

Crystal and Molecular Structures of Binuclear Caesium Complexes with 1,3-Calix[4]-*bis*-crown-6 and 1,3-Calix[4]-*bis*-benzo-crown-6

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(Received: 16 October 1995; in final form: 26 January 1996)

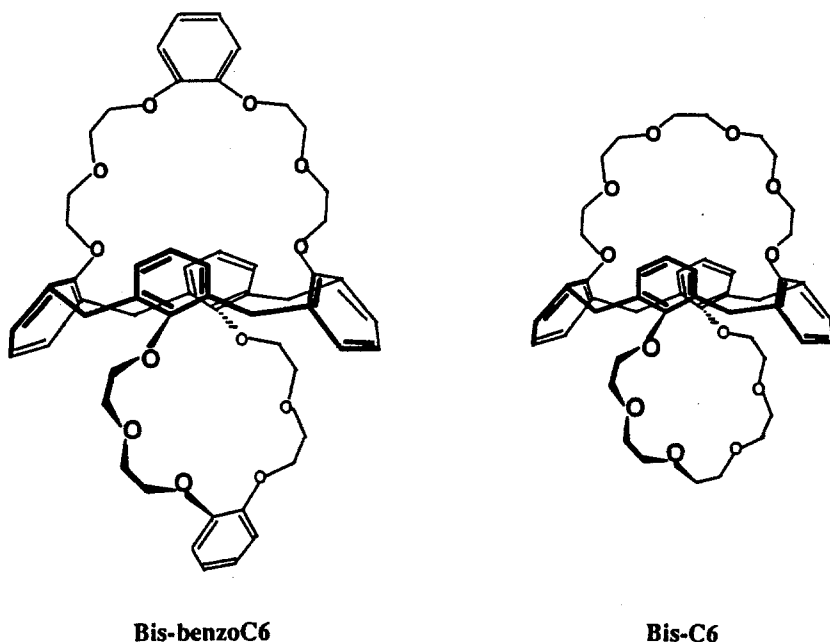
Abstract. The crystal structures of two binuclear complexes between caesium and 1,3-calix[4]-*bis*-crowns have been determined. $\text{Cs}_2\text{Bis-benzoC6}(\text{NO}_3)_2 \cdot 3\text{CHCl}_3$ (**1**) in which **Bis-benzoC6** is 1,3-calix[4]-*bis*-benzo-crown-6, crystallizes in the orthorhombic system: space group $Pca2_1$, $a = 19.513(10)$, $b = 15.382(5)$, $c = 23.708(9)$ Å, $V = 7116(5)$ Å³, $Z = 4$. Refinement led to a final conventional R value of 0.065 for 2321 reflections. The structure of (**1**) is analogous to those already reported with **Bis-C6** (in which **Bis-C6** is 1,3-calix[4]-*bis*-crown-6) and NO_3^- as a counter-ion. $\text{Cs}_2\text{Bis-C6}(\text{NCS})_2$ (**2**) crystallizes in the monoclinic system: space group $C2$, $a = 36.57(2)$, $b = 11.47(1)$, $c = 13.65(1)$ Å, $\beta = 109.03(5)^\circ$, $V = 5415(6)$ Å³, $Z = 4$. Refinement led to a final conventional R value of 0.063 for 2227 reflections. Compound (**2**) is made of dimers bridged by a disordered NCS^- ion. The crown ether chain conformations are discussed.

Key words. Bridged calix[4]arene, caesium complex, ditopic receptor, crystal structure.

Supplementary data relating to this article (atomic coordinates, anisotropic displacement parameters, bond distances and angles and observed and calculated structure factors) are deposited with the British Library as Supplementary Publication No. SUP 82199 (52 pages).

