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Crystal Structure
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[7,13-Bis(2-aminobenzyl)-1,4,10-trioxa-7,13-diazacyclopentadecane]-diisothiocyanatobarium(II)

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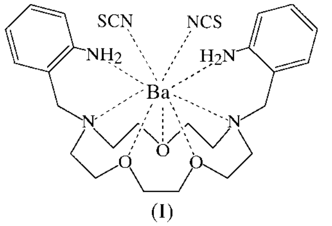
The X-ray crystal structure of the title complex, [Ba(NCS)$_2$-(C$_{24}$H$_{36}$N$_4$O$_3$)], indicates that the Ba^{II} cation is nine-coordinate in the solid state, being fully encapsulated by the organic receptor ligand. The receptor adopts a *syn* arrangement, with both pendant arms oriented on the same side of the crown moiety. The distance between the two amine N atoms is 3.911 (12) Å, while the pivotal N atoms are 5.322 (10) Å apart.

Comment

In a previous paper, we described a synthetic route for preparing a novel family of Schiff base lateral macrobicycles derived from bibracchial lariat ethers incorporating pendant aniline moieties and various dialdehyde functions, which structurally belong to the group defined as lateral macrobicycles (Esteban *et al.*, 1999). We have found that these compounds cannot be prepared by direct reaction between the organic precursors, but Ba^{II} can act as a template, thereby allowing access to the desired macrobicycles in high yields. The effectiveness of the Ba^{II} ion as a template in this case arises from the conformation that the metal ion induces in the bibracchial lariat ether precursor. Herein, we describe the X-ray crystal structure of one of these Ba intermediates, *viz.* the title complex, [Ba(*L*)(NCS)$_2$] [*L* is the bibracchial lariat ether 7,13-bis(2-aminobenzyl)-1,4,10-trioxa-7,13-diazacyclopentadecane], (I).



(I)

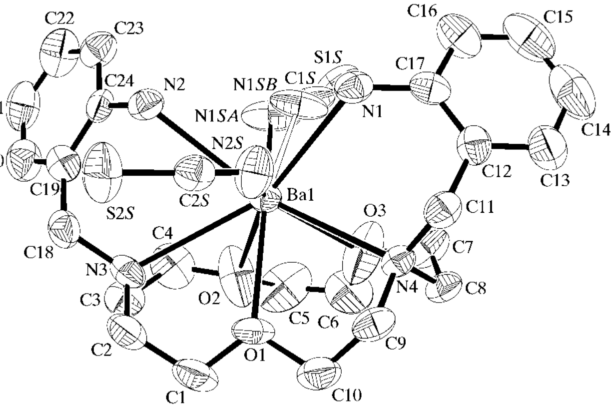


Figure 1
The X-ray crystal structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

In (I) (Fig. 1), the Ba^{II} ion is nine-coordinate, bound to the seven heteroatoms of *L* and the N atoms of two thiocyanate groups. The barium–donor-atom distances fall within the range found for the analogous perchlorate complex, [Ba(*L*)-(ClO$_4$)]$^+$, reported previously by Esteban *et al.* (1999). As in the perchlorate complex, the metal ion in (I), is almost symmetrically positioned with respect to the cavity of the organic receptor, and is situated 1.837 (4) Å above the pseudo-plane defined by the three O atoms and pivotal atom N4 of the bibracchial lariat ether. The coordination polyhedron (Fig. 2) may be described as a monocapped distorted square antiprism, with the donor atoms O1, O3, N1 and N2*S* defining the upper plane (mean deviation from planarity 0.034 Å) and the Ba^{II} ion 1.172 (5) Å from the plane. Due to the two-way disorder of thiocyanate atom N1*S* [occupancy factors 0.66 (8) for N1*SA* and 0.34 (8) for N1*SB*], the basal plane of the polyhedron may be considered as being defined by the donor atoms O2, N2, N3 and N1*SA* (mean deviation from planarity 0.099 Å), or by atoms O2, N2, N3 and N1*SB* (mean deviation from planarity 0.012 Å). Pivotal atom N4 is the cap of the polyhedron.

In (I), both pendant aniline arms of the receptor ligand are oriented on the same side of the macrocyclic plane, resulting in a *syn* conformation, in contrast with the *anti* conformation found for the free *L* ligand (Esteban *et al.*, 2000). This conformation was also found in the analogous perchlorate complex, but the presence of thiocyanate groups in the Ba coordination sphere of (I), instead of perchlorate groups,

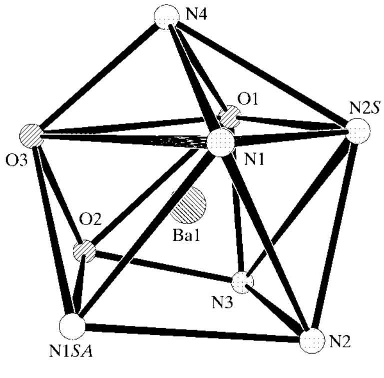


Figure 2
The coordination polyhedron of the Ba^{II} ion in (I).

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causes some structural changes. In (I), the distances between the two amine N atoms [N1$\cdots$N2 = 3.911 (12) Å] and the two pivotal N atoms [N3$\cdots$N4 = 5.322 (10) Å] are longer than those found in the perchlorate compound [N1$\cdots$N2 = 3.263 Å and N3$\cdots$N4 = 5.211 Å; Esteban *et al.*, 1999]. The N4—C11—C12 and N3—C18—C19 angles, with values of 113.6 (7) and 114.2 (8)°, respectively, are quite similar, and the planes containing the aromatic rings form a dihedral angle of 53.2 (3)°.

