Acta Cryst. (1996). C**52**, 2729-2731

Caesium Iodide Complex of 1,3-Calix[4]-*bis*-crown-6

Pierre Thuéry,[a] Martine Nierlich,[a] Véronique Lamare,[b] Jean-François Dozol,[b] Zouhair Asfari[c] and Jacques Vicens[c]

[a]*CEA, CE Saclay, SCM (CNRS URA 331), Bât. 125, 91191 Gif-sur-Yvette, France,* [b]*CEA, CE Cadarache, DCC/SEP/SETED, 13108 Saint-Paul-lez-Durance, France, and* [c]*EHICS, Laboratoire de Chimie Analytique et Minérale (associé au CNRS), 1 rue Blaise Pascal, 67008 Strasbourg, France*

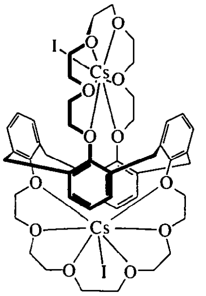
(*Received 18 March 1996; accepted 22 May 1996*)

Abstract

In [13,16,19,22,25,28,42,45,48,51,54,57-dodecaoxaheptacyclo[28.28.1.1^{11,40}.0^{5,58}.0^{7,12}.0^{29,34}.0^{36,41}]hexaconta-1(58),2,4,7,9,11,29,31,33,36,38,40-dodecaene-1κ^6O;2κ^6O]bis(iodocaesium) bis(acetonitrile) solvate, [$Cs_2I_2(C_{48}H_{60}O_{12})$].2$CH_3CN$, the calix[4]arene macrocycle, fixed in the 1,3-alternate conformation by two bridging –$(OCH_2CH_2)_5O$– units (denoted 1,3-calix[4]-*bis*-crown-6) forms a binuclear complex with caesium iodide. The two Cs^+ ions are each located at the centre of a coordination site defined by the six O atoms of a crown-ether chain and are bonded to six O atoms and iodide counterions; they also interact with the two closest benzene rings. This complex is isostructural with the previously reported structures of 'free' 1,3-calix[4]-*bis*-crown-6 and some of its complexes with caesium or potassium nitrate.

Comment

1,3-Calix[4]-*bis*-crown-6 and some of its derivatives have proven to be highly selective extractants for caesium ions with respect to sodium ions in a nitric medium (Hill *et al.*, 1994; Asfari *et al.*, 1995), which makes them interesting as potential tools for nuclear-waste recovery. We have reported previously the crystal structures of caesium, potassium and sodium complexes of this ligand, with nitrate or thiocyanate as counterions (Thuéry, Nierlich, Bressot, Lamare, Dozol, Asfari & Vicens, 1996; Asfari *et al.*, 1996; Thuéry, Nierlich, Lamare, Dozol, Asfari & Vicens, 1996). These structures have led to a better understanding of the complexing properties of this ligand, whose selectivity for caesium ions can be accounted for by complementarity and preorganization properties. Mononuclear or binuclear complexes can be formed depending on the metal/ligand ratio used during the synthesis. We report here the structure of the binuclear caesium complex with iodine as counterion and with acetonitrile solvate molecules, [Cs_2I_2(1,3-calix[4]-*bis*-crown-6)].2CH_3CN, (I).



(I)

