From *p*-Dimethoxybenzene to Crown-Benzenophanes, 4[◇]

Cation-Complexing Properties of Bis(*p*-phenylene-34-crown-10) – A Structural and Spectrophotometric Study

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The title compound **2**, an electron-rich macrocyclic paracyclophane of the coronand type, known to form a charge-transfer complex with paraquat, was found to encapsulate strontium cations and to bind to magnesium cations. X-ray analysis revealed that **2** forms a 2:1 (metal/substrate) complex with $Sr(ClO_4)_2$, in which the two benzene rings weakly overlap, whereas in the single crystals grown from $Mg(ClO_4)_2$, the metal cation prefers to lie outside the coronand (1:1 stoichiometry). In acetonitrile solution, cations were observed to trigger an hypsochromic shift of the UV absorption spectra, proportional to their size and charge density. The stoichiometries and binding constants were also determined by UV absorption titration in acetonitrile using the LETAGROP-SPEFO program for several monovalent and divalent cations. For Na^+, Ca^{2+}, and Sr^{2+}, 1:1 and 2:1 complexes were shown to be formed. In the free ligand, a weak interaction between the benzene rings was detected by fluorescence decay kinetic analysis, indicating the presence of two conformer populations within the nanosecond time scale. In solution, metal cations neither induce detectable excimer formation nor seem to have a strong influence on the fluorescence emission spectra, except a heavy atom quenching with $Sr^{2+}$and Ba^{2+}, in contrast to the effect observed in absorption. However, Sr^{2+} and Mg^{2+}induce a clear hypsochromic shift in the single crystal fluorescence spectra. Compound **2** was prepared by a new and efficient route which is compared to the previous procedures.

The design of sensoring devices capable of ion recognition has raised a considerable interest in the past thirty years[1]. Their broad applications to the selective detection of metal ions involved in biological processes[2a,b] (sodium, potassium, calcium, magnesium) as well as to pollution investigation[2c,d] (lead, mercury, cadmium, strontium, ...) underline the versatile features of these molecular probes.

Among the diverse detection methods presently available, optical-based techniques are often preferred as they satisfy threshold criteria of selectivity, sensitivity, and time response. As a result, small complexing molecules incorporating a chromophore subunit have been found to be excellent sensors since the complexation of an ionic analyte within the cavity can induce a related change in the optical properties[3].

Crown ethers connected to diversely substituted benzene rings proved to be efficient and easy to handle agents[4]. Since the discovery of the metal cation binding properties of bis-orthophenylene crown ethers **1** by Pedersen[5], extensive studies revealed that **1** forms complexes of various stoichiometries (1:1, 1:2, 2:1, 2:2) with alkaline or alkaline earth cations in solution or in the solid state[6]. The *p*-phenylene unit was also successfully incorporated into a wide range of crown compounds[7], particularly the electron-rich bis(*p*-phenylene-34-crown-10) (**2**) (denoted here as BBO_5O_5; Scheme 1) composed of two benzene rings (soft basic sites) linked by two tetraethylene glycol chains (hard basic sites) which confer a high conformational flexibility to the molecule.

Stoddart and coworkers[7b] showed that **2** readily accommodates a paraquat molecule within its large cavity (10.6 × 4.7 Å) to generate a 1:1 charge transfer complex, which

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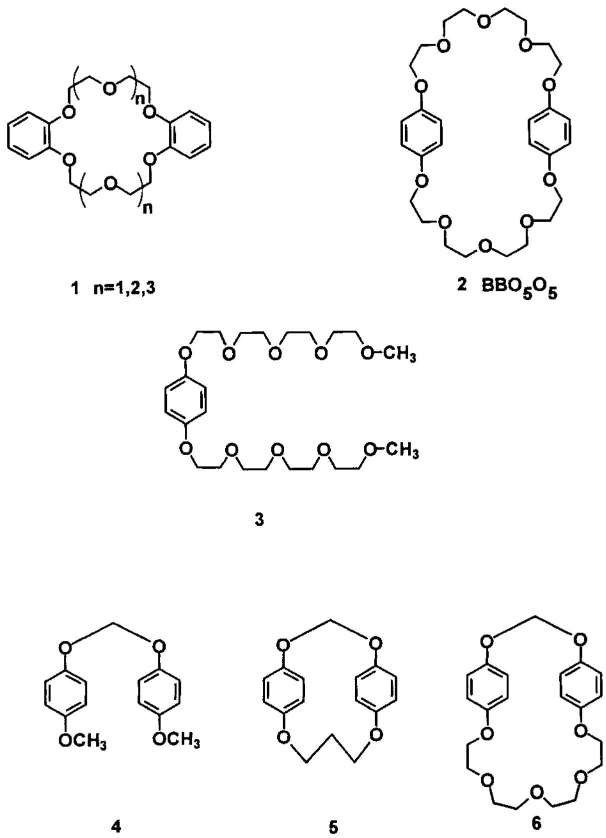
proved essential to the elegant synthesis of a new class of catenanes and rotaxanes[1f–7d].

Although **2** does not possess the typical structure of an ideal crown ether (alternation of one oxygen and two carbon atoms as in **1**) it was shown to form weak complexes of unknown stoichiometry with alkaline cations in solution[7c]. No data were available concerning divalent metal cations in solution or in the solid state.

In preceding papers[11,8] we investigated the gradual change of spectroscopic properties of molecules incorporating the paradimethoxybenzene subunit **4**, **5**, **6** (Scheme 1). Compounds **5** and **6** were found to behave as strained cyclophanes exhibiting an intramolecular interaction between the two benzene rings. Owing to its conformational mobility and larger size, BBO_5O_5 was expected not to display such an interaction.

Scheme 1



1 n=1,2,3

2 BBO_5O_5

3

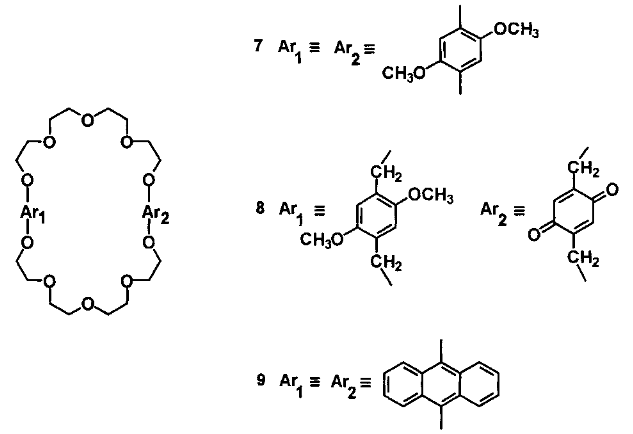
4

5

6

In this paper we report on the first X-ray structure analysis of single crystals of **2** associated to $Sr(ClO_4)_2$ and $Mg(ClO_4)_2$, respectively, as well as on the determination of the stoichiometry and association constants of some complexes in solution using UV absorption spectrometry. Interestingly, **2** was shown to display complexing properties in clear contrast to those of a previously studied anthraceno coronand analogue[3j] **9** (Scheme 2). We also describe the fluorescence properties of **2** in the presence and in the absence of cations and, finally, another useful stepwise method to synthesize **2**.

