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Outer-Sphere Association of *p*-Sulfonatothiacalix[4]arene and Tetrasulfonatomethylated Calix[4]resorcinarene with Cobalt(III) Tris(dipyridyl): The Effect on the Spectral and Electrochemical Properties of the Latter

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According to the ^{1}H NMR and X-ray data, the outer-sphere association of $[Co(dipy)_3]^{3+}$ with cyclophanic anions *p*-sulfonatothiacalix[4]arene and tetrasulfonatomethylated calix[4]resorcinarene is accompanied by the inclusion of the dipyridyl moiety of the former into the cavities of the cyclophanic anions in aqueous and aqueous–DMSO solutions and in the solid state. The first-step dissociation of *p*-sulfonatothiacalix[4]arene does not change the inclusion mode, but the increase in DMSO content leads to a shallower inclusion of $[Co(dipy)_3]^{3+}$. The electrochemical property changes of $[Co(dipy)_3]^{3+}$ with both receptors undergoing ion pairing indicate the stabilization of the tris(dipyridyl) cobalt complexes in lower oxidation states. The effect of the cyclophanic anions on the cyclic voltammograms of $[Co(dipy)_3]^{3+}$ correlates with the efficiency of binding of the latter with tetrasulfonatomethylated calix[4]resorcinarene and *p*-sulfonatothiacalix[4]arene.

Introduction

Recognition is a key phenomenon in supramolecular chemistry, as well as in nature. Recognition should possess two main processes: selective host−guest binding and signaling. The outer-sphere association of cobalt(III) and ruthenium(II) octahedral tris-chelates with DNA[1−3] is known to provide definite changes in the spectral and electrochemical properties of metal complexes, which serve as the signaling system. This is the reason that cobalt(III) and ruthenium(II) octahedral tris-chelates have been extensively studied as potential probes of DNA structure.[1−3] Water-soluble calixarenes, bearing ionized groups on their rims, have become increasingly important in supramolecular chemistry in recent decades.[4] Since tris-chelates of transition metal ions are able to form outer-sphere associations with DNA,[1−3] cyclic anions,[5−7] and water-soluble calixarenes,[8−13]

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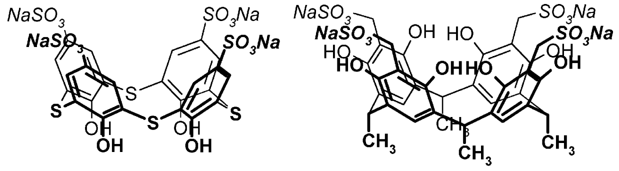
10.1021/ic050038i CCC: $30.25

Scheme 1



1 **2**

it is interesting to compare the spectral and electrochemical changes of the transition metal complexes provided by the outer-sphere association with polyanions of different structures. The hydrophobic cavity is the feature of cyclophanic polyanions that results in the insertion of moieties of the ligand of the metal ion into the hydrophobic cavity of calixarenes.[8−13] We have recently shown that the outer-sphere association of cobalt(III) tris(ethylendiaminate) with ionized calixarenes is accompanied by the insertion of the ethylendiaminate ring into the calixarene cavity which results in definite changes of spectropolarimetric properties of cobalt(III) tris(ethylendiaminate); these changes are contrary to those provided by the ion-pairing of DNA and cyclic polyanions.[12] The main reason for the spectropolarimetric changes is the inclusion of ethylendiaminate ring in the calixarene cavity; this results in an increase in the percentage of the least thermodynamically stable conformation, *ob*, whereas binding of the polyanions and DNA increases the percentage of the most stable conformation, *lel*, of the ethylendiaminate chelate rings.[12] We have now extended these studies to the effect of the outer-sphere association with cyclophanic polyanions on the spectral and electrochemical properties of cobalt(III) tris(dipyridyl) ($[Co(dipy)_3]^{3+}$) to compare it with the similar effect provided by DNA. Two water soluble cyclophanic anions, *p*-sulfonatothiacalix[4]arene (**1**) and tetrasulfonatomethylated calix[4]resorcinarene (**2**) (Scheme 1), were chosen as counterions for $[Co(dipy)_3]^{3+}$.