1. Introduction

The interest of calix[4]arenes constrained to the 1,3-*alternate* conformation by crown ether bridging for caesium complexation has recently been demonstrated [1,2]. These macrocycles could be used in liquid membrane techniques for caesium removal from medium-level radioactive waste [1]. More recently, we have used solution NMR studies and single-crystal X-ray diffraction to show that 1,3-calix[4]-*bis*-crown-6 (**Bis-C6**) can complex one or two caesium ions, depending on the crown/caesium stoichiometry [2]. In all cases, the caesium ion is bonded to the six ether oxygen atoms of the crown and to one or two oxygen atoms of the counter-



Scheme 1. Schematic representation of the calixcrowns **Bis-benzoC6** and **Bis-C6**.

ion; it also interacts with the terminal carbon atoms of two phenolic units [2]. The same trends have been found with caesium complexes of 1,3-calix[4]-*mono*-crown-6 [3,4]. Furthermore, the macrocycle **Bis-C6** presents the same conformation when 'free' and when complexed to one or two caesium ions bonded to bidentate nitrate ions, which suggests that the high complexing ability and selectivity for caesium are due to a preorganization of the ligand [2]. We report here the crystal structure of two caesium binuclear complexes: $\text{Cs}_2\text{Bis-benzoC6}(\text{NO}_3)_2 \cdot 3\text{CHCl}_3$ (**1**) and $\text{Cs}_2\text{Bis-C6}(\text{NCS})_2$ (**2**), in which **Bis-benzoC6** and **Bis-C6** are the calixcrowns represented in Scheme 1.

2. Experimental

2.1. SYNTHESIS

The reaction at room temperature between CsNO_3 (0.50 mmole) and **Bis-benzoC6** (0.25 mmole) in chloroform (4 mL), followed by filtration of unreacted CsNO_3 and slow evaporation of the solution, afforded colourless single crystals of (**1**) suitable for X-ray crystallography. Single crystals of (**2**) were obtained in the same way from CsNCS (0.70 mmole) and **Bis-C6** (0.35 mmole) in chloroform (15 mL), followed by recrystallization from chloroform/acetonitrile.

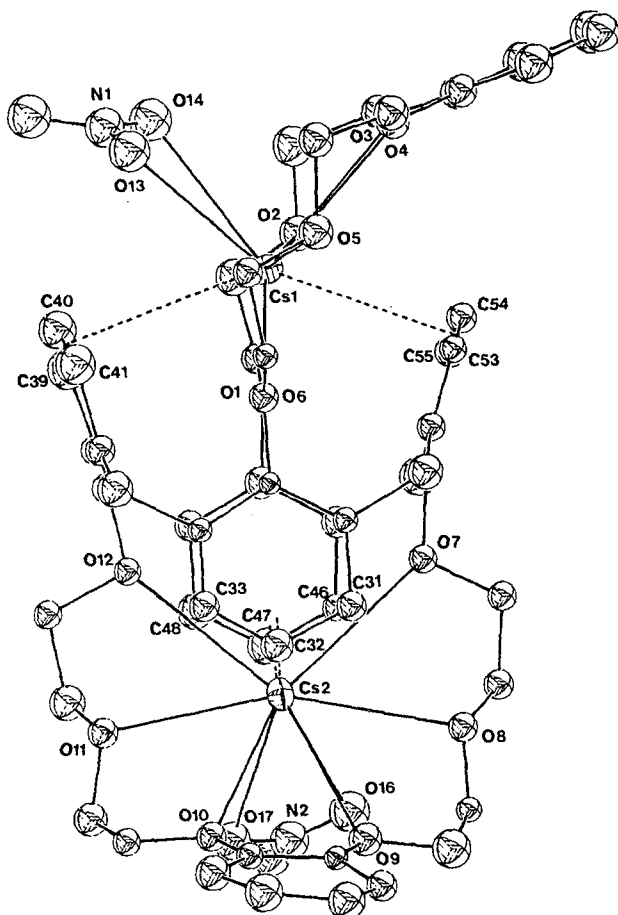


Figure 1. Molecular unit of $\text{Cs}_2\text{Bis-benzoC}_6(\text{NO}_3)_2 \cdot 3\text{CHCl}_3$ (**1**) (chloroform molecules omitted for clarity).