Scheme 2



1. X-ray Structure Determination of BBO_5O_5

In the solid state, BBO_5O_5 was shown to exist in two centrosymmetric crystallographically independent conformations in the same unit cell[9]. Both of them display an *open-box-shaped conformation* in which the benzene rings partially overlap; in one conformation, the aromatic plane-to-aromatic plane van der Waals distance is about 4.7 Å, whereas the center-to-center ring distance is ca. 7.2 Å; the length of the box is about 10.6 Å. Attempts to obtain suitable crystals of metal cation complexes of BBO_5O_5 met with success for Mg^{2+} and Sr^{2+}; their X-ray structures are described below, showing particularly the profound influence of the metal cations on the geometry of **2** which contrasts with the weak perturbations induced by the inclusion of paraquat[7b].

Mg^{2+}-Complex: Single crystals were grown at room temperature by slow evaporation of a CH_3OH/H_2O (7:3) solution of **2** and $Mg(ClO_4)_2$. The asymmetric unit cell contains one molecule of **2** for one molecule of $Mg(ClO_4)_2$ and also incorporates six molecules of water grouped around the cation located outside the crown ether part. The shape of the receptor is clearly different from that of the free ligand. Although the cation is not included into the crown ether part, its presence in the crystal (including that of the anions and the molecules of water) induces a closer proximity of the benzene rings: these are almost parallel and their mutual distances have decreased to 3.42 Å (plane-to-plane) and 5.35 Å (center-to-center). Nevertheless, their mutual interactions remain weak. The length of the molecule reaches 14.2 Å (Figure 1). The mean planes of the polyoxyethylene chains form an angle of about 50° with respect to the benzene rings. The cation Mg^{2+} is highly hydrated. The octahedron of coordination is almost perfect (Figure 2 and Table 1). Atomic coordinates and equivalent isotropic temperature factors are shown in Table 2. Bond lengths and angles are listed in Table 1a (for numbering see Scheme 3a).

Two types of Mg^{2+}/crown ether complexes are reported in the literature. An inclusion complex was observed[10] between benzo-15-C-5 and $Mg(SCN)_2$ in which the cation is situated inside the complexing cavity, the coordination number being equal to seven. In the case of 12-C-4, an ex-

Figure 1. Ball-and-stick representations of the [$Mg(ClO_4)_2 \cdot 6\ H_2O$] · **2** complex in the crystal

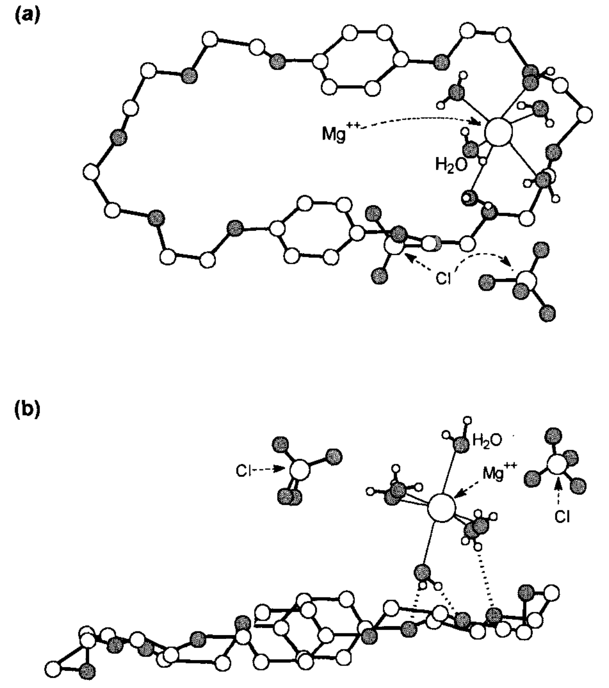


Figure 2. Octahedron of coordination of Mg^{2+} in the Mg^{2+} · **2** complex

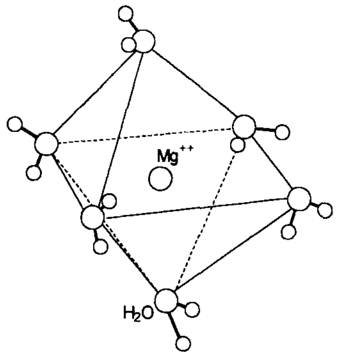


Table 1. Distances (Metal^{2+} ··· O) in the crystalline complexes; (a) [$Mg(ClO_4)_2 \cdot 6\ H_2O$] · **2** and (b) [$Sr(ClO_4)_2 \cdot 4\ H_2O$] ⊂ **2**; $r_{vdw}(O)$ = 1.51 Å, $r_i(Mg^{2+})$ = 0.65 Å, $r_i(Sr^{2+})$ = 1.13 Å[30]

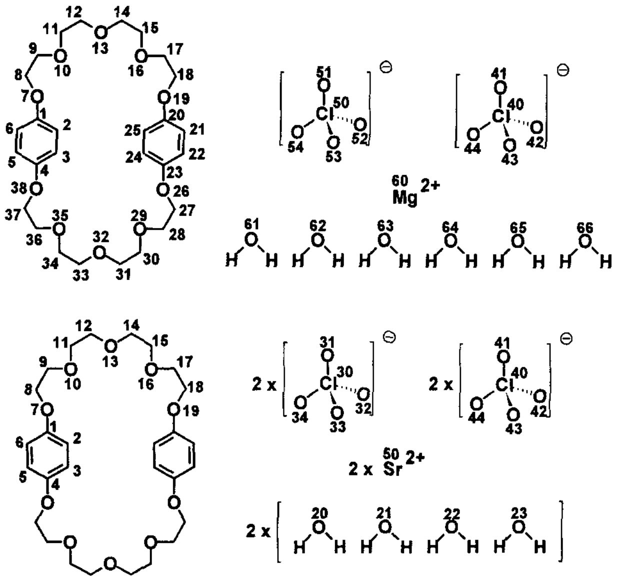
(1a)

