

# **A New Water Soluble Calixarene: 5,11,17,23-tetrasulphonato-25,27-di(hydroxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene. A Thermodynamic and Spectroscopic Investigation of Its Proton and Copper(II) Complexes.**

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**Abstract.** A new water soluble receptor 5,11,17,23-tetrasulphonato-25,27-di(hydroxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene was synthesized and characterized and its proton and copper(II) complexes were studied and compared with the analogous species of the fully carboxylated ligand 5,11,17,23-tetrasulphonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene.  $\Delta H^\circ$  and  $\Delta S^\circ$  values are crucial for understanding the peculiar acid-base properties of the ligand. EPR spectra together with the UV-VIS spectral data reveal the coordination stereochemistry of the copper(II) species.

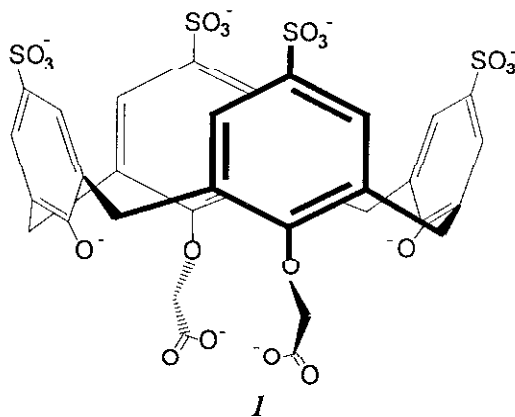
**Key words.** Water soluble calix[4]arenes, acid-base properties, thermodynamics, copper(II) complexes.

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## 1. Introduction

Calixarenes are macrocycles formed by phenolic oligomers that can be used both as building blocks and as platforms on which suitable ligands can be anchored to afford preorganized structures which can sequester selectively both ions and neutral molecules [1-9]. They can be modified with relative ease both at the upper and the lower rims [9-16]. Calix[4]arene-ester and -amide ligands in their fixed *cone* conformations have been shown to complex selectively  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . Their complexing properties have been recently reviewed [17]. Calix[4]arenes with amide pendants have been shown to complex  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ . This is of particular relevance, since these complexes are both soluble and highly luminescent [18]. Dicarboxylic acid derivatives have been designed for the selective extraction of divalent metal cations [19]. However, the need for selective functionalization has become a crucial point in the design and synthesis of new derivatized calixarenes, as underscored by several authors over the past decade [10-16]. On the other hand, water soluble calixarenes are utilized as enzyme mimicks. Using a water soluble derivatized calix[4]arene Shinkai *et al.* performed the regioselective cleavage of ribonucleoside 2',3'-cyclic phosphates [20]. For the past few years, we have been studying the complexing properties of water-soluble calixarenes [21-23] to design new calixarene-based receptors. The causative factors for the  $\text{pK}_a$  lowering of water-soluble calix[4]arenes and calix[6]arenes have been identified and discussed [21-23]. By dissecting the free energy term into  $\Delta H^\circ$  and  $\Delta S^\circ$  values, we have gained insight into the factors which determine the stability of proton complexes [22]. We have also shown that the calixarene molecular geometry has a strong influence on copper(II) complexation producing not only species with different stabilities but also different species [22].

We now report the synthesis of the new water-soluble calix[4]arene **I** which is selectively functionalized at the 1,3-(distal) positions with carboxylic pendants and locked in the *cone* conformation. The study has been carried out by a combination of several different techniques including potentiometry, thermogravimetry, calorimetry, as well as EPR, UV-VIS, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy.



## 2. Experimental

### 2.1 SYNTHESIS OF 5,11,17,23 TETRASULPHONATE-25,27 DIHYDROXYCARBONYL METHOXY-26,28 DIHYDROXY CALIX[4]ARENE OCTASODIUM SALT (*CONE* CONFORMATION).

