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A barium perchlorate complex with a lateral macrobicycle derived from 4,13-diaza-18-crown-6 containing a pyridine Schiff base spacer

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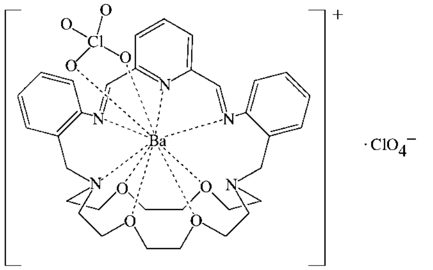
In the crystal structure of (perchlorato-κ^2O,O'))(28,31,36,39-tetraoxa-1,9,17,25,42-pentaazapentacyclo[23.8.5.$1^{11,15}$.$0^{3,8}$.$0^{18,23}$]-nonatriaconta-3,5,7,9,11,13,15,16,18,20,22-undecaene-κ^8N^1,N^9,N^{17},N^{42},O^{28},O^{31},O^{36},O^{39})barium(II) perchlorate, $[Ba(ClO_4)(C_{33}H_{41}N_5O_4)](ClO_4)$, the Ba^{II} cation is situated in the macrobicyclic cavity, bound to only eight of the nine available donor atoms of the Schiff base macrobicyclic receptor. The pivotal N5 atom does not belong to the coordination sphere of the Ba^{II} ion, in spite of its *endo* conformation with the lone pair directed towards the inside of the cavity. The Ba^{II} ion completes its coordination core with two O atoms of one bidentate perchlorate group.

Comment

Macropolycyclic structures delineate molecular cavities into which substrates can penetrate, forming complexes of which the geometry may be regulated *via* ligand design. According to the number of connecting bridges used for their construction and the nature of the subunits used as building blocks, a variety of macropolycyclic structures may be envisaged. Lateral macrobicycles are one of these structure types, although they have been investigated little to date. They are asymmetrical molecules with a structure based on the combination of two different binding units, one chelating and one macrocyclic (Lehn, 1980). We describe herein the X-ray crystal structure determination of the title barium complex, $[Ba(L)(ClO_4)](ClO_4)$, (I), where L is a Schiff base lateral macrobicycle formed by condensation of the two-armed crown ether N,N'-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 and 2,6-diformylpyridine. This kind of Schiff base lateral macrobicycle cannot be prepared by a direct reaction between the organic precursors, but Ba^{II} is able to template the reaction, thereby allowing the formation of the desired macrobicycles in high yield. In all cases, this metal ion remains trapped in the macrobicycle cavity, giving evidence of its behaviour as a permanent template.



(I)

The asymmetric unit of (I) contains the $[Ba(L)(ClO_4)]^+$ cation and a well separated perchlorate anion. Fig. 1 shows the structure of the cationic complex, while selected bond lengths and angles are given in Table 1. Unlike the analogue derived from the precursor N,N'-bis(2-aminobenzyl)-1,10-diaza-15-crown-5, where the Ba^{II} ion is coordinated to each donor atom of the macrobicyle (Esteban *et al.*, 1999), in (I) the sequestered Ba^{II} ion is only coordinated to eight of the nine available donor atoms of the macrobicycle. The long Ba$\cdots$N5 distance [3.690 (4) Å] indicates that the pivotal N5 atom does not belong to the coordination sphere of the Ba^{II} ion, in spite of its *endo* conformation with the lone pair directed towards the inside of the cavity. The Ba^{II} ion completes its coordination core with two O atoms of one perchlorate group acting as a bidentate ligand. The Ba—O5 and Ba—O6 distances indicate a weak interaction of the Ba^{II} ion with the perchlorate group, often described as 'semi-coordination' (Gowda *et al.*, 1984).

The fold of the macrobicyclic receptor around the metal ion allows donor atoms N1, N5, O2 and O4 of the crown moiety to be essentially coplanar [mean deviation from the plane of 0.0771 (19) Å], with the Ba^{II} ion located 1.032 (2) Å above it. The N3—C13—C14—N4 [−5.2 (6)°] and N3—C9—C8—N2 [−4.8 (6)°] torsion angles show that the imine groups are not

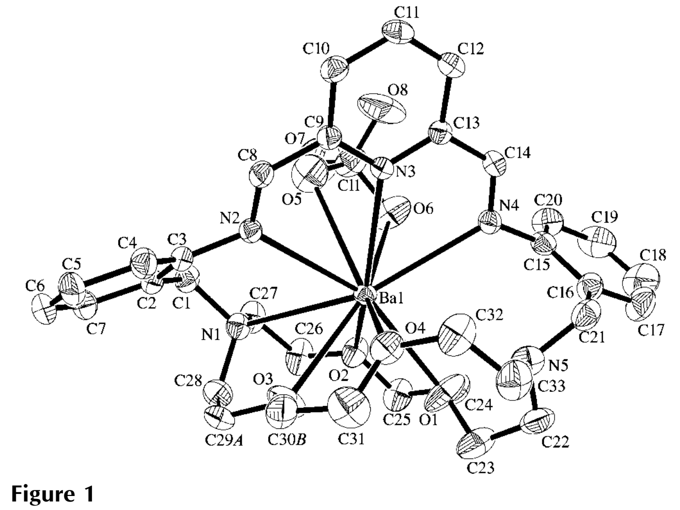


Figure 1
The molecular structure of the cation of (I), shown with 30% probability displacement ellipsoids. H atoms and the minor disorder component have been omitted for clarity.