Oxygen atoms of water	
$Mg^{2+}\cdots O(61)$	2.05(1)Å
$Mg^{2+}\cdots O(62)$	2.07(1)Å
$Mg^{2+}\cdots O(63)$	2.10(1)Å
$Mg^{2+}\cdots O(64)$	2.10(1)Å
$Mg^{2+}\cdots O(65)$	2.05(2)Å
$Mg^{2+}\cdots O(66)$	2.02(2)Å

(1b)

Oxygen atoms		Oxygen atoms of water	
$Sr^{2+}\cdots O(7)$	2.723(6)Å	$Sr^{2+}\cdots O(20)$	2.549(7)Å
$Sr^{2+}\cdots O(10)$	2.560(10)Å	$Sr^{2+}\cdots O(21)$	2.531(7)Å
$Sr^{2+}\cdots O(13)$	2.618(8)Å	$Sr^{2+}\cdots O(22)$	2.660(20)Å
$Sr^{2+}\cdots O(16)$	2.612(7)Å	$Sr^{2+}\cdots O(23)$	2.570(10)Å
$Sr^{2+}\cdots O(19)$	2.819(6)Å		

Scheme 3



ternal complex was formed with $MgCl_2 \cdot 6\ H_2O$, with a coordination number of six[11].

In the present work, the two complexing loops are flexible compared to the above-mentioned species and the cavity is not preformed. The small Mg^{2+} cation forms a molecular complex with six cation-coordinating water molecules as with 12-crown-4. Mg^{2+} is not directly chelated to the oxygen atoms of the macrocycle, but is connected in the lattice via hydrogen bonds to one crown ether molecule and its counterpart by the (x, $2 - y$, $1/2 + z$) symmetry and to the two perchlorate anions.

The projection of the cell along [010] reveals a two-dimensional network of alternating inorganic layers (hexahydrated magnesium ions) and organic layers **2** (Figure 3).

Sr^{2+} Complex: Single crystals were grown from $Sr(ClO_4)_2$ and **2** in CH_3OH/H_2O (7:3) solution at room temperature. **2** forms a 2:1 centrosymmetric complex where the Sr^{2+} cations lie inside two cavities (Figure 4). Each cation is coordinated to five oxygen atoms of **2** and four additional molecules of water. The distance between the cations is 8.82 Å. The mutual distances of the centrosymmetric – then parallel – benzene units are 3.60 Å (plane-to-plane, slightly increased compared to the complex of Mg^{2+}) and 4.50 Å (center-to-center). The length of the molecule reaches 13.7 Å. Similarly to the Mg^{2+} complex, the mean planes of the polyoxyethylene chains form an angle of about 53° with respect to the benzene units. The structure of the (2:1) Sr^{2+} complex is more compact than that of the (1:1) Mg^{2+} complex. In contrast to a similar (2:1) complex between Na^+ and an analogous bisanthraceno-coronand (AAO_5O_5 **9**)[12], the aromatic rings do not overlap in the 2 Sr^{2+} ⊂ **2** (Figure 4).

In the present work, the coordination number of Sr^{2+} is nine (as often found for this cation[13–16]), see Table 1b and

Figure 3. Two-dimensional diagram of the crystal structure $[Mg(ClO_4)_2 \cdot 6\ H_2O] \cdot$ **2** along the [010] direction

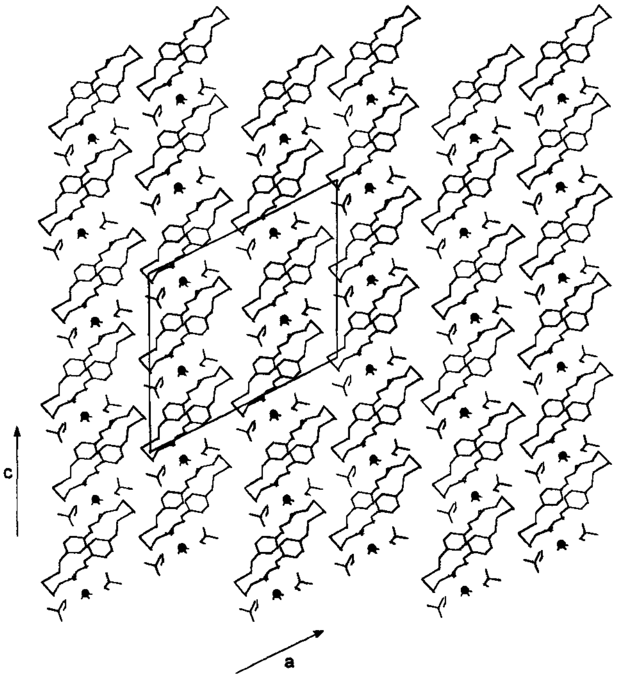
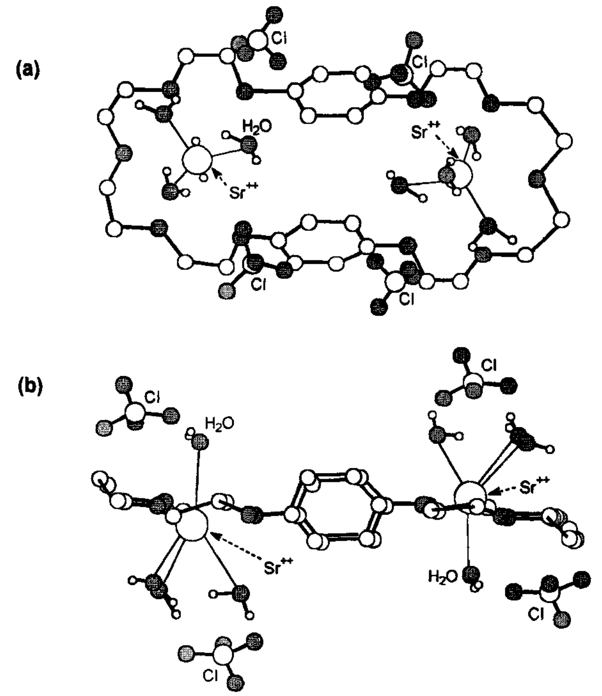


Figure 4. Ball-and-stick representations of the $[Sr(ClO_4)_2 \cdot 4\ H_2O] \cdot$ **2** complex in the crystal; in projection (b), the aromatic rings do not overlap



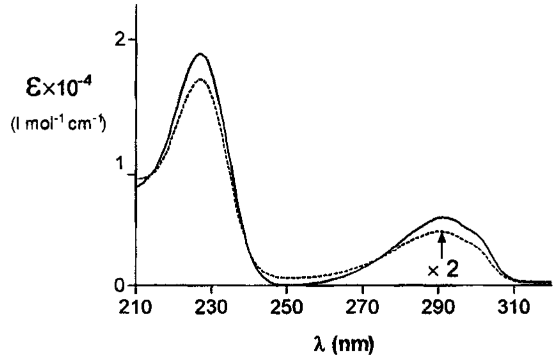
Scheme 3b for numbering. The nine oxygen atoms surrounding Sr^{2+} are situated at a distance varying from 2.53 to 2.82 Å. This distance is approximatively the sum of the ionic radius of Sr^{2+} and the van der Waals radius of oxygen (the shortest bonds involve the four molecules of water) except for the phenolic oxygens atoms no. 7, 19, 26 and 38. The perchlorate counter ions do not directly interact with Sr^{2+} but are linked via hydrogen bonds to the water molecules coordinating the cation. Moreover, it is important to mention that each aromatic ring is conjugated (via one n orbital) with one oxygen atom only.

