

# Complex Formation of Fe(II) and Fe(III) Ions with Octafunctionalized C-Methyl-calix[4]resorcinarene Possessing $-\text{OCH}_2\text{COOH}$ (K) Moieties

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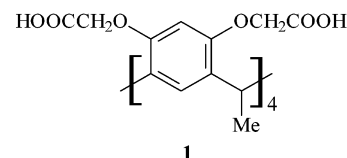
Received: September 23, 2002; In Final Form: February 19, 2003

The two common ionic forms of iron have quite different character with respect to polarizability. The Fe(III) is considered a harder Pearson acid than Fe(II). The octasubstituted C-methyl-calix[4]resorcinarene (**1**) with its carboxylate arms and aromatic rings can form both “hard” and “soft” ion binding sites, respectively. In this work the interactions of Fe(III) and Fe(II) ions with **1** were investigated by photoluminescence (PL) and quantum-chemical methods. The results suggest that Fe(II) ions form complexes with **1** favorably through cation– $\pi$  interactions, while the complexation of Fe(III) ions is mainly based on the chelate formation with the carboxylate moieties of the resorcinarene molecule. This observation makes **1** and its analogues promising candidates to be used in chemical sensors as special redox-sensitive host molecules.

## Introduction

Soon after the first syntheses of calixarenes, it was reported that they are capable of forming stable and selective complexes with ions and neutral molecules.<sup>1–3</sup> Ever since, a number of studies have been published about the factors controlling the thermodynamic and kinetic stability or selectivity of the resulting complexes.<sup>4–7</sup> In our previous papers,<sup>8,9</sup> the complexation behavior of calix[4]arene and 4-*tert*-butylcalix[6]arene (hosts) with neutral  $\pi$ -electron deficient 1-trifluoromethylbenzene derivatives (guests) in chloroform and dimethylformamide was reported. As a result of our investigation, the cavity shape<sup>10</sup> and also the solvent effect<sup>11</sup> on the stability of the complex could be determined. The results obtained on the complexation of calix[4]arene 1,3-phosphonic acid or phosphonic ester derivatives with 4-chloro-1-(trifluoromethyl)benzene showed the importance of  $\pi$ – $\pi$  interactions between the phenolic rings of the calixarene host and the neutral guest molecule.<sup>12</sup>

The interactions between Fe(II) or Fe(III) ions and aromatic  $\pi$  faces of biomolecules have been shown to play an important role in physiological processes.<sup>13</sup> Cation– $\pi$  interaction-linked sandwich complexes of iron are listed among reversible electrochemical mediators used in amperometric biosensors.<sup>14–16</sup> So far, great interest has been paid to the complexation studies of these metal ions in aqueous solution.<sup>17,18</sup> Owing to their polarizability, Fe(II) and Fe(III) ions are considered quite different. The species with the +2 oxidation state is “softer” than the “harder” Fe(III) cation. Octasubstituted C-methyl-calix[4]resorcinarene (**1**, Figure 1) can form both a “hard” and a “soft” ion binding site with its carboxylate arms and with the aromatic rings, respectively. Therefore, it appeared of interest to investigate its interactions with the two different iron ions.



**Figure 1.** Octafunctionalized C-methyl-calix[4]resorcinarene (**1**) investigated in this work.

## Results and Discussion

**Acid–Base Equilibria of the Interacted Species. pH Dependent Species Distribution of C-Methyl-calix[4]resorcinarene (**1**).** Table 1 summarizes the overall ( $\beta_i$ ) and stepwise ( $K_i$ ) protonation constants of **1**, determined as given in the Experimental Section. Figure 2 shows the distribution diagram of the different species. It can be clearly seen that, near pH = 7, compound **1** exists in double protonated form ( $\text{ResH}_2^{6-}$ , see Figure 2) and there is no considerable level of other species existing. Above pH = 10, the octa-anion form of **1** is dominant, and while decreasing the pH, penta- and tetraanions are formed. Below pH = 4, the acid–base titration suggests the association of resorcinarene molecules, probably through hydrogen bridges between the carboxylic acid arms, as was already described for resorcinarenes which have self-complementary hydrogen bonding sites.<sup>19</sup> Since at pH = 7 **1** has a well-defined protonation state and **1**-potassium salt,  $\text{FeCl}_2$ , and  $\text{FeCl}_3$  are soluble in water,<sup>20</sup> this pH value was chosen for the examination of the resorcinarene–iron interaction.

