

# Physicochemical behaviour of a dinuclear uranyl complex formed with an octaphosphinoylated *para-tert*-butylcalix[8]arene. Spectroscopic studies in solution and in the solid state



Flor de María Ramírez<sup>a,\*</sup>, Karen Palomares-Castillo<sup>a</sup>, Blanca Ocampo-García<sup>a</sup>, Enrique Morales-Avila<sup>b</sup>, Sabi Varbanov<sup>c</sup>

<sup>a</sup> Instituto Nacional de Investigaciones Nucleares, ININ, Carretera México-Toluca S/N, La Marquesa, Ocoyoacac C.P. 52750, Mexico

<sup>b</sup> Facultad de Química, Universidad Autónoma del Estado de México, C.P. 50120 Toluca, Mexico

<sup>c</sup> Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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## ABSTRACT

Spectrophotometric titrations of an octaphosphinoylated *para-tert*-butylcalix[8]arene ( $B_8bL^8$ ) by uranyl nitrate and vice versa in anhydrous ethanol indicate that the species with 2:1 (uranyl:calixarene) stoichiometry is the major complex in solution. Based on these results, a synthesis route was designed to isolate this complex. The latter is an orange, non-hygroscopic polycrystalline powder, with chemical formula  $[(UO_2)_2(NO_3)_4(B_8bL^8) \cdot 2H_2O] \cdot 2(H_2O)$ . (Compd. **1**), as ascertained by elemental analysis. Spectroscopic characterization of Compd. **1** in the solid and liquid states suggests that a neutral dinuclear uranyl calixarene complex was formed. MIR and FIR spectra indicate that, four phosphinoyl arms of the calixarene and two monodentate nitrates are bound to each 6-coordinate uranyl ion in the complex because no vibrational frequencies from un-coordinated O=P groups or from ionic nitrates are present; in addition the spectra reveal that water molecules form intramolecular hydrogen bonding with monodentate nitrates. The de-convoluted luminescence and XPS spectra obtained in the solid state point to a similar chemical environment around each uranyl ion, as confirmed by the mono-exponential decay of the luminescence. The more rigid conformation acquired by the calixarene in the complex and the non-symmetrical arrangement of the coordinated nitrates result in a particular feature of the emission spectra at 77 K. No evidence of cation-cation interaction was found. A rough approach to the molecular structure of the complex by molecular modelling based on the experimental findings yielded a molecule that was useful for understanding the physicochemical behaviour of Compd. **1**.

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## 1. Introduction

The specific and versatile properties of calixarenes have led to many interesting applications in chemistry, technology and bio-sciences [1]. Advances in calixarene complexation have been recently reviewed [2–4]. From the point of view of coordination chemistry, the recognition ability of calixarenes towards metal cations, strengthened by proper functionalization [3–5], has been widely demonstrated and used in separation processes [2]. The complexation selectivity of calixarenes towards cations has often been explained in terms of the size-fit concept because calixarenes

form more stable complexes with cations the ionic diameter of which matches the size of the calixarene cavity.

However, apart from this concept, it has also been proven that the stability of a complex depends on others factors, such as the affinity of its donor groups towards a specific cation, the ability of the receptor to fulfil the coordination sphere, as well as the stereochemical orientation of the ligating arms, which can be properly tuned by positioning them in the upper or lower rims. Therefore, the stoichiometry of calixarene complexes can also be adjusted. Calixarene coordination chemistry with f-elements has been mainly focused on the separation of 4f (Ln: lanthanides) from 5f elements (An: actinides) [1a,2,6] and on studying photophysical properties, [1a,6,7] often with respect to developing luminescent bioprobes [8].

Regarding actinides more specifically, uranyl being the most studied species of the series, a large number of uranyl complexes

\* Corresponding author.

E-mail addresses: [flor.ramirez@inin.gob.mx](mailto:flor.ramirez@inin.gob.mx) (F.M. Ramírez), [Karen.Palomares@tevamexico.com](mailto:Karen.Palomares@tevamexico.com) (K. Palomares-Castillo), [blanca.ocampo@inin.gob.mx](mailto:blanca.ocampo@inin.gob.mx) (B. Ocampo-García), [enrimorafm@yahoo.com.mx](mailto:enrimorafm@yahoo.com.mx) (E. Morales-Avila), [varbanov@orgchm.bas.bg](mailto:varbanov@orgchm.bas.bg) (S. Varbanov).

have been reported [2,9–14], with the aim of establishing a relationship between their chemical structure and optical spectra, as well as studying their solution behaviour [15,16]. Semi-empirical and first-principles studies [12,14] have also been essential for deciphering electronic and vibronic states and the nature of the chemical bonds [14]. Recently, photophysical property studies of uranyl complexes with organic ligands have substantially increased in number [16b,17]. Here, we focus on the structure, bonding and application of dinuclear uranyl complexes that are formed with organic ligands. In recent decades, uranyl cation–cation interactions (CCI's) have been evidenced in polynuclear uranyl(VI) and uranyl(V) complexes formed with organic ligands [18,19]. To the best of our knowledge, however, no clear evidence of such an interaction has been found in dinuclear uranyl calixarene complexes.

It has been reported in the literature a bimetallic uranyl complex structure obtained by initial deprotonation of *p*-*tert*-butylcalix[8]arene, two of the four uranyl oxo moieties interact with protonated triethylammonium cations, and the overall structure is stabilized by hydrogen-bonded water and acetonitrile molecules. The phenolic units adopt a conformation that is close to that observed for the free *p*-*tert*-butylcalix[8]arene, which is commonly described as a pleated loop, although it has a distortion towards a saddle shape [20b].

The crystal structures of dinuclear uranyl complexes that are formed with no functionalised parent calixarenes, where the calixarenes are partially or totally de-protonated reveal the presence of bridges between the uranium of the uranils by counter-ions such as carbonate, acetate, nitrates, hydroxides or coordinated water molecules or/and these entities bridging the uranyl oxygen ions where the oxygens can be the donors [10,21a,b]. These and other studies maintain current attention on the exciting fundamental aspects of the uranyl compounds and the control of their physicochemical properties and chemical behaviour, which are of particular importance in the nuclear industry and in natural environments. In this direction, we have been involved in the study of the coordination chemistry of uranyl complexes that are formed with *n*-phosphinoylated *para*-*tert*-butylcalix[*n* = 4–8]arenes as well as the capability of these calixarenes towards the separation of uranyl and thorium from acidic-nitrate media and from lanthanides in these media under a salt effect or not [6].

In general, the calix[8]arenes and their derivatives adopt the pleated-loop, 1,2 alternate, 1,2,3,4 alternate, cone and  $\frac{3}{4}$  cone conformations in the solid state. In solution, the *para*-*tert*-butylcalix[8]arene ligands do not always maintain such conformations due to the solvent influence in the conformational arrangement of the calixarenes, which can break intramolecular hydrogen bonding in the calixarene or interact somehow with the cavity or the rim substituents [2,5,20]. In their metal complexes, the pleated loop and pinched conformations appear to be the preferred conformations that are adopted, although other conformations have been reported [20,21a,b]. The particular scaffold and conformations of calix[8]arenes and of their derivatives are the basis of the supramolecular assemblies of their metallic and organic complexes, and therefore, they have gained considerable attention from the researchers in this field [20,21]. However, little work has been performed on functionalised calix[8]arenes and their complexes.

In the specific case of the neutral octa-phosphinoylated *para*-*tert*-butylcalix[8]arene macrocyclic receptor  $B_8bL^8$ , no solid state structure of it and its lanthanide complexes has been achieved, but the structural arrangement of  $B_8bL^8$  studied in methanol solution by temperature-dependent  $^1H$  and  $^{31}P$  NMR spectroscopy has indicated that the calix[8]arene adopts a cone conformation, which is maintained in its 1:1 lutetium complex [7e].

In fact, to the best of our knowledge, only some crystal structures of dinuclear metallic calix[8]arene complexes formed with f-elements have been obtained, with partial or total de-protonated calixarenes [7a,10b,20a,21b].

Here, we present and discuss the results from the study of uranyl complexation with an octaphosphinoylated *para*-*tert*-butylcalix[8]arene,  $B_8bL^8$ , Fig. 1, in solution and those from the isolated bimetallic uranyl complex in the solid state and in solution.

## 2. Material and methods

### 2.1. Starting materials and equipment

Absolute anhydrous MeOH and EtOH from Baker and Hycel, *N*, *N*-dimethylformamide (DMF) and spectrophotometric grade  $CHCl_3$ ,  $CH_2Cl_2$  and  $CH_3CN$  from Aldrich were used without further purifications but were dried before use on 3 Å molecular sieve previously dried under a vacuum at 0.01333 Pa and 120 °C and kept inside a glove box. 5,11,16,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56 octakis(dimethylphosphinoyl)methyleneoxy)calix[8]arene, ( $B_8bL^8$ ), was prepared as previously reported [7e] and further purified from acetonitrile and dried before use. Diisopropyl ether and  $UO_2(NO_3)_2 \cdot 6H_2O$  were purchased from Merck.

UV–Vis and diffuse reflectance spectra were recorded on a Perkin–Elmer Lambda 35 spectrophotometer with double beam and an integration sphere, using 1-cm quartz cells and MgO pellets containing approx. 5% of the dispersed sample, respectively. ATR–FTIR spectra were measured in the range 500–4400  $cm^{-1}$  on a Perkin Elmer System 2000 spectrometer with an ATR platform (Pike Technologies). Far-infrared spectra (30–700  $cm^{-1}$ ) were acquired under nitrogen atmosphere on a Spectrum 400 Perkin Elmer spectrometer fitted with an ATR platform (Diamond GladiATR, Pike Technologies). Low resolution emission and excitation luminescence spectra of solutions and powdered samples were recorded at 291 K and 77 K on a Perkin Elmer LS-55 spectrofluorimeter (200–900 nm) in both fluorescence and phosphorescence modes. The lifetimes of the complexes and starting materials were measured in frozen solution at 77 K. The solutions were prepared in a mixture of DMF–MeOH (60:20 v/v). The lifetimes in Table 1 are the averages of at least five determinations.

The uranium content was determined by neutron activation analysis (NAA) using the SIRCA position (Capsules Rotary Irradiation Automatic System) of the TRIGA Mark III nuclear reactor of ININ and by X-ray photoelectron spectroscopy (XPS). X-ray photo-

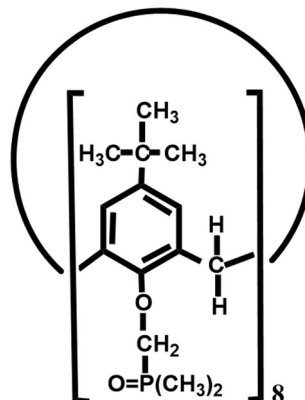


Fig. 1. Schematic representation of the  $B_8bL^8$  calixarene ligand.

**Table 1**  
Lifetimes ( $\tau$ ) of uranyl salt, calixarene ligand and dinuclear uranyl calixarene complexes in DMF-MeOH at 77 K.

Compds./ $\tau$	Excitation wavelength (nm)	Emission wavelength (nm)	Emission wavelength (nm)	Excitation wavelength (nm)	Emission wavelength (nm)	Emission wavelength (nm)
Compd. <b>3</b>	270	497	543	327	497	543
$\tau$ (ms)		$1.64 \pm 0.05$	$1.32 \pm 0.02$		$1.80 \pm 0.03$	$1.15 \pm 0.09$
Compd. <b>2</b>	270	446				
$\tau$ (ms)		$126.08 \pm 6.12$				
Compd. <b>1</b>	270	498	543	327	498	543
$\tau$ (ms)		$0.52 \pm 0.01$	$0.46 \pm 0.01$		$0.31 \pm 0.01$	$0.38 \pm 0.01$
Compd. <b>1a</b>	270	497	543	327	497	543
$\tau$ (ms)		$0.84 \pm 0.01$	$0.73 \pm 0.01$		$0.45 \pm 0.01$	$0.39 \pm 0.01$

electron spectroscopy spectra were acquired on a Jeol JPS 9200 spectrometer equipped with a Mg K $\alpha$  X-ray source (1253.6 eV). The source was operated at 10 kV/20 mA and calibrated using Au 4f<sub>7/2</sub> (84.0 eV) and Ag 3d<sub>5/2</sub> (368.2 eV) from foil samples. The samples were introduced into an ultra-high vacuum (UHV) chamber of the spectrometer ( $1.40 \times 10^{-6}$  Pa) and measured at 297 K. The spot size in the beam was 100  $\mu$ m. The pressure did not change during the analysis, and 10 scans for Au 4f were performed with an energy step size of 0.1 eV. The binding energies were referenced to the C1s peak at 284.3 eV. Shirley background was subtracted from all spectra to perform the peak fitting with a symmetric Gauss-Lorentz sum function (SpecSurf software). Surface elemental composition of Compd. **1** (uranyl calixarene complex tetrahydrate) and Compd. **1a** (uranyl calixarene complex bihydrate) was determined by fitting and integrating the U4f, P2p, O1s, N1s and C1s bands using theoretical sensitive factor provided by the manufacturer of the XPS apparatus. To evaluate the confidentiality of the elemental contents of Compds. **1** and **1a** determined by this technique, the contents of C, O, P in Compd. **2** (B<sub>8</sub>bL<sup>8</sup> calixarene ligand) and U, N, O in Compd. **3** (uranyl nitrate hexahydrate) were simultaneously measured.