The diameter of the cation matches well the size of the ligand cavity, which in turn, is able to adapt its own shape to the Sr^{2+} cations.

2. UV Absorption Spectroscopy

a) Free Ligand: The spectrophotometric studies were conducted in CH_3CN rather than CH_3OH to solubilize a sizeable amount of salts and to achieve larger binding constants[3j]. In contrast to compounds **4** and **5**, the UV spectrum of **2** resembles that of the reference compound **3** (Figure 5, one notes only a slight hyperchromic effect). This indicates (i) that in **2** the two benzene rings, in acetonitrile, seem to behave independently from each other in the ground state (no significant solvent effect was observed either), and (ii) that the juxtanuclear oxygen n orbitals are conjugated with the aromatic π clouds[8b] as in the reference compound **3**.

Figure 5. UV absorption spectra of **2** (—) and **3** (---) in CH_3CN at +20°C



b) In the Presence of Salts: The dominant feature is a *hypsochromic shift* induced by the presence of cations on both absorption bands (291 and 226.5 nm); the larger the *size* (compare Li^+ and Na^+ or Ca^{2+} and Sr^{2+}) and the *charge density* of the cation (compare Na^+ and Ca^{2+}), the stronger the *shift* (Table 2). This effect is connected with the coordination of the *phenolic* oxygen atoms with the encapsulated cation, which raises the energy of the electronic transitions by decreasing the conjugation of the oxygen lone pairs with the benzene ring[17]. Interestingly, Mg^{2+} was found to have no influence on the UV transitions (Figure 6).

3. Fluorescence Emission Spectroscopy

3.1 Stationary State Spectra

a) The Free Ligand: The comparison of the fluorescence emission spectrum of **2** in CH_3CN with that of the reference monochromophoric molecule **3** (Figure 7) shows only small differences (vide infra the fluorescence lifetimes) with no detectable excimer emission (the excimer maximum wave-

Figure 6. UV absorption spectra of **2** in the absence (—) and in the presence of cations $NaClO_4$ (- - -), $Sr(ClO_4)_2$ (···) in CH_3CN at +20 °C, respectively

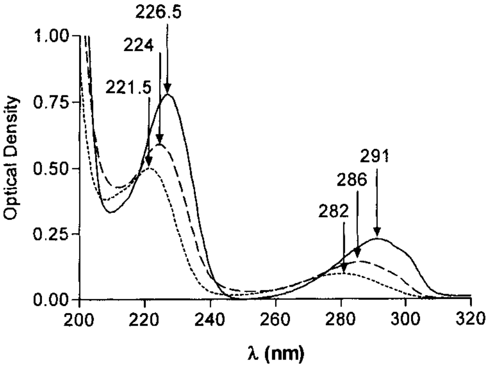
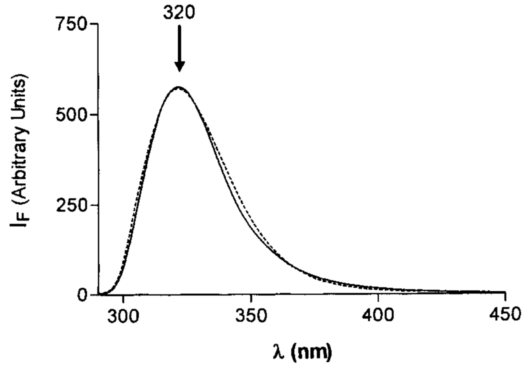


Table 2. Maximum wavelengths of the UV spectra of **2** ($c \approx 10^{-5}$ M) free of salt and in the presence of a large excess ($c \approx 10^{-1}$ M) of perchlorate salts in CH_3CN at +20 °C; $\Delta\tilde{\nu}$ represents the hypsochromic shifts

Added salt	None	$Li(ClO_4)$	$Na(ClO_4)$	$Mg(ClO_4)_2$	$Ca(ClO_4)_2$	$Sr(ClO_4)_2$	$Ba(ClO_4)_2$
λ_1 (nm)	291	289.8	286	291	284	282	282
$\Delta\overline{\nu}_1$ (cm^{-1})	—	142	601	0	847	1097	1097
λ_2 (nm)	226.5	226.2	224	226.5	223	221.5	221
$\Delta\overline{\nu}_2$ (cm^{-1})	—	59	493	0	693	997	1099
Ionic radii[30] (Å)	—	0.68	0.95	0.65	0.99	1.13	1.35

length is known[8b] to appear at ca. 370 nm). However, the fluorescence quantum yield (ϕ_F: 0.18) is lower than that of the reference **3** (ϕ_F: 0.24), presumably as a result of some intramolecular bichromophoric quenching. Thus, the benzenic subunits of BBO_5O_5 do not behave completely independently in the relaxed excited singlet state (vide infra the transient kinetic analysis).

Figure 7. Corrected fluorescence spectra normalized at 320 nm of **2** (—) and of the reference molecule **3** (---) in CH_3CN at +20 °C ($c \approx 2.5 \times 10^{-5}$ M, $\lambda_{exc} = 280$ nm)



b) In the Presence of Salts: In the presence of the salts investigated, the fluorescence emission spectra (CH_3CN) exhibit a small hypsochormic shift ($\Delta\tilde{\nu} \approx 200$ cm^{-1}) and some quenching increasing with the salt concentration[19c] (Figure 8 and Table 3), except for Mg^{2+} which shows no detectable influence; the quenching, significant for Sr^{2+} and Ba^{2+}, could be attributed mainly to a heavy-atom effect[19a,c]. That there is *virtually no difference* in the *position* and the *shape* of the emission spectrum whatever the nature of the cation (in contrast to the absorption spectra) might be related, at least in part, to a *relaxed excited state* where the cations are *no longer associated with the phenolic oxygen* atom with the result that the fluorescence spectrum resembles that of the free ligand (Figure 8). Evidence of such phenomena was very recently given for related complexing systems where *nitrogen* atoms are directly linked with the aromatic ring[19a,b]. Further experiments involving femtosecond or picosecond spectroscopy are necessary to shed more light on this question.