This compound was obtained (and characterized) for the first time as a by-product of the synthesis of 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)-calix[4]arene in the *partial cone* conformation [22]. The product of interest was isolated from the product mixture which contained only 10% of the desired product by reverse phase column chromatography (Lichrosorb RP 18; eluent: H<sub>2</sub>O). The separation progress was monitored by TLC (silica gel, n-PrOH:H<sub>2</sub>O:AcOEt:NH<sub>3</sub>=5:3:2:1). The enriched mixture, free of starting material but still containing the *partial cone* derivative, was passed through a silica gel column (eluent: n-PrOH:H<sub>2</sub>O=76:24) until a single spot was obtained by TLC (silica gel, eluent: n-PrOH:H<sub>2</sub>O:AcOH = 12:5:3). The product was dissolved in a minimum amount of water, filtered and treated with acetone to induce precipitation (slightly acidic solution). The resulting suspension was kept at 4 °C overnight and filtered. The solid was dried *in vacuo* to produce **1** as a white powder in 5% yield. mp = 250-2°C (dec.); IR (KBr) 3700-3100 (bs), 1620 (s), 1200 (s), 1050(s) cm<sup>-1</sup>; <sup>1</sup>H NMR (D<sub>2</sub>O) δ 3.67 (d, 4H, Ar-CH<sub>2</sub>-Ar, H<sub>eq</sub>, J=13.8 Hz), 4.40 (d, 4H, Ar-CH<sub>2</sub>-Ar, H<sub>ax</sub>), 4.53 (s, 4H, O-CH<sub>2</sub>-CO), 7.32 (s, 4H, ArH), 7.69 (s, 4H, ArH); <sup>13</sup>C NMR (D<sub>2</sub>O) δ 33.3 (t, Ar-CH<sub>2</sub>-Ar), 77.3 (t, O-CH<sub>2</sub>-CO), 129.1 (d, Ar *meta*), 136.0 (s, Ar *ortho*), 130.0, 142.0 (s, Ar *para*), 157.5 (s, Ar *ipso*), 178.5 (s, C=O); *m/z* (negative ion LSIMS): 859.5 [M - 1]<sup>-</sup> for C<sub>32</sub>H<sub>28</sub>O<sub>20</sub>S<sub>4</sub>. An alternative synthetic route was devised in an attempt to improve the yield [24]. However, the product obtained by the alternative route does not have the same degree of purity (*i.e.*>98%) of **1** as was obtained by the method described above.

### 2.2. PREPARATION OF SOLUTIONS

Copper (II) solutions were standardized with EDTA, as recommended by Flaschka [25]. HNO<sub>3</sub> and NaOH solutions were standardized with tris(hydroxymethyl)aminomethane and potassium hydrogen phthalate (both Merck primary standards), respectively. NaNO<sub>3</sub> (RPE) was used as received.

### 2.3. POTENTIOMETRIC MEASUREMENTS.

All potentiometric measurements were conducted at  $25.0 \pm 0.1$  °C under an atmosphere of pre-humidified nitrogen with the previously described home-assembled, computerized potentiometric titration device [21]. Dispensers, cells, electrodes and meters were all purchased from Metrohm. To avoid systematic errors and verify the reproducibility, each experiment was carried out in parallel using different reading times for each meter. Values of  $E^\circ$ ,  $E_j$ ,  $K_w$  and the Nernstian slope were determined in separate experiments and the meters were calibrated on the  $\text{pH} = -\log[\text{H}^+]$  scale.

### 2.4. CALORIMETRIC AND THERMOGRAVIMETRIC MEASUREMENTS

The calorimetric measurements were carried out at  $25.0000 \pm 0.0002$  °C using a LKB Thermal Activity Monitor (TAM) equipped with a 2.5 mL stainless steel cell. At least two electrical calibrations were performed for each run. The calorimeter was also checked chemically every other week. All protonation experiments were performed by titrating a ligand solution of appropriate pH with acid. This procedure allows better  $\Delta H^\circ$  values to be obtained, since protonation heats do not overlap with the heat liberated by water formation, as it would be the case if the ligand were titrated with a base. The ligand concentration, metal/ligand ratio, pH range investigated and number of data points collected in both the potentiometric and calorimetric experiments are shown in Table I.

Thermogravimetric data were obtained by means of a Mettler TA 3000 (sensitivity =  $2.5 \times 10^{-6}$  g). An *ca* 10 mg sample was heated in air (heating rate =  $10 \text{ K min}^{-1}$ ) from room temperature up to 900 °C.

### 2.5 CALCULATIONS

Potentiometric data were refined using SUPERQUAD [26]. This package makes it possible to check also the initial ligand and/or acid concentration.  $\Delta H^\circ$  values were obtained using the program DOEC [27], whereas distribution diagrams were obtained by means of DISDI [28].

### 2.6. SPECTROSCOPIC MEASUREMENTS

NMR experiments were carried out in  $\text{D}_2\text{O}$  at 25°C using a Bruker AC-200 spectrometer and the chemical shifts ( $\delta$ , ppm) were externally referenced to DSS. Samples usually had a concentration of  $5 \times 10^{-3} \text{ mol dm}^{-3}$ . EPR spectroscopic measurements were carried out with a Bruker ER 200D

spectrometer controlled by an ESP3220 data system and equipped with a standard low temperature device.

Table I. Experimental conditions for potentiometric and calorimetric measurements conducted at 25 °C and  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ).