2.2. CRYSTAL DATA

Crystals of both compounds were sealed in glass capillaries. The lattice parameters were obtained from the least-squares refinement of the setting angles of 25 reflections ($8 < \theta < 12^\circ$). Data were collected with an Enraf-Nonius CAD4 diffractometer using $\text{Mo-K}\alpha$ radiation (0.71073 \AA) in the range $1 < \theta < 20^\circ$, in the $\omega/2\theta$ scan mode. The intensity decay was estimated from three standard reflections, measured every 60 mn (not significant for (**1**); -1.7% in 37 hours for (**2**), linearly corrected). The data were corrected for Lorentz-polarization effects. Absorption effects were empirically corrected [5] (transmission coefficients $T_{\min} = 0.89$ and $T_{\max} = 1.00$ for (**1**), $T_{\min} = 0.93$ and $T_{\max} = 1.00$ for (**2**)).

The structures were solved by the heavy-atom method and refined by full-matrix least-squares on F . Hydrogen atoms were located at their ideal positions ($\text{C-H } 0.95 \text{ \AA}$, $B \ 6 \text{ \AA}^2$) and constrained to ride their parent carbon atom. Analytical

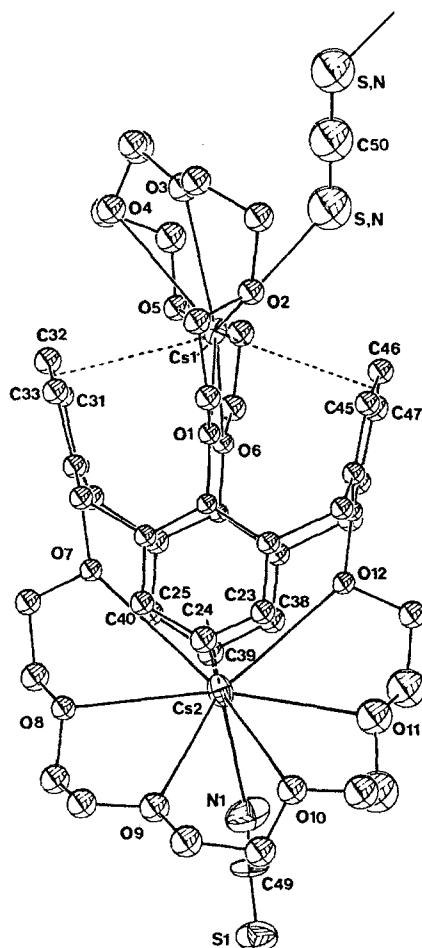


Figure 2. Molecular unit of $\text{Cs}_2\text{Bis-C6(NCS)}_2$ (2).

scattering factors for neutral atoms [6] were corrected for the anomalous dispersion components f' and f'' . The two enantiomorphs have been checked and gave the same results. All calculations were performed on a VAX 4200 computer with the Enraf-Nonius MolEN system [7].

$\text{Cs}_2\text{Bis-benzoC6(NO}_3)_2 \cdot 3\text{CHCl}_3$ (1)

$\text{Cs}_2\text{C}_{59}\text{H}_{63}\text{N}_2\text{O}_{18}\text{Cl}_9$, formula weight = 1673.05. Orthorhombic, space group $Pca2_1$ (No. 29); $a = 19.513(10)$, $b = 15.382(5)$, $c = 23.708(9)$ Å, $V = 7116(5)$ Å³; $Z = 4$; $D_x = 1.562$ g cm⁻³; $\mu = 14.2$ cm⁻¹; crystal size: $0.60 \times 0.60 \times 0.30$ mm³. Data collected at 273 K. 2321 observations with $I > 3\sigma(I)$, out of 3420 unique reflections measured, were used. Refinement of 370 parameters (anisotropic ther-

