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A barium perchlorate complex with a lateral macrobicycle derived from 1,10-diaza-15-crown-5 containing a phenol Schiff base spacer

Fernando Avecilla, David Esteban, Carlos Platas-Iglesias, Andres De Blas and Teresa Rodríguez-Blas*

Departamento de Química Fundamental, Universidade da Coruña, Campus da Zapateira s/n, E-15071 A Coruña, Spain
Correspondence e-mail: mayter@udc.es

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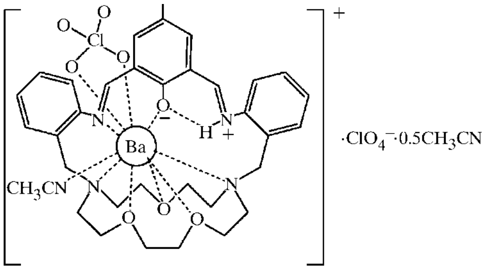
In the crystal structure of (acetonitrile-κ*N*)[13-methyl-39-oxido-1,17,25-triaza-9-azonia-28,31,36-trioxapentacyclo[23.8.5.$1^{11,15}$.$0^{3,8}$.$0^{18,23}$]nonatriaconta-3,5,7,9,11,13,15(39),16,18,20,22-undecaene-$\kappa^7N^1,N^{17},N^{25},O^{28},O^{31},O^{36},O^{39}$](perchlorato-$\kappa^2$-*O*,*O*′)barium(II) perchlorate acetonitrile hemisolvate, $[Ba(ClO_4)(C_2H_3N)(C_{33}H_{40}N_4O_4)]ClO_4{\cdot}0.5CH_3CN$, the barium(II) cation is asymmetrically situated in the macrobicyclic cavity and is bound to seven of the eight heteroatoms of the macrobicyclic ligand, to the N atom of an acetonitrile molecule and to two O atoms of one perchlorate group. The azonia N atom is not coordinated to the barium(II) cation and is involved in an intramolecular hydrogen-bonding interaction with the oxido O atom.

Comment

In a previous work (Esteban *et al.*, 1999), we reported a novel family of Schiff base lateral macrobicycles that contain two different binding units, *viz.* a rigid and unsaturated N_2X set, (X = N and O) and a flexible and cyclic N_2O_n set linked by aromatic bridges. These macrobicycles, which are the first examples of lateral macrobicycles containing imine groups, are structurally derived from bibracchial lariat ethers that incorporate pendant aniline moieties. We have found that the macrobicycles cannot be prepared by a direct reaction between the organic precursors, but barium can act as a template, thereby facilitating the formation of the desired macrobicycles in high yields. In all cases, the barium(II) ion acts as a permanent template, remaining trapped in the macrobicyclic cavity. We describe herein the X-ray crystal structure determination of one of these barium complexes, $[Ba(ClO_4)(CH_3CN)(L)]ClO_4{\cdot}0.5CH_3CN$, (I), where L is the macrobicycle formed by condensation of the bibracchial lariat ether *N*,*N*′-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 and 2,6-diformyl-4-methylphenol.

The asymmetric unit of (I) contains the $[Ba(ClO_4)(CH_3CN)(L)]^+$ cation, a well separated perchlorate anion and half a molecule of acetonitrile. Fig. 1 shows the structure of the cationic complex, while selected bond lengths and angles are given in Table 1. The barium(II) ion is bound to seven of the eight heteroatoms of L, to the N atom of an acetonitrile molecule and to two O atoms of one perchlorate group. The X-ray data suggest that imine atom N1 and phenol donor O4 are involved in an intramolecular hydrogen-bonding interaction (Table 2). The relevant distances (N1—H1N = 0.97 Å and O4···H1N = 1.72 Å) also indicate that proton transfer from the phenol group to imine atom N1 has occurred, as previously found in related complexes (Esteban *et al.*, 2002). As a result, N1 does not belong to the coordination sphere of the barium(II) ion, which consequently is situated asymmetrically in the macrobicyclic cavity. All the barium-donor atom distances fall within the range found in the literature.



(I)

The torsion angles N2—C7—C6—C1 [5.8 (6)°] and N1—C32—C2—C1 [−0.7 (6)°] indicate that the coordinated imine group is just slightly rotated from coplanarity with the phenol

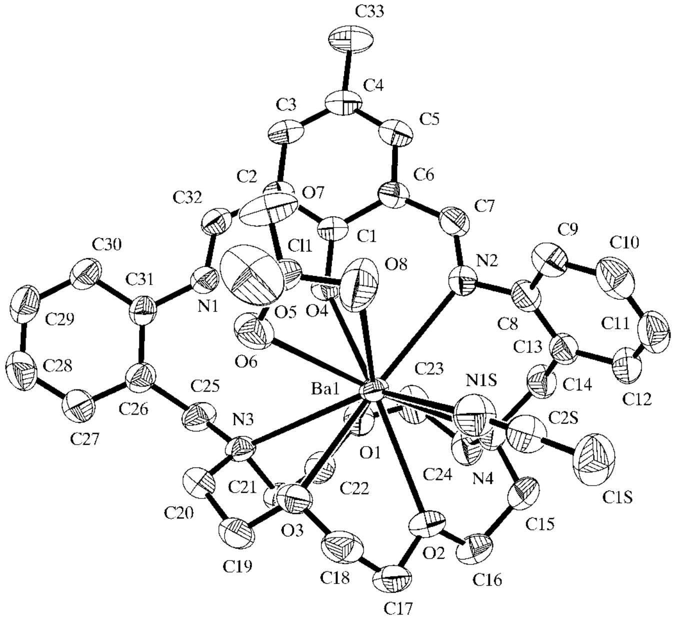


Figure 1
A view of the $[Ba(ClO_4)(CH_3CN)(L)]^+$ cation, showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