Concentrations ( $\text{mol dm}^{-3}$ ).					
$C_L$	$C_M$	Titrant NaOH	Titrant $\text{HNO}_3$	pH range	n° of points
0.00268		0.1017		2.5-11.0	72
0.00411		0.0999		2.4-11.0	73
0.00326		0.0999		2.4-7.0	67
0.00317		0.1007		2.4-7.0	43
0.00397		0.0996		2.4-7.5	62
0.00351		0.1009		2.4-8.5	55
0.00389		0.1006		2.4-7.2	57
0.00270	0.00255	0.1007		2.4-9.0	92
0.00356	0.00325	0.0996		2.4-7.7	48
0.00340	0.00197	0.0996		2.6-6.2	37
0.00270	0.00255	0.1007		2.4-7.5	55
0.00271			0.0811	2.2-7.0	10
0.00223			0.0811	2.5-7.0	10
0.00220			0.0811	2.5-7.5	10
0.00266			0.0811	2.6-8.0	10
0.00194			0.0811	2.6-7.5	20
0.00248			0.0811	2.5-7.5	24
0.00259			0.0811	2.5-7.0	13

Frozen solution spectra were recorded at 150 K. Parallel spin Hamiltonian parameters ( $g_{\parallel}$  and  $A_{\parallel}$ ) were calculated directly from the experimental spectra, after standardizing the klystron frequency by means of the DPPH radical ( $g_{\parallel} = 2.0036$ ). IR spectra were obtained in KBr by a Perkin-Elmer 684 infrared spectrophotometer, whereas UV-VIS spectra were obtained with a HP-8542A meter controlled by a HP-Vectra system. The solutions had a  $\text{Cu}^{2+}/L$  ratio of 1:1.1 and  $[\text{Cu}^{2+}] = 0.00253 \text{ mol dm}^{-3}$ . Each solution containing copper(II) and

the ligand was studied as a function of the pH in order to obtain information on the stereochemistry of the species detected by the potentiometric investigation. LSIM spectra were obtained with a double-focusing Kratos MS 50S instrument equipped with the standard LSIMS source and a DS90 data system. The cesium ion gun was operated at 20 keV. The instrument was scanned from  $m/z$  3000 to 100 with a scan rate of 10 s/decade. The accelerating voltage was 8 kV. LSIM spectra were obtained in the negative mode using 3-nitro-benzylalcohol (TNB) acidified with sulphuric acid as matrix. Cesium iodide was used to calibrate the instrument.

Further details can be found in References 22, 23 and 29.

### 3. Results and Discussion

The  $^1\text{H-NMR}$  spectrum of **1** (Figure 1) clearly shows that the compound has a *cone* conformation [1]. The  $^1\text{H-NMR}$  spectrum shows a single AX system for the methylene bridge protons with a remarkable chemical shift difference between the axial and equatorial protons [30] ( $\Delta\delta_{(\text{Hax-Heq})} = 0.73$  ppm)

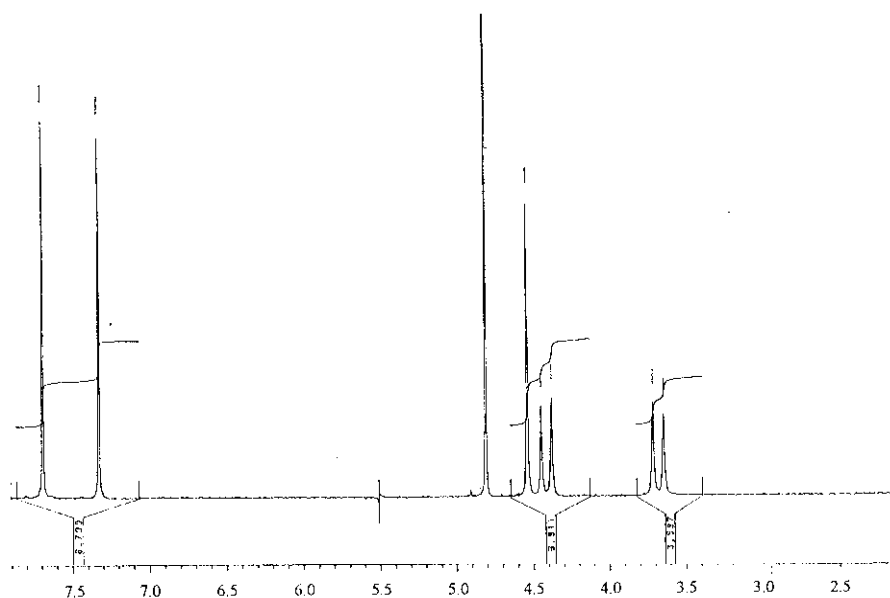


Figure 1.  $^1\text{H NMR}$  spectrum of the calix[4]-tetrasolf-bis-carboxylate **1** in  $\text{D}_2\text{O}$ .