## 2.2. Solution studies

Spectrophotometric titrations were performed at 291 K on the UV-Vis spectrophotometer mentioned above. The calixarene was titrated with the uranyl salt, and vice versa, in anhydrous ethanol. In a typical experiment, 5 mL of a  $5.74 \times 10^{-4}$  M solution of B<sub>8</sub>bL<sup>8</sup> was titrated by a solution of  $5.74 \times 10^{-4}$  M uranyl nitrate (20 aliquots of 0.5 mL, 5 of 0.8 mL, and 5 of 1.3 mL); in total, 31 spectra were recorded for [Uranyl]/[B<sub>8</sub>bL<sup>8</sup>] ratios from 0 to 4.1. Alternatively, 3 mL of a  $6.01 \times 10^{-4}$  M uranyl nitrate solution was titrated by a solution of  $5.74 \times 10^{-4}$  M B<sub>8</sub>bL<sup>8</sup> (17 aliquots of 0.350 mL, 8 of 0.700 mL, and 3 of 2 mL); 29 spectra were recorded for [B<sub>8</sub>bL<sup>8</sup>]/[Uranyl] ratios ranging from 0 to 5.59. Both series of experiments were conducted in the glove box, and the titrant was delivered by 5 cm<sup>3</sup> and 1 cm<sup>3</sup> micropipettes. The resulting spectra were statistically analysed by the Origin Pro 8.0 software. The experimental results revealed the presence of species with 1:1(M:L), 1:2 and 2:1 stoichiometries and free ligand and uranyl ions.

## 2.3. Synthesis of the uranyl complexes

In a two-necked flask fitted with a magnetic stirrer, a nitrogen inlet and a condenser joined to a drying tube containing blue silica gel, were added 25.2 mg (0.0111 mmol) of B<sub>8</sub>bL<sup>8</sup>·6H<sub>2</sub>O and 4 mL of absolute anhydrous ethanol. The slightly yellow solution was heated at 65 °C under an ultrapure nitrogen atmosphere under magnetic stirring. A solution of uranyl nitrate (15.3 mg, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) (0.0275 mmol) in 2.8 mL of EtOH (lemon-yellow) was added dropwise via a dropping funnel, and once the temperature reached again 65 °C, the reaction mixture turned intense

yellow, which five minutes later changed into a reddish-amber colour. The temperature was maintained for 2.5 h, and then, increased to 71 °C; the reaction mixture was maintained under vigorous stirring and N<sub>2</sub> atmosphere for 4 h. Once the heating was stopped, the reaction medium was further stirred until room temperature was reached. The mother liquor was turbid; it was refrigerated overnight at -22 °C, and no precipitate was observed, even when diisopropyl ether or anhydrous chloroform was slowly added. It was centrifuged for 25 min with a speed of 75 rpm; a precipitate formed that was collected and washed with anhydrous dichloromethane, before drying for 24 h at 20 °C under a vacuum at 0.01333 Pa. The dried precipitate was washed with anhydrous absolute ethanol three times and dried again for 24 h at 20 °C and for 48 h at 47 °C and 24 h at 55 °C under the same vacuum. The liquid from the centrifugation was concentrated to 30% of the total volume on a rotary evaporator. The concentrated liquid was centrifuged, and the recovered precipitate was also dried under a high vacuum, washed with dichloromethane and dried again, and washed with ethanol and finally dried for 24 h at 20 °C, for 2 days at 45–50 °C and 24 h at 55 °C, under 0.01333 Pa vacuum. The two precipitates were weighted and analysed separately; the reaction yield was 50% for (**1**), and 25% for the second precipitate (**1a**). The complexes were dissolved in dried EtOH and acetonitrile or a mixture of DMF-MeOH solvents dried inside the glove-box. Compd. **1** was analysed by UV-Vis, MIR, FIR, NAA, diffuse reflectance (DR), XPS and luminescence in DMF-MeOH and solid state, both at 291 K and at 77 K. Due to the low yield, (**1a**) was not analysed by UV-Vis, FIR and DR.

## 2.4. Molecular modelling

B<sub>8</sub>bL<sup>8</sup> was modelled by DFT (Density Functional theory) and by the sequential application of AugmentedMM3/CONFLEX/AugmentedMM3/MOPAC-PM5/MOPAC-PM5-COSMO procedures. Both computational molecular modelling methods yielded the same calixarene structure. However, COSMO evaluates the effect of the solvent on the stabilization of a structure, in particular, a polar solvent (water); and therefore to ensure complex molecules with the minimum energies and conformers with the lowest energies, the resulting calixarene structure calculated by this procedure was the basis for simulating the dinuclear uranyl complex molecule by using Augmented MM3/CONFLEX procedures. These procedures are part of the CAChe Work SystemPro 5.02 programme package for Windows (Fujitsu Ltd., 2000–2001).

## 3. Results and discussion

### 3.1. Solution studies

#### 3.1.1. Speciation

To ascertain the stoichiometry of the main species formed between B<sub>8</sub>bL<sup>8</sup> and uranyl in organic media, the ligand was titrated

with the uranyl salt and vice versa in anhydrous ethanol; both titrations were followed by UV–Vis spectrophotometry. The spectrum of the free ligand presents two maxima at 270.3 and 276.9 nm and a comparatively weaker band centred at 350 nm; the latter corresponds to an intraligand charge transfer (ILCT), previously reported at 360 nm in methanol [7e]. All spectra (Fig. 2) from each titration were statistically analysed using Origin Pro 8.0 software only, due to the lack of the SPECFIT/32 programme used in our previous investigations on calixarene and f-elements [6a,d,7d]. Three wavelength intervals of the spectra are observed 267–270 nm (ligand), 330–400 nm (ligand) and 420–425 nm (uranyl).

It is important to point out that the concentration values of the ligand and the uranyl salts used for the titrations were chosen on purpose with the aim of analysing the band between 420 and 425 nm which corresponds to uranyl ions (uranyl presents a fine vibronic structure between 350–490 nm with maximum absorption bands between 400–460 nm) [16]. It is observed that the graphs of the absorbance versus the molar fraction of the uranyl salt or the ligand resulted in curves similar to that obtained by the Job's methods for weak complexes [1a]. The graphs are presented in Figs. S1 and S2 (supplemental material) and reveal coordination of uranyl to  $B_8L^8$ . Therefore, it is proposed that the presence of more than one complex species in the titration medium is the reason why the plots are curves more than the formation of weak complex species. The deviation from the typical Job's plots was expected [1a] therefore, the number of

species in solution has been determined by multiple-peak fitting of the absorption bands with Gaussian functions (see Figs. S1 and S2 and Tables S1 and S2). The fit revealed the presence of 5 species, four complexed species, free uranyl nitrate or free ligand. It was observed that titrating the calixarene with the uranyl salt two species with the same 2 M:1 L stoichiometry were formed. Thus the quantitative analysis for the three main species (ML) gave the following percentages of the 1:2, 1:1, and two 2:1 species: 38.2%, 17.6%, and 31.7% when the ligand is titrated and the fifth species is the free uranyl nitrate, 12.5% (Fig. S1 and Table S1) while titrating the uranyl salt with the calixarene 5 species were also revealed where one species with 1:3 stoichiometry was formed. The quantitative analysis for the four main species gave the following percentage of the 1:3, 1:2, 1:1, and 2:1 species: 13.4%, 14.6%, 17.1% and 36.2% when uranyl is titrated and the fifth species is the free calixarene ligand, 18.7% (Fig. S2 and Table S2). The percentages obtained from the two series of experiments are similar for the 1:1 and 2:1 species but substantially differ for the 1:2 species.

These results and those from the literature [10a,b] in which it is demonstrated that calix[8]arenes form 2:1 complexes with 4f-elements and uranyl permitted us to establish the experimental conditions for the synthesis of the dinuclear complex, a metal:ligand ratio equal to 2.5 being adequate.

### 3.1.2. Solution studies of the isolated complex

Inside a glove box, solutions of the dinuclear uranyl calixarene complex (**1**,  $3.75 \times 10^{-5}$  M)  $B_8L^8$  (**2**,  $1.35 \times 10^{-4}$  M) and uranyl nitrate salt (**3**,  $5.72 \times 10^{-4}$  M) were prepared in a dried mixture of DMF–MeOH because Compd. **1** was partially soluble in methanol and ethanol. Compd. **1** was partially soluble in acetonitrile whereas the mononuclear uranyl calixarene complexes that formed with phosphinoylated *para-tert*-butylcalix[4-6]arenes [6a,c] and phosphinoylated *para-tert*-octylcalix[4]arene [6d] were soluble, and this difference can be considered as a physical evidence for the formation of the dinuclear complex. A dinuclear lutetium complex formed with Compd. **2** also revealed low solubility in methanol [7e].

The UV–Vis spectra of Compds. **1**, **2** and **3** solutions in the DMF–MeOH mixture were recorded and Fig. S3 shows these spectra from 250 nm to 550 nm for Compds. **1** and **2** and from 300 nm to 550 nm for Compd. **3**, the three compounds solutions showed spectra with specific features. Therefore, to have a more accurate assignment of the absorption bands, a multi-peak Lorentzian model was applied (from 200 nm to 550 nm region). The correlation factor was  $R^2 = 0.9975$  and  $\chi^2 = 6 \times 10^{-5}$ . The absorption spectrum of Compd. **2** revealed two unresolved bands at 225 and 246 nm, which were assigned to  $\pi \rightarrow \pi^*$  transitions that are mainly located on the phosphinoyl groups; there was a semi-split band at 268 (molar absorption coefficient,  $\epsilon = 6222 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 277 nm, and a non-resolved weak band at 314 nm which were assigned to the  $\pi \rightarrow \pi^*$  transitions and  $n \rightarrow \pi^*$  transitions, respectively that are mainly located on the phenyl rings. The latter could be the result of the interaction of the rings with the solvent mixture. A band observed at 416 nm ( $\epsilon = 622 \text{ M}^{-1} \text{ cm}^{-1}$ ) was assigned to the intraligand charge transfer state (ILCT), which was already observed in the absorption spectrum of the ligand at 360 nm in methanol [7e], ( $1.7 \times 10^{-4}$  M) and at 350 nm in ethanol ( $5.7 \times 10^{-4}$  M) in this work. The large red shift observed in the DMF–MeOH solvent mixture (60:20 v/v) is possibly due to the high polarity of the DMF (Fig. S3), mainly. Interaction with the phosphinoyl arms as well as the calixarene cavity cannot be ruled out.

