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Synthesis and crystal structure of a caesium α-cyanobenzothiazole-α-carbaldehyde oximate complex with a crown ether (L): new evidence for the stability of $[Cs_2L_3]^{2+}$ club sandwiches

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The reaction of Cs_2CO_3, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and α-cyanobenzothiazole-α-carbaldehyde oxime (Hcbto) resulted in the formation of $[Cs_2(18\text{-crown-}6)_3][H(cbto)_2]_2\cdot 2Hcbto\cdot 2H_2O$. X-Ray diffraction analysis revealed a genuine club sandwich centrosymmetric structure for the complex cation $[Cs_2(18\text{-crown-}6)_3]^{2+}$ with one of the crown ligands placed between the two caesium atoms, and is important evidence for the stability of such macrocyclic complexes. The metal atoms adopt twelve-fold co-ordination in a distorted hexagonal-antiprismatic geometry. The 'central' 18-crown-6 molecule displays longer co-ordination interactions Cs–O [3.393(5)–3.636(5), average *ca.* 3.511(5) Å] than the 'border' crown ligand [3.152(7)–3.431(8), average *ca.* 3.265(8) Å]. The caesium atom deviates from the mean plane of the six oxygen atoms by 2.167(1) Å in the first case and 1.640(3) Å in the second. Hydrogen bonding is considered to be important in the crystal packing.

Crown ethers are selective complexing agents for a wide variety of cations, including alkali-, alkaline-earth-metal, lead(II) and thallium(I) ions, and interactions in the M^{n+}–crown ligand systems have been studied in solution as well as in the solid state.[1–5] It was shown that the behaviour of practically every metal ion towards the crown ligands may be controlled by varying its counter anion.[2] Thus, although the cavity of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) seems to be too small to give centrosymmetric complexes $[M(18\text{-crown-}6)]^+$ with most large cations (Rb^+, Tl^+ or Cs^+),[1] such complexes in the solid state may be stable in the case of centrosymmetric single charged counter anions. Hydrogen halides HX_2^- (X = F or Cl),[6] nitrates ($X = NO_3$)[6] or more complex oximates ($X = ONCZ^1Z^2$; Z^1, Z^2 = CN, $CONH_2$ or Heteraryl)[7] may be suggested as suitable anions in this context. Recently we described the crystal structure of an unprecedented thallium(I) hydrogen α-cyanobenzothiazole-α-carbaldehyde oximate complex with 18-crown-6, in which the large thallium atom (ionic radius 1.50 Å[6]) resides exactly in the centre of the crown ether cavity.[7]

We were not successful in the preparation of such compounds for caesium (ionic radius 1.67 Å[6]). Under the conditions used 2:3 caesium–18-crown-6 complexes were isolated, which represent a rarely encountered type of macrocyclic compounds, the so-called triple decker club sandwiches.[1,2,8] The factors affecting the structures of such crown ether complexes are not readily comprehensible[1,2] and crystal structure studies of these species are of special interest in this context. To date only one example of a triple decker club sandwich cation has been reported[8] and practically in all M^{n+}–crown ether systems, reported earlier to have 2:3 stoichiometry, the additional crown ether molecule is not bound to the metal centre but held loosely in the lattice.[2] Herein we describe the synthesis and crystal structure of a new genuine $[Cs_2(18\text{-crown-}6)_3]^{2+}$ club sandwich compound.

Results and Discussion

The structure of the compound $[Cs_2(18\text{-crown-}6)_3][H(cbto)_2]_2\cdot 2Hcbto\cdot 2H_2O$ (Hcbto = α-cyanobenzothiazole-α-carbaldehyde oxime) is depicted in Figs. 1–3. The lattice comprises complex cations $[Cs_2(18\text{-crown-}6)_3]^{2+}$, accompanied in a 1:2 proportion by hydrogen oximate anions $[H(cbto)_2]^-$ and frag-