The spectrum also shows a singlet ( $\delta = 4.53$  ppm, 4H) that is attributed to the two  $-\text{OCH}_2\text{COOH}$  methylene protons and two distinct singlets ( $\delta = 7.69$  ppm, 4H;  $\delta = 7.32$  ppm, 4H) in the aromatic proton region for the aromatic protons which are *meta* with respect to the hydroxo and hydroxocarbonylmethoxy groups, respectively. The presence of a single AX system for the Ar-CH<sub>2</sub>-Ar methylene protons demonstrates that the two  $-\text{OCH}_2\text{COOH}$  groups occupy the 1 and 3 positions on the lower rim. If this were not the case, the Ar-CH<sub>2</sub>-Ar protons would appear as three AX (or AB) systems, in a 1:2:1 ratio, corresponding to the three different types of bridging methylene groups. The <sup>13</sup>C-NMR spectrum exhibits only one signal ( $\delta = 33.3$  ppm) for the Ar-CH<sub>2</sub>-Ar carbon atoms, which further supports both the structure and conformation of **1**. Complete assignment of the <sup>13</sup>C-NMR signals is reported in the Experimental.

The thermogravimetric analysis of the compound indicates that water loss is complete below 200 °C. The anhydrous compound decomposes above 300 °C. The water content amounts to *ca.* 20 % of the starting material. This supports the result obtained by SUPERQUAD that, under the experimental conditions described above, the ligand contains 13 water molecules.

The pH range 2.5-11.0 was firstly explored to determine the protonation constants of the ligand (Table I). However, since a sharp pH jump was detected just above the neutrality region, our investigation was restricted to the pH range 2.5-7.5, where two buffered regions exist. The first and second buffered regions are ascribed to neutralization of the carboxylic and phenolic protons, respectively. A titration curve is shown in Figure 2. Superposition of the calculated curve gives an idea of the goodness of fit. The protonation constants extracted from the titration curves are reported in Table II. In the same table are included for comparison the log K values previously determined for calix[4]-tetrasulf-tetracarb [22] and *p*-hydroxybenzene sulphonic acid [23], as well as for phenoxyacetate [31]. No significant differences were observed when NaOH (the titrant usually employed) was replaced with KOH. This indicates that neither cation is significantly complexed by the calixarene in aqueous solution. Table II shows that two protonation constants fall in the pH range 3.0-3.7 and two in the range 6.5-7.0. In any case, the pH range in which the ligand loses two protons is narrow and this made it necessary to collect a large number of data points (see Table I). Comparison with the data for the fully carboxylated ligand indicates that the last two protonation constants of calix[4]-tetrasulf-bis-carb are for protonation of the carboxylate groups, whilst the first two constants are for protonation of the phenolate groups. It is noteworthy that protonation of the phenolate oxygens takes place at pH values significantly lower than those for protonation of the *p*-hydroxybenzenesulphonic acid. This is due to the particular conformation for this class of compounds. For calix[4]tetrasulphonate, the simplest member of the series, it has been shown

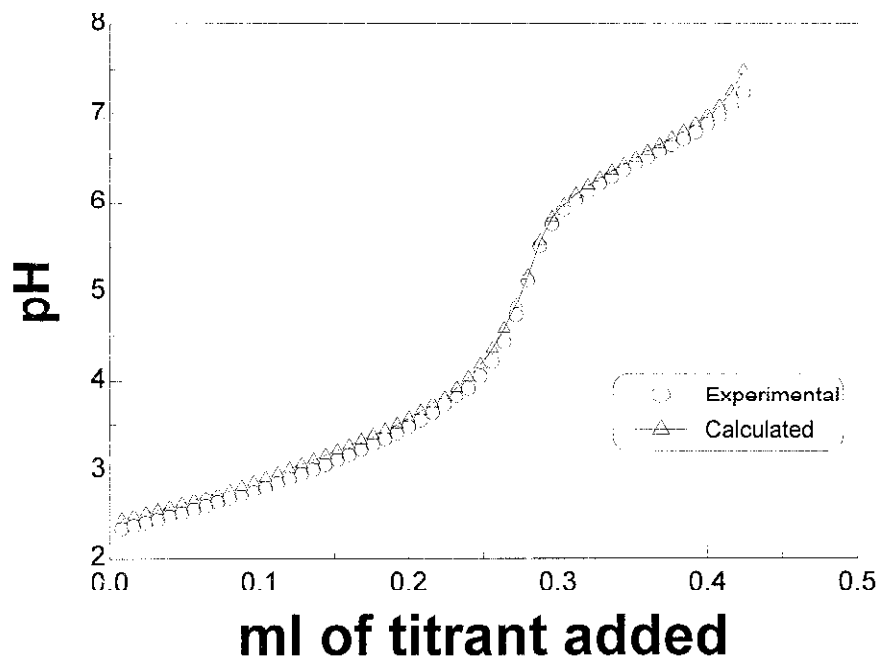


Figure 2. Calculated and experimental curves for the titration of calix[4]-tetrakisulf-bis-carboxylate *I* with NaOH;  $C_L = 3.5 \times 10^{-3} \text{ mol dm}^{-3}$ .

that the preorganization of the system together with stabilization due to hydrogen bond formation is responsible for a pK lowering of *ca.* 5 log units [21].