The present compound is isostructural with 'free' 1,3-calix[4]-*bis*-crown-6 and some of its mononuclear and binuclear caesium nitrate complexes (Asfari *et al.*, 1996), as well as with its potassium nitrate complex (Thuéry, Nierlich, Lamare, Dozol, Asfari & Vicens, 1996). The complex molecule possesses a twofold symmetry axis which contains the two methylene-bridge C atoms, C24 and C25. The caesium-ion environment comprises an iodine ion at a distance of 3.7140 (5) Å (the sum of the ionic radii is 3.87 Å; Lide, 1992) and the six O atoms of the ether chain, with distances ranging from 3.172 (4) to 3.510 (5) Å [mean value 3.3 (1) Å]. The six O atoms are planar within ±0.464 (3) Å, with the caesium ion at a distance of 0.76 Å from this mean plane. The existence of π interactions between the Cs and the three terminal atoms of the two closest benzene rings can be inferred from the rather short contacts, ranging from 3.273 (5) to 3.770 (5) Å [mean value 3.6 (2) Å]; this was also observed in the previous structures and is in agreement with NMR experiments (Asfari *et al.*, 1996). Using the notation proposed for the characterization of crown-ether conformations (Fyles & Gandour, 1992), the conformation of the ether chain was $g^+g^-g^+g^-g^+$ (where g indicates a *gauche* O—C—C—O angle) in the previous isostructural complexes of 1,3-calix[4]-*bis*-crown-6. In the present case, the conformation is described by the sequence $g^+g^-g^+g^+g^-$. Furthermore, one of the *anti*-C—O—C—C angles is particularly distorted from its ideal value [103.6 (8)°]. The same trend has been found in 'crown-2' of the binuclear complex of caesium thiocyanate (Thuéry, Nierlich, Bressot, Lamare, Dozol, Asfari & Vicens, 1996). We have shown previously that 1,3-calix[4]-*bis*-crown-6 is preorganized for the complexation of caesium bonded to a bidentate nitrate counterion, but has to undergo some reorganization to complex a caesium ion bonded to monodentate counterions such as nitrate (Asfari *et al.*, 1996) or, to a lesser extent, thiocyanate (Thuéry, Nierlich, Bressot, Lamare, Dozol, Asfari & Vicens, 1996). In the present case, at variance with the preceding ones, the reorganization of the ether chains may not be sufficient to change the crystal packing and the resulting space group.

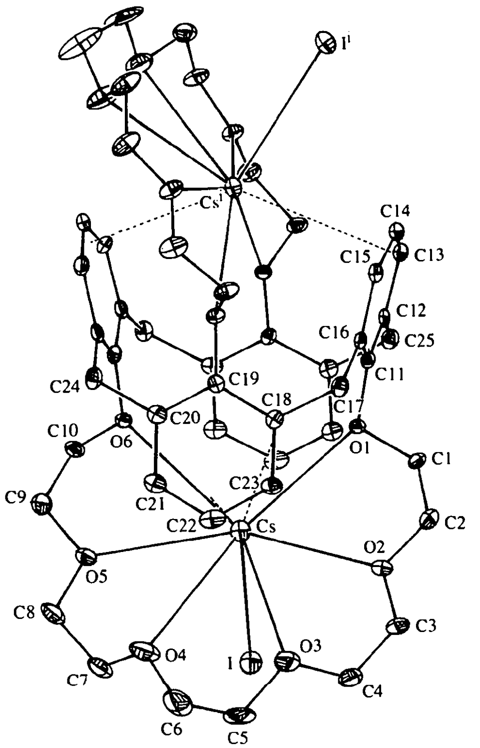


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title complex (solvent molecules and H atoms have been omitted) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. Caesium–benzene ring π interactions are shown as dashed lines. [Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.]

Experimental

The title compound, (I), was obtained by reaction of 1,3-calix-[4]-*bis*-crown-6 and an excess of caesium iodide in chloroform at room temperature, followed by filtration of unreacted caesium iodide. Recrystallization from a 1:1 chloroform/acetonitrile solution provided single crystals suitable for X-ray structure determination.

Crystal data

$[Cs_2I_2(C_{48}H_{60}O_{12})].2C_2H_3N$
$M_r = 1430.73$
Monoclinic
$C2/c$
$a = 18.150\,(9)$ Å
$b = 17.990\,(9)$ Å
$c = 17.365\,(6)$ Å
$\beta = 97.39\,(3)°$
$V = 5623\,(7)$ Å^3
$Z = 4$
$D_x = 1.690$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–$12°$
$\mu = 2.429$ mm^{-1}
$T = 295$ K
Irregular
$0.60 \times 0.50 \times 0.40$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.30$, $T_{\max} = 0.38$
2858 measured reflections
2625 independent reflections
2281 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.01$
$\theta_{\max} = 20°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 17$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: not significant