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ring, whereas the uncoordinated imine group is rigorously coplanar with the phenol ring. The phenol ring forms a dihedral angle of 67.43 (11)° with the plane containing the benzyl ring attached to the coordinated imine atom N2 and an angle of 32.31 (20)° with the plane containing the second aromatic ring. This difference in the fold of the receptor may be due to the coordination of the barium(II) ion, which, in order to maximize the interaction with the seven coordinated heteroatoms of the macrobicycle, forces the torsion and fold of this part of the receptor, so diminishing the degree of π conjugation and increasing the stress on this side of the receptor. In addition, donor atoms O1, O3, N3 and N4 of the crown moiety are essentially coplanar (the mean deviation from the plane is 0.0044 Å), with the barium ion lying 1.5018 (18) Å above the plane.

The distance between the two imine N atoms (N1 and N2) is 5.376 (4) Å, which is 0.37 Å longer than the distance found in the analogous perchlorate complex in which the macrobicyclic receptor contains a pyridine Schiff base spacer (Esteban *et al.*, 1999). The distance between the two pivotal N atoms (N3 and N4) is 5.169 (4) Å, which is 0.22 Å shorter than the distance found in the analogous complex containing the pyridine spacer.

Experimental

Single crystals of $[Ba(ClO_4)(CH_3CN)(L)]ClO_4 \cdot 0.5CH_3CN$ suitable for X-ray crystallographic analysis were grown by slow diffusion of diethyl ether into an acetonitrile solution of the previously reported complex $[Ba(ClO_4)_2(EtOH)(L)]$ (Esteban *et al.*, 1999).

Crystal data

$[Ba(ClO_4)(C_2H_3N)(C_{33}H_{40}N_4O_4)]$-$ClO_4 \cdot 0.5C_2H_3N$
$M_r = 954.51$
Triclinic, $P\overline{1}$
$a = 9.5691$ (8) Å
$b = 14.8261$ (13) Å
$c = 15.7110$ (13) Å
$\alpha = 101.726$ (2)°
$\beta = 101.994$ (2)°
$\gamma = 91.566$ (2)°
$V = 2129.2$ (3) Å^3

$Z = 2$
$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 862 reflections
$\theta = 1.4$–28.3°
$\mu = 1.12$ mm^{-1}
$T = 293$ (2) K
Block, orange
0.55 × 0.40 × 0.40 mm

Data collection

Bruker SMART CCD diffractometer
φ–ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.577$, $T_{max} = 0.662$
14 862 measured reflections
10 257 independent reflections

8410 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 28.3°$
$h = -12 \rightarrow 10$
$k = -19 \rightarrow 16$
$l = -19 \rightarrow 20$
50 first frames intensity decay: 1.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.126$
$S = 1.02$
10257 reflections
547 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.087P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.33$ e Å^{-3}
$\Delta\rho_{min} = -1.56$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Ba1—O4	2.596 (2)	Ba1—O6	2.928 (3)
Ba1—O1	2.741 (2)	Ba1—N1*S*	2.963 (4)
Ba1—O2	2.827 (2)	Ba1—O8	2.980 (4)
Ba1—O3	2.838 (3)	Ba1—N4	3.096 (3)
Ba1—N2	2.884 (3)	Ba1—N3	3.243 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O4	0.97	1.72	2.556 (4)	142

Atoms O9, O10 and O12 of one perchlorate group were disordered [site-occupancy factor of 0.52 (2) for O9*A*, O10*A* and 012*A*], as were atoms C3*S* and N2*S* of an acetonitrile molecule [site-occupancy factor of 0.103 (13) for C3*SA* and N2*SA*], and 93 restraints were imposed. The site O11 is occupied by two non-separable, but not completely coincident, disordered atoms. The refinement converged with anisotropic displacement parameters for all non-H atoms, except for C3*SA*, C3*SB*, C4*S*, N2*SA* and N2*SB*, which were refined isotropically. The positions of all H atoms, except H1N, were calculated geometrically, and a riding model was used in their refinement. Atom H1N, which is involved in an intramolecular hydrogen bond, was found in a difference electron-density map and then refined riding on atom N1. The H atoms of the solvent (non-coordinated acetonitrile) were not included. The minimum and maximum final electron-density peaks were 0.86 and 0.89 Å from Ba1, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: FA1006). Services for accessing these data are described at the back of the journal.

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