**Potassium Content.** The total potassium content of the aqueous solution of **1**- $\text{K}^+$  salt was determined with flame photometry. The results show a resorcinarene–potassium ratio of 1:8. Potentiometric measurements with an ion-selective  $\text{K}^+$  electrode were carried out to estimate the free (noncomplexed with **1**) potassium content of the solution having pH = 7. Contrary to the total potassium content, only two free potassium ions were found for a resorcinarene molecule in a  $10^{-2}$  M solution of **1**. However, when decreasing the concentration, in the solution which has  $10^{-4}$  M **1**- $\text{K}^+$  salt, 7.98 free potassium ions were determined for a resorcinarene molecule. This result

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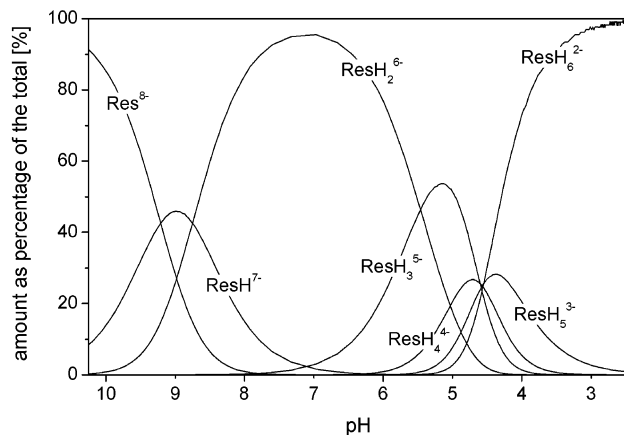
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**TABLE 1: Stepwise and Overall Protonation Constants of C-Methyl-calix[4]resorcinarene Derivative (1) in Aqueous Solution ( $I = 0.1$  M Tetraethylammonium Perchlorate)<sup>a</sup>**

| species formed                  | $\log K_i$ | $\log \beta_i$ |
|---------------------------------|------------|----------------|
| ResH <sup>7-</sup>              | 9.20 (4)   | 9.20           |
| ResH <sub>2</sub> <sup>6-</sup> | 8.75 (4)   | 17.95          |
| ResH <sub>3</sub> <sup>5-</sup> | 5.46 (5)   | 23.41          |
| ResH <sub>4</sub> <sup>4-</sup> | 4.60 (5)   | 28.01          |
| ResH <sub>5</sub> <sup>3-</sup> | 4.57 (5)   | 32.58          |
| ResH <sub>6</sub> <sup>2-</sup> | 4.55 (6)   | 37.13          |

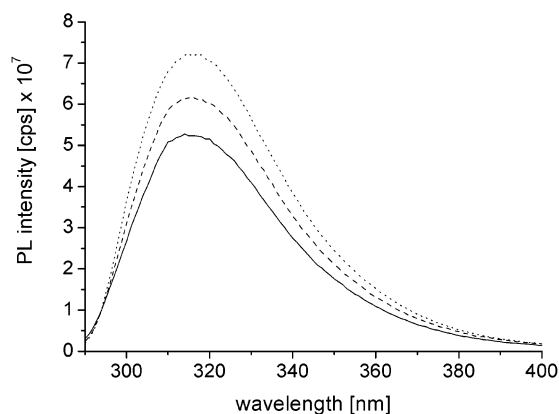
<sup>a</sup> Values in parentheses are the standard deviations of the last significant figure.

**Figure 2.** Distribution diagram of the differently protonated C-methyl-calix[4]resorcinarene derivative (1) as a function of pH.

predicts that **1**-K<sup>+</sup> salt exists in totally dissociated form below the concentration  $10^{-4}$  M. Above this concentration, astonishingly, resorcinarene **1** in aqueous solutions can bind K<sup>+</sup> ions in stable forms. On the basis of quantum-chemical calculations, the phenol ether oxygen atoms and/or the phenol ether oxygen atoms with the assistance of the carboxylate groups are involved in stabilizing the potassium cations by coordinative and ionic interactions. A similar finding was published for calixarene carboxylate derivatives.<sup>21</sup> Toward elimination of the effect of potassium complexation with respect to the interaction of **1** with iron ions, the concentrations of **1** below  $10^{-4}$  M were used for spectroscopic measurements.