The Compd. **1** spectrum revealed two shoulders at 220 and 245 nm and the strongest band at 268 nm ( $\epsilon = 16,800 \text{ M}^{-1} \text{ cm}^{-1}$ ) with shoulders at 278 and 298 nm, with the latter 16 nm blue shifted with respect to that of Compd. **2**. The intriguing band is

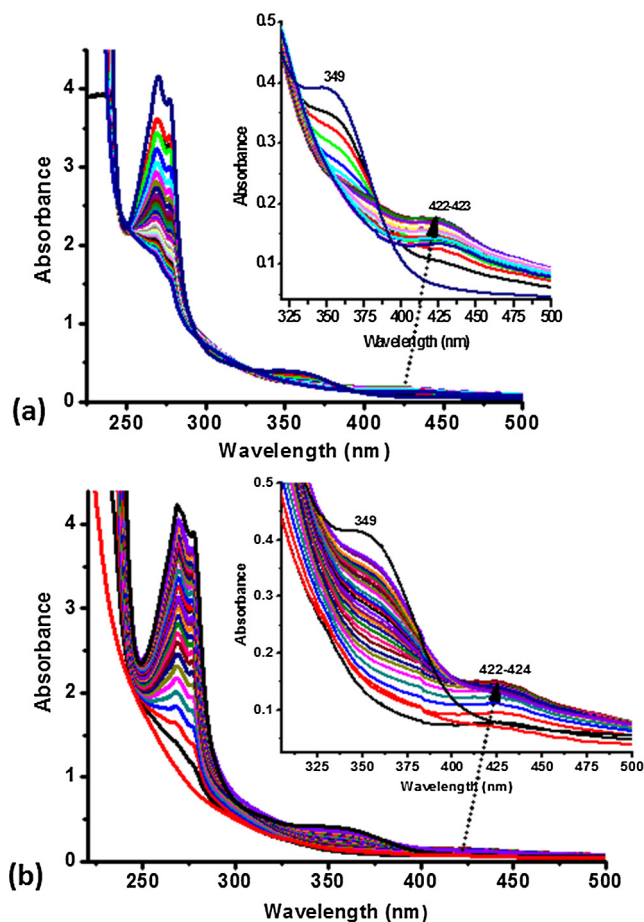


Fig. 2. Spectrophotometric UV–Vis titrations: (a) Titrating the calixarene ligand ( $5.74 \times 10^{-4}$  M) with uranyl nitrate salt ( $5.74 \times 10^{-4}$  M) in ethanol, (b) titrating the uranyl nitrate salt ( $6.01 \times 10^{-4}$  M) with the calixarene ligand ( $5.74 \times 10^{-4}$  M) in ethanol. Analysed band: 423 nm.

the one centred at 404 nm ( $\epsilon = 906 \text{ M}^{-1} \text{ cm}^{-1}$ ), which is observed at the same position in a 5 times more concentrated solution; it could be assigned to a blue shift of the ILCT band (416 nm) from Compd. **2** or from the vibronic structure of the coordinated uranyl ions in the complex. Therefore, the uranyl nitrate salt spectrum was also recorded.

Bands between 400 and 470 nm result from a vibronic structure due to coupling of symmetric O–U–O stretching vibrations to electron transfer transitions (LMCT) [16a,b,d]. The spectrum of the uranyl nitrate in the DMF–MeOH solvent mixture does not reveal any significant band at approximately 400–465 nm. The solvent type and the compound concentration affect the ILCT state position, and in the present case, it can overlap with the absorption bands from the vibronic structure from the complexed uranyl. The LMCT band position is not very sensitive to the solvent but is sensitive to the coordination of the uranyl. Thus, the band centred at 404 nm in the Compd. **1** spectrum seems to come from the ILCT state, which is blue shifted by the coordination to the uranyl ions. This shift and the significant decrease in the absorbance of the bands assigned to the O=P transitions or its disappearance confirmed the interaction of uranyl ions with the calixarene through the phosphinoylated arms.

### 3.2. Solid state studies

#### 3.2.1. Elemental content

The synthesised complex was an orange, non-hygroscopic polycrystalline powder. However, all attempts to grow mono-crystals failed.

Elemental Analysis (EA) of U, C, O, P and N of Compd. **1** was conducted by XPS. The uranium content was confirmed by NAA; four samples of Compd. **1** were analysed, and an average percentage equal to  $16.42 \pm 0.41\%$  of uranium was found. By XPS, the uranium content was 16.55%, which is also in good agreement with the calculations for a minimum formula of Compd. **1** ( $\text{UO}_2)_2(\text{C}_{112}\text{H}_{168}\text{O}_{16}\text{P}_8)(\text{NO}_3)_4(\text{H}_2\text{O})_4$ , MW = 2878.48 g/mol (Calc. C:46.73, H:6.16, N:1.95, O: 20.01, P:8.61, U:16.54%; Found (XPS): C: 46.77, O: 19.43, P: 8.51, U: 16.55%). Samples of Compd. **1a** were also analysed by XPS, and we found the same content of uranium as in Compd. **1** but with a lower content of water and a higher content of carbon and phosphorous; the uranyl content by NAA was  $16.62 \pm 0.41\%$ , and the best fit with the calculation was  $(\text{UO}_2)_2(\text{C}_{112}\text{H}_{168}\text{O}_{16}\text{P}_8)(\text{NO}_3)_4(\text{H}_2\text{O})_2$ , MW = 2842.45 g/mol (Calc. C:47.33, H:6.10, N:1.97, O: 19.14, P:8.72, U:16.75%; Found (XPS): C: 46.99, O: 18.83, P: 8.79, U: 16.55%).

Two water molecules is the only difference between the isolated compounds **1** and **1a** with the same stoichiometry uranyl:calixarene ligand which is curiously in agreement with two uranyl:calixarene species with 2uranyl:1calixarene stoichiometry formed during the titration of the calixarene ligand with uranyl salt in ethanol (Section 3.1.1).

#### 3.2.2. Infrared spectra

The IR spectra of the solid samples of Compd. **1**, Compd. **2**, and Compd. **3** were recorded by IR in the Medium IR (MIR) and FAR IR (FIR) regions. Table S3 presents the most important vibrational frequencies in the MIR region and in Fig. 3, the FIR spectra are given.

Because the coordination of the uranyl ions to the calixarene ligand is through the phosphinoyl pendant arms [6a,c,d] the interaction provokes a significant change in the main region of the vibrational frequencies of the  $\text{O}=\text{P}(\text{CH}_3)_2\text{CH}_2-$  arms; the very strong band at  $1154 \text{ cm}^{-1}$  and a strong band at  $1114 \text{ cm}^{-1}$  of the ligand are observed in the complex at 1092 and  $1052 \text{ cm}^{-1}$ , and there is a red shift of  $62 \text{ cm}^{-1}$  for both bands, which maintains the intensity ratio that is observed in the free ligand. This indicates that the shifted bands effectively correspond to the

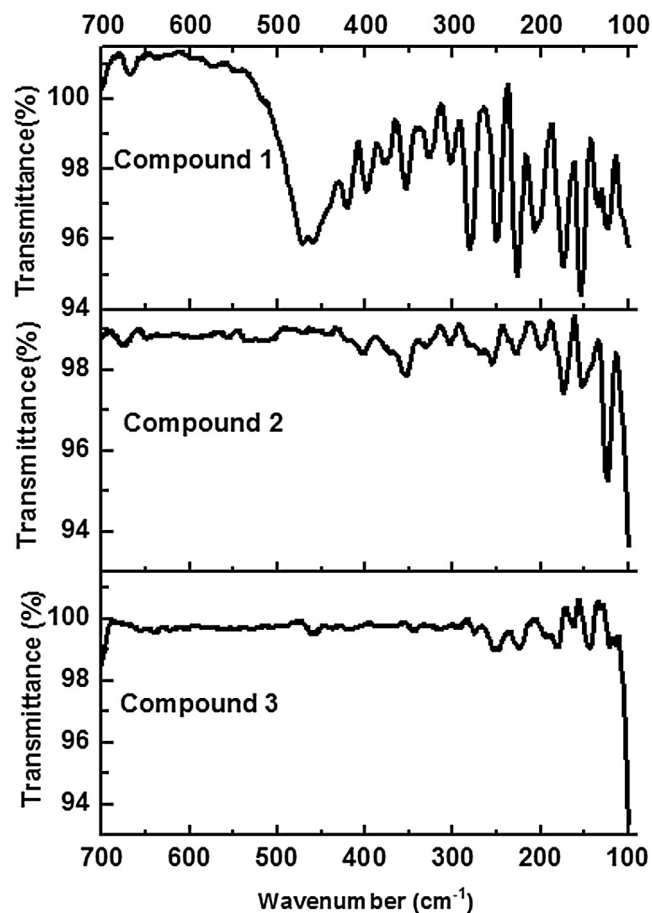


Fig. 3. FIR spectra of the dinuclear uranyl calixarene complex (top), the calixarene ligand (middle) and the uranyl nitrate hexahydrate (bottom).

vibration frequencies of the phosphinoyl groups after complexation. The extent of the shift to lower energies of the main bands confirmed that the two uranyl ions share the eight  $\text{O}=\text{P}(\text{CH}_3)_2\text{CH}_2-$  arms of the octameric phosphinoylated calixarene, with four per cation. In addition, the band at  $1022 \text{ cm}^{-1}$  that corresponds to the phenyl-oxy groups ( $=\text{C}-\text{O}-\text{CH}_2$ -arm) in Compd. **2** changed very little in the Compd. **1** spectrum, which suggests that this functional group does not interact with the uranyl ions or water molecules. It is noted that the vibration frequencies at  $1472$  and  $1296 \text{ cm}^{-1}$  assignable to the  $P-\text{CH}_3$  groups are strong bands in the Compd. **2** spectrum but are very weak in the Compd. **1** spectrum, as a consequence of the strong coordination of the  $-\text{CH}_2\text{P}(\text{O})(\text{CH}_3)_3$  arms to the two uranyl ions. The overall results indicate that the structural arrangement of the calixarene is almost maintained in the complex.

Weak Bands at  $1519$ ,  $1458$  and  $806 \text{ cm}^{-1}$  that correspond to mono-coordinate nitrates were observed in the spectrum of Compd. **1**. Comparatively, in the spectrum of the uranyl nitrate hexahydrate, medium and strong bands associated with monodentate and bidentate nitrates and weak bands that correspond to ionic nitrates were observed (Table S3). Bands assigned to coordinate nitrates are observed at least as medium strong bands in other uranyl complexes formed with smaller phosphinoylated calixarenes [6a,c,d]. Although nitrate groups are oxyanion highly coordinative, their coordination mode in particular to uranyl depends on the interplay between ligand–metal attractions, interligand repulsion, and solvation. In polar solvents that are capable of donating an electron pair or in compounds that contain water molecules, their tendency is to coordinate in a

monodentate mode [9a,b,c,22]. Therefore, it was expected that two monodentate nitrates were bonded to each uranyl ion. This coordination mode leaves two oxygens of the nitrate free to interact with the medium. In Compd. **1**, no ionic nitrate band was observed. According to EA, at most four water molecules are present in Compd. **1**.

MIR results reveal a weak semi-broad band that is centred at  $3343\text{ cm}^{-1}$  and is assignable to hydrogen-bonded water molecules and very weak bands of free water molecules in the lattice. Therefore, it is suggested that at least two water molecules that form hydrogen bonding must be part of the dinuclear uranyl complex  $[(\text{UO}_2)_2(\text{NO}_3)_4(\text{B}_8\text{bL}^8)\cdot 2\text{H}_2\text{O}]\cdot 2(\text{H}_2\text{O})$ . The free oxygens of the nitrates were the best candidates for interacting with such molecules. No evidence of coordinated water was found in the spectrum of Compd. **1**. In the spectrum of Compd. **3**, bands that correspond to coordinated water molecules ( $3079\text{ cm}^{-1}$ ) and to water molecules from hydration and crystallization are present as medium-weak bands and were observed in the MIR spectrum ( $3548$ ,  $3506$ ,  $3289\text{ cm}^{-1}$ ). The spectrum of Compd. **2** also showed bands from water molecules ( $3293$ ,  $1749$ ,  $1731\text{ cm}^{-1}$ ). It has been widely demonstrated experimentally and theoretically that nitrates can also form intramolecular and intermolecular strong hydrogen bonds through each of the three oxygen atoms [9a,b,21–23]. A very stable arrangement is formed in which the water molecules bridge the nitrate oxygen bonds through hydrogen bonds. It is well known that water molecules can diffuse into the material and become trapped there, especially if the material contains voids that can hydrogen-bond water molecules, as is the case of the titled calixarene, Compd. **2**, which is highly hygroscopic and is obtained with a variable number of water molecules. Thus, the content of water molecules can go from 8 to 2. Water and phosphinoyl groups present a high affinity for the uranyl ion, and therefore, it was important to conduct the reaction under an inert atmosphere. All of this experimental and theoretical information suggests that in Compd. **1**, the nitrates that are coordinated to one uranyl ion are also hydrogen bonded to the coordinated nitrates of the other uranyl ion through water molecules that are favoured by the intrinsic nature of Compd. **2**.

The IR of Compd. **1a** revealed no water in the lattice, and therefore, we clearly observed the band at  $3220\text{ cm}^{-1}$  from the intramolecular hydrogen bond, which in the spectrum of Compd. **1** is overlapped by the water molecules in the lattice and, therefore, the band position is not the same band.