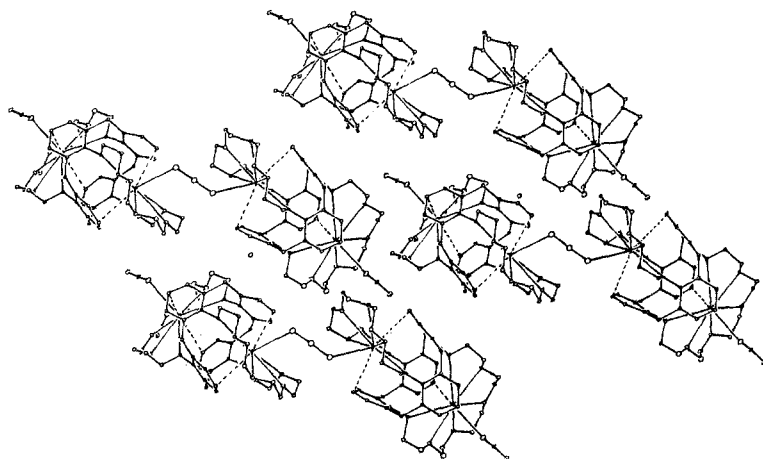


Figure 3. Crystal packing of $\text{Cs}_2\text{Bis-C6(NCS)}_2$ (**2**) (the isolated atoms are the carbons of disordered thiocyanate ions).

mal parameters for Cs atoms). The final R values were $R = 0.065$ and $R_w = 0.075$ ($w = 1/\sigma^2(F)$). Maximum residual density: 0.87 e/\AA^3 .

$\text{Cs}_2\text{Bis-C6(NCS)}_2$ (**2**)

$\text{Cs}_2\text{C}_{50}\text{H}_{60}\text{N}_2\text{O}_{12}\text{S}_2$, formula weight = 1210.98. Monoclinic, space group $C2$ (No. 5); $a = 36.57(2)$, $b = 11.47(1)$, $c = 13.65(1) \text{ \AA}$, $\beta = 109.03(5)^\circ$; $V = 5415(6) \text{ \AA}^3$; $Z = 4$; $D_x = 1.485 \text{ g cm}^{-3}$; $\mu = 14.7 \text{ cm}^{-1}$; crystal size: $0.60 \times 0.45 \times 0.35 \text{ mm}^3$. Data collected at 295 K. 2227 observations with $I > 3\sigma(I)$, out of 2690 unique reflections measured, were used. Refinement of 290 parameters (anisotropic thermal parameters for Cs, S(1), N(1), C(49) and C(51); S, N and C(50) have been found, then fixed in the subsequent refinements). The final R values were $R = 0.063$ and $R_w = 0.085$ ($w = 1/\sigma^2(F)$). Maximum residual density: 1.01 e/\AA^3 .

3. Discussion of Results

ORTEP [8] drawings of the molecular units of (**1**) and (**2**) and of the crystal packing of (**2**) are represented in Figures 1–3, and selected bond lengths given in Table I. In contrast to **Bis-C6**· $4\text{CH}_3\text{CN}$ (**3**), $\text{CsBis-C6(NO}_3)_2 \cdot 2\text{CH}_3\text{CN}$ (**4**) and $\text{Cs}_2\text{Bis-C6(NO}_3)_2 \cdot 2\text{CH}_3\text{CN}$ (**5**) described elsewhere [2], the molecule of (**1**) does not possess any symmetry element and its packing is different from that of the three former compounds. However, the environment of the caesium ion is analogous to the one in (**4**) and (**5**): each Cs is bonded to six ether oxygen atoms with Cs—O distances ranging from $3.09(2)$ to $3.48(2)$ (mean value $3.3(2) \text{ \AA}$), to two nitrate oxygen atoms, with distances ranging from $3.14(3)$ to $3.30(3)$ (mean value

Table I. Selected bond lengths (Å) in compounds (1) and (2) (bond lengths and angles of the macrocycles do not deviate from the usual values).