Dissection of the  $\Delta G^\circ$  values into the  $\Delta H^\circ$  and  $\Delta S^\circ$  values gives further insight into the factors responsible for such behaviour. The  $\log K_1$  value (see Table II) for protonation shows that the first proton is entering a fairly stabilized anionic system (the four negative charges on the sulphonate groups are omitted for simplicity). In fact the  $\log K_1$  value for *I* is significantly lower than that for *p*-hydroxybenzenesulphonate ( $\log K = 8.62$ ) [23]. The second proton is entering a fairly stabilized system as indicated by the  $\log K_2$  value for *I* that is also lower than the  $\log K$  of *p*-hydroxybenzenesulphonic acid and is comparable to  $\log K_1$ . The  $\log K_3$  and  $\log K_4$  values are typical of protonation of carboxylate groups. A comparison with the thermodynamic values for *p*-hydroxybenzenesulphonic acid indicates that the lowering of the first protonation constant for *I* is largely due to a less favorable entropic contribution (9 vs 27.6  $\text{cal mol}^{-1} \text{ deg}^{-1}$ ) whereas the lowering of the second protonation constant results mainly from a markedly unfavorable enthalpic contribution (1.0 vs -3.5  $\text{kcal mol}^{-1}$ ).



Table II. The log K values and thermodynamic parameters for the protonation of calix[4]bis-carb<sup>a</sup>, calix[4]tetracarb<sup>b</sup>, *p*-hydroxybenzenesulfonic acid<sup>c</sup> and phenoxyacetate<sup>d</sup> at 25°C and I = 0.1 mol dm<sup>-3</sup> (NaNO<sub>3</sub>)<sup>e</sup>.

Reaction				log K	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )	$\Delta H^\circ$ (kcal mol <sup>-1</sup> )	$\Delta S^\circ$ (cal mol <sup>-1</sup> deg <sup>-1</sup> )	
<b>calix[4]bis-carb<sup>a</sup> (I)</b>								
L	+	H	$\rightleftharpoons$	HL	6.86(1)	9.35(1)	-6.8(5)	8(2)
HL	+	H	$\rightleftharpoons$	H <sub>2</sub> L	6.58(1)	-8.97(1)	1.0(3)	34(1)
H <sub>2</sub> L	+	H	$\rightleftharpoons$	H <sub>3</sub> L	3.66(2)	-4.99(3)	-1.6(4)	11(1)
H <sub>3</sub> L	+	H	$\rightleftharpoons$	H <sub>4</sub> L	3.00(2)	-4.09(3)	0.7(4)	16(1)
<b>calix[4]tetracarb<sup>b</sup></b>								
L	+	H	$\rightleftharpoons$	HL	4.57	-6.23	-0.5	19.1
HL	+	H	$\rightleftharpoons$	H <sub>2</sub> L	3.97	-5.41	-1.1	15.7
H <sub>2</sub> L	+	H	$\rightleftharpoons$	H <sub>3</sub> L	3.27	-4.46	0.4	16.3
H <sub>3</sub> L	+	H	$\rightleftharpoons$	H <sub>4</sub> L	3.03	-4.13	3.0	24.0
<b><i>p</i>-hydroxybenzenesulfonic acid<sup>c</sup></b>								
L	+	H	$\rightleftharpoons$	HL	8.62	-11.8	-4.0	28
<b>phenoxyacetate<sup>d</sup></b>								
L	+	H	$\rightleftharpoons$	HL	3.16	-4.31	1.12	18

<sup>a</sup> This work. <sup>b</sup> Reference 22. <sup>c</sup> Reference 23. <sup>d</sup> Reference 31. <sup>e</sup> Standard deviations are given in parentheses. Charges are omitted for the sake of clarity

This is quite peculiar. Usually for a *hard-hard* interaction [32], the first protonation step is accompanied by a large entropic change (due to the release of water molecules into the solvent bulk) and by almost no enthalpic change. In

our case: i) the entropic contribution value indicates that the complexation of the first proton causes neither the release of a considerable number of molecules into the bulk of the solvent (as it would be expected ( $\Delta S \gg 0$ ) for a classical *hard-hard* interaction [32]) nor a significant order-disorder change; and ii) the much higher than expected enthalpic contribution ( $-6.8 \text{ kcal mol}^{-1}$ ), shows that at this stage virtually no ion-dipole bonds are destroyed, whereas a “strong” stabilizing interaction is taking place.