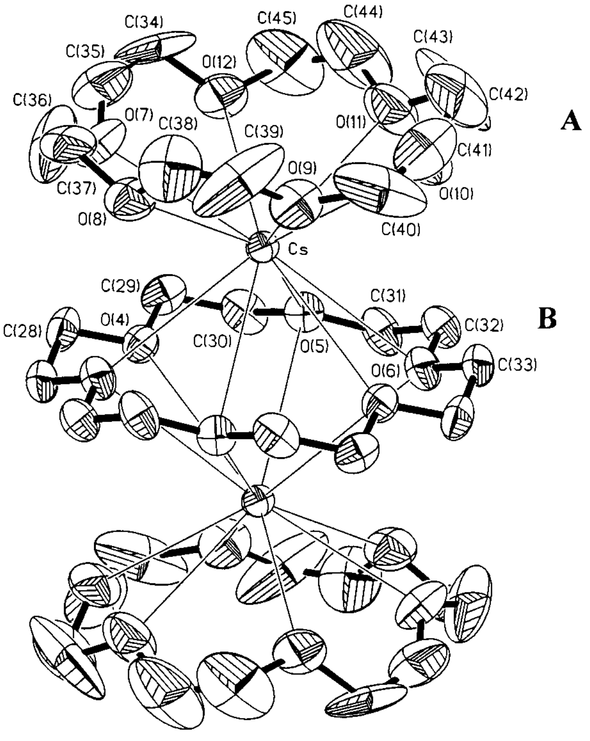
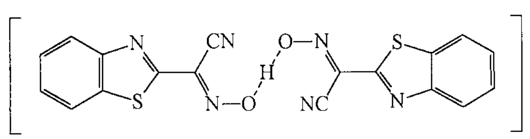
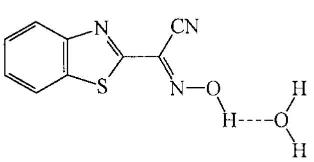


Fig. 1 Perspective view of the $[Cs_2(18\text{-crown-}6)_3]^{2+}$ club sandwich cation represented by 30% probability ellipsoids for thermal motion and showing the atom numbering scheme. Hydrogen atoms are omitted for clarity



$[H(cbto)_2]^-$



$Hcbto\cdot H_2O$

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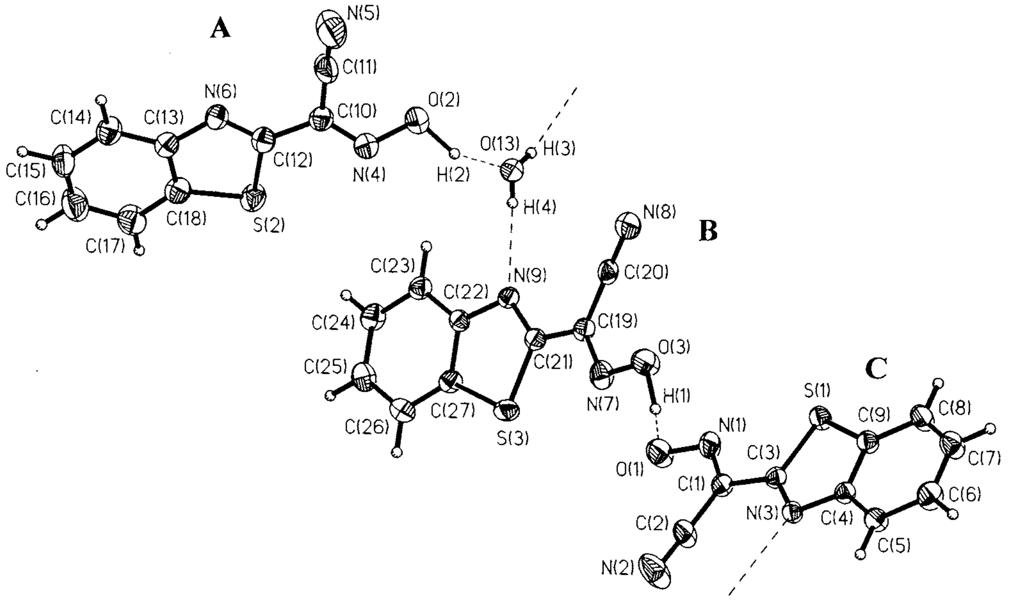

Fig. 2 Perspective view, with 40% probability ellipsoids, of the $[H(cbto)_2]^-$ and $Hcbto{\cdot}H_2O$ moieties, showing the atom numbering scheme