<i>Compound 1</i>			
Cs(1)—O(1)	3.26(2)	Cs(2)—O(7)	3.23(2)
Cs(1)—O(2)	3.09(2)	Cs(2)—O(8)	3.13(2)
Cs(1)—O(3)	3.47(2)	Cs(2)—O(9)	3.47(2)
Cs(1)—O(4)	3.45(3)	Cs(2)—O(10)	3.48(2)
Cs(1)—O(5)	3.19(2)	Cs(2)—O(11)	3.09(2)
Cs(1)—O(6)	3.23(2)	Cs(2)—O(12)	3.23(2)
Cs(1)—O(13)	3.30(3)	Cs(2)—O(16)	3.25(3)
Cs(1)—O(14)	3.15(3)	Cs(2)—O(17)	3.14(3)
Cs(1)···C(39)	3.89(4)	Cs(2)···C(31)	3.53(4)
Cs(1)···C(40)	3.56(4)	Cs(2)···C(32)	3.38(4)
Cs(1)···C(41)	3.65(4)	Cs(2)···C(33)	3.56(3)
Cs(1)···C(53)	3.47(4)	Cs(2)···C(46)	3.74(3)
Cs(1)···C(54)	3.33(3)	Cs(2)···C(47)	3.57(4)
Cs(1)···C(55)	3.60(3)	Cs(2)···C(48)	3.77(3)
<i>Compound 2</i>			
Cs(1)—O(1)	3.24(2)	Cs(2)—O(7)	3.47(2)
Cs(1)—O(2)	3.15(2)	Cs(2)—O(8)	3.18(2)
Cs(1)—O(3)	3.17(2)	Cs(2)—O(9)	3.30(2)
Cs(1)—O(4)	3.37(2)	Cs(2)—O(10)	3.68(2)
Cs(1)—O(5)	3.08(2)	Cs(2)—O(11)	3.22(3)
Cs(1)—O(6)	3.18(1)	Cs(2)—O(12)	3.20(1)
Cs(1)—S _N	3.442(1)	Cs(2)—N(1)	3.22(4)
Cs(1)···C(31)	3.47(2)	Cs(2)···C(23)	3.38(3)
Cs(1)···C(32)	3.35(3)	Cs(2)···C(24)	3.33(3)
Cs(1)···C(33)	3.57(3)	Cs(2)···C(25)	3.69(3)
Cs(1)···C(45)	3.54(2)	Cs(2)···C(38)	3.59(3)
Cs(1)···C(46)	3.34(3)	Cs(2)···C(39)	3.47(3)
Cs(1)···C(47)	3.62(2)	Cs(2)···C(40)	3.83(3)

3.2(1)) Å, and it interacts with the three terminal carbon atoms of two phenolic units, with Cs···C distances ranging from 3.33(3) to 3.89(4) (mean value 3.6(2)) Å. The conformation of the crown ether chains was analogous in (3), (4), (5) and in the half of Cs₂**Bis-C6**(NO₃)₂ (6) that corresponds to a bidentate nitrate ion [2]. In the notation of Fyles and Gandour [9], it can be described as $g^+g^-g^+g^-g^+$. For compound (1), the torsion angles, given in Table II, are near to the *anti* ideal value of 180° for C—O—C—C bonds, and to the *gauche* one of 60° for O—C—C—O bonds, with the exception of the one corresponding to the aromatic ring: the conformation can be described as $g^+g^-0g^+g^-$. The six ether oxygen atoms are in

Table II. Successive torsion angles ($^{\circ}$) of the crown ether chains in compounds (1) and (2). C_{calix} indicates the carbon atoms of the phenolic units. Crown 1 corresponds to Cs(1), crown 2 to Cs(2).