Stabilization of the quadruple negatively charged lower rim in *I* cannot arise from hydrogen bonding due to protons. In fact at the pH of interest, the system is fully deprotonated. All of these factors lead to the conclusion that the lowering of  $\log K_1$  for *I* may be ascribed to hydrogen bonding due to a water molecule bridging the distal phenolate oxygens.

This conclusion is corroborated by the thermodynamic changes associated with the second protonation step. At this stage the attachment of the second proton onto the second phenolate oxygen destroys the favorable hydrogen bond network ( $\Delta H > 0$ ) and confers to the system a relatively greater flexibility ( $\Delta S > 0$ ). In other words in the fully deprotonated system a water molecule acts as a clip. This (O---H-O-H---O) clip is then replaced by a somewhat more efficient one (O---H<sup>+</sup>---O) in the monoprotinated system and is lost as the system takes up the second proton.

Although microsolvation effects are known to play an important role both in chemical and biological processes [33], they are very difficult to detect. To the best of our knowledge, this is one of the few examples reported in the literature for a macrocycle [34,35] which shows how microsolvation effects can significantly affect the complexing characteristics of a ligand.

The third and fourth protonation steps, *i. e.* the protonation of the two carboxylate groups, shows some peculiarities indicating that very likely the two groups influence one another. This seems to be a characteristic of calix[4]arenes with carboxylic groups in the 1,3-(distal) positions on the lower rim [21]. Protonation of the first carboxylate group shows a small but favourable  $\Delta H^\circ$  value ( $-1.6 \text{ kcal mol}^{-1}$ ) whilst protonation of the second carboxylate group involves an almost negligible enthalpic contribution ( $0.7 \text{ kcal mol}^{-1}$ ). The favorable enthalpic value associated with the third protonation step indicates that very likely the third proton entering the anionic system bridges the two carboxylate groups. If this were not the case, one would expect an almost negligible enthalpic contribution. This interpretation is corroborated by both the  $\Delta H^\circ$  and  $\Delta S^\circ$  values obtained for the fourth protonation step. Entrance of the fourth proton destroys the hydrogen bonds and this is reflected by the unfavourable enthalpic contribution but by a favorable  $\Delta S^\circ$  value that can only arise from an increased degree of freedom of the two carboxylate groups. At this stage the favourable entropic contribution cannot result from a desolvation

effect of a lower rim anionic system that is already largely desolvated [32]. This interpretation is also supported by the thermodynamic values associated with the fourth protonation step of the fully carboxylated calix[4]arene, for which the process described above had been shown to occur [22].

We also investigated copper(II) complex formation with compound *I* to compare the complexing capability of calix[4]-tetrasolf-biscarb *I* with that of calix[4]-tetrasolf-tetracarb. Potentiometric analysis shows that two species form in the pH range 2.5-8.5, namely [CuL] and [CuLOH] (L=*I*). There are also indications of the formation of a bis-hydroxo species ([CuI.(OH)<sub>2</sub>]). However, fitting simultaneously the two hydroxo species turned out to be impossible due to the limited number of data points that could be collected over the pH range in which the species form. For this reason the curve analysis was not extended above pH 8.5. Below this pH the bis-hydroxo species forms in low percentage and can be neglected. Table III and Figure 3 show log β values and distribution diagrams for these species, respectively. Data in Table III reveal that the species formed by calix[4]bis-carb *I* are more stable than the analogous species formed by the fully carboxylated ligand.

Table III. Logβ values for Cu(II) complex formation with calix[4]-tetrasolf-bis-carb<sup>a</sup> and calix[4]-tetrasolf-tetra-carb<sup>b</sup> at = 25°C and I=0.1 mol dm<sup>-3</sup> (NaNO<sub>3</sub>)<sup>c</sup>.

Reaction		logβ
<b>calix[4]-tetrasolf-bis-carb<sup>a</sup> (<i>I</i>)</b>		
Cu + L	$\xrightarrow{\leftarrow}$ [CuL]	5.82(1)
Cu + L + H <sub>2</sub> O	$\xrightarrow{\leftarrow}$ [CuLOH] + H	1.72(5)
<b>calix[4]tetra-carb<sup>b</sup></b>		
Cu + L + 2H	$\xrightarrow{\leftarrow}$ [CuLH <sub>2</sub> ]	11.27
Cu + L + H	$\xrightarrow{\leftarrow}$ [CuLH]	8.45
Cu + L	$\xrightarrow{\leftarrow}$ [CuL]	4.63

<sup>a</sup>This work. <sup>b</sup> Reference 22. <sup>c</sup> Standard deviations are given in parentheses. Charges are omitted for the sake of clarity.