Experimental Section

Materials. Receptors **1** and **2** as well as $[Co(dipy)_3](ClO_4)_3$ (**3**) were synthesized using methods from the literature.[14−16]

Safety Note. Perchlorate salts of metal complexes are potentially explosive and should be handled with care. In particular, they should never be heated as solids.[17]

Spectral Measurements. The ^{1}H NMR spectra were recorded on Bruker DRX-300 and DRX-600 spectrometers operating at 300.13 and 600.13 MHz, respectively, in unbuffered D_2O, in the presence of Tris-buffer ($C = 10^{-2}$ M) and HCl ($C = 10^{-2}$ M) in D_2O, and in D_2O−DMSO-d_6 mixtures with 10, 20, and 50 vol % of the latter at 293 K. The signals for the residual protons of the deuterated solvent D_2O ($\delta_H = 4.86$ at 293 K) were used as the references for the chemical shifts. The ^{1}H NMR titration was carried out by adding aliquots of a solution of **1** to a solution of **3** with the concentrations of **3** varying from 3×10^{-3} to 1.5×10^{-3} M and the concentrations of **1** varying from 5×10^{-4} to 1×10^{-2} M. The log β values and the CIS values of **3** were deduced using the well-known Benesi−Hildebrandt procedure.[18]

UV−vis spectra were recorded on a Perkin-Elmer Lambda 35 UV−vis spectrophotometer using a 10 mm cell. The UV−vis spectra of **3** in unbuffered aqueous solutions ($C = 5 \times 10^{-3}$ M) were recorded in the absence and presence of various amounts of **1** ($C = 1{-}5 \times 10^{-3}$ M).

Crystal Structure of 4. A single crystal of **4**, $2(C_{30}H_{24}CoN_6)$, $C_{24}H_{11}O_{16}S_8$, ClO_4, $4(H_2O)$, $M = 2038.29$, was mounted with mother liquer in a glass capillary and transferred to an Enraf-Nonius CAD4 automatic four-circle diffractometer (graphite monochromator, Cu K_α radiation (1.54184 Å), $\omega/2\theta$ scan method, $\theta \leq 74.11°$). Twenty-five centered reflections gave a refined monoclinic unit cell with the following dimensions: $a = 17.366(7)$ Å, $b = 22.2492(15)$ Å, $c = 29.0904(19)$ Å, $\beta = 102.22(4)°$, $V = 10985(5)$ Å^3, $Z = 4$, $\mu(\mathrm{Cu}\ K_\alpha) = 4.58$ mm^{-1}, $\rho = 1.23$ (g cm^{-3}), and $T = 293(2)$ K. A total of 11 238 reflections, of which 7433 were unique, were measured. The stability of the crystals and the experimental conditions was checked every 2 h using three control reflections, and the orientation was monitored every 200 reflections by centering two standards. Corrections for Lorentz and polarization effects were applied. The structure was solved in space group $P2_1/c$ by direct methods and difference Fourier syntheses using the SIR program[19] and the MolEN package[20] and refined using the full-matrix least-squares method and the SHELXL97[21] program. All non-hydrogen atoms were refined anisotropically; H-atoms were located in ΔF maps and were included in the structure-factor calculations with fixed positional and thermal parameters. The final R values were $R = 0.0795$ and $R_w = 0.1632$ for 2880 unique reflections with $I \geq 2\sigma$. All calculations were carried out on a PC using the WinGX[22] suite of programs.

pH-metric Measurements. The pH-metric measurements were carried out in a thermostatically controlled cell at 25 ± 0.1 °C with an I-130 Ionomer meter; the error was less than 0.05 pH unit. A HCl (1×10^{-2} M) solution was used as the titrant. The pH meter was calibrated by a series of buffer solutions. The pHs of **1** ($C = 2 \times 10^{-3}$ M) and a 1/1 mixture of **1** and **3** were recorded in the range of pH 2.0−3.0. No extra salts were added during the pH measurements to maintain a definite value of ionic strength and avoid undesirable association equilibriums.

Cyclic Voltammograms. Cyclic voltammograms (CVs) were recorded using a PI-50-1 potentiostat with a N307/2 XY recorder. The potential scan rate was 100 mV s^{-1}. A glass-carbon electrode ($d = 2$ mm) pressed in Teflon served as the working electrode. The electrode was polished prior to each measurement. The potentials were measured versus Ag/AgCl/0.1 M KCl.