**Effect of Complexation on PL Spectra.** To investigate the interaction of **1** with Fe(II) or Fe(III) ions,  $10^{-4}$  M aqueous solutions of **1**-K<sub>8</sub> salt, FeCl<sub>2</sub>, and FeCl<sub>3</sub> were prepared and the PL spectra were recorded. Figure 3 shows the PL spectra of  $10^{-4}$  M aqueous solutions of **1** in the absence and also in the presence of  $10^{-4}$  M FeCl<sub>2</sub> or FeCl<sub>3</sub> salts, by using 280 nm for excitation. The experiments were carried out at pH = 7.0, buffered by Tris, after adjusting the ionic strength with [Et<sub>4</sub>N]-[ClO<sub>4</sub>] solution (0.1 M).

Evaluating the spectra, it could be seen that the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> induced changes on the spectra. The shapes of the PL spectra are very similar: the maximum intensity was obtained at nearly 312 nm in cases of both pure **1** and **1** with FeCl<sub>2</sub> solutions. In the case of solutions of **1** with FeCl<sub>3</sub>, the maximum of PL spectra appeared at 318 nm, which is as small as a 6 nm shift from the 312 nm original value. While there were no major changes in fluorescence wavelength, the change in intensity was significant in each case (see Figure 3 as a representative example). The resorcinarene showed lower PL intensity in the presence of iron ions. According to our earlier<sup>9–12</sup> and some other results,<sup>22</sup> it was supposed that the spectral changes observed were induced by the weak interaction of resorcinarene host with Fe<sup>2+</sup> and Fe<sup>3+</sup> guest ions.

**Figure 3.** Spectral change of C-methyl-calix[4]resorcinarene derivative (1) obtained in the absence (dotted) and in the presence of  $10^{-4}$  M FeCl<sub>2</sub> (solid) or FeCl<sub>3</sub> (dashed) salts.

**Determination of Thermodynamic Properties.** To investigate the interaction of **1** with Fe(II) or Fe(III) ions,  $10^{-4}$  M aqueous stock solutions of **1**, FeCl<sub>2</sub>, and FeCl<sub>3</sub> were prepared. Following our earlier methodology based on PL measurements<sup>9–12</sup> using the Job's method, the 1:4 resorcinarene–iron complex formation can be assumed for both Fe(II) and Fe(III). Therefore, the following considerations were taken into account to evaluate the Job's curves, where the symbol C stands for the resorcinarene; M is the Fe<sup>2+</sup> or Fe<sup>3+</sup> ion; CM, CM<sub>2</sub>, CM<sub>3</sub>, and CM<sub>4</sub> are the individual types of complexes formed in the studied systems; and K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>, and K<sub>4</sub> denote the formation constants of the individual complexes, respectively. Assuming that the observed PL signal varies linearly with the concentrations,  $\Delta F$  in such a system is described by eq 1

$$\Delta F = f_{CM}[CM] + f_{CM_2}[CM_2] + f_{CM_3}[CM_3] + f_{CM_4}[CM_4] \quad (1)$$

wherein  $\Delta F = F - F_0$  is the difference between the PL intensity observed and the PL intensity of the resorcinarene with the same setup. The  $f_{CM}$ ,  $f_{CM_2}$ ,  $f_{CM_3}$ , and  $f_{CM_4}$  measurements the PL signal could be observed for the individual CM<sub>i</sub> ( $i = 1, 2, 3, 4$ ) species relative to the PL signal of pure resorcinarene species at the same concentrations. By definition,

$$f_{CM_i} = \frac{F([C]) - F([CM_i])}{F([C])} \Big|_{[CM_i]=[C]} \quad (i = 1, 2, 3, 4) \quad (2)$$