In the MIR region, the uranyl salt presents a very strong band at  $938\text{ cm}^{-1}$  and a defined medium strong shoulder at  $960\text{ cm}^{-1}$ , which correspond to the asymmetrical vibration, and a weak band at  $869\text{ cm}^{-1}$ , which corresponds to the symmetrical vibration of the uranyl cation while in Compd. **1**, one medium band is observed at  $950\text{ cm}^{-1}$  and a shoulder at  $924\text{ cm}^{-1}$ . A very weak band at  $876\text{ cm}^{-1}$  was observed. The shift of bands demonstrate the interaction of the uranyl ions with the ligand and the change of their absorbance ratio suggests a slight perturbation of the  $\text{UO}_2^{2+}$  centrosymmetric environment by the coordination. However, the symmetry of the calixarene is affected because the aryl-ring vibrations ( $936$  and  $896\text{ cm}^{-1}$ ) are not observed.

In the FIR region (Fig. 3), two weak bands are located at  $250$  and  $225\text{ cm}^{-1}$ , which correspond to the stretching vibrations of the uranyl of Compd. **3** while in the Compd. **1** spectrum are strong bands. Two strong bands at  $209$  and  $202\text{ cm}^{-1}$  were observed which correspond to monocoordinated nitrates to uranyl ions [9a,b,c,23a,b]. The calixarene spectrum reveals a medium intense band at  $125\text{ cm}^{-1}$  which can be associated to water molecules in the calixarene cavities or hydrogen bonded to the phosphinoylated groups of the pendant arms in the lower rim [6a,7b,d].

A weak band from the aromatic C–H out-of-plane bending vibrations of the phenyl rings of the calixarene appeared at  $668\text{ cm}^{-1}$ , this vibration was observed at  $677\text{ cm}^{-1}$  in Compd. **2**.

The Compd. **1** spectrum showed a new and wide strong complex band between  $510$  and  $428\text{ cm}^{-1}$  with two maxima at  $471$  and  $458\text{ cm}^{-1}$ . From  $550$  to  $420\text{ cm}^{-1}$ , the spectra of Compds. **2** and **3** reveal negligible absorptions but in that of Compd. **2** could be identified an extremely weak band at  $471\text{ cm}^{-1}$  and in **3** a very weak band at  $458\text{ cm}^{-1}$  [9a,b,23a,b]. Bending vibrations down to  $500\text{--}200\text{ cm}^{-1}$  have been also reported for  $\text{--C--P=O}$  functional groups and for coordinated  $\text{O=P}$  and nitrates to uranyl as well as bending vibrations of  $\text{UO}_2^{2+}$  at  $246\text{--}262\text{ cm}^{-1}$ . [9,23a,b]. Bending vibrations from lattice water and water molecules forming hydrogen bonding with nitrates have been also reported in the region of the wide strong band [9a,b,6d,23a,b].

Hence in Compd. **1** spectrum the two maxima that arise from the wide strong complex band correspond to the bending vibrations of the phosphinoyl groups ( $471\text{ cm}^{-1}$ ) coordinated to the two uranium central atoms and to hydrogen bonded water molecules to the coordinated nitrates ( $458\text{ cm}^{-1}$ ). The sharp medium-strong bands between  $430$  and  $220\text{ cm}^{-1}$  with respect to those of Compds. **2** and **3** confirm a change of symmetry of the calixarene molecule as result of the strong U–OP bonds formed with the uranyl ions and no strong perturbation of the uranyl (VI) ions which was expected since the hydrogen bonding is formed between the nitrates coordinated to the uranyl ions.

The coordination of the phosphinoyl groups to uranyl cations which has a significant effect in the C–P=O bending vibrations and the hydrogen bonding of water molecules formed between the nitrates coordinated to the two uranyl cations caused the new wide strong band. In several dinuclear uranyl complexes that are formed with calixarenes, it is common to find water molecules hydrogen bonded to oxo, phenoxo and ether oxygen atoms [20a–c,21a,b] as well as counter ions such as carbonates, carbamates, and/or nitrates and solvent molecules that are involved in hydrogen bonding between the uranyl centres [20a–c,21a,b].

It is proposed that the weak band centred at  $3343\text{ cm}^{-1}$  and the strong one centred at  $458\text{ cm}^{-1}$  correspond to intramolecular hydrogen bonding, forming a bridge between the mono-coordinated nitrates from one uranyl ion to the other uranyl or between the two nitrates of each uranyl cation in the dinuclear complex.

Thus, based on the MIR and FIR results and the literature, it is proposed that the features of the IR spectra are characteristic of the dinuclear uranyl calixarene complex.

### 3.2.3. Solid state diffuse reflectance electronic absorption spectra

The DR spectra of Compds. **1**, **2** and **3** were recorded. The reflectance bands in the  $200\text{--}700\text{ nm}$  range were analysed. In the calixarene spectrum was observed a slightly structured reflectance band that was centred at  $224$  and  $234\text{ nm}$  and it was assigned to  $\pi \rightarrow \pi^*$  (P=O) transitions. A broad band centred at  $275$  and  $335\text{ nm}$  with a semi-shoulder at  $344\text{ nm}$  was assigned to the  $\pi \rightarrow \pi^*$  (C=C-phenyl) transitions. According to the DR spectrum of Compd. **2**, the broad band centred at  $416\text{ nm}$  in the UV–Vis spectrum in solution (Fig. S3) which corresponded to ILCT, it is composed by at least three transitions located at  $377$ ,  $394$  and  $429\text{ nm}$  (Fig. S4).

The typical diffuse reflectance absorption spectra of uranyl ions are observed between  $310$  and  $520\text{ nm}$  [16a,b]. Bands identified in the spectrum of Compd. **3** at  $319\text{ nm}$ ,  $346\text{ nm}$ ,  $351\text{ nm}$ ,  $390$ ,  $417$ ,  $438\text{ nm}$  (shoulder),  $445\text{ nm}$  and shoulders at  $464\text{ nm}$  and  $481\text{ nm}$  were associated with the vibronic structure from the symmetric stretching vibrations of the uranyl ions [16a,b]. The spectrum of Compd. **1** clearly reveals the presence of the calixarene, uranyl ions and nitrates. The bands from the  $\pi \rightarrow \pi^*$  (P=O) transitions

centred at 227 and 232 nm were 3 nm red shifted and 2 nm blue shifted, respectively, compared to those of free ligand as a consequence of the coordination to uranyl and in agreement with the tendency observed by IR in which the strength of the  $P=O \rightarrow UO_2^{2+}$  bond is not exactly the same for the two uranyl ions. The strong and blue-shifted structured band at 265 nm corresponded to the  $\pi \rightarrow \pi^*$  (C=C-phenyl) transitions. The large shift ( $1372\text{ cm}^{-1}$ ) with respect to that of the free ligand revealed the significant effect of the coordinated uranyl ions in the calixarene cavity. Transitions between 310 nm and 370 nm from the uranyl ions are masked by those at 335 nm and 344 nm from the  $\pi \rightarrow \pi^*$  (C=C-phenyl) transitions of the coordinated calixarene which contribute to the absorbance. A well-defined and structured band centred at 294 nm was associated with mono-coordinate nitrates [23c].

The vibronic structure from the symmetric stretching vibrations of the uranyl ions (310–510 nm) is simpler in the Compd. **1** spectrum than in the Compd. **3** spectrum [Fig. S4]. The bands observed as shoulders in Compd. **3** are observed in Compd. **1** as the main bands, and the semi-flat blue-shifted bands that were centred at 433 nm and 460 nm were observed. The separation between them of 28 nm in the complex and approx. 27 nm in the salt indicated correspondence to the uranyl ions.

### 3.2.4. Luminescence studies

A study of the photophysical properties of Compd. **1** was performed. These studies included (1) measurements of powder samples in metallic plates at 291 K, (2) measurements of powder in capillary cells at 291 K, (3) measurements of powder and frozen solutions in capillary cells at 77 K, using  $\lambda_{\text{exc}} = 327\text{ nm}$  and  $\lambda_{\text{exc}} = 270\text{ nm}$ ; we selected the most relevant results at 77 K, which are collected in Table S4. The excitation and emission spectra were recorded in the fluorescence and phosphorescence modes at 291 K in solid state and solution (DMF-MeOH) and at 77 K in solid and frozen solutions (Figs. 4 and 5, and Figs. S5 and S6). Here, we focused on those recorded in phosphorescence mode, to evaluate the extent of the energy transfer from the calixarene to the uranyl cations in the complex. After normalization of the spectra, it was found that the energy transfer  $^3\pi\pi^* \rightarrow UO_2$  exciting the ligand ( $\lambda_{\text{exc}} = 270\text{ nm}$ ) was 86.5%, and the energy transfer exciting the uranyl centres ( $\lambda_{\text{exc}} = 327\text{ nm}$ ) was 87.3%, which was expected for a pure stable compound; in both cases, the band at 463 nm from the  $^3\pi\pi^*$  state almost disappeared (Fig. 4). The energy transfer  $^1\pi\pi^* \rightarrow ^3\pi\pi^*$  is not complete in Compd. **2** because even at 77 K, the  $^1\pi\pi^*$  state (304–308 nm) is still observed that can be the result from an incomplete intersystem crossing process [6d].

However, a careful analysis of the dinuclear uranyl complex spectra at  $\lambda_{\text{exc}} = 270\text{ nm}$  in powder and frozen solution, indicated that the lowest  $^1\pi\pi^*$  state is located at about 314 nm, the energy lowering of the  $^1\pi\pi^*$  state is apparently due to the ligand coordination to the uranyl cations in benefit of a better energy transfer to the  $^3\pi\pi^*$  state (463 nm).

**3.2.4.1. Emission spectra.** At 291 K and in powder, the emission spectra of Compd. **1** in the fluorescence and phosphorescence modes are similar to those at 77 K. The features of the emission spectrum, band positions and their intensity ratio changed with respect to that of Compd. **3**, the emission bands are shifted by approximately 10 nm to lower energies in powder at 77 K, under the same excitation energy (Fig. 4, Table S4). At 291 K, the luminescence of Compds. **1** and **3** in DMF-MeOH solution is partially quenched. At 77 K, the spectrum from DMF-MeOH frozen solution of the complex (Fig. S6) and that of the powdered sample were similar. When accounting for the fact that the solvent mixture is polar and DMF can coordinate to the uranyl ions, the similarity between those spectra suggests that Compd. **1** is stable in such a