Classic polarograms were recorded on a LKD-4 $x{-}y$ recorder using polarograph PU-1. The potential scan rate was 10 mV s^{-1}. A capillary with a mercury flow rate of 12.29 mg s^{-1} was used. The drop time was 0.5 s. The polarization curves were recorded in three electrode modes; the platinum wire and the silver electrode Ag/0.01 M $AgNO_3$ in MeCN were used as auxiliary and reference electrodes, respectively.

The electrochemical measurements of **3** ($C = 2 \times 10^{-3}$ M), 5/1, 2/1, 1/1, and 1/2 mixtures of **3** and **1**, and 5/1, 1/1, 1/3, and 1/6

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Table 1. CIS values of **3** in Aqueous Solutions at Various pHs and in Aqueous−DMSO Solutions with Various Concentrations of DMSO

	CIS					
proton number[b]	D_2O, pH 2.8−3.0	D_2O, pH 7.1	D_2O, pH 2.0	D_2O−10% DMSO-d_6	D_2O−20% DMSO-d_6	D_2O−50% DMSO-d_6
6	−0.51	−0.51	−0.46	−0.44	−0.39	−0.28
5	−0.44	−0.42	−0.42	−0.37	−0.32	−0.24
4	−0.59	−0.64	−0.59	−[a]	−[a]	−0.34
3	−0.3	−0.29	−0.29	−0.25	−0.23	−0.16

[a] CIS value cannot be accurately determined because of the overlap with the signal of **1**. [b] Numbered protons of dipyridyl fragments are shown in Figure 1.

mixtures of **3** and **2** were performed in DMSO−H_2O (20 vol % of DMSO) in the presence of 0.1 M $NaClO_4$ with 1×10^{-2} M Tris as the buffer system.

The dissolved oxygen was removed by bubbling nitrogen through the solution; all measurements were carried out at 22 ± 0.1 °C.

Results and Discussion

According to our recently published data,[12] conductivity and ^1H NMR spectroscopy methods revealed that **3** forms outer-sphere associations with receptors **1** and **2** in aqueous and aqueous−DMSO media (aqueous−DMSO medium is required to avoid the precipitation of the complex formed between **2** and **3**). As long as receptors **1** and **2** possess four aromatic rings, their anisotropic effects on the chemical shifts of vicinal protons were used to control the proximity of the guests to the hosts and as a measure of their association. The ^1H NMR titrations of **3** by receptors **1** and **2** were recorded in unbuffered D_2O and D_2O−DMSO-d_6 with 20 vol % of the latter.[12] The apparent association constants (β) and the limiting chemical shifts or complexation-induced shifts (CIS) of **3** were deduced from the ^1H NMR titration data using a 1/1 binding model. The data indicate that the interaction of **3** with **1** ($\log \beta > 4$) is tighter than that of **3** with **2** ($\log \beta = 3.47 \pm 0.07$) in an aqueous−DMSO (20 vol %) solution.[12] Compounds **1** and **2** in aqueous media exhibit acidic properties because of the dissociation of the phenolic groups. According to the data from the literature, compound **1** is a much stronger acid than **2** (pK_1 values in aqueous medium are 2.18 and 9.0 for receptors **1**[23] and **2**,[11] respectively). Thus, under the pH conditions of the ^1H NMR titration in unbuffered D_2O and D_2O−DMSO-d_6 (20 vol %) (pH 2.5−3.0) receptor **1** is an equilibrium mixture of tetra- ($\mathbf{1}^{4-}$) and penta-anions ($\mathbf{1}^{5-}$), in which the formation degrees (α) of $\mathbf{1}^{5-}$ and $\mathbf{1}^{4-}$ vary with increased concentration of **1**, while **2** is in the $\mathbf{2}^{4-}$ form at pH 5.9−6.4 in unbuffered D_2O−DMSO-d_6 (20 vol %). The appearance of an electron-donating phenolate group upon changing from $\mathbf{1}^{4-}$ to $\mathbf{1}^{5-}$ increases the π-electron density of the hydrophobic cavity, and this, in turn, may facilitate guest binding and provide enhanced anisotropic effects on the chemical shifts of the guest protons.[24] This compels us to repeat the NMR titration of **3** by **1** at definite pH values to distinguish the upfield sifts caused by $\mathbf{1}^{4-}$ from those caused by $\mathbf{1}^{5-}$. This is the reason that the ^1H NMR titration measurements were carried out in the presence of HCl at pH 2, where the α-values of $\mathbf{1}^{4-}$ and $\mathbf{1}^{5-}$ are 70% and 30%, respectively, and in the presence of Tris-buffer at pH 7.1, where the α-value of $\mathbf{1}^{5-}$ is 100%. Figure 1 illustrates the ^1H NMR titration data in the presence of Tris-buffer at pH 7.1; the data obtained at pH 2 and 2.8−3.0 are not shown because of their proximity to the titration data obtained at pH 7.1. The CIS values of **3** ion-paired with **1**, deduced from the ^1H NMR titration measurements at pH 2, 2.8−3.0, and 7.1, are very close (Table 1); thus, the dipyridyl protons of **3** exhibit the same upfield shift when ion-paired with both $\mathbf{1}^{4-}$ and $\mathbf{1}^{5-}$. Although the binding constant between **1** and **3** is very high ($\log \beta > 4$) and cannot be accurately evaluated from the ^1H NMR data, it is possible to reveal which form of **1** ($\mathbf{1}^{4-}$ or $\mathbf{1}^{5-}$) has a tighter association with **3**. Because counterion binding can shift the dissociation equilibrium, pH-metric titration data enable us to study the effect of ion-pairing with **3** on the first-step deprotonation of **1**. The pH-metric titration of both $\mathbf{1}^{4-}$ and $\mathbf{1}^{5-}$ in the presence of **3** at a 1/1 concentration ratio was carried out at a pH range from 3.1 to 2.0. The data (Figure 2) indicate that the deviation between titration curves A and B is nearly within experimental error. Thus, the pH-