	Compound 1		Compound 2	
	Crown 1	Crown 2	Crown 1	Crown 2
C2 _{calix} —C1 _{calix} —O—C	−87(3)	−81(3)	−88(2)	−88(2)
C3 _{calix} —C1 _{calix} —O—C	97(3)	94(3)	87(2)	88(2)
C1 _{calix} —O—C—C	163(2)	−166(2)	−171(2)	169(2)
O—C—C—O	69(3)	−76(3)	−62(2)	70(2)
C—C—O—C	162(2)	−168(2)	−161(2)	162(2)
C—O—C—C	−167(2)	164(2)	−58(3)	−176(2)
O—C—C—O	−77(2)	73(3)	−66(3)	−78(2)
C—C—O—C	−179(2)	−169(2)	−166(2)	−173(2)
C—O—C—C	176(2)	−175(2)	169(2)	174(2)
O—C—C—O	5(4)	0(3)	68(3)	65(3)
C—C—O—C	−173(2)	174(2)	178(2)	170(3)
C—O—C—C	176(2)	−179(2)	97(3)	98(3)
O—C—C—O	68(3)	−71(2)	65(3)	84(4)
C—C—O—C	175(2)	−176(2)	−171(2)	153(4)
C—O—C—C	−165(2)	153(2)	−157(2)	−163(3)
O—C—C—O	−74(3)	73(3)	−68(2)	−53(4)
C—C—O—C4 _{calix}	−169(2)	171(2)	−178(2)	177(2)
C—O—C4 _{calix} —C5 _{calix}	−84(3)	−87(3)	−94(2)	−101(2)
C—O—C4 _{calix} —C6 _{calix}	93(3)	90(3)	91(2)	82(2)

a plane within $\pm 0.36(2)$ and $0.31(2)$ Å for crowns 1 and 2 respectively, the caesium atoms being at $0.675(2)$ and $0.697(1)$ Å from these mean planes: this geometry is nearly identical to those found in compounds (4), (5), and in crown 1 of (6).

As can be seen in Figure 3, Cs₂Bis-C6(NCS)₂ (2) is made of dimeric assemblies located around a binary axis, with the formula [Cs₂Bis-C6(NCS)]₂(NCS), in which two NCS (N(1)—C(49)—S(1)) are bonded to Cs(2) by the nitrogen atom, and the other one (S₂N—C(50)—S₂N) is shared by two Cs(1) ions. The C atom of the bridging NCS lies on the twofold axis, hence N and S atoms cannot be distinguished. The Cs(1)—S₂N distance ($3.442(1)$ Å) is longer than Cs(2)—N(1) ($3.22(4)$ Å). The Cs(2)—N(1) bond length is comparable to the Cs—NCS distances already published [10]. Some examples of NCS[−] ions bridging two ions and bonded by both N and S, comparable to the one described here, have been reported in the case of transition metal ions [11]. The Cs—O distances range from $3.08(2)$ to $3.68(2)$ (mean value $3.3(2)$) Å and the Cs⋯C interaction distances from $3.33(3)$ to $3.83(3)$ (mean value $3.5(2)$) Å. Another NCS[−] ion per dimeric unit is present in the structure: located on the twofold axis and not bonded, it is disordered and only the central carbon atom can be resolved (C(51)). The conformations of the two crown ether chains are somewhat different. In crown 1 (bonded to Cs(1)), two

C—O—C—C angles are *gauche* ones, and the O—C—C—O angles correspond to $g^-g^-g^+g^+g^-$: the same conformation has been found in crown 2 of Cs₂**Bis-C6**(NO₃)₂ (**6**), corresponding to a caesium atom bonded to a monodentate nitrate ion [2]. In crown 2 (bonded to Cs(2)), only one C—O—C—C angle is far from the *anti* value, and the O—C—C—O angles correspond to $g^+g^-g^+g^+g^-$. The six ether oxygen atoms are in a plane within $\pm 0.80(1)$ and $0.57(2)$ Å for crowns 1 and 2, respectively, the caesium atoms being at $0.347(1)$ and $0.822(2)$ Å from these mean planes: these values confirm the analogy between crown 1 of (**2**) and crown 2 of (**6**). This result confirms the conclusion of the investigation of compounds (**3–6**) [2]: the macrocycle **Bis-C6** is preorganized to bond to caesium atoms with bidentate counter-ions, but has to undergo some reorganization to bond to caesium with monodentate counter-ions (nitrate in (**6**), thiocyanate in (**2**)).

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