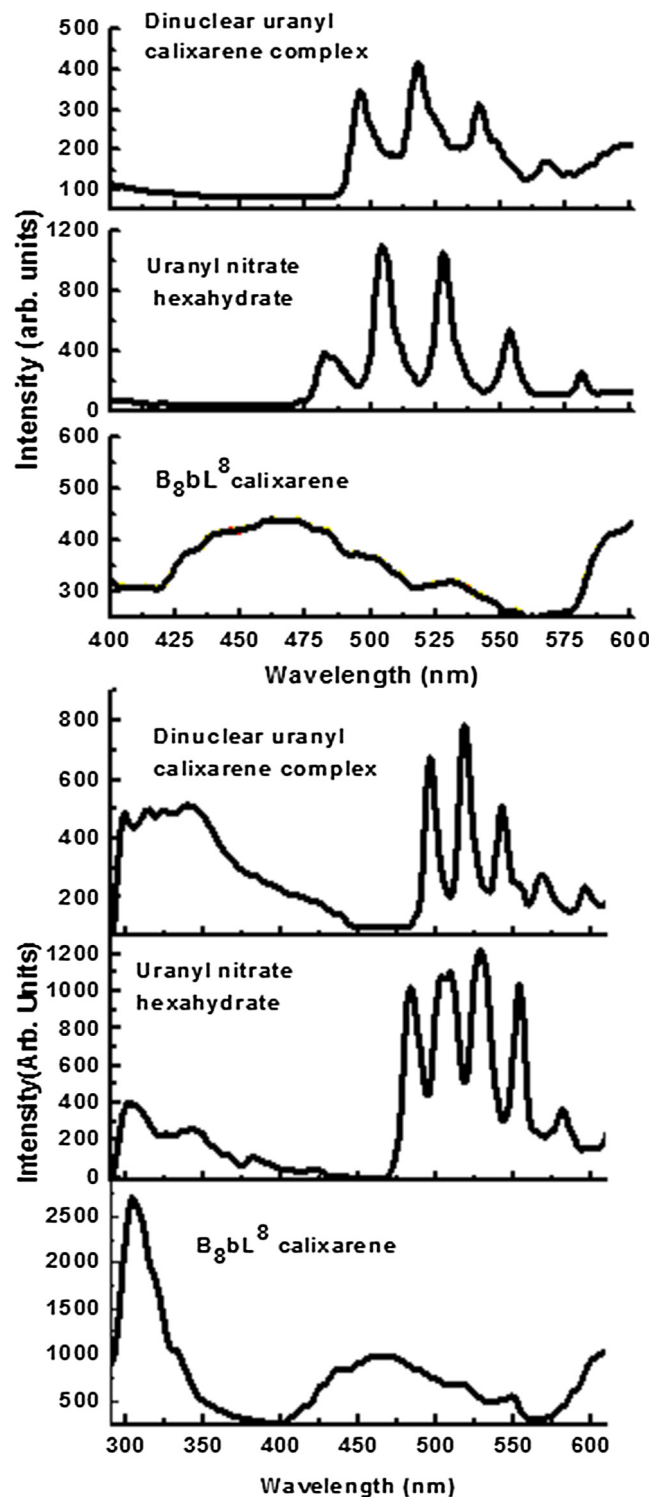
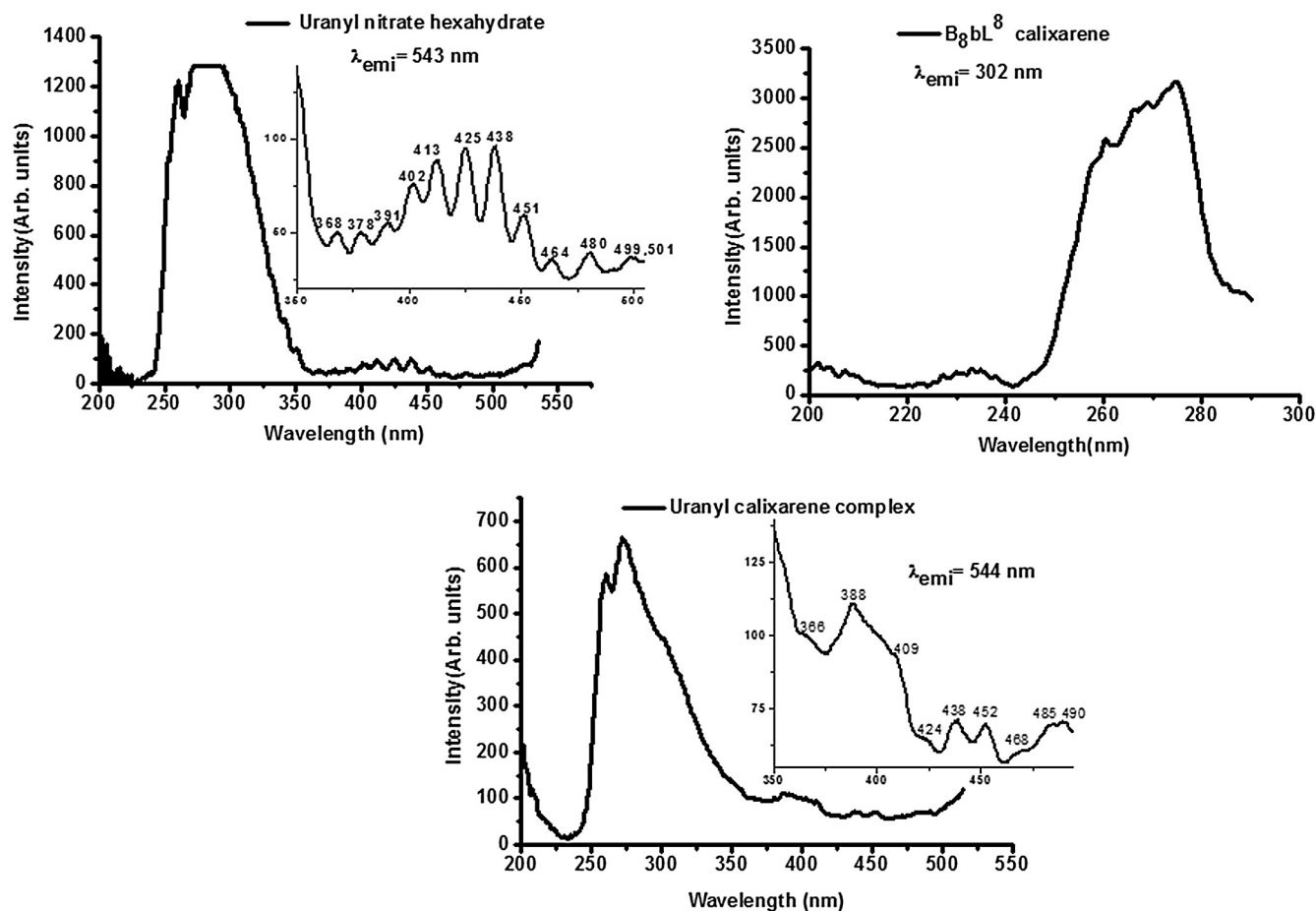


Fig. 4. Phosphorescence emission spectra in powder at 77 K of Compd. **1** (top), Compd. **3** (middle) and Compd. **2** (bottom), (a)  $\lambda_{\text{exc}} = 327\text{ nm}$  (top). (b)  $\lambda_{\text{exc}} = 270\text{ nm}$  (bottom).

polar solution and the uranyl ions maintain their chemical environments as in the solid state. The opposite occurs in the Compd. **3** spectrum, at 291 K and 77 K, which reveals that DMF is partially coordinated to the uranyl ions because the uranyl emission bands are 10 nm red shifted with respect to those of the free uranyl ions in acetonitrile [6a] and of the uranyl salt in the solid state (Fig. 4 and Table S4); the features of the spectrum and the band



**Fig. 5.** Fluorescence excitation spectra in DMF-MeOH frozen solution at 77 K of Compd. **3** (top on the left, with inset of the region from 350 to 505 nm), Compd. **2** (top on the right) and Compd. **1** (bottom in the middle, with inset of the region from 350 to 500 nm).

positions are somehow similar to those from uranyl complexes [6a, c,d].

This finding indicates that water molecules that coordinate to uranyl in Compd. **3** in the solid state are interchanged in solution by DMF molecules. It has been demonstrated that DMF coordinates to uranyl [24]. In powder at 77 K, the spectrum of Compd. **1** is quite asymmetric and is partially resolved; the phosphorescence spectra are given in Fig. 4. Two uranyl ions coordinated to the same calixarene ligand and to nitrate ions are in a similar chemical environment. This was better revealed when exciting the uranyl ion, (Fig. 4a) than when exciting the ligand (Fig. 4b).

To confirm that more than one uranyl band is involved in the spectra, the spectra of Compd. **1** and Compd. **3** obtained from exciting the uranyl ion in the solid state at 77 K, were deconvoluted. The results from the deconvolution are given in Table S4. The deconvoluted spectrum reveals two bands at 495.81 nm and 501.26 nm which correspond to the lowest excited states of uranyl and it confirms the presence of two uranyl(VI) centres in the complex molecule; each vibronic band has two bands (Table S4). These states correspond to the  $E(0-0)$  transitions which is formally a magnetic dipole transition, and it acquires appreciable electric dipole character for non-centrosymmetric environments [6]. Hence, the band positions from the experimental spectrum and those from its deconvolution demonstrate that effectively two uranyl ions are in a similar chemical environment in Compd. **1**.

It is interesting to note the particular features of the Compd. **1** spectrum when it is excited mainly at 270 nm (Fig. 4b) in phosphorescence mode. It is observed between 300–470 nm, a broad structured band in powder or frozen solution at 77 K.

The emission spectra of the frozen solution of Compd. **1** (Fig. S6) revealed two important aspects, (1) when it is excited at 327 nm, a better resolution of the spectrum is seen and it allowed us to find the position of the first transition state ( $E_{0-0}$  phonon transition) of each uranyl ion in the dinuclear complex, with certainty,  $U1E_{0-0} = 20,080 \text{ cm}^{-1}$  and  $U2E_{0-0} = 19,841 \text{ cm}^{-1}$ , and (2) when it is excited at 270 nm, the mean vibronic spacing ( $\nu_{sp}$ ) for each uranyl centre is practically the same,  $U1\nu_{UO} = 862 \text{ cm}^{-1}$  and  $U2\nu_{UO} = 860 \text{ cm}^{-1}$  in agreement with the results in powder  $U1\nu_{UO} = 856 \text{ cm}^{-1}$  and  $U2\nu_{UO} = 861 \text{ cm}^{-1}$ . These facts point to a calixarene shared by the two uranyl centres in a similar manner which is maintained in solution.

The broad complex band observed in the FIR spectrum of Compd. **1** (Fig. 3) is assumed to be due to the effect that the hydrogen bonding formed between the coordinated nitrates exerts in the molecular structure of Compd. **1**. The similarity between the emission spectra in the solid and solution of Compd. **1** at 77 K suggests that the new dinuclear uranyl calixarene complex in polar organic solvents maintains its geometrical arrangement which keeps the hydrogen-bonded water molecules between the nitrates coordinated to the uranyl ions. It can be assumed that the coordinated calixarene to the two uranyl ions maintains its conformation in solution.

**3.2.4.2. Excitation spectra.** Fig. 5 shows the excitation spectra in frozen solution of DMF-MeOH at 77 K for Compds. **1**, **2**, and **3**. In the features of the excitation fluorescence spectrum of Compds. **1** and **3**, the intensity ratio of the bands from the uranyl ion corresponds to eight-coordinate uranium (VI) centres (six-coordinate uranyl



(VI) ion), which is in agreement with the features of the corresponding emission spectra [6a,c,d]. The bands of the vibronic structure of uranyl in the excitation and emission spectra of Compd. **3** in solution are observed to be different from those observed in the solid state, which is due to the substitution of water molecules by DMF molecules of the solvent. The excitation spectrum at  $\lambda_{\text{emi}} = 544$  nm for Compd. **1** reveals a specific features in which the bands at 438 and 452 are wider and of equal intensity, while in Compd. **3**, they are less wide and have different intensities. At 77 K, the excitation spectrum from Compd. **3** after exciting at  $\lambda_{\text{emi}} = 497$  nm ( $E_{0-0}$  phonon transition) presents the same vibronic structure that the spectrum after exciting at  $\lambda_{\text{emi}} = 543$  nm. In the excitation spectrum of Compd. **1**, each of the bands observed in the spectrum at  $\lambda_{\text{emi}} = 544$  nm are slightly unfolded (412.5, 415.8; 419.7, 422.7; 424.9, 426.5; 437.1, 439.6; 446.4, 449.7; 455.1, 458.7 nm), which confirms that the chemical environment of the uranyl ions in Compd. **1** is not exactly the same.

The luminescence spectra of Compd. **1** are slightly affected by the medium because of the conformation acquired by  $B_8bl^8$  which shields the coordinated cation centres from it. Somehow, the water molecules which are not coordinated to uranyl ions and are in the lattice or probably inside the cavity, contribute to the spectra feature and the extent of its photophysical parameters as vibronic fine structure (from  $E_{0-0}$ ), the mean vibronic spacing ( $\nu_{\text{sp}}$ ) and the difference between the position of the  $E_{0-0}$  phonon transitions of each uranyl ion ( $\Delta E_{0-0}$ ). Thus, in powder at 77 K, at 327 excitation wavelength,  $\Delta E_{0-0} = 280$   $\text{cm}^{-1}$  and  $\Delta \nu_{\text{sp}} = 62$   $\text{cm}^{-1}$  were found, while in frozen solution at 77 K,  $\Delta E_{0-0} = 239$   $\text{cm}^{-1}$  and  $\Delta \nu_{\text{sp}} = 29$   $\text{cm}^{-1}$  were found. Under the same experimental condition in Compd. **1a**, which differs from Compd. **1** in that it has two fewer water molecules, these parameters were  $\Delta E_{0-0} = 274$   $\text{cm}^{-1}$  and  $\Delta \nu_{\text{sp}} = 50$   $\text{cm}^{-1}$  and  $\Delta E_{0-0} = 280$   $\text{cm}^{-1}$  and  $\Delta \nu_{\text{sp}} = 52$   $\text{cm}^{-1}$  in frozen solution, the parameters are very similar, in contrast to those of Compd. **1**.