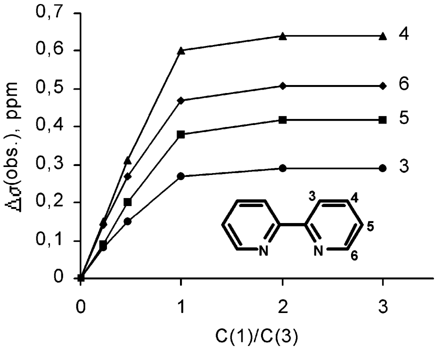

Figure 1. Upfield shift ($\Delta\delta_H$) of the aromatic protons of **3** as a function of C_1/C_3 in D_2O at pH 7.1.

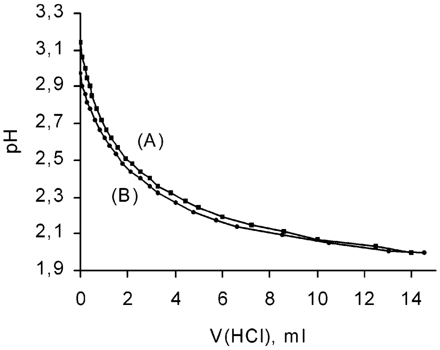

Figure 2. pH-metric titration curves of **1** (A) and **1** in the presence of equimolar amounts of **3** (B).

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metric and NMR titration data indicate that both **1**$^{4-}$ and **1**$^{5-}$ bind **3** with the same efficiency (log $\beta > 4$) and provide the same CIS values. So, although, in aqueous solution, **1** exists as an equilibrium mixture of **1**$^{4-}$ and **1**$^{5-}$, the equilibrium shift between **1**$^{4-}$ and **1**$^{5-}$ does not have an effect on the experimentally observed upfield shifts of **3** with the increasing concentration of **1** in unbuffered solutions.

The comparison of CIS values, deduced from the NMR titration data in aqueous and in aqueous−DMSO media with 20 vol % of the latter, indicates that the ion-pairing between **1** and **3** in aqueous media provides more upfield shift of **3** than that in aqueous−DMSO media (Table 1). A further increase of the DMSO content results in a further decrease of the CIS values of **3** (Table 1).