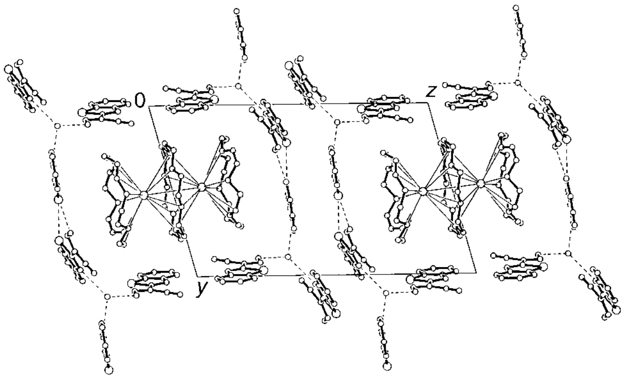

Fig. 3 Fragment of the crystal structure. Projection on the *yz* plane

Table 1 Selected bond lengths (Å) and angles (°) for $[Cs_2(18\text{-crown-}6)_3][H(cbto)_2]_2{\cdot}2Hcbto{\cdot}2H_2O$

Cs–O(4)	3.636(5)	O(3)–N(7)	1.299(5)
Cs–O(4a)*	3.416(5)	N(1)–C(1)	1.298(6)
Cs–O(5)	3.393(5)	N(4)–C(10)	1.290(6)
Cs–O(5a)*	3.636(5)	N(7)–C(19)	1.315(6)
Cs–O(6)	3.546(5)	C(1)–C(2)	1.422(7)
Cs–O(6a)*	3.442(5)	C(10)–C(11)	1.434(9)
Cs–O(7)	3.152(7)	C(19)–C(20)	1.413(7)
Cs–O(8)	3.397(7)	C(1)–C(3)	1.450(6)
Cs–O(9)	3.182(7)	C(10)–C(12)	1.449(7)
Cs–O(10)	3.220(7)	C(19)–C(21)	1.445(6)
Cs–O(11)	3.413(8)	C(2)–N(2)	1.134(7)
Cs–O(12)	3.227(7)	C(11)–N(5)	1.119(8)
S(1)–C(3)	1.740(4)	C(20)–N(8)	1.143(6)
S(2)–C(12)	1.741(5)	C(3)–N(3)	1.286(5)
S(3)–C(21)	1.744(4)	C(12)–N(6)	1.291(6)
O(1)–N(1)	1.305(5)	C(21)–N(9)	1.297(5)
O(2)–N(4)	1.353(5)		
O(4)–Cs–O(5)	46.5(1)	C(28)–O(4)–C(29)	115.0(6)
O(4)–Cs–O(6a)*	45.9(1)	C(30)–O(5)–C(31)	117.9(7)
O(4)–Cs–O(7)	74.9(2)	C(32)–O(6)–C(33)	117.7(7)
O(4)–Cs–O(9)	151.1(2)	C(3)–S(1)–C(9)	88.6(2)
O(5)–Cs–O(6)	47.2(1)	C(12)–S(2)–C(18)	88.4(2)
O(5)–Cs–O(8)	152.1(2)	C(21)–S(3)–C(27)	89.1(2)
O(5)–Cs–O(9)	157.7(2)	C(1)–N(1)–O(1)	113.9(4)
O(6)–Cs–O(7)	154.1(2)	C(10)–N(4)–O(2)	111.5(4)
O(7)–Cs–O(8)	51.6(2)	C(19)–N(7)–O(3)	113.0(4)
O(7)–Cs–O(12)	51.9(3)	C(1)–C(2)–N(2)	178.2(7)
O(8)–Cs–O(9)	49.6(2)	C(10)–C(11)–N(5)	178.3(7)
O(10)–Cs–O(11)	49.4(3)	C(19)–C(20)–N(8)	177.4(5)
Cs–O(4)–Cs(a)*	75.8(1)	N(1)–C(1)–C(3)	117.1(4)
Cs–O(5)–Cs(a)*	76.1(1)	N(4)–C(10)–C(12)	120.1(5)
Cs–O(6)–Cs(a)*	76.7(1)	N(7)–C(19)–C(21)	116.5(4)

* Symmetry transformation used to generate equivalent atom: $-x$, $1 - y$, $2 - z$.