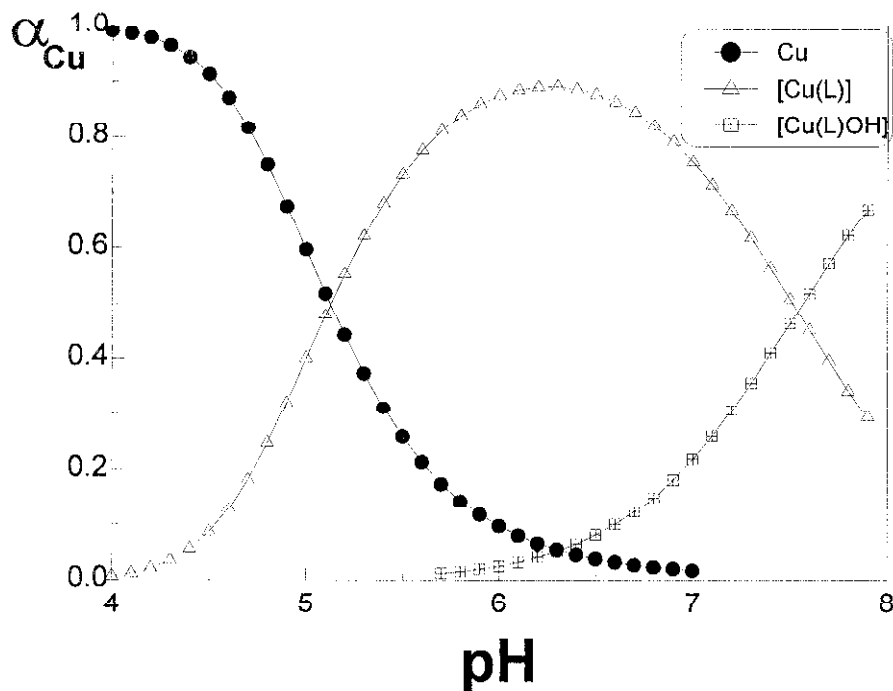


Figure 3. Distribution diagram for the Cu(II)-calix[4]-tetrasulf--biscarboxylate system.  $[Cu] = [L] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ . Charges are omitted for simplicity.

An EPR and UV-VIS spectroscopic study was conducted to provide information on i) the number of donor atoms coordinated to copper(II); ii) the geometry of the complex; and iii) the ground state of copper(II). EPR spectra were obtained in the pH range 4-9 (Table IV). Figure 4 shows the parallel portion of the EPR spectrum of the copper(II) complexes as a function of the pH. The values reported in Table IV show that below pH 4 the species is  $[Cu(H_2O)_6]^{2+}$ . As the pH increases, signals for two new species appear. According to the potentiometric results the new signals are attributed to  $[CuL]^{2-}$  and  $[CuLOH]^{3-}$ . Although a strictly quantitative correlation of the speciation and EPR data is not possible since the latter are obtained under quite different temperature conditions (150 K) [36], both the distribution diagram (Figure 3) and the EPR spectra show that the "second species" forms at the expenses of  $[CuL]^{2-}$ .

Table IV. Spin Hamiltonian parameters<sup>a</sup> for the Cu(II)-calix[4]-tetrasulf-bis-carboxylate system.<sup>b</sup>

[Cu(H <sub>2</sub> O) <sub>6</sub> ]		pH	[Cu(L)(H <sub>2</sub> O)]		[Cu(L)(OH)]		
$g_{  }$	$A_{  }^c$		$g_{  }$	$A_{  }$	$g_{  }$	$A_{  }$	
2.427(3)	130(2)						
		4.0	2.294(3)	172(2)	---	---	
		5.0	2.299(3)	174(2)	---	---	
		6.0	2.299(3)	173(2)	2.266(3)	178(2)	
		7.0	2.294(3)	172(2)	2.260(3)	178(2)	
		8.0	2.294(3)	172(2)	2.261(3)	177(2)	
		9.0	2.294(3)	172(2)	2.260(3)	177(2)	
		10.0	---	---	2.259(3)	177(2)	

<sup>a</sup> Estimated errors in the last digit are shown in parentheses. <sup>b</sup> Charges of the species are omitted for simplicity. <sup>c</sup> Hyperfine coupling constants in  $10^4 \text{ cm}^{-1}$ .

