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Bis[μ-2-(1,4,7,10-tetraoxa-13-azacyclopentadeca-13-yl)cyclohepta-2,4,6-trien-1-one]bis[bis(thiocyanato)barium(II)]

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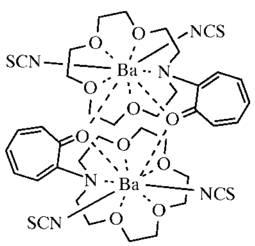
In the title complex, $[Ba_2(NCS)_4(C_{17}H_{25}NO_5)_2]$, each Ba^{2+} cation is coordinated by one N atom, four O atoms of the macrocyclic unit, two N atoms of thiocyanate unit and one O atom from each of the tropone units.

Comment

Recently, we have prepared several aza-crown ethers having a tropone system and their guest cation complexes. By addition of metal thiocyanates, the original absorption bands of the organic molecule at 355 and 417 nm disappeared and a new absorption band appeared around 332 nm, suggesting that the conformation of the 2-aminotropone moiety changes (Takeshita *et al.*, 1995). The X-ray crystallographic analysis of the $Ca(NCS)_2$ complex of *N*-(tropon-2-yl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (ttapd) showed that the Ca^{2+} ion is eight-coordinated, which includes four ether O atoms, one azacrown N, two thiocyanate N atoms and one tropone O atom instead of an O atom from the solvent, such as methanol or water (Kubo, Yamamoto *et al.*, 1999). From the results of the association constants determined by the absorption spectral changes of ttapd for various guest cations, ttapd showed Ba^{2+} ion selectivity (Takeshita *et al.*, 1995). The stoichiometry of the complexation between ttapd and Ba^{2+} ion was confirmed as n:n (n = 1 or 2), at least in acetonitrile, by the molar-ratio method. However, the cavity of ttapd seems to be too small to accommodate a Ba^{2+} ion and ttapd also lacks one potential coordination site, if one assumes a normal Ba^{2+} ion coodination number of nine. In order to reveal the detailed structure of ttapd and the Ba^{2+} ion complex, the barium thiocyanate complex, (I), has been investigated by X-ray crystallographic analysis.



(I)

The title complex has 2:2 stoichiometry with C_i symmetry. The structure of (I) is distinct from those of 2,5,8,11,14-pentaoxapentadecane–$Ba(NCS)_2$–$2H_2O$ (Wei *et al.*, 1987), 1,4,7,10,13,16-hexaoxacyclooctadecane–$Ba(NCS)_2$–H_2O (Wei *et al.*, 1988) and 10-methyl-9-[2-methyl-4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]acridinium–$Ba(ClO_4)_2$–CH_3CN (Häming *et al.*, 1990). Each Ba^{2+} ion of complex (I) has nine-coordination, which includes four ether O atoms (O1, O2, O3 and O4), one azacrown N1 atom, two thiocyanate N atoms (N2 and N3), one tropone O5 atom and one O atom from the other tropone, O5^i [symmetry code: (i) $2 - x$, $-y$, $1 - z$]. One N atom (N1) and four O atoms (O1, O2, O3, and O4) of the azacrown are coordinated on one side of Ba1, and the two thiocyanate N atoms (N2 and N3) and the two tropone O atoms (O5 and O5^i) on the opposite side. The dihedral angles between the least-squares azacrown plane defined by O1/O2/O3/O4/N1 and the tropone ring defined by C11–C17/O5 is 116.1 (1)°, while the two BaNCS planes intersect at 76.5 (5) and 50.6 (2)° to the azacrown plane, respectively.

The average value [2.846 (3) Å] of four Ba1—O ether distances is similar to those found in $Ba(NCS)_2$–2,5,8,11,14-pentaoxapentadecane [2.878 (3) Å; Wei *et al.*, 1987], $Ba(NCS)_2$–1,4,7,10,13,16-hexaoxacyclooctadecane [2.835 (6) Å; Wei *et al.*, 1988] and to the sum of the ionic and van der Waals radii (2.87 Å = 1.47 + 1.40 Å; Shannon, 1976; Lide, 1990). The Ba1—O5 distance [2.789 (2) Å] is significantly shorter than the Ba1—O ether distances and the Ba1—O5^i distance [2.937 (2) Å]. The Ba1—N1 distance [3.096 (3) Å] is shorter than those of 10-methyl-9-[2-methyl-4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]acridinium–$Ba(ClO_4)_2$–CH_3CN [3.260 (8) Å; Häming *et al.*, 1990] and *N,N′*-bis(1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane–$Ba(NCS)_2$–H_2O [3.127 (5) Å; Kubo, Sakurai *et al.*, 1999] and is similar to the sum of the ionic and van der Waals radii (3.02 Å = 1.47 + 1.55 Å; Shannon, 1976; Lide, 1990), indicating fairly strong coordination of 2-aminotropone to the Ba^{2+} ion.