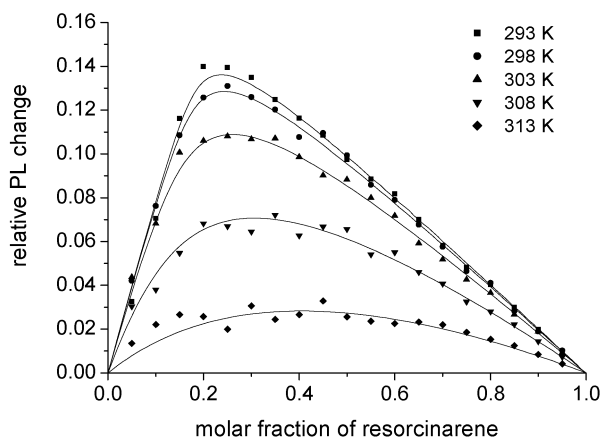
Using the expressions for the total concentration of the resorcinarene (eq 3), the theoretical change of the PL signal in the studied system can be obtained by eq 4.

$$C_0 = [C] + K_1[C][M] + K_1K_2[C][M]^2 + K_1K_2K_3[C][M]^3 + K_1K_2K_3K_4[C][M]^4 \quad (3)$$

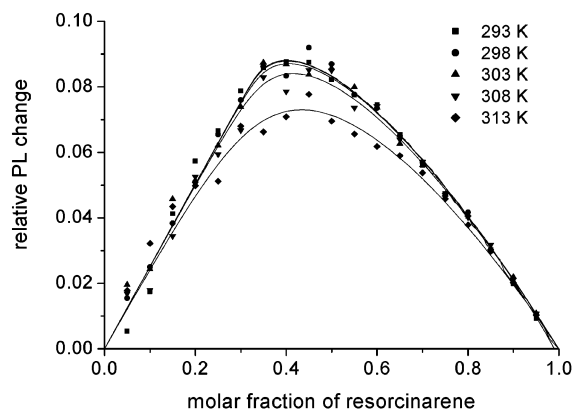
$$M_0 = [M] + K_1[C][M] + 2K_1K_2[C][M]^2 + 3K_1K_2K_3[C][M]^3 + 4K_1K_2K_3K_4[C][M]^4 \quad (4)$$

$$F - F_0 = (C_0\{f_{CM}K_1[M] + f_{CM_2}K_1K_2[M]^2 + f_{CM_3}K_1K_2K_3[M]^3 + f_{CM_4}K_1K_2K_3K_4[M]^4\}) / (1 + K_1[M] + K_1K_2[M]^2 + K_1K_2K_3[M]^3 + K_1K_2K_3K_4[M]^4) \quad (5)$$

wherein  $C_0$  is the analytical concentration of resorcinarene,  $[C]$  is the equilibrium concentration of resorcinarene,  $M_0$  and  $[M]$  are the analytical and equilibrium concentrations of the Fe<sup>2+</sup>



**Figure 4.** Job's plots of *C*-methyl-calix[4]resorcinarene derivative (1)-Fe<sup>2+</sup> complexes at different temperature.



**Figure 5.** Job's plots of *C*-methyl-calix[4]resorcinarene derivative (1)-Fe<sup>3+</sup> complexes at different temperatures.

ions, respectively, and  $K_i$  ( $i = 1, 2, 3, 4$ ) is the complex formation constant. Using eq 5, the values of  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$  as well as  $f_{CM}$ ,  $f_{CM_2}$ ,  $f_{CM_3}$ , and  $f_{CM_4}$  could be optimized iteratively: First, eqs 3 and 4 are solved numerically for given values of the formation constants and the  $f_{CM}$ ,  $f_{CM_2}$ ,  $f_{CM_3}$ , and  $f_{CM_4}$  coefficients. Then, using the equilibrium concentration of the Fe<sup>2+</sup> ions for the given parameters, the theoretical change of the PL signal can be calculated.

However, it is known that the equilibrium in similar systems strongly depends on the temperature.<sup>12</sup> The thermodynamic parameters for the individual complexes formed in the resorcinarene-Fe<sup>2+</sup> system can be determined from the thermal dependencies using the van't Hoff equation:

$$\ln K_i = -\frac{\Delta G_i}{RT} = -\frac{\Delta H_i}{RT} + \frac{\Delta S_i}{R} \quad (i = 1, 2, 3, 4) \quad (6)$$

where  $\Delta G_i$  is the Gibbs free energy change,  $\Delta S_i$  is the entropy change, and  $\Delta H_i$  is the enthalpy change associated with the complex formation. Using eq 6, inserting this expression of the formation constants into eqs 3–5, the fluorescence change in eq 5 can be expressed as a function of the  $\Delta H_i$  and  $\Delta S_i$  values and the  $f_{CM}$ ,  $f_{CM_2}$ ,  $f_{CM_3}$ , and  $f_{CM_4}$  coefficients.