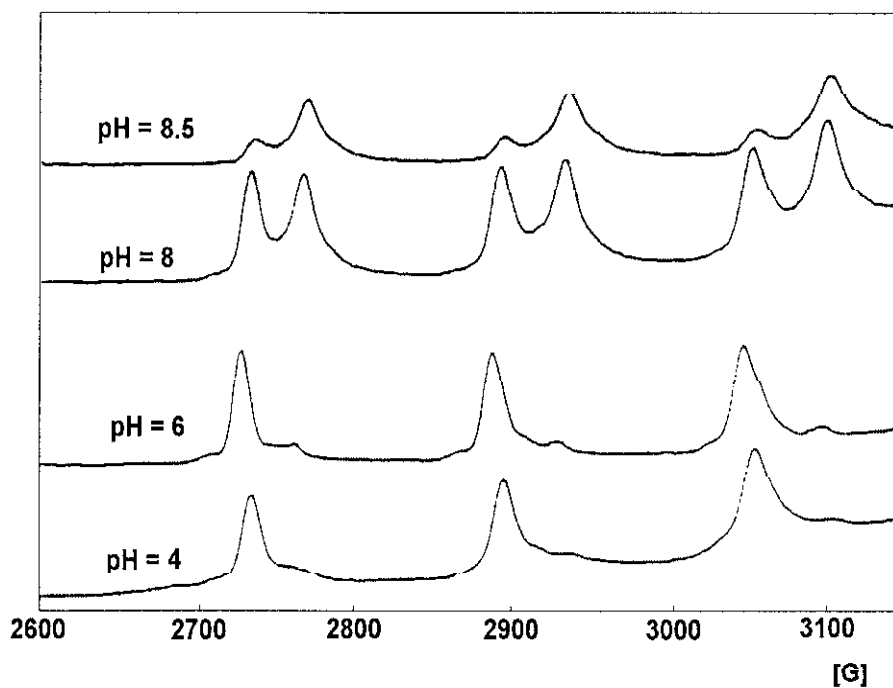


Figure 4. pH dependence of the parallel portion of the EPR spectra for the Cu(II)-calix[4]-tetrasulf-bis-carboxylate system.

In addition, the decrease of  $g_{||}$  and the increase of  $A_{||}$  observed for the "second species" (Table IV) clearly indicates that copper(II) is experiencing a stronger field and thus, in line with the potentiometric results, the "second species" can only be  $[\text{CuLOH}]^{3-}$ . As to the geometry of these complexes, very likely  $[\text{CuL}]^{2-}$  involves the simultaneous coordination of the two carboxylate and the two phenolate oxygens with the metal. However, more pronounced changes of  $g_{||}$  and  $A_{||}$  would be expected for the formation of a di-negatively charged species. In fact for tetrahydroxo and the bis-oxalato copper(II) complexes, these parameters are  $g_{||} = 2.252$  and  $A_{||} = 186$  and  $g_{||} = 2.235$  and  $A = 183$ , respectively [37]. The higher  $g_{||}$  and the lower  $A_{||}$  obtained for our complex ( $[\text{CuL}]^{2-}$ ) could result from either a tetrahedrally distorted or a five-coordinated (square base pyramid) complex. Since the ambiguity concerning the complex geometry cannot be resolved on the basis of the Hamiltonian parameters only, UV-VIS spectra were taken over the pH range 4-9. The optical spectra show both  $d-d$  and charge transfer bands, the  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  values of which are reported in Table V.

Table V.  $\lambda$  and  $\epsilon$  values for the Cu(II)-calix[4]-tetrasulf-bis-carboxylate system.

pH	$\lambda_1, (\epsilon_1)^a$	$\lambda_2, (\epsilon_2)$	$\lambda_3, (\epsilon_3)$
6.2	724 (215)	658 (268)	454 (1246)
8.5	655 (107)	591 (154)	417 (733)

<sup>a</sup> The units are nm and  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  for  $\lambda$  and  $\epsilon$ , respectively.

Below pH 4, the UV-VIS spectra showed the presence of both the free ligand and  $\text{Cu}^{2+}$ . Above pH 5, the visible spectrum showed two  $d-d$  transition bands. In the presence of a di negative charge on the coordination site, these parameters strongly favor a square pyramidal geometry. As the pH is further increased, the two  $d-d$  bands shift to higher frequencies whereas  $\epsilon$  values decrease. These results are in good agreement with both the potentiometric and EPR results, which indicate the simultaneous presence of two species in this pH region, *i.e.*  $[\text{Cu}(\text{L})(\text{H}_2\text{O})]^{2-}$  and  $[\text{Cu}(\text{L})(\text{OH})]^{3-}$ . Thus, on the basis of the experimental results, these complex species very likely have a square-pyramidal geometry. In other words, the complex species  $[\text{Cu}(\text{L})]^{2-}$  has a five-coordinate arrangement, involving four oxygens of the ligand and a water molecule. Thus more appropriately, the species should be indicated as  $[\text{Cu}(\text{L})(\text{H}_2\text{O})]^{2-}$ . As the pH increases, the complex still maintains this geometry, but the water molecule

loses a proton. As anticipated, electronic spectra also show charge transfer bands which could be either LMCT or MLCT. Although we are inclined to believe that these are LMCT bands, we cannot exclude *tout court* that they might be MLCT bands, since the simultaneous coordination of two phenolate anions is also known to give rise to MLCT bands [38].

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