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coplanar with the pyridine group, although the loss of planarity is less than that found in the analogue derived from *N*,*N*′-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 (corresponding values of −11.5 and 4.9°). The pyridine ring forms a dihedral angle of 83.3 (1)° with the plane containing the benzyl ring attached to imine atom N4 and 49.4 (2)° with the plane containing the second aromatic ring. The distance between the two imine atoms (N2 and N4) is 4.961 (4) Å, whereas that between the two pivotal atoms (N1 and N5) is 6.384 (4) Å.

Experimental

Single crystals of [Ba(*L*)(ClO$_4$)](ClO$_4$), (I), suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into an acetonitrile solution of the previously reported complex Ba(*L*)(ClO$_4$)$_2$ (Esteban *et al.*, 1999).

Crystal data

[Ba(ClO$_4$)(C$_{33}$H$_{41}$N$_5$O$_4$)](ClO$_4$)
M_r = 907.95
Orthorhombic, *Pbca*
a = 17.6868 (7) Å
b = 20.6923 (8) Å
c = 20.7567 (8) Å
V = 7596.5 (5) Å^3
Z = 8
D_x = 1.588 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6140 reflections
θ = 1.8–28.3°
μ = 1.25 mm^{-1}
T = 293 (2) K
Prism, colourless
0.60 × 0.10 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.520, $T_{\max}$ = 0.917
53 172 measured reflections
9421 independent reflections
6140 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
$\theta_{\max}$ = 28.3°
$h = -23 \rightarrow 22$
$k = -27 \rightarrow 27$
$l = -20 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.092
S = 1.07
9421 reflections
498 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0141P)^2 + 16.3465P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.58 e Å^{-3}
$\Delta\rho_{\min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ba1—O4	2.773 (3)	Ba1—N4	2.928 (3)
Ba1—O1	2.785 (3)	Ba1—N1	2.979 (3)
Ba1—O3	2.816 (3)	Ba1—N2	2.990 (3)
Ba1—O2	2.866 (3)	Ba1—O6	3.012 (4)
Ba1—N3	2.919 (3)	Ba1—O5	3.045 (4)
O4—Ba1—O1	86.37 (10)	O3—Ba1—N2	72.89 (11)
O4—Ba1—O3	57.90 (11)	O2—Ba1—N2	126.66 (9)
O1—Ba1—O3	83.64 (14)	N3—Ba1—N2	57.05 (9)
O4—Ba1—O2	132.42 (10)	N4—Ba1—N2	113.90 (9)
O1—Ba1—O2	55.72 (9)	N1—Ba1—N2	68.20 (9)
O3—Ba1—O2	87.55 (11)	O4—Ba1—O6	154.99 (12)
O4—Ba1—N3	78.45 (10)	O1—Ba1—O6	94.43 (12)
O1—Ba1—N3	136.29 (11)	O3—Ba1—O6	147.07 (12)
O3—Ba1—N3	119.68 (11)	O2—Ba1—O6	65.04 (11)
O2—Ba1—N3	148.61 (9)	N3—Ba1—O6	83.93 (11)
O4—Ba1—N4	90.45 (10)	N4—Ba1—O6	64.94 (11)
O1—Ba1—N4	82.88 (12)	N1—Ba1—O6	90.60 (12)
O3—Ba1—N4	146.26 (10)	N2—Ba1—O6	108.13 (10)
O2—Ba1—N4	109.61 (10)	O4—Ba1—O5	135.52 (10)
N3—Ba1—N4	56.84 (9)	O1—Ba1—O5	136.68 (11)
O4—Ba1—N1	113.48 (10)	O3—Ba1—O5	124.13 (12)
O1—Ba1—N1	104.19 (11)	O2—Ba1—O5	89.89 (10)
O3—Ba1—N1	58.51 (10)	N3—Ba1—O5	62.62 (10)
O2—Ba1—N1	59.41 (9)	N4—Ba1—O5	85.87 (11)
N3—Ba1—N1	119.48 (9)	N1—Ba1—O5	72.62 (11)
N4—Ba1—N1	155.19 (10)	N2—Ba1—O5	64.67 (9)
O4—Ba1—N2	76.77 (9)	O6—Ba1—O5	43.54 (10)
O1—Ba1—N2	155.93 (12)		

Atoms C29 and C30 of the crown moiety were disordered [site-occupancy factor of 0.593 (10) for atom C29*A* and 0.26 (3) for atom C30*A*], and 76 similarity restraints were imposed. These restraints were applied to the bonds C28—C29*A*, C28—C29*B*, O3—C29*A*, O3—C29*B*, O3—C30*A*, O3—C30*B*, C30*A*—C31 and C30*B*—C31. The positions of all H atoms were calculated geometrically and a riding model was used in their refinement, with C—H distances in the range 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); 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: JZ1570). Services for accessing these data are described at the back of the journal.

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