Refinement

Refinement on F
$R = 0.025$
$wR = 0.038$
$S = 1.879$
2281 reflections
317 parameters
$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$
Cs	0.48414 (2)	0.27674 (2)	0.04312 (2)	3.769 (8)
I	0.37970 (2)	0.34614 (2)	−0.14078 (2)	4.705 (9)
O1	0.5878 (2)	0.3766 (1)	0.1760 (2)	2.67 (6)
O2	0.6253 (2)	0.3725 (2)	0.0161 (2)	4.05 (7)
O3	0.6134 (3)	0.2440 (2)	−0.0828 (2)	6.6 (1)
O4	0.5070 (2)	0.1238 (2)	−0.0770 (2)	7.5 (1)
O5	0.3865 (2)	0.1298 (2)	0.0105 (2)	4.57 (8)
O6	0.3975 (2)	0.1853 (2)	0.1685 (2)	2.87 (6)
N	0.6808 (3)	0.0445 (4)	−0.2136 (4)	9.2 (2)
C1	0.6090 (3)	0.4388 (3)	0.1306 (3)	3.9 (1)
C2	0.6611 (3)	0.4166 (3)	0.0759 (3)	4.2 (1)
C3	0.6701 (3)	0.3575 (3)	−0.0422 (3)	5.3 (1)
C4	0.6275 (4)	0.3152 (3)	−0.1072 (3)	5.8 (1)
C5	0.5796 (5)	0.1987 (4)	−0.1465 (3)	13.0 (2)
C6	0.5574 (4)	0.1339 (5)	−0.1298 (4)	11.5 (2)
C7	0.4360 (3)	0.1081 (4)	−0.1067 (3)	6.2 (1)
C8	0.3922 (3)	0.0795 (3)	−0.0499 (3)	6.0 (2)
C9	0.3453 (3)	0.1033 (3)	0.0676 (3)	5.8 (1)
C10	0.3320 (3)	0.1584 (3)	0.1233 (3)	4.3 (1)
C11	0.6026 (2)	0.3873 (2)	0.2559 (2)	2.52 (9)
C12	0.5623 (2)	0.4401 (2)	0.2927 (3)	2.8 (1)
C13	0.5848 (3)	0.4524 (3)	0.3717 (3)	3.4 (1)
C14	0.6419 (3)	0.4115 (3)	0.4121 (3)	3.8 (1)
C15	0.6775 (3)	0.3570 (2)	0.3755 (3)	3.4 (1)
C16	0.6580 (2)	0.3428 (2)	0.2958 (3)	2.8 (1)
C17	0.6994 (2)	0.2847 (3)	0.2562 (3)	3.3 (1)
C18	0.6521 (2)	0.2233 (2)	0.2146 (3)	2.8 (1)
C19	0.6041 (2)	0.1791 (2)	0.2517 (2)	2.45 (9)
C20	0.5565 (2)	0.1275 (2)	0.2113 (3)	2.9 (1)
C21	0.5627 (3)	0.1156 (3)	0.1333 (3)	3.6 (1)
C22	0.6146 (3)	0.1549 (3)	0.0970 (3)	4.1 (1)
C23	0.6568 (3)	0.2091 (3)	0.1374 (3)	3.6 (1)
C24	1/2	0.0833 (4)	1/4	3.7 (2)
C25	1/2	0.4845 (3)	1/4	3.3 (1)
C26	0.7118 (3)	0.0093 (3)	−0.2511 (3)	4.9 (1)
C27	0.7522 (3)	−0.0368 (3)	−0.2978 (3)	4.4 (1)

Table 2. *Selected geometric parameters (Å, °)*

Cs—I	3.7140 (5)	C8—O5	1.399 (7)
Cs—O1	3.313 (3)	O5—C9	1.401 (8)
Cs—O2	3.172 (4)	C9—C10	1.428 (8)