Intermolecular nuclear Overhauser effects between host and guest protons can provide additional support for the host−guest complex formation discussed above.[25] Intermolecular nuclear Overhauser effects (NOEs) were observed between the protons of **2** and **3**,[12] whereas no effects were seen for the mixture of **1** and **3** in aqueous−DMSO medium with 10 and 20 vol % of the latter. Strong NOEs between the aromatic proton of **1** and CH(6) of **3** in D_2O (see Supporting Information, 2D NOESY spectra) indicates that they are closer together in the aqueous medium than in the aqueous−DMSO medium. Thus, the CIS values at various concentrations of DMSO (Table 1) along with 2D NOESY NMR (NOE) data in aqueous and aqueous−DMSO (10 and 20 vol % DMSO) solutions indicate that the ion-pairing between **1** and **3** has a deeper inclusion of the dipyridyl moieties of **3** into the cavity of **1** in an aqueous medium than it has in an aqueous−DMSO medium. If the high solvating capacity of DMSO toward cations is taken into account,[26] it is natural to assume that the more efficient solvation of **3** is the main cause of its less efficient inclusion into the cavity of **1** in aqueous−DMSO solutions than in aqueous solutions.

X-ray diffraction analysis is a powerful tool for the determination of the structure of the host−guest complex. The slow evaporation of diluted aqueous solutions ($C = 1-5 \times 10^{-3}$ M) of **1** and **3** with various concentration ratios for **1** and **3** results in the growth of two types of crystals suitable for single-crystal X-ray diffraction analysis. The first type of crystal grows from 0.5/1, 1/1, and 1.5/1 solutions of **1** and **3**; the second type occurs only at excess concentrations of **1** where the pH is 2.5, and thus, **1** is an equilibrium mixture of **1**$^{4-}$ and **1**$^{5-}$. According to the X-ray data, the asymmetric part of the monoclinic crystals (first type) contains one **1**$^{5-}$ anion, two $[Co(dipy)_3]^{3+}$ cations, one ClO_4^- anion, and four H_2O molecules (**4**). One $[Co(dipy)_3]^{3+}$ complex is included in the calixarene cavity, and another one interacts with the calixarene aromatic units outside the cavity (Figure 3).

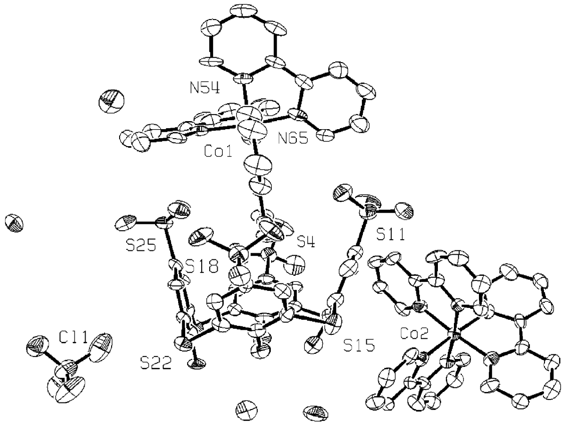

Figure 3. ORTEP view of the molecular geometry of compound **4**. Hydrogen atoms are not shown for clarity.

The analysis of the crystal structure of the second type of crystal is in progress to date and will be published later. The preliminary results show that the unit cell parameters and the supramolecular structure of the second type of crystal are quite different from those of the first type. In particular, the asymmetric part of the trigonal crystal (second type) contains one anion of **1**, one $[Co(dipy)_3]^{3+}$, one $Na(H_2O)_6^+$ cation, and eight H_2O molecules. This composition indicates that **1** is in the form **1**$^{4-}$.

The inclusion of $[Co(dipy)_3]^{3+}$ into the cavity of **1**$^{5-}$ in the crystal of **4** is driven by face to face and edge to face interactions. This interaction is facilitated by the conformation of the calixarene anions which is very close to a 1.3-diplanar conformation (dihedral angles between facing phenolic moieties of 31.33° and 78.60°) which is more asymmetric than that adopted by the *p*-sulfonatocalix[4]arene anion for the inclusion of $[Ni(phen)_3]^{2+}$ into its cavity.[13] In particular, in the crystal structure of **4** the distances between aryl centroids of dipyridyl and calixarene are 4.78(1) and 5.06(1) Å which corresponds to the dihedral angles between the dipyridyl and calixarene aromatic fragments; they are 29.68(3)° and 4.99(3)°, respectively. The C−H···π-interactions between the dipyridyl hydrogens and the aromatic rings of the calixarene moieties stabilize the arrangement of $[Co(dipy)_3]^{3+}$ within the cavity of **1**. The second $[Co(dipy)_3]^{3+}$ interacts with the thiacalixarene molecules via face to face π-stacking and C−H(dipy)···O(SO_3) hydrogen bonding (the closest CH···O distance is 2.57 Å). The analysis of the supramolecular structure of **4** reveals the up−down face to face π-stacking only between those thiacalixarenes which are centrosymmetric to each other. The distance between the aryl centroids of face to face interacting calixarenes (a and b in Figure 4) is 3.66(1) Å, and the dihedral angle is 0°. Each calixarene anion in the pair has $[Co(dipy)_3]^{3+}$ in its cavity. A pair of up−down face to face interacting thiacalixarenes with $[Co(dipy)_3]^{3+}$ in their cavities constitutes a supramolecular synthon. These synthons are situated along the crystallogragic axis *0a*. There is no direct face to face interaction between the synthons because the second $[Co(dipy)_3]^{3+}$ cation limits their proximity. Thus the 1D supramolecular structure is provided only by the interaction of the thiacalixarene couples with the outer $[Co(dipy)_3]^{3+}$ cations via face to face π-stacking and C−H(dipy)···O(SO_3) hydrogen bonding.