To determine these thermodynamic properties experimentally, the Job's method at five different temperatures selected in the 15–35 °C range with a step size of 5 °C was applied. The thermodynamic parameters associated with the  $K_i$  values were determined from the Job's curves (Figures 4 and 5) by an iterative solution of eqs 3–5 using the expression of  $K_i$  values from eq 6.

**TABLE 2: Thermodynamic Parameters<sup>a</sup> of Complexation of *C*-Methyl-calix[4]resorcinarene Derivative (1) with Fe(II) Ions**

| coordination step | log $K_i$ | log $\beta_i$ | $\Delta G^\circ$ (kJ·mol <sup>-1</sup> ) | $\Delta H^\circ$ (kJ·mol <sup>-1</sup> ) | $\Delta S^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> ) |
|-------------------|-----------|---------------|--|--|--|
| 1                 | 5.13 (4)  | 5.13          | -29.25 (7)                               | -58.21 (3)                               | -97.18 (2)   |
| 2                 | 4.96 (4)  | 10.09         | -28.30 (7)                               | -57.12 (3)                               | -96.71 (2)   |
| 3                 | 4.91 (5)  | 15.00         | -28.01 (8)                               | -56.82 (2)                               | -96.68 (2)   |
| 4                 | 4.77 (5)  | 19.77         | -27.21 (8)                               | -55.65 (2)                               | -95.43 (2)   |

<sup>a</sup> log  $K_i$ , log  $\beta_i$ , and  $\Delta G^\circ$  values are calculated at  $T = 298$  K.

**TABLE 3: Thermodynamic Parameters<sup>a</sup> of Complexation of *C*-Methyl-calix[4]resorcinarene Derivative (1) with Fe(III) Ions**

| coordination step | log $K_i$ | log $\beta_i$ | $\Delta G^\circ$ (kJ·mol <sup>-1</sup> ) | $\Delta H^\circ$ (kJ·mol <sup>-1</sup> ) | $\Delta S^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> ) |
|-------------------|-----------|---------------|--|--|--|
| 1                 | 6.83 (4)  | 6.83          | -38.98 (9)                               | -77.17 (6)                               | -128.16 (2)  |
| 2                 | 6.52 (4)  | 13.35         | -37.18 (9)                               | -76.28 (6)                               | -131.21 (3)  |
| 3                 | 0.26 (4)  | 13.61         | -1.51 (11)                               | -21.23 (5)                               | -66.19 (3)   |
| 4                 | 0.13 (4)  | 14.74         | -0.76 (11)                               | -19.69 (6)                               | -63.52 (3)   |

<sup>a</sup> log  $K_i$ , log  $\beta_i$ , and  $\Delta G^\circ$  values are calculated at  $T = 298$  K.

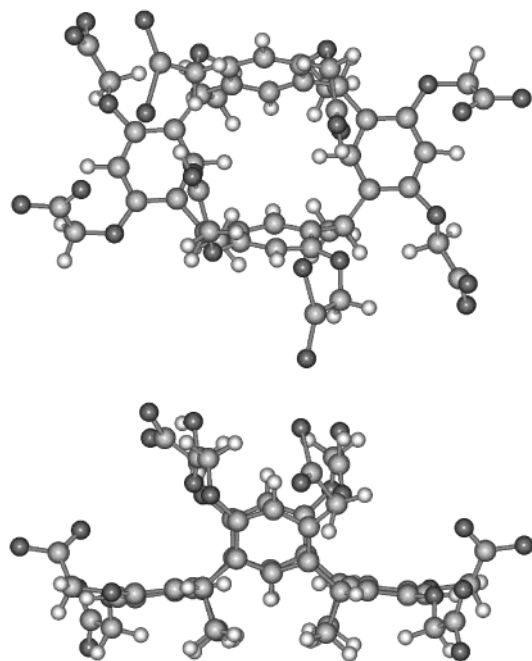
**TABLE 4: Interaction Energies of the Complexation of *C*-Methyl-calix[4]resorcinarene Derivative with Iron Ions at Different "Phenol Ether" or "Carboxylic" Sites**