Cs—O3	3.458 (5)	C10—O6	1.423 (6)
Cs—O4	3.510 (5)	O6—C19^{i}	1.394 (6)
Cs—O5	3.192 (4)	O1—C11	1.393 (6)
Cs—O6	3.286 (3)	C11—C12	1.401 (7)
Cs· · ·C13^{i}	3.770 (5)	C11—C16	1.397 (7)
Cs· · ·C14^{i}	3.489 (5)	C12—C13	1.397 (7)
Cs· · ·C15^{i}	3.709 (5)	C12—C25	1.501 (6)
Cs· · ·C21	3.509 (5)	C13—C14	1.386 (8)
Cs· · ·C22	3.273 (5)	C14—C15	1.375 (7)
Cs· · ·C23	3.559 (5)	C15—C16	1.407 (8)
O1—C1	1.449 (6)	C16—C17	1.505 (7)
C1—C2	1.478 (7)	C17—C18	1.524 (7)
C2—O2	1.398 (6)	C18—C19	1.397 (7)
O2—C3	1.405 (7)	C18—C23	1.378 (8)
C3—C4	1.491 (9)	C19—C20	1.394 (7)
C4—O3	1.383 (7)	C20—C21	1.389 (8)
O3—C5	1.45 (1)	C20—C24	1.520 (7)
C5—C6	1.28 (1)	C21—C22	1.393 (8)
C6—O4	1.39 (1)	C22—C23	1.376 (8)
O4—C7	1.355 (8)	N—C26	1.111 (8)
C7—C8	1.437 (9)	C26—C27	1.426 (9)
I—Cs—O1	126.73 (5)	O1—C11—C12	120.2 (5)
I—Cs—O2	91.31 (7)	O1—C11—C16	116.7 (4)
I—Cs—O3	79.99 (9)	C12—C11—C16	123.1 (5)
I—Cs—O4	80.7 (1)	C11—C12—C13	116.8 (5)
I—Cs—O5	85.14 (7)	C11—C12—C25	122.7 (4)
I—Cs—O6	120.22 (6)	C12—C13—C14	121.2 (5)
O1—Cs—O2	53.93 (8)	C13—C12—C25	120.5 (4)
O2—Cs—O3	51.1 (1)	C13—C14—C15	120.7 (5)
O3—Cs—O4	49.4 (1)	C14—C15—C16	120.6 (5)
O4—Cs—O5	49.5 (1)	C15—C16—C11	117.3 (5)
O5—Cs—O6	53.23 (8)	C15—C16—C17	119.9 (5)
C11—O1—C1	113.9 (4)	C11—C16—C17	122.8 (5)
O1—C1—C2	112.2 (4)	C16—C17—C18	115.9 (4)
C1—C2—O2	110.8 (4)	C17—C18—C19	122.7 (5)
C2—O2—C3	112.8 (4)	C17—C18—C23	119.6 (5)
O2—C3—C4	110.6 (5)	C19—C18—C23	117.7 (5)
C3—C4—O3	109.9 (6)	C18—C19—C20	122.0 (5)
C4—O3—C5	111.4 (6)	C19—C20—C21	118.1 (5)
O3—C5—C6	117.0 (9)	C19—C20—C24	122.3 (4)
C5—C6—O4	121.5 (7)	C21—C20—C24	119.6 (5)
C6—O4—C7	116.9 (6)	C20—C21—C22	120.5 (5)
O4—C7—C8	113.4 (6)	C21—C22—C23	119.6 (5)
C7—C8—O5	112.5 (6)	C18—C23—C22	121.8 (5)
C8—O5—C9	114.1 (5)	C12—C25—C12^{i}	115.6 (6)
O5—C9—C10	113.3 (5)	C20—C24—C20^{i}	116.9 (6)
C9—C10—O6	114.1 (5)	N—C26—C27	178.7 (8)
C10—O6—C19^{i}	113.5 (4)		
C12—C11—O1—C1	68.6 (5)	C5—C6—O4—C7	103.6 (8)
C16—C11—O1—C1	−112.0 (4)	C6—O4—C7—C8	164.6 (6)
C11—O1—C1—C2	123.5 (4)	O4—C7—C8—O5	60.9 (7)
O1—C1—C2—O2	69.8 (5)	C7—C8—O5—C9	−179.0 (5)
C1—C2—O2—C3	172.9 (4)	C8—O5—C9—C10	−172.5 (5)
C2—O2—C3—C4	−175.8 (4)	O5—C9—C10—O6	−63.7 (6)
O2—C3—C4—O3	−69.5 (6)	C9—C10—O6—C19^{i}	−125.1 (4)
C3—C4—O3—C5	−173.4 (6)	C10—O6—C19^{i}—C18^{i}	−69.2 (5)
C4—O3—C5—C6	−173.3 (7)	C10—O6—C19^{i}—C20^{i}	110.7 (4)
O3—C5—C6—O4	56 (1)		