ments of composition $Hcbto{\cdot}H_2O$. The geometrical parameters of the three unique fragments (cbto) do not exhibit essential differences and agree satisfactorily with results obtained from a crystallographic investigation of the $[Tl(18\text{-crown-}6)][H(cbto)_2]$ and $Cs[H(cbto)_2]{\cdot}H_2O$ complexes.[7]

The centrosymmetric $[Cs_2(18\text{-crown-}6)_3]^{2+}$ cation has a 'club sandwich' structure with one of the crown ligands placed between the two caesium atoms (Figs. 1 and 3). The latter adopt twelve-fold co-ordination in a distorted hexagonal-antiprismatic geometry. Thus, in accordance with the most convenient classification of the crown ether complexes, this is a case of complete encapsulation of the caesium atoms by 18-crown-6.[1,2] Both the unique 18-crown-6 molecules are bound to the metal, and the Cs–O separations are within the range 3.152(7)–3.636(5) Å (Table 1), which only slightly exceeds the values for the standard bonding distances (3.03–3.34 Å[2–4]) for the caesium–crown systems. It should be noted here that the 'central' 18-crown-6 molecule (B, Fig. 1) displays longer co-ordination interactions [3.393(5)–3.636(5), average *ca.* 3.511(5) Å], than the 'border' (A) one [3.152(7)–3.431(8), average *ca.* 3.265(8) Å]. The caesium atom deviates from the mean plane of six oxygen atoms by 2.167(1) Å in the first case and 1.640(3) Å in the second. The latter value is typical of the large Cs^+ cation co-ordinated to an 18-crown-6 molecule.[2–4]

Evidently, the caesium–central crown interaction is slightly weaker, in accord with data reported for the unique $[Cs(\mu\text{-}18\text{-crown-}6)Cs]^{2+}$ systems (Table 2).[8–12] It is important, however,[1,2] that in accordance with a centrosymmetric structure of the $[Cs_2(18\text{-crown-}6)_3]^{2+}$ moiety in the present compound, the central crown molecule maintains equally effective Cs–O interactions on both axial sides simultaneously. Thus the cation $[Cs_2(18\text{-crown-}6)_3]^{2+}$ can be regarded as an example of the almost perfect club sandwich structure.[8]

Although, the cation $[Cs_2(18\text{-crown-}6)_3]^{2+}$ has also been observed in the crystal structure of $[Cs_9(18\text{-crown-}6)_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$,[8] its formation, in accordance with Bajaj and Poonia,[2] should be described as the result of the additional moiety–moiety interactions under forcing conditions. Thus, the Cs–O separations in this case have a much

Table 2 Geometry of the Cs(μ-18-crown-6)Cs fragment in crystal structures

Cation	Anion	Cs–O/Å		Cs···Cs/Å	d^a/Å	Ref.
		Range	Average			
$[Cs_2(18\text{-crown-6})]^{2+}$	$[(p\text{-}MeC_6H_4)N{=}NNN{=}N(C_6H_4Me\text{-}p)]^-$	3.207(7)–3.510(8)	3.382(8)	3.940(4)	1.970(4)	9
$[Cs_2L]^{2+b}$	S_6^{2-}	3.11(1)–3.55(1)	3.33(1)	4.022(4)	2.011(4)	10
$[Cs_2(18\text{-crown-6})]^{2+c}$	$[SO_4(AlMe_3)_3]^{2-}$	3.13(1)–3.49(1)	3.29(1)	3.923(4)	1.785(5)	11
		3.34(1)–3.59(1)	3.49(1)		2.135(5)	
$[\{Cs(18\text{-crown-6})\}_\infty]^{\infty+}$	$[(TcNCl_4)_\infty]^{\infty-}$	3.34(1)–3.68(1)	3.51(1)	4.275(4)	2.138(4)	12
$[Cs_2(18\text{-crown-6})_3]^{2+c}$	$[Rh_{22}(CO)_{35}H_x]^{5-}$,	3.29(8)–4.25(8)	3.75(8)	4.755(4)	2.41(8)	8
	$[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$	3.35(8)–3.96(8)	3.70(8)		2.34(8)	
$[Cs_2(18\text{-crown-6})_3]^{2+}$	$[H(cbto)_2]^-$	3.393(5)–3.636(5)	3.515(5)	4.335(1)	2.167(1)	This work

[a] Deviation of cation from the mean oxygen atoms plane. [b] L = Dibenzo-18-crown-6 = 6,7,9,10,17,18,20,21-octahydrodibenzo[*b*, *k*][1,4,7,10,13,16]-hexaoxacyclooctadecine. [c] The central 18-crown-6 molecule forms unequal axial contacts with caesium atoms.