3.2 Transient Kinetic Analysis in Solution

The fluorescence decay of **2** in the absence and in the presence of a large excess of salts was recorded by the single photon-timing technique; the data are listed in Table 4 (some measurements were also made in CH_3OH where the same trends were observed). Three conclusions can be drawn: (i) in contrast to the reference molecule **3**, whose decay clearly follows a single exponential function, a biex-

Figure 8. Corrected fluorescence spectra of the free ligand **2** (—) ($c = 2.85 \times 10^{-5}$ M, $\lambda_{exc} = 280$ nm) and in the presence of a large excess (10^{-1} M) of $Ca(ClO_4)_2$ (···), $NaClO_4$ (---), $Sr(ClO_4)_2$ (–·–), $Ba(ClO_4)_2$ (–··–) in CH_3CN at +20 °C ($\lambda_{exc} = 280$ nm), respectively

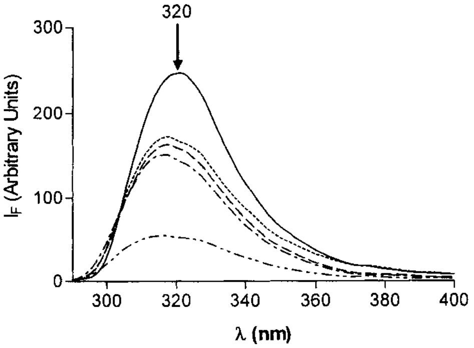


Table 3. Corrected fluorescence-emission maximum wavelength and quantum yield of **2** ($c \approx 2.5 \times 10^{-5}$ M) in the absence and in the presence of an excess of perchlorate salt ($c \geq 10^{-1}$ M, $\lambda_{exc} = 280$ nm) in degassed CH_3CN at +20 °C

Added salt	none	$Na(ClO_4)$	$Ca(ClO_4)_2$	$Sr(ClO_4)_2$	$Ba(ClO_4)_2$
λ_{max}	320	318	318	318	318
Φ_F	0.18	0.15	0.16	0.09	0.05

ponential function is necessary for compound **2**. This means that BBO_5O_5 displays two conformer populations in the excited state within the nanosecond range, one of which could explain the higher fluorescence quenching found for **2**. (ii) Mg^{2+} also induces a biexponential decay in solution perhaps through a weak interaction between BBO_5O_5 and the hydrated salt. (iii) The single exponential decay for the strontium inclusion complex ($1/\lambda = 2.63$ ns) could be assigned to the occurrence of only one fluorescent species similar to that revealed in the crystal ($1/\lambda = 2.60$ ns) (see Table 4). This interpretation also applies to Ca^{2+}.

Table 4. Fluorescence decay ($\lambda_{exc} = 289$ nm) of degassed diluted ($c \approx 10^{-5}$ M) solutions (CH_3OH and CH_3CN) of **2** at +20°C in the absence and in the presence of perchlorate salts ($c \geqslant 10^{-1}$ M)[a]; A_1 and A_2 are the preexponential factors, $1/\lambda_n$ the time constants and χ^2 the statistical factor

Solvent	Cation	λ_{obs}	A_1	$1/\lambda_1$ (ns)	A_2	$1/\lambda_2$ (ns)	χ^2	Ionic radii[30] (Å)
CH_3CN	none	330	0.7	0.78	0.8	3.75	1.04	—
"	Na^+	"	1.0	1.17	0.4	4.81	1.10	0.98
"	Mg^{2+}	"	0.5	1.08	0.8	2.76	1.06	0.78
"	Ca^{2+}	"	—	—	1.1	2.84	1.15	1.06
"	Sr^{2+}	"	—	—	1.1	2.63	1.14	1.27
"	Ba^{2+}	"	1.4	0.78	0.0	5.49	1.13	1.43
CH_3OH	none	316	1.0	0.62	0.4	4.42	1.03	—
"	Na^+	306	0.4	0.59	0.2	4.46	1.00	0.98
"	Na^+	350	1.3	0.69	0.4	4.61	1.06	0.98

[a] The decay of the reference molecule **3** was found to follow a single exponential curve under the same experimental conditions: $1/\lambda_1 = 2.68$ ns in CH_3CN.

3.3 Single-Crystal Fluorescence Emission

Figure 9. Corrected fluorescence-emission spectra of single crystals of **2** (—) and of its $Mg(ClO_4)_2$ (---) and $Sr(ClO_4)_2$ (···) complexes

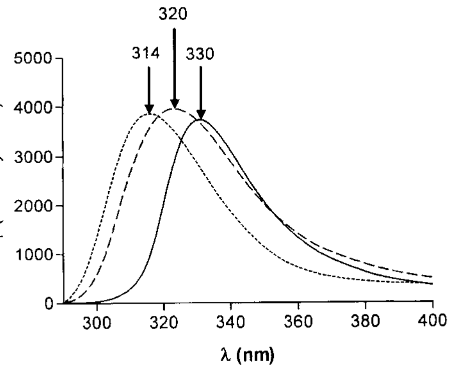


Table 5. Fluorescence emission maximum wavelength of single crystals of free **2**, (Mg^{2+}, **2**), (2 $Sr^{2+} \subset$ **2**); A represents the preexponential factor, $1/\lambda$ the time constant and χ^2 the statistical factor

	λ_{max} (nm)	A	$1/\lambda$ (ns)	χ^2
2	330	0.24	2.06	1.02
Mg^{2+}, **2**	320	0.11	1.60	1.30
$2Sr^{2+}\subset$**2**	314	0.69	2.60	1.07

The single-crystal fluorescence emission of **2** and its Mg^{2+} and Sr^{2+} complexes was recorded in order to tentatively compare the spectra of known structures (solid state) with those of unknown structures (preferred conformations in fluid solution at room temperature as in similar cases AAO_5O_5[3j], anthophorene[20], and **6**[8b]) (see Figure 9 and Table 5). The spectra differ from those of the acetonitrile solutions and the fluorescence decays, *single exponentials*, are in agreement with the presence of only one fluorescent conformer population in the crystal. Regarding the maximum emission wavelength, one observes that free **2** undergoes a bathochromic shift compared to the compound in solution and that the divalent cations *induce a hypsochromic effect*. These spectral shifts could be assigned to the degree of coordination between the metal cations and the phenolic oxygen atoms (as mentioned above). For the free ligand, the conjugation is probably more efficient in the crystal ($\lambda = 330$ nm) than in fluid medium ($\lambda = 320$ nm) in which BBO_5O_5 experiences a higher conformational mobility. These observations are in contrast to those in solution. It is likely that the rigidity of the crystalline phase *prevents the dissociation between the phenolic oxygen atoms and the complexed cation* in the relaxed excited state. Hence, the blue shift effect is related to that occurring in the UV spectra in acetonitrile (Table 2).