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

Data were corrected for Lorentz–polarization effects. The structure was solved using *SHELXS*86 (Sheldrick, 1985) which gave the main part of the structure. Missing atoms were found by subsequent Fourier differences. H atoms were included as riding atoms at calculated positions (C—H = 0.95 Å, B = 6 Å^2). Analytical scattering factors for neutral atoms were corrected for $\Delta f'$ and $\Delta f''$. All calculations were performed on a VAX4000-200 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1233). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Asfari, Z., Bressot, C., Vicens, J., Hill, C., Dozol, J. F., Rouquette, H., Eymard, S., Lamare, V. & Tournois, B. (1995). *Anal. Chem.* **67**, 3133–3139.

Asfari, Z., Naumann, C., Nierlich, M., Thuéry, P., Bressot, C., Lamare, V., Dozol, J. F. & Vicens, J. (1996). *New J. Chem.* In the press.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Fyles, T. M. & Gandour, R. D. (1992). *J. Incl. Phenom.* **12**, 313–332.

Hill, C., Dozol, J. F., Lamare, V., Rouquette, H., Eymard, S., Tournois, B., Vicens, J., Asfari, Z., Bressot, C., Ungaro, R. & Casnati, A. (1994). *J. Incl. Phenom.* **19**, 399–408.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lide, D. R. (1992). Editor. In *Handbook of Chemistry and Physics*, 72nd ed. Boca Raton: CRC Press.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Thuéry, P., Nierlich, M., Bressot, C., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1996). *J. Incl. Phenom.* **23**, 305–312.

Thuéry, P., Nierlich, M., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1996). *J. Incl. Phenom.* Submitted.

Acta Cryst. (1996). C**52**, 2731–2734

A Mixed-Metal Pentanuclear Complex Containing Linked Ni^{II}N$_2$S$_2$ and Cu^{I}I Units

STEPHEN FOX, ROBERT T. STIBRANY, JOSEPH A. POTENZA* AND HARVEY J. SCHUGAR

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903, USA. E-mail: potenza@xstal.rutgers.edu

(*Received 24 July 1995; accepted 29 January 1996*)

Abstract

Bis[(1S,2S)-*trans*-3,3′-(1,2-cyclohexanediyldinitrilo)bis-(2-methylpropane-2-thiolato)]-1$\kappa^4N^1,N^{1'},S^1,S^{1'}$;2$\kappa^4N^2$,-$N^{2'},S^2,S^{2'}$;3$\kappa^2S^1,S^{2'}$;4$\kappa^2S^{1'},S^2$;5$\kappa^2S^{1'},S^{2'}$-triiodo-3$\kappa I$,4$\kappa I$,-5$\kappa I$-tricopper(I)dinickel(II) bis(acetonitrile) solvate, [{Ni(C$_{14}$H$_{28}$N$_2$S$_2$)}$_2$(CuI)$_3$].2CH$_3$CN, is one of a number of possible novel pentanuclear complexes formed from M^{II}N$_2$S$_2$ units with available donating thiolate ligands. In the title compound, three Cu^{I}I groups bridge