The tropone moiety of complex (I) shows pronounced bond alternation similar to those of ttapd–$Ca(NCS)_2$ (Kubo, Yamamoto *et al.*, 1999) and tropone (Barrow & Mills, 1973) and its ring system deviates from planarity; the angle of the intersection between the least-squares planes *A* (defined by C11, C12, C17 and O5) and *B* (defined by C12, C13, C16 and

C17) is 20.5 (2)°, while that between the least-squares planes *B* and *C* (defined by C13–C16) is 170.2 (3)°.

Experimental

Ttapd was condensed with aza-15-crown-5 ether and 2-(*p*-toluenesulfonyloxy)tropone in toluene and EtOH (Takeshita *et al.*, 1995). Single crystals of (I) were obtained by slow evaporation of an equimolar mixture of $Ba(NCS)_2$ and ttapd in CH_3CN.

Crystal data

$[Ba_2(NCS)_4(C_{17}H_{25}NO_5)_2]$
$M_r = 576.88$
Triclinic, $P\bar{1}$
$a = 11.668 (5)$ Å
$b = 12.445 (5)$ Å
$c = 8.918 (5)$ Å
$\alpha = 96.697 (5)°$
$\beta = 106.143 (5)°$
$\gamma = 106.720 (5)°$
$V = 1163.8 (9)$ Å^3
$Z = 2$
$D_x = 1.646$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.71$–$18.11°$
$\mu = 1.919$ mm^{-1}
$T = 296 (2)$ K
Prism, yellow
0.30 × 0.27 × 0.23 mm

Data collection

Enraf–Nonius FR590 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
$T_{min} = 0.570$, $T_{max} = 0.643$
5850 measured reflections
5597 independent reflections
4973 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.97°$
$h = -14 \rightarrow 15$
$k = -16 \rightarrow 0$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 2.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.070$
$S = 1.147$
5597 reflections
272 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 1.0237P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0092 (5)

Table 1
Selected geometric parameters (Å, °).

Ba1—N2	2.762 (3)	N3—C19	1.144 (5)
Ba1—N3	2.784 (3)	O5—C11	1.255 (4)
Ba1—O5	2.789 (2)	S1—C18	1.619 (4)
Ba1—O4	2.804 (3)	S2—C19	1.623 (4)
Ba1—O2	2.838 (3)	C11—C17	1.433 (5)
Ba1—O3	2.858 (3)	C11—C12	1.475 (4)
Ba1—O1	2.882 (2)	C12—C13	1.378 (4)
Ba1—O5^i	2.937 (2)	C13—C14	1.403 (6)
Ba1—N1	3.096 (3)	C14—C15	1.349 (7)
Ba1—Ba1^i	4.6697 (19)	C15—C16	1.396 (7)
N1—C12	1.413 (4)	C16—C17	1.343 (6)
N2—C18	1.149 (5)		
N2—Ba1—N3	82.41 (12)	O3—Ba1—O1	82.20 (8)
N2—Ba1—O5	78.26 (10)	O5—Ba1—O5^i	70.75 (7)
N3—Ba1—O5	112.09 (10)	O4—Ba1—N1	59.41 (7)
O4—Ba1—O3	59.38 (8)	O1—Ba1—N1	58.42 (7)
O2—Ba1—O3	57.58 (8)	N2—C18—S1	179.2 (4)
O2—Ba1—O1	57.77 (8)	N3—C19—S2	179.6 (4)
O1—C1—C2—O2	62.0 (4)	O4—C7—C8—N1	−59.8 (4)
O2—C3—C4—O3	54.0 (5)	N1—C9—C10—O1	−65.7 (4)
O3—C5—C6—O4	−56.4 (6)		

Symmetry code: (i) $2 - x, -y, 1 - z$.

All H atoms were placed at ideal positions and constrained to ride on the atom to which they are bonded. The H-atom isotropic displacement parameters were fixed to $1.2U_{eq}$ of the riding atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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