4. Stoichiometry and Binding Constants

The stoichiometry of the complexes and binding constants of **2** were determined with the LETAGROP-SPEFO program[21] for each selected salt. The UV spectra were recorded for solutions of increasing salt content, the concentration of the ligand being kept constant. The titration ends when no shift is observed any more between two consecutive spectra (Figure 10). Fitting of the experimental data with the program reveals the occurrence of a mixture of 1:1 and 2:1 complexes (metal/ligand) at any concentration, the latter prevailing for the highest concentrations (see distribution diagram for Sr^{2+}, Figure 10). For Ba^{2+}, no satisfactory agreement between experimental and calculated data could be obtained. The binding constant values are listed in Table 6.

These values should be compared with those determined by Cram et al.[7c] for the complexation of alkali metal cations by **2** using the extraction technique ($CHCl_3/H_2O$). The association constant for Na^+ was found under their experimental conditions to be log $K = 3.0$ without any clear-cut evidence for the stoichiometry. It is also interesting to compare our data with those obtained for "genuine" coronands such as 15-C-5 log $K_{Na^+} = 4.9$ in acetonirile (potentiometry[22]) or benzo-15-C-5 log $K_{Na^+} = 4.55$ in acetonitrile (polarography[22]). Besides, the related coronand **1** ($n = 3$) incorporating the bis-orthophenyl subunit was found by polarography to form a 1:1 complex with $NaClO_4$ in acetonitrile[6]; the association constant was reported to be log $K = 3.6$. However, X-ray analysis of the single crystals of the Na^+ complex showed a 2:1 stoichiometry in the solid state[23]; the two cations are localized in the plane delineated by the oxygen atoms of the two polyoxyethylene bridges. The large cavity includes both cations, the aromatic rings being maintained far apart from each other. Interest-

Figure 10. (a) Titration in CH_3CN at +20°C of a solution of **2** (2.23×10^{-5} M) by $Sr(ClO_4)_2$: a: 0 M, b: 4×10^{-3} M, c: 10^{-2} M, d: 2×10^{-2} M, e: 4×10^{-2} M, f: 8×10^{-2} M, g: 10^{-1} M, h: 1.2×10^{-1} M; (b) LETAGROP-SPEFO calculated spectra (solid lines) from experimental data (symbols) from which the binding constants are determined; (c) computed distribution diagram as a function of salt concentration: free **2** (○), $Sr^{2+} \subset$ **2** (□), 2 $Sr^{2+} \subset$ **2** (△) (after binding constants determination)

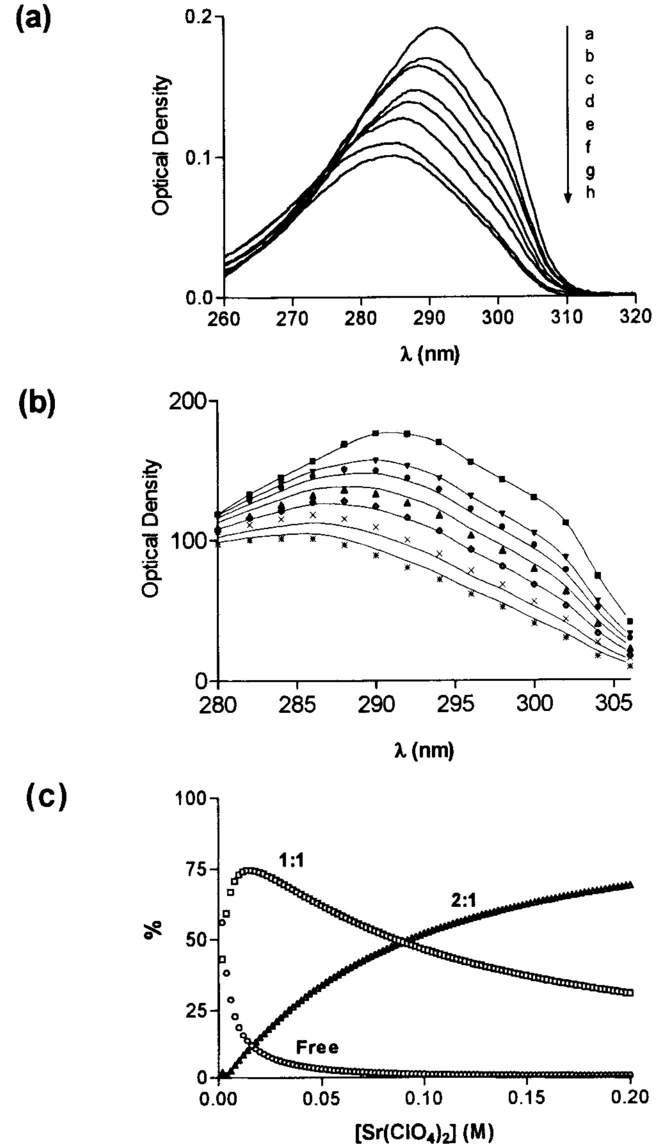


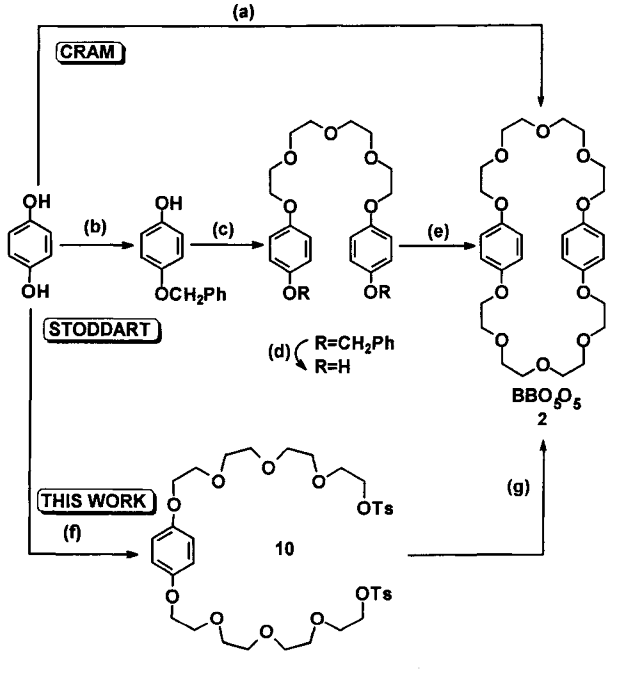
Table 6. Association constants in CH_3CN, at +20°C, of **2** with Na^+, Ca^{2+} and Sr^{2+} (counterion ClO_4^-) determined from the UV absorption spectral data with the LETAGROP-SPEFO program (β = $K_{11} \cdot K_{12}$); the stoechiometry was found to be 1:1 and 2:1 (metal/ligand)

	$\log K_{11}$	$\log K_{12}$	$\log \beta$
Na^+	2.81±0.1	1.35±0.02	4.16
Ca^{2+}	2.58±0.01	1.05±0.16	3.64
Sr^{2+}	3.26±0.06	1.40±0.1	4.65

ingly, compound **7** (the tetramethoxy derivative of **2**) forms also a 2:1 complex with NaSCN in the solid state[24], the benzene rings being stacked nearly parallel (distance 3.5 Å); however, the stoichiometry in solution is not known. A similar 2:1 complex was mentioned[25] for **8** with NaSCN.