| guest ion | coordination step | $E_{\text{inter}}(\text{phenol ether})$ (kJ·mol <sup>-1</sup> ) | $E_{\text{inter}}(\text{carboxylic})$ (kJ·mol <sup>-1</sup> ) |
|-----------|-------------------|---|---|
| Fe(II)    | 1                 | -43.17  | -18.36  |
|           | 2                 | -42.93  | -18.04  |
|           | 3                 | -42.57  |   |
|           | 4                 | -42.96  |   |
| Fe(III)   | 1                 | -14.13  | -69.13  |
|           | 2                 | -13.96  | -67.39  |
|           | 3                 | -13.74  |   |
|           | 4                 | -13.55  |   |

Tables 2 and 3 summarize the thermodynamic parameters for the complexation of *C*-methyl-calix[4]resorcinarene (1) with iron ions. In the case of Fe(II) ions as guests (Table 2), the enthalpy, entropy, and also the Gibbs free energy changes of the different complexation steps are nearly the same. However, the complexation of 1 with Fe(III) ions show quite different thermodynamic behavior (Table 3). The 1:1 and 1:2 complex formation results in similar enthalpy-entropy changes, which are higher than the appropriate values found for the Fe(II) ion. Nevertheless, the 1-Fe(III) complex formation with 1:3 or 1:4 stoichiometry is not supported due to the very low interaction energy derived from these stoichiometries.

The interaction between the resorcinarene derivative and iron ions detected by PL studies was examined in this work also by quantum-chemical methods using the HyperChem package<sup>23</sup> with the following calculation procedure. Each type of iron ions was separately fixed in a "hard" and in a "soft" ion binding cavity of the resorcinarene: one of them to the carboxylate arms and the other one to the phenolic units. Beginning from these initial conditions, when the stable conformation of the resorcinarene-iron system was found, full geometry optimization was done for the complex and the total energy of the unforced state was used to determine the interaction energy  $E_{\text{inter}}$ .<sup>8–12</sup> Table 4 summarizes these results. It can be clearly seen that the Fe(II) ions form much more stable complexes with the phenol ether rings of the resorcinarenes than with the carboxylate arms. On the other hand, the Fe(III) ions form about five times stronger complexes with the carboxylate arms than with the phenol ether rings. The quantum-chemical investigations suggest that Fe(II) ions seem to form complexes with 1 through cation- $\pi$  interactions in a favorable way, while the complexation of Fe(III) ions is mainly based on the chelate formation





**Figure 6.** Top and side views of the optimized structure of *C*-methyl-calix[4]resorcinarene derivative (**1**).

with the carboxylate moieties of the resorcinarene. Thus, our findings are in accordance with a close analogy published recently<sup>24</sup> and also with several results reported for similar “redox-switch”-like compounds: interconversion between two distinct states takes place by ligand exchange, such as some photochromic materials that undergo reversible, light-induced cyclizations,<sup>25</sup> rotaxanes in which macrocyclic structures shuttle between two stations on a rodlike molecule,<sup>26</sup> catenates in which redox processes of a guest ion promote swinging motions of two rings relative to each other,<sup>27</sup> and triple-stranded helices that undergo electron-induced translocation of an iron atom between neighboring cavities.<sup>28</sup>

The significant difference in the number of coordinated Fe(II) or Fe(III) ions can be interpreted by the structural property of host **1**. The geometry optimization of the given species shows that the CH<sub>3</sub> groups on the methylene bridges are located in “*all-cis*” (rccc) position and the molecule exists in a “boat” (*C*<sub>2v</sub>) conformation where two opposite rings are nearly parallel, while the other two rings are almost entirely flattened (see Figure 6). Evaluating the data derived for the interaction energy of protons with **1**, the protonation of the carboxylate moieties on rings 1 and 3 was found as the most probable way, which just results in the folding of these carboxylate arms through hydrogen bonding. As an inference, these carboxylate groups cannot take part in the cation complexation any more. This is in agreement with both the experimental and theoretical results supporting resorcinarene–Fe(III) complex formation with 1:2 stoichiometry; that is, the number of the complexed Fe(III) ions is limited to two.