Other important parameters for Compd. **1** in powder at 77 K were the U–O<sub>yl</sub> bond length. The  $\nu_{\text{sp}}$  corresponds to the symmetric stretching frequency of uranyl observed in Raman or IR therefore, it is a parameter used for calculating the U–O<sub>yl</sub> bond length using the equation reported [25]. Thus a  $\nu_{\text{sp}} = 831$   $\text{cm}^{-1}$  yielded 177.98 pm for U(1)–O bond length and a  $\nu_{\text{sp}} = 769$   $\text{cm}^{-1}$  yielded 184.42 pm, for U(2)–O bond length and their corresponding fwhh (full width at half height) were 5.2 nm and 5.8 nm, respectively.  $E_{10-0} = 20,161$   $\text{cm}^{-1}$  and  $E_{20-0} = 19,881$   $\text{cm}^{-1}$  were the first transition states (0–0 phonon transitions) of Uranyl-**1** and Uranyl-**2** of the dinuclear complex, respectively. The spectrum was deconvoluted, and the main parameters were  $E_{0-0} = 20,169$   $\text{cm}^{-1}$  with  $\nu_{\text{sp}} = 835$   $\text{cm}^{-1}$  for **U1** and  $E_{0-0} = 19,950$   $\text{cm}^{-1}$  with  $\nu_{\text{sp}} = 792$   $\text{cm}^{-1}$  for **U2**; U(1)–O bond length = 177.60 pm and U(2)–O bond length = 181.90 pm and their fwhh = 5.4 and 5.6 nm, respectively. The extent of the parameters from the experimental spectrum and the good agreement with those from its deconvolution confirmed the existence of a dinuclear calixarene complex in which water molecules are part of the coordination polyhedron without direct coordination with the uranium centres and with low vibronic contribution from the medium, that is, the water molecules are in the second coordination sphere of the uranyl centres and are released in solution. For the uranyl salt, the  $E_{0-0}$  was split:  $E_{0-0} = 20,726, 20,572$   $\text{cm}^{-1}$  with  $\Delta E_{0-0} = 154$   $\text{cm}^{-1}$  and  $\nu_{\text{sp}} = 877$   $\text{cm}^{-1}$  and the U–O<sub>yl</sub> bond length = 173.71 pm and fwhh = 6.4 nm; its deconvolution only fit well for one band at  $E_{0-0} = 20,750$   $\text{cm}^{-1}$  and  $\nu_{\text{sp}} = 893$   $\text{cm}^{-1}$  and U–O<sub>yl</sub> bond length = 172 pm and fwhh = 7.1 nm.

The features of the luminescence spectra of Compd. **1** as well the parameters indicate no cation-cation interactions because in complexes where cation-cation interactions exist, the lumines-

cence spectra are quite different from those of uranyl ions that do not have this type of interactions [19a].

**3.2.4.3. Lifetimes.** The luminescence lifetimes ( $\tau$ ) of uranyl ions are strongly dependent on the coordination environment and the state of the medium. To evaluate these effects, the  $\tau_s$  of Compds. **1**, **2** and **3** were measured in frozen DMF–MeOH mixture solutions at 77 K under two exciting wavelengths,  $\lambda_{\text{exc}} = 270$  nm and  $\lambda_{\text{exc}} = 327$  nm. The luminescence decay was monoexponential in the three cases, and the lifetimes are given in Table 1. The lifetimes of Compd. **1** were longer when it was excited through the calixarene ligand than through the uranyl centres, by approximately 40%, from analysing the  $E_{0-0}$  transition band and approximately 17% when analysing the band at 543 nm, which is associated with the molecular structure. This finding demonstrates the energy transfer from the excited triplet state of the calixarene to the first excited state of the uranyl ions. The shorter lifetimes exciting the uranyl ions can be due to the deactivation of the excited uranyl ions as a consequence of the water molecules hydrogen bonded between the coordinated nitrates, with a significant contribution from the released water molecules to the medium. This finding is demonstrated by the extent of the lifetimes of Compd. **1a**. The lifetimes of this complex were 38% longer than for Compd. **1**, which suggests that the conformation of the calixarene in these complexes is not the same but exciting the uranyl centres at 327 nm and analysing at 543 nm, the lifetimes were the same for both compounds. The latter demonstrates that in Compd. **1** and Compd. **1a**, the oxidation states of the two uranyl ions ( $\text{UO}_2^{2+}(\text{VI})$ ) are maintained, their inner coordination spheres (CN = 8 for the uranium atom) are the same but their environment are not. The larger lifetimes of **1a**, which are 0.84 ms and 0.45 ms for the  $E_{0-0}$  transitions exciting at 270 nm and at 327 nm, respectively, were due to the absence of free water molecules, which confirmed that deactivation of the uranyl excited state by the hydrogen bonding between the nitrates is not significant but it is the presence of free water molecules and the acquired conformation of the calixarene in the complexes. The monoexponential luminescence decay of the dinuclear uranyl complexes demonstrates that the first coordination sphere of each of the two uranyl ions are the same and the eight phosphinoyl arms from the calixarene are strongly coordinated to the two uranyl ions ( $\text{UO}_2^{2+}$ ) as a consequence, the calixarene mobility is restricted. In conclusion, in Compd. **1**, when the uranyl ion was excited and the emission band associated to the first excitation state (497–498 nm) was analysed, the lifetime was 40% shorter than that found when the ligand was excited, and 17% shorter analysing the band at 543 nm which imply that radiative energy from the ligand is transferred to the excited state of the uranyl ions that share it (each one coordinates four phosphinoylated arms), and they re-emit it as one because both are in a similar geometrical arrangement of the calixarene and nitrate ligands in which each one of the two coordinated nitrates of one uranium centre are hydrogen bonded by water molecules to each one of the two coordinated nitrates of the other uranium centre. According to the approximate modelling of the complex molecule to be discussed below and the features of the emission spectra and the associated photophysical parameters, one of the uranyl ions is slightly exposed to the medium, mainly because of the conformation that is acquired by the calixarene.

The same study was performed on Compd. **3**. In contrast to the findings from acetonitrile at 77 K, where the band positions and lifetime corresponded to the free uranyl ions [6a], in the DMF–MeOH mixture, these bands are approximately 10–12 nm red shifted as a consequence of the complexation of uranyl ions with DMF molecules after some of the water molecules are replaced by DMF molecules which is reflected in its lifetime. Thus, exciting the uranyl ion and analysing the band emission at

543 nm, the lifetime of the no-free uranyl ions was three times longer than that of the dinuclear calixarene complexes. This finding indicates that de-coordination of phosphinoyl arms from both uranyl ions can be ruled out. The lifetime of Compd. **3** in the solid state at room temperature was 0.750 ms, after excitation with a nitrogen laser [23b]. It is noteworthy that the long lifetime found for the  $B_8bL^8$  in its frozen DMF-MeOH solution was  $126 \pm 6$  ms, while in the powdered sample at 77 K, the lifetime was 2.61 ms for  $B_8bL^8 \cdot 5H_2O$  [7e]. It has been already reported [7d] a  $\tau = 83 \pm 4$  ms for  $B_6bL^6 \cdot 4H_2O$  in frozen  $CH_3CN$  solution at 77 K; thus, it is not strange to find such a lifetime for  $B_8bL^8$  in such a highly polar solvent mixture, which is able to remove the water molecules from the free calixarene compound and to restrict the mobility of the calixarene molecule.

### 3.2.5. XPS spectra

X-photoelectron spectroscopy of Compds. **1**, **2** and **3** was performed (Figs. 6 and 7 and Table 2). The survey spectrum of each compound was its fingerprint. For Compd. **1**, the XPS spectra of the U4f, P2p, O1s, and C1s orbitals of the core electron levels are presented; the XPS spectra of the U4f and O1s orbitals of Compd. **3**, and the C1s, P2p and O1s orbitals of Compd. **2** were analysed for comparison with Compd. **1**. Additionally, in the present work, the binding energy range ( $\sim 15$  to  $\sim 50$  eV) of the inner valence molecular orbitals was analysed for U6p and O2s [26].

It has been established that the extent of the covalent and/or ionic character of the bonding and the coordination geometry and coordination numbers, among other factors, determine the binding energies (BE) of the uranyl orbitals [26,27a,c]. In Compd. **1**, no reduction of the uranyl ions occurs and the absence of the U5f orbital from the  $U^{4+}$  ion at 1.9 eV confirmed this assumption (Fig. S7). The elemental content of Compd. **2**, was also determined by XPS in order to increase the confidentiality of the elemental content determined by this technique for Compd. **1** and to evaluate the BE positions of the P and O orbitals after coordination to uranyl ions (Table 2).

3.2.5.1. U(4f) spectra (core electron levels). The uranium spectrum from Compd. **1** reveals two main peaks, (U(4f<sub>7/2</sub>) and U(4f<sub>5/2</sub>), which are flanked on their left sides with semi-weak structured shake-up satellite bands, and on the right side of each main band, we observed a weak unresolved band similar to satellites centred at 377.36 eV and 378.37 eV (U4f<sub>7/2</sub>) and 388.30 eV and 389.38 eV

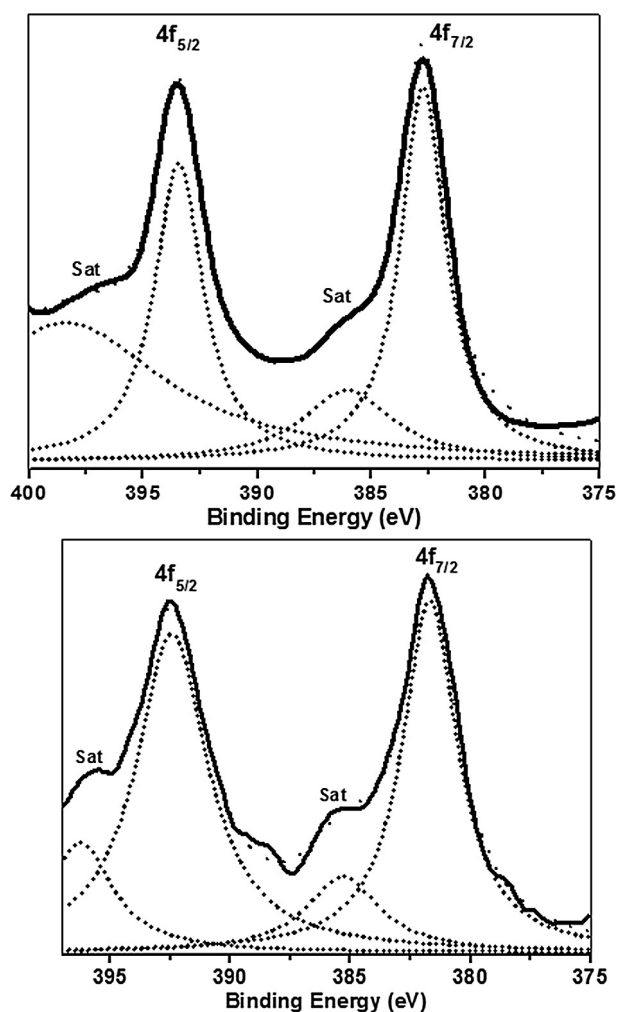


Fig. 6. XPS spectra of the U4f orbitals of the core electron levels of Compd. **1** (bottom), Compd. **3** (top).