Experimental

The title complex was prepared according to Esteban *et al.* (1999). Slow diffusion of diethyl ether into a solution of the complex in acetonitrile gave single crystals of (I) suitable for X-ray analysis.

Crystal data

$[Ba(NCS)_2(C_{24}H_{36}N_4O_3)]$
$M_r = 682.07$
Monoclinic, $P2_1$
$a = 10.4878$ (2) Å
$b = 12.2591$ (2) Å
$c = 11.9750$ (3) Å
$\beta = 95.029$ (1)°
$V = 1533.71$ (5) Å^3
$Z = 2$

$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 331 reflections
$\theta = 1.4$–28.3°
$\mu = 1.47$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ/ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.758$, $T_{max} = 0.930$
11 420 measured reflections

5697 independent reflections
3718 reflections with $I > 2\sigma(I)$
$R_{int} = 0.075$
$\theta_{max} = 28.3°$
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 16$
$l = -15 \rightarrow 15$

Table 1
Selected geometric parameters (Å, °).

Ba1—O1	2.727 (5)	Ba1—N1	2.877 (8)
Ba1—O3	2.771 (7)	Ba1—N2	2.921 (8)
Ba1—N1*SB*	2.776 (15)	Ba1—N2*S*	2.950 (8)
Ba1—N1*SA*	2.788 (11)	Ba1—N4	2.999 (7)
Ba1—O2	2.790 (9)	Ba1—N3	3.020 (7)
O1—Ba1—O3	86.8 (3)	N1*SB*—Ba1—N2*S*	126.4 (6)
O1—Ba1—N1*SB*	157.8 (10)	N1*SA*—Ba1—N2*S*	134.3 (10)
O3—Ba1—N1*SB*	72.3 (13)	O2—Ba1—N2*S*	148.5 (3)
O1—Ba1—N1*SA*	152.0 (10)	N1—Ba1—N2*S*	61.6 (2)
O3—Ba1—N1*SA*	75.2 (6)	N2—Ba1—N2*S*	68.7 (2)
N1*SB*—Ba1—N1*SA*	13.9 (9)	O1—Ba1—N4	62.31 (19)
O1—Ba1—O2	78.2 (3)	O3—Ba1—N4	61.0 (2)
O3—Ba1—O2	57.2 (3)	N1*SB*—Ba1—N4	111.1 (16)
N1*SB*—Ba1—O2	84.2 (7)	N1*SA*—Ba1—N4	122.6 (7)
N1*SA*—Ba1—O2	74.1 (11)	O2—Ba1—N4	106.4 (3)
O1—Ba1—N1	121.3 (2)	N1—Ba1—N4	69.1 (2)
O3—Ba1—N1	97.1 (3)	N2—Ba1—N4	139.9 (2)
N1*SB*—Ba1—N1	69.9 (9)	N2*S*—Ba1—N4	72.1 (2)
N1*SA*—Ba1—N1	82.6 (11)	O1—Ba1—N3	62.1 (2)
O2—Ba1—N1	148.7 (2)	O3—Ba1—N3	113.3 (2)
O1—Ba1—N2	112.7 (2)	N1*SB*—Ba1—N3	119.2 (14)
O3—Ba1—N2	156.0 (2)	N1*SA*—Ba1—N3	105.4 (10)
N1*SB*—Ba1—N2	86.1 (14)	O2—Ba1—N3	59.3 (2)
N1*SA*—Ba1—N2	81.3 (5)	N1—Ba1—N3	149.6 (2)
O2—Ba1—N2	111.3 (3)	N2—Ba1—N3	68.0 (2)
N1—Ba1—N2	84.8 (2)	N2*S*—Ba1—N3	94.6 (2)
O1—Ba1—N2*S*	73.5 (2)	N4—Ba1—N3	124.3 (2)
O3—Ba1—N2*S*	133.0 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1*C*$\cdots$N2*S*	0.92	2.15	2.986 (12)	151
N2—H2*D*$\cdots$S2*S*	1.01	2.76	3.700 (9)	155
N1—H1*D*$\cdots$S1*S*^{i}	1.01	2.86	3.577 (9)	128
N2—H2*C*$\cdots$S1*S*^{i}	1.06	2.46	3.466 (9)	157

Symmetry code: (i) $1 - x, y - \frac{1}{2}, 1 - z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.099$
$S = 1.05$
5697 reflections
353 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.91$ e Å^{-3}
Absolute structure: Flack (1983), with 1709 Friedel pairs
Flack parameter = 0.02 (2)

The crystal of (I) presented a disorder of the N atom of one isothiocyanate group, and 27 restraints were imposed. These restraints were applied to the bonds N1*SA*—C1*S*, N1*SB*—C1*S*, Ba1—N1*SA* and Ba1—N1*SB*, and the site-occupancy factor was 0.66 (8) for N1*SA*. That the correct direction of the polar axis in $P2_1$ had been chosen was established by refinement of the Flack parameter [0.02 (2); Flack, 1983]. The positions of all H atoms were calculated geometrically (C—H distances in the range 0.93–0.97 Å) and a riding model was used in their refinement, except for the H atoms involved in hydrogen bonds to the isothiocyanate moieties (H1*C*, H1*D*, H2*C* and H2*D*), which were first located in a difference density map. Atoms H1*C* and H1*D* were restricted to a distance of 1.01 Å from the corresponding heteroatom. These four H atoms were then refined as riding on their respective heteroatoms.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); program used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1001). Services for accessing these data are described at the back of the journal.

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