Table 3 Geometry of the hydrogen bonding

Donor (D)	Hydrogen atom (H)	Acceptor (A)	Separation (Å)			Angle D–H···A/°
			D–H	A···H	D···A	
O(3)	H(1)	O(1)	1.17(10)	1.32(10)	2.478(5)	170(8)
O(2)	H(2)	O(13)	1.06(9)	1.52(9)	2.520(5)	155(7)
O(13)	H(3)	N(3b)*	0.78(7)	2.16(8)	2.930(6)	170(7)
O(13)	H(4)	N(9)	0.71(6)	2.18(6)	2.877(6)	165(7)

* Symmetry transformation used to generate equivalent atom: −1 + *x*, 1 + *y*, *z*.

wider range [3.29(8)–4.32(8) Å, Table 2][8] than those observed for the present compound and other caesium–18-crown-6 species.[8–12] Another comparable structural precedent is the unique crystal structure of a [Cs(18-crown-6)][$TcNCl_4$] complex,[12] containing polymeric cations $[\{Cs(18\text{-crown-6})\}_\infty]^{\infty+}$ of an ‘infinite sandwich’. In this case the Cs–O [average *ca.* 3.51(1) Å] and Cs···Cs [4.275(4) Å, Table 2] separations are actually equal to those observed in the present compound (Tables 1, 2), suggesting the close structural resemblance in the Cs(μ-18-crown-6)Cs bridging.

The central 18-crown-6 molecule (B) is centrosymmetric and exists in the D_{3d} conformation, the most stable conformation for this ligand in complexes with metal ions.[13] Both the C–O [1.357(8)–1.377(9), average *ca.* 1.36(1) Å] and C–C [1.42(1)–1.44(1), average *ca.* 1.43(1) Å] distances are slightly shortened with respect to the standard separations in crown ethers (C–O 1.43 ± 0.02, C–C 1.49 ± 0.02 Å[14]). This phenomenon is well known for macrocyclic compounds and has been ascribed to an artificial effect arising from curvilinear vibrations.[12,15] The high thermal motion of the atoms of the border 18-crown-6 molecules (A) (Fig. 1) indicates possible disorder, which may be attributed to the large size of the $[Cs_2(18\text{-crown-6})_3]^{2+}$ cation and the insensitivity of the packing to the conformation of the crown molecules.[8,12,16] The high thermal motion precludes further discussion. We note, however, that the oxygen atoms O(7)–O(12) are actually coplanar, the maximum deviation from their mean plane being *ca.* 0.046(6) Å.

Considering the club sandwich cation stability of the present compound, it is suggested that moiety–moiety interactions are important in the packing of the anionic part of the structure. A similar conclusion was reached by Baldas *et al.*[12] for [Cs(18-crown-6)][$TcNCl_4$].

There are four types of hydrogen bonds involving both the NOH groups and water of crystallization (Table 3). The strong, nearly symmetrical, hydrogen bond O(1)···O(3) of *ca.* 2.478(5) Å connects the appropriate fragments L (B and C, Fig. 2) in the hydrogen oximate anion $[H(cbto)_2]^-$, which is a typical feature, *cf.* [Tl(18-crown-6)][$H(cbto)_2$] documented earlier.[7] The hydrogen bonding involving fragments of composition Hcbto·H_2O links the neighbouring anions [(*x*, *y*, *z*) and (−1 + *x*, 1 + *y*, *z*)] to give chains along the 0*y* direction (Figs. 2 and 3). The distance O(2)···O(13) in the Hcbto·H_2O fragment of *ca.* 2.520(5) Å and both the distances O(13)···N(9) 2.877(6) and O(13)···N(3b) (−1 + *x*, 1 + *y*, *z*) 2.930(6) Å together with the appropriate angles at the hydrogen atoms (Table 3) also indicate relatively strong hydrogen bonding.[6,17]