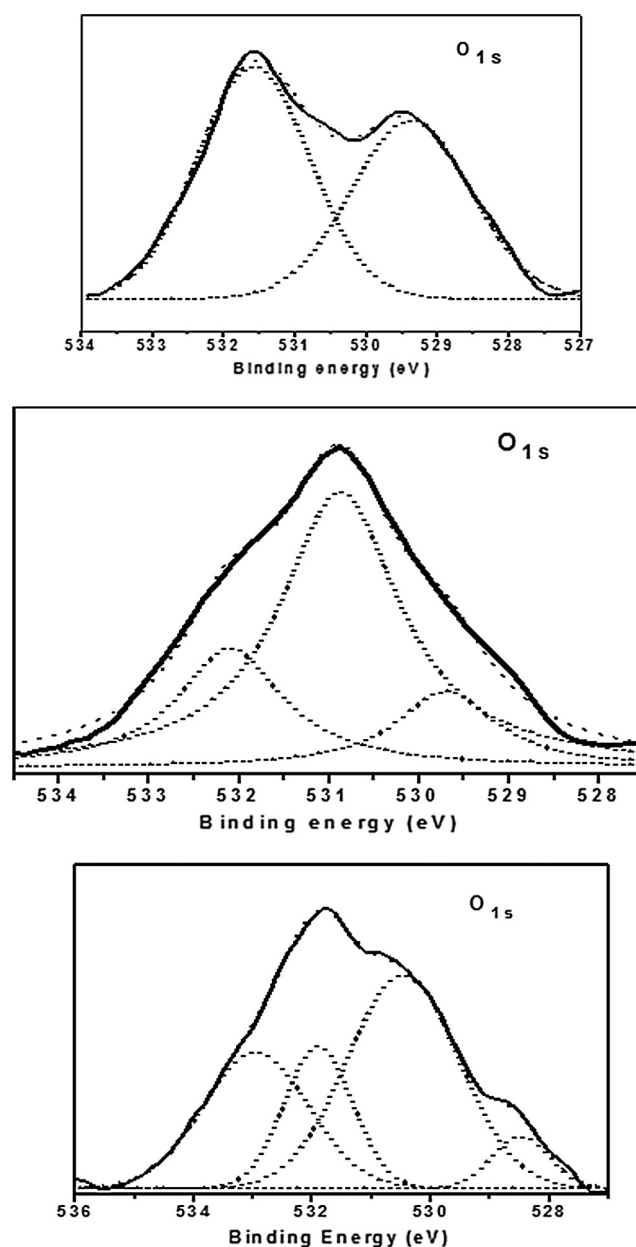


Fig. 7. XPS spectra of the O1s orbitals of the core electron levels of Compd. **2** (top), Compd. **1** (middle), Compd. **3** (bottom).

**Table 2**  
Selected binding energies (BE) of uranium (VI), oxygen, phosphorus and carbon.<sup>a</sup>

Levels	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·6H <sub>2</sub> O Compd. <b>3</b>		(UO <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> (B <sub>8</sub> bl <sup>8</sup> )·4H <sub>2</sub> O Compd. <b>1</b>		B <sub>8</sub> bl <sup>8</sup> ·2-6H <sub>2</sub> O Compd. <b>2</b>	
	BE /eV, $\Delta$ sat /eV	Fwhh /eV	BE /eV, $\Delta$ sat/eV	fwhh /eV	BE/eV	fwhh /eV
U4f <sub>7/2</sub>	382.8	2.3	381.7	2.8		
U4f <sub>7/2</sub> (sat)	386.1		385.3			
$\Delta$ U4f <sub>7/2</sub> (sat)	3.3		3.6			
U4f <sub>5/2</sub>	393.5	2.5	392.4	3.6		
U4f <sub>5/2</sub> (sat)	398.4		396.3			
$\Delta$ U4f <sub>5/2</sub> (sat)	4.9		3.9			
U4f <sub>5/2</sub> -U4f <sub>7/2</sub>	10.7		10.7			
O1s	533.00, 531.9, 530.5, 528.5	1.8, 1.2, 1.9, 1.0	532.1, 530.9, 529.7, 527.6	1.4, 1.6, 1.32	531.6, 529.3	2.1, 2.4
P2p <sub>3/2</sub>			132.9	2.2	132.0	2.2
C1s			283.9 (main)	2.3	284.1 (main)	2.2

<sup>a</sup> Experimental conditions: spots diameter = 100  $\mu$ m; 10 kV/20 mA, 200 W.

(U4f<sub>5/2</sub>). The 4f spectrum of Compd. **1** (Fig. 6, bottom) is more featured than that of the Compd. **3** spectrum (Fig. 6, top). Both spectra were deconvoluted into Gaussian–Lorentzian functions, and the best fit yielded two major well-defined peaks at 381.7 eV ( $J = 7/2$ ) and 392.4 eV ( $J = 5/2$ ) for Compd. **1** and at 382.8 eV and 393.5 eV for Compd. **3**, with both separated by 10.7 eV. (Table 2). The binding energies of the 4f core electron orbitals for the coordinated UO<sub>2</sub><sup>2+</sup> ions in Compd. **1** are red shifted by 1.1 eV with respect to those of Compd. **3**, mainly as a result of the coordination of the uranium centres to the phosphinoylated calixarene arms. Additionally, the spectra were treated with a multippeak model for Lorentzian and Gaussian functions; we confirmed only one peak for 4f<sub>7/2</sub> and one for the 4f<sub>5/2</sub> orbitals, which indicates the presence of only one species. The fwhh of these peaks is 2.8 and 3.6 eV, respectively, which is larger than those found for the mononuclear uranyl(VI) calixarene complexes formed with a smaller tetra-phosphinoylated calixarene [6c]. Therefore, the larger fwhh in Compd. **1** must be due to the perturbation of U4f orbitals of the two uranyl (VI) ions sharing the same octa-phosphinoylated calixarene.

The shake-up satellite band features depend on the bonding environment and could therefore also be useful in estimating the covalent/ionic character of the U–ligand bonds [26]. However, a precise correlation is not presently available. In Compd. **1**, the centred binding energies associated with the very pronounced shake-up satellite band yielded  $\Delta E$ (sat) equal to 3.6 ( $J = 7/2$ ) and 3.9 eV ( $J = 5/2$ ), which is typical of uranyl(VI) ions; an average of 4.0 (2.4–4.5) was reported, which also corroborates that there was no reduction of the uranyl ions. In Compd. **3**, the  $\Delta E$ (sat) is quite different for the two 4f orbitals (Table 2), which can be the result of mono- and bi-coordinated nitrates and water molecules coordinated to the uranium centre because the position of the satellite peak with respect to the photoelectron peak (4f) depends on the energy difference between the ground state and the higher orbital to which the valence electrons of uranium are excited and the valence of the elements and the type and number of its nearest-neighbours. In particular,  $\Delta E$ (sat) tends to decrease with the increasing covalent character of the U–ligand bonds. Thus, the  $\Delta E$ (sat) values found for Compd. **1** point to strong U–O=P interactions.

**3.2.5.2. O1s and P2p spectra (core electron levels).** It has recently been demonstrated that the nature of the ligands influences the BE of the uranyl oxygen atoms [6c,27b]. In most of the compounds reported to date, BE(O1s) lies in the range of 530.8–533.9 eV (fwhh = 2 eV). Therefore, in the previous work on the uranyl complex spectra formed with a smaller analogue calixarene [6c], the bands centred at 531.2 and 530.9 eV were assigned to uranyl oxygen atoms and phosphoryl oxygen atoms, while those centred at 532.8 and 532.6 eV correspond to the other oxygen atoms (phenoxy, nitrate and water molecules).

The O1s level spectra of Compds. **1**, **2**, and **3** (Fig. 7) were specific for each compound, which allowed us to visualize the interaction modes of the water molecules that are present in these compounds. According to the discussions above, in the dinuclear uranyl complex, each uranium atom from the two uranyl ions is directly bonded to four P=O groups from the calixarene and two nitrates in a monodentate mode. Other oxygens come from the water molecules, which are not directly bonded to the uranium atom but are in the lattice and hydrogen bonded in the complex. For each uranium ion, a CN = 6 from the ligand and nitrates and a CN = 2 from the “yl” oxygens from the uranyl ion would fulfil a CN = 8 by each uranium atom. In the spectrum of Compd. **2**, (Fig. 7 top) two peaks are observed, and the best fit of the spectrum was also for two peaks; the area ratio between them indicates that the peak centred at 531.6 eV corresponds to the water molecules and phenoxy oxygens, and the peak at 529.3 eV corresponds to the phosphinoyl oxygens from the pendent arms. The corresponding area ratio and height ratio with the correlation factor R<sup>2</sup> of 0.997 corresponded to the oxygen atom ratio of Compd. **2** as a bihydrate calixarene.

The spectrum of the O1s levels of Compd. **3** was complex (Fig. 7 bottom), and after deconvolution, the adequate fitting yielded four bands: from right to left, those from 528.5 to 530.5 correspond to uranyl oxygens and coordinated water molecules, and those from 531.9 to 533 eV correspond to lattice water and coordinated nitrates [6c,27b].

The spectrum of the O1s levels from Compd. **1** (Fig. 7, middle) was a broad peak with a maximum at 530.9 eV. The spectrum was deconvoluted, and the best fit by Gaussian–Lorentzian functions confirmed the peak with a maximum at 530.9 eV and revealed two peaks under the semi shoulders, at 532.1 eV and at 529.7 eV. The latter belongs to the O1s orbitals from the OP group of the calixarene, which is blue shifted with respect to the free calixarene (0.4 eV). It is clear that there is a contribution from the O1s orbitals of the uranyl oxygen ions at 530.9 eV; this band is enriched by the O1s phenoxy group band of the calixarene. The band at approximately 532.1 eV represents the O1s from water molecules and nitrates, which was red shifted by at least 0.9 eV with respect to those from Compd. **3**.

The spectrum of the P2p levels of phosphorus in the O=P groups that are coordinated to uranyl is affected by the U–OP bond strength. A stronger coordination of U–OP means significant PO  $\rightarrow$  U electron transfer; then, the photoelectron energy of P2p increases by 0.9 eV with respect to Compd. **2**. Deconvolution and any attempt of fitting more than one peak failed because the fwhh was 2.0 eV as that of the free calixarene. The XPS results confirmed the existence of one dinuclear uranyl complex that shares the same calixarene, where the coordinated nitrates also interact with water molecules that form part of the Compd. **1** structure.

**3.2.5.3. U6p and O2s (inner valence molecular orbitals) spectra.** The binding energy range of these orbitals goes from  $\sim 15$  to  $\sim 50$  eV. The analysis of these orbitals allows us to have a better understanding of the extent of the interactions in the chemical bonds of the species that are formed with uranyl ions. In particular, the spectrum of Compd. **1** shows finer and more pronounced structure than that of Compd. **3**. In the U6p–O2s binding energy range from  $\sim 12$  to 35 eV, the most extended peaks are for U6p<sub>3/2</sub> and O2s electrons shifted to higher energies with respect to those of Compd. **3**; in Compd. **1** those from O2s electrons also include the O2s orbital contribution from Compd. **2** (Fig. S8).

These spectra were deconvoluted, and from the binding energies, we obtained parameters such as  $\Delta U6p_{3/2} = 3.23$  eV and 3.04 eV. With these values in the equation [26]  $R_{U(1,2)-O} = 0.149 + 0.138(\Delta U6p_{3/2} + 1.59)^{-1}$ , we calculated the U–Oyl bond lengths for the two uranyles in the complex U(1)–O bond length = 177.63 pm and U(2)–O bond length = 178.81 pm, which differ from those of the deconvoluted luminescence spectrum obtained in powder at 77 K.

The difference was 0.03 pm for the shorter uranyl (U(1)–O bond length = 177.60 pm) and 3.09 pm for the longer uranyl (U(2)–O bond length = 181.90 pm). The U(2)–O bond length obtained from the luminescence spectrum has some uncertainty because the vibronic band positions are not completely defined since vibronic contribution from the coordinated nitrates and hydrogen bonded water can not be ruled out; therefore, the U–O bond lengths of the uranyl ions obtained from the XPS parameters were considered to be the best for the dinuclear uranyl complex which corroborated the same coordination sphere of each uranyl ions but not very similar environment that was already proposed by the other spectroscopic techniques. Nevertheless, the values of the U–O<sub>yl</sub> bond lengths obtained by XPS and Luminescence differ only by 3%.

### 3.2.6. Molecular modelling

In the present work, the experimental results found for the dinuclear uranyl complex formed with the B<sub>8</sub>BL<sup>8</sup> calixarene in ethanol and nitrates as counter ions would be better understood by the structure but attempts to obtain suitable single crystals for Compd. **1** and also for the calixarene receptor failed. In addition, modelling the molecular structure of Compd. **1** is a truly complicated task. Thus far, some DFT and other theoretical calculations of uranyl complexes have been reported [28]. The distortion effect that macrocycles can suffer when they are coordinated to f-elements and the loss of the linearity in the case of the uranyl (VI) ion by the size and conformation effects of the macromolecule have caused limitations on obtaining a truly well-modelled uranyl calixarene complex molecule. In fact, the complete molecule of a uranyl calix[4]arene molecule has already been modelled by DFT calculations [6c], but the found geometrical parameters did not allow us to propose a molecule as representative of the complex. Based on this experience and considering the higher complexity and size of the calixarene, in the complex discussed in the present work, no attempt at modelling the dinuclear calixarene complex by DFT calculations was made, but attempts for the free B<sub>8</sub>BL<sup>8</sup> calixarene were performed for which the conformation and structural parameters were very similar to that discussed below.