Finally, the formation of a 2:1 complex raises the question of cooperativity[26]. In contrast to the analogous anthraceno coronand **9**, which was found to display a *positive* cooperative effect[3j] with $NaClO_4$ in CH_3CN, **2** clearly shows a *negative* effect ($K_{12}/K_{11} \ll 1/4$) for the three cations considered (Table 6), presumably because of electrostatic repulsion between the cations separated by 9 Å from each other. In the case of bisanthracene **9**, the repulsion might be attenuated by the π electron shield of the larger rings and by some entropic effect as well.

Scheme 4. Synthetic routes for the preparation of **2** from hydroquinone; (a) $TsOCH_2(CH_2OCH_2)_3CH_2OTs$ (TEGBT) (1 mol-equiv.), reflux in dioxane, 1-butanol and NaOH. – (b) $C_6H_5CH_2Cl$, K_2CO_3, DMF, room temperature. – (c) TEGBT, NaH, DMF, 80°C. – (d) H_2, Pd/C, $MeOH/Et_2O$. – (e) TEGBT (1 mol-equiv.), NaH, THF, reflux. – (f) TEGBT (3 mol-equiv.), K_2CO_3, acetone, reflux. – (g) Hydroquinone (1 mol-equiv.), K_2CO_3, acetone, reflux, high dilution (for overall yields, see text)



5. Synthesis

Compound BBO_5O_5 was first prepared by Cram et al.[7c] by a one-pot procedure from hydroquinone and α,ω-tetraethyleneglycol bistosylate (Scheme 4); **2** was isolated by column chromatography in ca. 8% yield; the method has the advantage of simplicity for a multigram preparation (2.1 g from 15 g of hydroquinone). Another route was explored by Stoddart et al.[1e] using the four-step procedure outlined in Scheme 4 (overall yield 13%) which offers the opportunity to modify the nature and size of the second chain in step (e). We chose a two-step procedure via the so-called "crab intermediate" according to the method used for the anthracene analog **9**[3j] and similar preparations described by others[1a]; the overall yield was found to be 20%. This process is also versatile, making it possible to introduce a different chromophoric group in the second step (g).

6. Summary and Conclusion

The flexibility of BBO_5O_5, **2**, an electron-rich macrocyclic paracyclophane of the coronand type, allows the two *p-dialkoxybenzene* moieties to behave almost independently from each other as observed in fluid solution by UV absorption and fluorescence emission spectroscopy. In acetonitrile solution, cations were observed to induce a blue shift in the UV spectra (150–1100 cm^{-1}) whereas they virtually do not affect the fluorescence emission maximum wavelength, presumably as a result of a photodissociation between the phenolic oxygen atoms and the cation in the excited state. Whereas the fluorescence spectra of paradimethoxybenzene, **3** and **2** are similar, their decay rates were found to be single and biexponential, respectively; this reflects intramolecular interactions between the chromophores in the macrocycle. Neither in solution nor in the solid state **2** was found to form an excimer, in contrast to all the molecules containing the paradialkoxybenzene unit (**4**–**6**) studied before. The ability of compound **2** to bind to metal cations was shown in the solid state and acetonitrile solutions; in the latter, the stoichiometries and association constants were determined for several metal cations. **2** displays a good affinity for metal cations as compared with other dibenzo crown ethers and can form *biscoronates*, especially with alkaline earth cations.

The present results constituting part 4 of the title series illustrate the similarity and differences (UV absorption, fluorescence emission, cation binding ability, stoichiometry) of various members of this kind of molecules and may be useful to understand the possible influence of metal cations on the photochemical reactivity of compound **2**.

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Experimental Section

General Methods: Solvents for synthesis were dried according to standard procedures: THF (from Na/benzophenone ketyl), DMF (from CaH_2), and CH_3CN (from P_2O_5). – Thin-layer chromatography (TLC): Aluminum sheets coated with silica gel 60 (Merck 5554). – Column chromatography: silica gel 60 (Merck 9385, 230–400 mesh). – Melting points were determined with a Kofler block. – A microbalance (Mettler ME 30, sensitivity 1 μg) was used to weigh the samples for spectroscopic measurements. – ^1H-NMR spectra: Hitachi R-1200, (60 MHz) and Bruker AC250 (250 MHz) instruments. – Mass spectra: Fisons Instrument (AutoSpec-EQ). – IR spectra: Perkin-Elmer model 412 instrument. – UV spectra: Hitachi U-3300 spectrophotometer. Fluorescence spectra: Hitachi F-4500. The fluorescence quantum yields were determined by using fluorene as standard[18a]. The samples (concentration $<10^{-5}$ M) were degassed by freeze-pump-thaw cycles on a high-vacuum line and sealed under vacuum.

Fluorescence decay measurements were performed by using the single-photon timing technique as already described[3j]. The experimental decay profiles were fitted by using the Decan 1.0 program[27]. The quantum yield (fluorescence, reaction, ...) and lifetimes were determined with an *accuracy of approximately 10%.*

Spectroscopic grade solvents were used for spectrophotometric measurements. No fluorescent contaminants were detected upon excitation in the wavelength region of experimental interest.

1,11-Bis(p-tolylsulfonyloxy)-3,6,9-trioxaundecane was prepared as described in ref.[28].