Between the hydrogen-bonded chains in the crystal, considerably shortened van der Waals contacts S(1)···S(2c) (1 + *x*, *y*, *z*) 3.461(2) Å are observed (r_s ⟨van der Waals⟩ 1.85 Å[6]), which connect neighbouring chains [(*x*, *y*, *z*) and (1 + *x*, *y*, *z*)] into layers running parallel to the *xy* plane (Fig. 3). A similar type of sulfur–sulfur interactions was described earlier for thiadiazole derivatives.[18] The layers pack one on top of the other, yielding linear channels running down the 0*x* direction. These are filled with the large $[Cs_2(18\text{-crown-6})_3]^{2+}$ cations (Fig. 3). Apparently, the cations are held inside the channels by electrostatic forces, which is typical for structures involving large cations.[19] Thus, we may conclude that the crystal packing of the present compound differs from that of $[Cs_9(18\text{-crown-6})_{14}]^{9+}$-$[Rh_{22}(CO)_{35}H_x]^{5-}$$[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$ and therefore cannot be an obvious reason to discuss the $[Cs_2(18\text{-crown-6})_3]^{2+}$ cation structure in terms of forced conditions.[1,2] Moreover, for similar systems the stability of the higher ‘club sandwiches’ with 18-crown-6 may be assumed.[12]

Experimental

The compounds Cs_2CO_3 and 18-crown-6 were commercial products of reagent grade, used without further purification. The oxime was prepared as described previously.[20]

Preparation of caesium–18-crown-6 derivative

To a hot solution of the oxime (0.202 g, 1.0 mmol) in 95% ethanol (40 cm^3) was added Cs_2CO_3 (0.163 g, 0.5 mmol). The mixture was stirred for 20 min and then 18-crown-6 (0.264 g, 1.0 mmol) and additional Hcbto (0.202 g, 1.0 mmol) were added. The clear yellow solution obtained on standing yielded yellow prismatic crystals suitable for X-ray diffraction. The yield was 0.51 g (65% with respect to the oxime used) (Found: C, 47.1; H, 4.4; N, 11.0. Calc. for $C_{90}H_{104}Cs_2N_{18}O_{26}S_6$: C, 46.8; H, 4.5; N, 10.9%).

Crystallography

Measurements were made on an Enraf-Nonius CAD-4 diffractometer with Mo-Kα radiation (λ = 0.710 73 Å) operating in the ω–2θ scan mode. Accurate unit-cell parameters and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 24 reflections in the range 13 < θ < 15 °. The essential experimental conditions and resulting crystal data are given in Table 4. The structure was solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation using

Table 4 Crystal data for $[Cs_2(18\text{-crown-}6)_3][H(cbto)_2]_2\cdot 2Hcbto\cdot 2H_2O$

Formula	$C_{90}H_{104}Cs_2N_{18}O_{26}S_6$
M	2312.1
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.598(2)
b/Å	13.465(3)
c/Å	20.235(4)
α/°	75.31(3)
β/°	89.99(3)
γ/°	71.42(3)
U/Å^3	2637.4(9)
Z	1
D_c/g cm^{-3}	1.456
μ(Mo-Kα)/cm^{-1}	8.89
F(000)	1184
θ Range for data collection/°	1.0–22.5
Total number of reflections	7349
Number of unique reflections	6896 (R_{int} 0.023)
Number of observed reflections [$I > 2\sigma(I)$]	5701
Data used	6895
Parameters refined	656
$R1$(obs.), $R1$(all data)	0.044, 0.067
$wR2$(obs.), $wR2$(all data)	0.119, 0.132
Goodness of fit on F^2	1.082
Data-to-parameter ratio	10.5
Maximum, minimum difference peaks/e Å^{-3}	0.49, −0.44

SHELXS 86 and SHELXL 93.[21,22] Absorption corrections were not applied. All O-bonded hydrogen atoms were located from the Fourier-difference syntheses and refined isotropically. The positions of the CH hydrogen atoms were idealized and included in the calculations with their isotropic U values invariant at 0.08 Å^2. Judging by the large values of U [0.152(3)–0.39(3) Å^2] and poor bond distances and angles in the OCH_2-CH_2O linkage of macrocyclic molecule A (Fig. 1) this molecule is disordered. All attempts to divide the oscillatory movement between two positions with partial occupancies of 50% were not successful.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/397.

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