolecular hydrogen-bonding interactions involving the pivot and imine N atoms [N2···N1 = 2.743 (3) Å; Table 2], and this conformation is, in fact, quite different from that observed when a metal ion is placed inside its cavity (Avecilla *et al.*, 2003). The lateral aromatic rings of H₂L²⁺ form a dihedral angle of 85.32 (9)°, whereas the plane of the pyridine ring forms a dihedral angle of 54.87 (10)° with the plane containing the benzene ring. The imine groups are not coplanar with the pyridine moiety, as indicated by the torsion angle N2–C4–C3–N3 of 15.7 (5)°. This deviation from planarity is considerably greater than that found in the

**Figure 1**

The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms (with the exception of H1N and H1NA) have been omitted for clarity. Atoms labelled with the suffix *A* are at the symmetry position $(2 - x, y, \frac{3}{2} - z)$.

corresponding Ba complex (Avecilla *et al.*, 2003). Likewise, the fold of the macrobicyclic causes an important approach between the two pivot N atoms [$N1 \cdots N1A = 5.257(5) \text{ \AA}$], which are $6.384(4) \text{ \AA}$ apart when a Ba ion is trapped in the macrobicyclic cavity (Avecilla *et al.*, 2003). Moreover, the distance between the two imine N atoms (N2 and N2A) is $5.138(4) \text{ \AA}$, *ca* 0.35 \AA longer than that found in $[\text{Ba}(L)]^{2+}$.

Experimental

Single crystals of $(\text{H}_2L)(\text{ClO}_4)_2$ suitable for X-ray crystallographic analysis were grown by addition of a dilute solution of perchloric acid in acetonitrile to a solution of $[\text{Pb}(L)](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ in the same solvent (molar ratio 2:1), followed by slow diffusion of diethyl ether into the resulting solution.

Crystal data

$\text{C}_{33}\text{H}_{43}\text{N}_5\text{O}_4^{2+} \cdot 2\text{ClO}_4^-$
 $M_r = 772.62$
 Monoclinic, $C2/c$
 $a = 9.5092(2) \text{ \AA}$
 $b = 19.1979(2) \text{ \AA}$
 $c = 20.6024(5) \text{ \AA}$
 $\beta = 96.880(1)^\circ$
 $V = 3734.02(13) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.374 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 951 reflections
 $\theta = 2.9\text{--}28.2^\circ$
 $\mu = 0.24 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Block, colourless
 $0.40 \times 0.35 \times 0.30 \text{ mm}$

Table 1

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

N1—C15	1.501(4)	O1—C14	1.427(4)
N1—C12	1.501(4)	N2—C4	1.261(3)
N1—C11	1.509(4)	N2—C5	1.425(3)
O1—C13	1.418(4)		
C15—N1—C12	112.8(2)	C16—O2—C17	113.3(2)
C15—N1—C11	113.8(2)	C4—N2—C5	119.8(2)
C12—N1—C11	109.9(2)	N2—C4—C3	123.5(3)
C13—O1—C14	113.1(3)		

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.910$, $T_{\max} = 0.931$
 13 616 measured reflections
 4630 independent reflections

2771 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -12 \rightarrow 12$
 $k = -23 \rightarrow 25$
 $l = -21 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.214$
 $S = 1.06$
 4630 reflections
 262 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.101P)^2 + 2.7759P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997b)
 Extinction coefficient: 0.0030(7)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
N1—H1N \cdots N2	0.89(3)	2.07(3)	2.743(3)	131(2)

The O atoms of one perchlorate anion were disordered (site-occupancy factors of 0.5 for atoms O5A, O6A, O5B and O6B). 42 restraints were imposed and applied to the Cl—O bonds of the perchlorate anion. Atom H1N, which is involved in an intramolecular hydrogen bond, was found in a difference electron-density map and then refined riding on the coordinates of atom N1. The positions of all other H atoms were calculated geometrically and a riding model was used in their refinement, with C—H distances in the range $0.93\text{--}0.97 \text{ \AA}$ and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SHELXTL* (Sheldrick, 1997a); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1108). Services for accessing these data are described at the back of the journal.

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