The B<sub>8</sub>BL<sup>8</sup> calixarene was modelled by using the COSMO procedure (Section 2.4) in order to simulate the effect of the ethanol solvent in the calixarene conformation during the synthesis of the complex. The minimum energy of the most stable B<sub>8</sub>BL<sup>8</sup> calixarene conformer was 57 kcal mol<sup>-1</sup>, and the heat of formation under the solvent effect was -1028 kcal/mol, with an average bond angle of 112.02°  $\pm$  4.27° of the -phenyl-CH<sub>2</sub>-phenyl- moieties. This neutral octa-phosphinoylated *para-tert*-butylcalix[8]arene molecule adopted a pleated loop-like conformation (Fig. 8a, b), with the eight lower rim arms arranged in two groups that are oriented in

the opposite direction of the octa-phenoxy platform, which is above and below the calixarene platform (Fig. 8b).

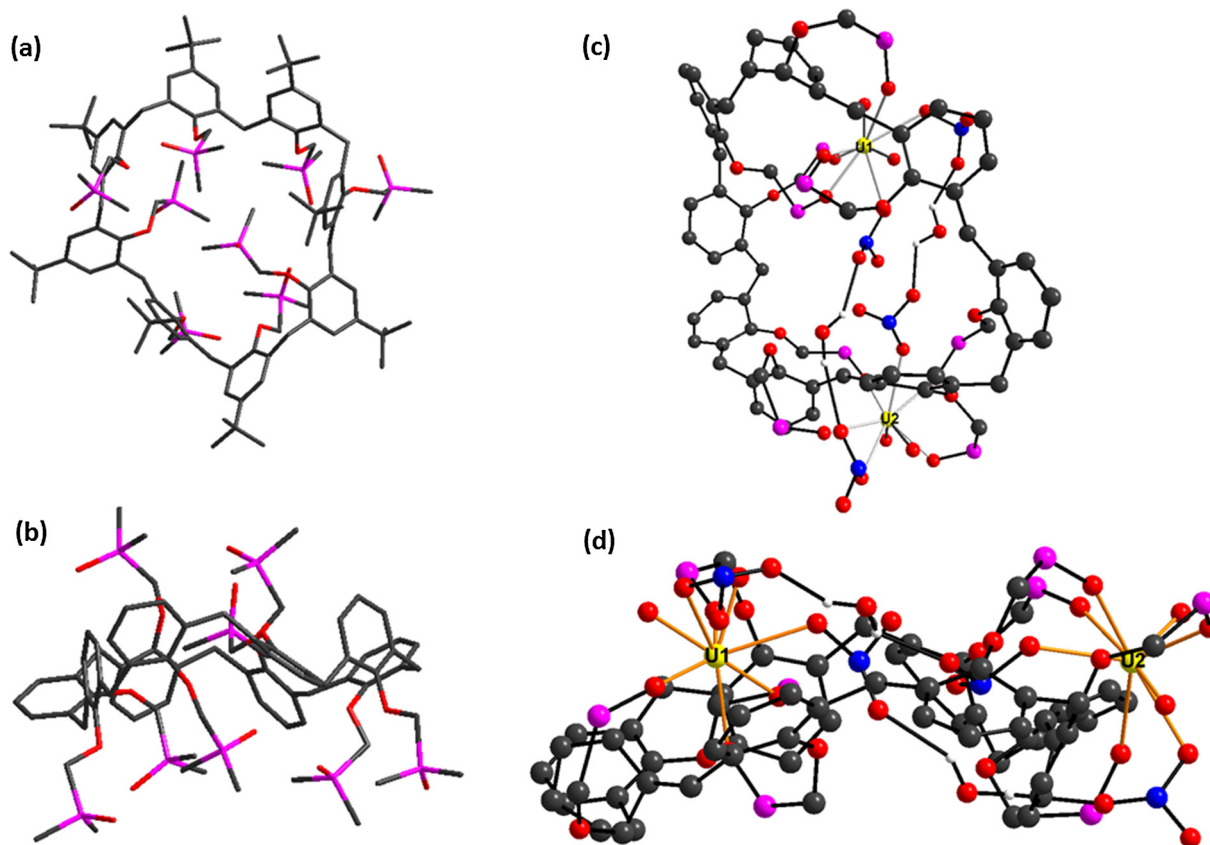
In order to achieve a better understanding of the experimental results a semi-qualitative visualization of the dinuclear uranyl complex molecule was attempted by semi-empirical calculations using as a base the modelled calixarene molecule and the spectroscopic results for building the complex molecule. Because of the lack of 5f-parameters in these procedures and the linearity of the uranyl centres, the uranyl ions were left in the calculation in unconfigured hybridization forms, in other words, in a free coordination polyhedral geometry. Thus, several possible structures were built and calculated; the best optimized complex molecule with the lowest minimum energy and the most stable conformer was that in which four OP groups of the neutral calixarene and two nitrates were coordinated to each uranium centre (U1, U2) and the mono-coordinate nitrates were hydrogen bonded with water molecules from one uranium centre (U1) to the other (U2): the (UO<sub>2</sub>)<sub>2</sub>(B<sub>8</sub>BL<sup>8</sup>)(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> molecule (Fig. 8c, d). Although this calculated molecule has geometrical deficiencies, it is a good tri-dimensional representation of the complex molecule.

In the complex, the calixarene adopted a distorted pleated loop-like conformer (Fig. 8c, d); each of the two uranyl centres is in a six-coordinate distorted geometry; the parameters of the coordination polyhedron of uranyl-**1** were the following: U–OP average bond lengths equal to 2.396  $\pm$  0.062 Å with bond angles equal to 148  $\pm$  9°, and for the two mono-coordinate nitrates U–ONO<sub>2</sub>, the bond lengths were 2.589 and 2.637 Å and the bond angle was 118.4°. The parameters of the coordination polyhedron for uranyl-**2** were as follows: U–OP average bond lengths equal to 2.447  $\pm$  0.117 Å and with bond angles equal to 149  $\pm$  17°, whereas the U–ONO<sub>2</sub> bond lengths were equal to 2.645 and 2.746 Å and the bond angle was 121.3°. We propose that the elongation of the U–ONO<sub>2</sub> bonds (typically 2.52–2.54 Å) can be the result of the hydrogen bonds from 1.873 to 2.322 Å, formed between the water molecules and the mono-coordinate nitrates (–OON–O··HOH··ONOO–). Nevertheless, the geometrical parameter values are in the intervals of those reported for calixarene uranyl complex structures and other uranyl complexes also formed with oxygen donor ligands [20,21,22e,f,28a]. The U1··U2 distance was 10 Å, which is too long for cation–cation interactions (<5 Å) [19a,c] and which agrees with the results from the spectroscopic results, in particular, the features of the luminescence spectra and the lifetimes, which does not indicate any cation (uranyl)–cation (uranyl) interactions or any hydrogen bonding between water molecules and uranyl oxygens. In the structural arrangement of the modelled dinuclear complex molecule, it can be observed that one uranyl centre is partially included in the calixarene cavity and in the lower rim holding the phosphinoyl arms while the other is mostly located in the lower rim and partially shielded by *para-tert*-butyl substituents in the upper rim (Figs. 8 and S9). Therefore, one uranyl centre is more exposed to the medium than the other centre.

The coordination modes of nitrates in uranyl complexes substantially affect the coordination geometry of the uranyl ion coordinated to organic ligands [22]. Further, in the structural arrangement of the molecule, one of the two mono coordinated nitrates of each uranyl is inside the cavities and the other is oriented outside. The two water molecules that are hydrogen bonded to the coordinated nitrates are located partially inside the calixarene cavity.

### 3.2.7. Discussion: correlation of experimental data with the calculated structures

Uranyl cations can accommodate 4, 5 and 6 donor ligands in the equatorial plane which results convenient for complexation with the B<sub>8</sub>BL<sup>8</sup> calixarene. The reaction of B<sub>8</sub>BL<sup>8</sup> with uranyl



**Fig. 8.** Modelled molecule of Compd. **2** (a) Top view of the calixarene ligand using the sequential Augmented MM3/CONFLEX/MOPAC-PM5-MOPAC-PM5/COSMO calculations, (b) Side view of the calixarene ligand, (c and d) A rough approximation to the molecule of Compd. **1** using Augmented MM3/CONFLEX calculations, (c) Top view of the dinuclear uranyl calixarene molecule where each uranyl ion is in a hexacoordinate polyhedron, (d) Side view of the complex molecule. *Tert*-butyl, methyl groups and all hydrogen atoms from the calixarene were removed for clarity. Colour coding: C: dark grey, O: red, N: blue, P: purple, U: yellow. (Colour online.)

nitrates in stoichiometric ratio 2 M:1 L in ethanol yielded a dinuclear calixarene complex, Compd. **1**. The spectroscopic results pointed to a molecule where each uranyl ion coordinates four phosphinoylated arms and each one fulfils a CN = 6 since the uranyl oxygens count as 2 donors. MIR results showed the absence of free phosphinoylated arms and the two bands from the stretching vibrations of the phosphinoyl groups strongly red-shifted by  $66\text{ cm}^{-1}$  with respect to the free ligand which demonstrates the coordination of the eight phosphinoylated arms and the strong interaction with the uranyl ions, fact that is strengthened by the increased absorbance of the bending vibrations of the  $\text{—CP=O}$  groups in the FIR region. Stretching vibrations bands from mono-coordinated nitrates are present and bands due to ionic nitrates and coordinated water molecules were absent. Instead a broad band associated to hydrogen bonding was revealed in the far infrared. Therefore, the coordination of two monodentate nitrates to each uranyl ion was proposed which results in a final CN = 8 for each uranium central atom in agreement with IR results was the feature of the luminescence spectra typical of hexa-coordinate uranyl(VI) ions and where two bands due to two  $E_{0-0}$  phonon transitions close in energy indicated the existence of two emitting uranyl (VI) centres in a hexa-coordinate geometry. In addition, the mono-exponential luminescence decay confirmed this assumption and also suggested the restriction of the calixarene mobility by its complete coordination to the uranyl centres. The similarity between the emission spectra in the solid and solution of Compd. **1** at 77 K in polar organic solvents indicated that the coordination geometry for both uranium centres are maintained, the hydrogen bonding between the coordinated nitrates to the uranyl ions is not broken.

Then it can be assumed that the coordinated calixarene to the two uranyl ions maintains its conformation in solution. It is the distorted pleated loop-like conformation of the calixarene and the hydrogen bonding between the uranyl nitrates which leave one of the uranyl centre more exposed to the environment than the other. XPS results confirmed the uranyl (VI) oxidation state in the complex and the U–O uranyl bond lengths of each uranyl centre correlate well with those calculated from the luminescence parameters. The modelled  $B_8bl^8$  ligand acquired a pleated loop-like conformation (Fig 8a, b) which is maintained though distorted, in the modelled dinuclear uranyl complex (Fig 8c, d). It is observed in Fig 8c, d, that effectively one uranyl centre is more exposed to the medium than the other uranyl centre. In spite of the flaw concerning the  $\text{O=U=O}$  bond angle, the geometrical parameters as bond lengths, bond and dihedral angles, the approximate coordination polyhedra of the uranyl centres and the structural arrangement of the calculated complex molecule correlate well with the experimental results.

#### 4. Conclusions

The octaphosphinoylated *para-tert*-butylcalix[8]arene ( $B_8bl^8$ ) forms a dinuclear complex with uranyl nitrate ( $[(UO_2)_2(NO_3)_4(B_8bl^8)_2 \cdot 2H_2O] \cdot 2(H_2O)$ ), Compd. **1**. Thus far, the spectroscopic results already discussed together the molecular modelling results of the complex molecule and of the free calixarene allow us to conclude that the two uranyl (VI) ions have the same type of coordination geometry where each one has four coordinated phosphinoylated arms and two mono-coordinated nitrates puckered in their equato-

rial planes. The calixarene keeps the pleated loop-like conformation of the calixarene in the complex molecule and this together the hydrogen bonding between the nitrates favoured the stability of the complex in solution and also the good energy transfer from the calixarene ligand to the uranyl centres as revealed by the luminescence results. This work is a little contribution to the exciting field of calixarenes and their complexes. The results inspired us to prove the B<sub>8</sub>BL<sup>8</sup> calixarene as extractant of uranyl from aqueous media simulating those used in the treatment of nuclear wastes (article in progress).

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2016.11.016>.

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