1,4-Bis[1-(p-tolylsulfonyloxy)-3,6,9-trioxaundecyloxy]benzene (**10**)[29]: K_2CO_3 (62.1 g, 0.45 mol) in dry acetone (800 ml) was placed under nitrogen in a two-necked flask equipped with a condenser and a dropping funnel. The mixture was heated at reflux for 10 min. Hydroquinone (10 g, 90.9 mmol) and 1,11-bis(*p*-tolylsulfonyloxy)-3,6,9-trioxaundecane (225.9 g, 0.45 mol) in dry acetone (600 ml) were added simultaneously during 2 h. After refluxing for 2 d, the mixture was cooled down to room temp. and filtered; then the solvent was removed in vacuo. The residue was washed with H_2O (3 × 200 ml) and then dissolved in CH_2Cl_2 (200 ml). The solution was washed once with an aqueous solution of NaOH (10%, 150 ml), then twice with pure H_2O (2 × 200 ml). The organic phase was dried with Na_2SO_4 and the solvent removed in vacuo. Column chromatography [silica gel, ethyl acetate/petroleum ether (60–80 °C), 3:1] of the obtained brown oil afforded 1,4-bis[1-(*p*-tolylsulfonyloxy)-3,6,9-trioxaundecyloxy]benzene as a colorless oil (56 g, 80%). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.23 (6H, s), 3.29–4.05 (32H, m), 6.76 (4H, s), 7.24–7.27 (4H, d), 7.69–7.73 (4H, d). – ^{13}C NMR: δ = 21.59, 68.02, 68.63, 69.22, 69.82, 70.51, 70.62, 70.72, 115.52, 127.93, 129.78, 133.05, 144.44, 153.06.

1,4,7,10,13,20,23,26,29,32-Decaoxa[13.13]-(1,4)-benzenophane (BBO_5O_5, **2**): To a refluxing suspension of K_2CO_3 (7 g, 51 mmol) in dry acetone (300 ml), a solution of 1,4-bis[1-(*p*-tolylsulfonyloxy)-3,6,9-trioxaundecyloxy]benzene (3.66 g, 4.7 mmol) and hydroquinone (0.54 g, 4.9 mmol) in dry acetone (40 ml) was added dropwise under nitrogen over 24 h. Refluxing was continued for 2 d and, after cooling, the reaction mixture was filtered and the solvent removed in vacuo. The residue was treated with H_2O (50 ml) and CH_2Cl_2 (3 × 50 ml). The combined organic extracts were washed with an aqueous solution of NaOH (10%, 150 ml) and twice with pure H_2O (2 × 50 ml), then dried with Na_2SO_4 and the solvent was removed in vacuo. Column chromatography (silica gel, ethyl acetate) of the resulting brown oil afforded BBO_5O_5, **2** as a white solid. Crystallization from methanol, yielded colorless needles (600 mg, 25%). – M.p. 92 °C (ref.[7c] 93–94 °C; ref.[1e] 87–88 °C). – ^1H NMR (CD_3COCD_3, 250 MHz): δ = 3.55–3.61 (16H, m), 3.75–3.84 (8H, m), 3.90–3.95 (8H, m), 6.75 (8H, s). – ^{13}C NMR: δ = 69.0, 70.4, 71.4, 71.5, 116.3, 154.1. – UV (acetonitrile): λ_{max} [nm] (ε) = 226.6 (1.9×10^4), 290.8 (5.6×10^3). – LSIMS: *m/z* 536 [$M^{+\bullet}$].

1,4-Bis(1-methoxy-3,6,9-trioxaundecyloxy)benzene (**3**): Dry THF (10 ml), CH_3OH (40 ml) and NaOH (830 mg, 21 mmol) were placed under nitrogen in a three-necked flask fitted with a condenser. The temperature was set to 80 °C. A solution of 1,4-bis[1-(*p*-tolylsulfonyloxy)-3,6,9-trioxaundecyloxy]benzene (4 g, 5.2 mmol) in CH_3OH (10 ml) was added dropwise during 30 min. After 20 h the reaction mixture was cooled down to room temp., H_2O (50 ml) was added and the solution was acidified to ca. 2 pH (HCl 10%). The solution was extracted twice with CH_2Cl_2 (2 × 50 ml). The combined organic layers were washed with H_2O (50 ml), dried with $MgSO_4$, filtered and the solvent was removed in vacuo. The colorless oil obtained was identified as 1,4-bis(1-methyl-4,7,10,13-tetraoxatridecyloxy)benzene (2.18 g, 86%). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.18–4.05 (6H, s), 3.32–3.36 (4H, m), 3.37–3.54 (20H, m), 3.86–3.89 (4H, m), 6.65 (4H, s). – ^{13}C NMR: δ =

58.80, 67.88, 69.67, 70.46, 70.62, 71.78, 115.38, 152.9. – UV (acetonitrile): λ_{max} (nm) (ε) = 226.9 (9.2 × 10^3), 290.4 (2.4 × 10^3). – EI: *m*/*z* 490.2 [M^+]. – HRMS: calcd. 490.2777, found 490.2757.

Table 7. Crystal data, data-collection conditions, structure determination, and refinement characteristics

	Mg^{2+} complex	Sr^{2+} complex
formula	$C_{28}H_{40}O_{10}$, $Mg(ClO_4)_2$, 6 H_2O	$C_{28}H_{40}O_{10}$, 2[$Sr(ClO_4)_2$, 4 (H_2O)]
mass	867.9	1253.4
symmetry cell	monoclinic	monoclinic
space group	Cc	$P2_1/n$
cell parameters	a = 19.696(15)	a = 10.054(3)
	b = 10.603(3)	b = 10.023(3)
	c = 21.820(15) Å	c = 14.323(4) Å
	β = 116.07(3) °	β = 105.53(3) °
	Z = 4	Z = 2
cell volume	4093 $Å^3$	2501 $Å^3$
cell measurement	20 reflect. (10 to 14°)	25 reflect. (7 to 13°)
crystal	needle, colourless	flat prism, colourless
	0.58 x 0.13 x 0.08 mm^3	0.6 x 0.2 x 0.1 mm^3
meas. density	1.408 $g.cm^{-3}$	1.671 $g.cm^{-3}$
F_{000}	1824 e^-	1272 e^-
X-ray	Enraf-Nonius CAD4, 293 K	Enraf-Nonius CAD4, 293 K
measurement	λ(MoKα) = 0.7093 Å	λ(CuKα) = 1.54070 Å
	θ/2θ scan	θ/2θ scan
	θmax = 25°	θmax = 65°
absorpt. corr.	psi-scan (T = 0.964 to 1.0)	none
measured refl.	2526	3872
observed refl.	1579 (I>3σ(I))	3347 (I>3σ(I))
data reduction	local program	local program
structure sol.	Mithril[31]	Mithril[31]
refinement	local programs	local programs
	least squares, block diagonal	block diagonal
	703 parameters	419 parameters
final R factor	0.046	0.070
final Rw	0.036	0.080
weigth	w = 1/[σ^2(F) + 0.0004 F^2)]	w = 1/[σ^2(F) + 0.0004 F^2)]
resid. density	± 0.2 $e^-/Å^3$	± 0.3 $e^-/Å^3$ (0.7 $e^-/Å^3$ around Sr)

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