## Conclusion

Using our earlier successfully employed methodology based on PL measurements and the Job’s method, the complex formation of octasubstituted *C*-methyl-calix[4]resorcinarene with both Fe(II) and Fe(III) ions was studied in parallel with quantum-chemical calculations. In agreement with the experiments, the quantum chemical investigations suggest that Fe(II) ions seem to form complexes with **1** through cation– $\pi$  interactions in a favorable way, while the complexation of Fe(III) ions is mainly based on the chelate formation with the carboxylate moieties

of the resorcinarene molecule. This observation makes **1** and its analogues promising candidates as special, redox-sensitive host molecules to be used in chemical sensors.

## Experimental Section

The host compound was prepared by the hydrolysis of octaethoxycarbonyl(methoxy)-*C*-methyl-calix[4]resorcinarene<sup>29</sup> with boiling alcoholic KOH, and the octapotassium salt of **1** was precipitated from the reaction mixture in essentially pure form. The product was dried in vacuo at 120 °C (0.1 mmHg/3 h) before use. The <sup>13</sup>C and <sup>1</sup>H NMR spectra were recorded in D<sub>2</sub>O with a Bruker Avance DRX-500 instrument, and the series of signals indicated the presence of a single conformer. Selected <sup>13</sup>C NMR data:  $\delta$  = 20.10 (CH<sub>3</sub>), 30.93 (bridge-CH-), 68.99 (CH<sub>2</sub>O), 171.51 (CO) ppm. The <sup>1</sup>H NMR spectrum was not informative due to strong broadening of signals.

Solvents were distilled before use by standard methods. The experiments were carried out at pH = 7.0 using TRIS/Tris(hydroxymethyl)aminomethane/Merck buffer. The exact pH value was reached with addition of 0.1 M HCl. Ionic strength was set by using 0.1 M tetraethylammonium perchlorate (Sigma-Aldrich) background salt, as recommended in the literature.<sup>30</sup> All measurements were carried out under purified nitrogen atmosphere.

The acidity of the host *C*-methyl-calix[4]resorcinarene (**1**) derivative was studied by potentiometry. The potentiometric investigations of acid–base equilibria were carried out by using 10<sup>−2</sup> M HCl at 25.0 ± 0.1 °C with ionic strength 0.1 M ([Et<sub>4</sub>N][ClO<sub>4</sub>]). The protonation was studied in aqueous solution with **1** at a concentration of 10<sup>−2</sup> M. Values of the stepwise protonation constants *K*<sub>*i*</sub> and the overall protonation constants  $\beta$ <sub>*i*</sub> of resorcinarene **1** were computed. The potentiometric data were obtained by using several titrations, each including not less than 250 points, and the experimental data were analyzed by the HyperQuad 2000 (Protonic Software) computer program.<sup>31–33</sup>

The potential readings were taken in stirred solutions via an Orion 420Aplus pH meter (ORION Research, Inc., Beverly, MA, USA). The pH values were determined with a combined electrode (Triode pH Electrode, Thermo Orion, Beverly, MA, USA) filled with saturated NaCl to prevent precipitation of KClO<sub>4</sub> at the junction.<sup>34</sup>

**Potassium Measurements.** *Reagents.* Reagent grade potassium ionophore III (BME-44), poly(vinyl chloride) (PVC) high molecular weight, bis(2-ethylhexyl) sebacate (DOS), and potassium tetrakis(4-chlorophenyl)borate were all obtained from Fluka. Tetrahydrofuran (THF) solvent was purchased from Aldrich. All solutions were prepared with chemicals of the highest available quality. Standard solutions were prepared from NaCl, KCl, LiNO<sub>3</sub>, and FeCl<sub>2</sub>·6H<sub>2</sub>O (Aldrich).

*Preparation of the Potassium Selective Electrode.* A coated wire type ion selective potassium electrode was used in these measurements. To prepare it, a copper wire was soldered as electric contact onto one end of a silver wire (Aldrich, o.d. 1.5 mm, length 60 mm). The other end of the wire was melted in a flame to form a small sphere with about 2 mm diameter at the end. The soldered section was coated with heat shrinking Teflon tubing and sealed by moving a soldering iron near it. The sphere and a silver wire stem of about 10 mm were left out of the insulating coating. This section was dipcoated by the plasticized PVC based K<sup>+</sup> ion selective membrane coating BME 44 ionophore.

Doing the dip coating, the silver wire was 10 times dipped into the ion selective cocktail. Between each dip, 10 s waiting

time was allowed for evaporation of the THF solvent. In this way, a membrane with an estimated thickness of about 5  $\mu\text{m}$  was obtained.

The ion selective cocktail was prepared by dissolving high molecular weight PVC (150 mg), BME44 (5.18 mg), bis(2-ethylhexyl) sebacate (DOS) (300 mg), and potassium tetrakis-(4-chlorophenyl)borate lipophilic salt (2.81 mg) in 4.5 mL of tetrahydrofuran, as was described in detail earlier.<sup>35</sup>

**Experimental Configuration of Potassium Measurements.** A Ag/AgCl electrode (Radelkis) placed into a reference half cell containing 0.1 M NaCl solution was used as reference. The measurement half cell was connected to the reference cell by a U shaped 5% agar bridge prepared with 0.1 M LiNO<sub>3</sub> electrolyte. A coated wire type ion selective potassium electrode prepared in our laboratory was used for the measurements. It was calibrated with standard KCl solutions in the concentration range 10<sup>-5</sup> to 10<sup>-2</sup> M. The equation EMF [mV] = 56.8 log  $c_{[\text{K}^+]}$  + 225.8 represents the calibration curve with  $R^2 = 0.9929$ . To avoid the interaction of the ligand and the PVC membrane as a source of error, the "standard addition slope by dilution" method<sup>36</sup> (SASD) was used. According to this method, after electrode potential measurement ( $E_1$ ) in the sample, the appropriate volume of the known standard is added and  $E_2$  is measured (the concentration is about doubled by the addition). Knowing the total volume, the same volume of water is added (double dilution) and the electrode potential is measured again ( $E_3$ ). From  $E_2 - E_3$  the slope can be calculated, and that value was used for calculating the sample concentration from  $E_2 - E_1$ . The procedure was repeated in the range 10<sup>-2</sup> to 10<sup>-4</sup> M 1-K<sup>+</sup>. The slope of the calibration and the value calculated from SASD measurements were compared, and an average deviation of 1.2% was found.

The potassium content of the solutions was followed during the titration via an ORION 420Aplus benchtop pH/ISE meter (ORION Research, Inc., Beverly, MA, USA). The potentiometric measurements were performed at constant temperature (25  $\pm$  0.1  $^\circ\text{C}$ ). A Grant thermostat (Grant LTD6G, Grant Instruments) was used for temperature controlling. The total potassium content of the samples was measured with a Perkin-Elmer 372 type atomic absorption spectrophotometer operating in atomic emission mode.

**Photoluminescence Detection.** A highly sensitive Fluorolog  $\tau 3$  spectrofluorometric system (Jobin-Yvon/SPEX) was used to investigate the photoluminescence (PL) spectra of the different solutions. For data collection a photon counting method with 0.2 s integration time was used. Excitation and emission bandwidths were set to 2 nm. A 1 mm layer thickness of the fluorescent probes with front face detection was used to eliminate the inner filter effect. A wavelength of 280 nm was chosen for excitation, and 312 nm, for the emission peak of the spectra. A Grant thermostat (Grant LTD6G, Grant Instruments) was used for temperature controlling. The stoichiometry and stability constants of the complexes were determined by an application of Job's method.<sup>37</sup>

**Quantum-Chemical Calculations.** The equilibrium conformation of the resorcinarene derivative and its complexes with iron ions was studied with a semiempirical AM1 (Austin Model) method,<sup>38</sup> followed by ab initio HF/6-31G\* calculations. The Fletcher-Reeves geometry optimization method was used for the investigation of the conformers. The interaction energy of the studied species was described at an ab initio level using an HF/6-31G\* calculation. TIP3P method<sup>39</sup> with extension to the solvent used<sup>40</sup> was applied for considering the solvent effect.

All types of calculations were carried out with a HyperChem Professional 5.1 program package.<sup>23</sup>

**Acknowledgment.** The financial support of Hungarian Scientific Research Fund (OTKA T035047, OTKA T037403), Hungarian National Committee of Technological Development (OMFB 97-20-MU0086), and Francelab Co. (France) are highly appreciated.

## References and Notes

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