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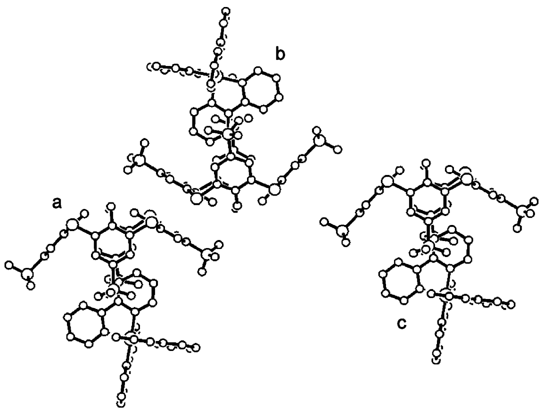

Figure 4. One-dimensional supramolecular structure in the crystal of **4**. Hydrogen atoms are not shown for clarity. Two independent [Co(dipy)$_3$]$^{3+}$ cations situated between thiacalixarenes b and c are not shown.

Although the packing mode of the second type of crystal differs from that of **4**, the supramolecular synthon also consists of up−down face to face interacting calixarene units with [Co(dipy)$_3$]$^{3+}$ in their cavities, which is unlike the crystal structure presented in the work of Nichols, Raston, and Steed[13] in which the supramolecular synthon is one *p*-sulfonatocalix[4]arene anion with [Ni(phen)$_3$]$^{2+}$ in its cavity. The inclusion mode of [Co(dipy)$_3$]$^{3+}$ in the cavity of **1**$^{4-}$ is similar to that of **1**$^{5-}$ which is in accordance with above mentioned ^{1}H NMR data in solutions. The up−down face to face π-stacking interaction between the inclusion complexes of *p*-sulfonatothiacalix[4]arene units very often provides a so-called bilayer supramolecular structure.[27−29] The assembly of the inclusion complexes of **1**$^{4-}$ with [Co(dipy)$_3$]$^{3+}$ results in a tubular superstructure, which is unlike the tubular structure of the assembly of *p*-sulfonatocalix[4]arene inclusion complexes,[30] provided by the up−up arrangement of calixarene units. It is also interesting to note that, unlike the [Ni(dipy)$_3$]$^{2+}$−*p*-sulfonatocalix[4]arene system[13] in which the presence of the equilibrium mixture of tetra- and penta-anions results in a crystal structure with both tetra- and penta-anions, the system of [Co(dipy)$_3$]$^{3+}$ and **1** has two different crystal structures which are dependent on the form of **1** (**1**$^{4-}$ and **1**$^{5-}$).

It is known[2,3] that the binding of the cobalt(III) polypyridyl complex to DNA through intercalation results in hypochromism and a red-shift of its $\pi-\pi$ bands because of the stacking interactions between the aromatic chromophore of the complex and the base pairs of DNA. The absorbance of **1** restricts the analysis of the $\pi-\pi$ bands of **3** in the region of 200−340 nm, while there is no significant effect of the ion-pairing with **1** on the ϵ and λ_{max} of the shoulders at 350 and 450 nm from the $\pi-\pi$ and charge-transfer transitions of **3**. The absorbance of **2** at 350−450 nm restricts the analysis of the effect of **2** on the spectral features of **3**.

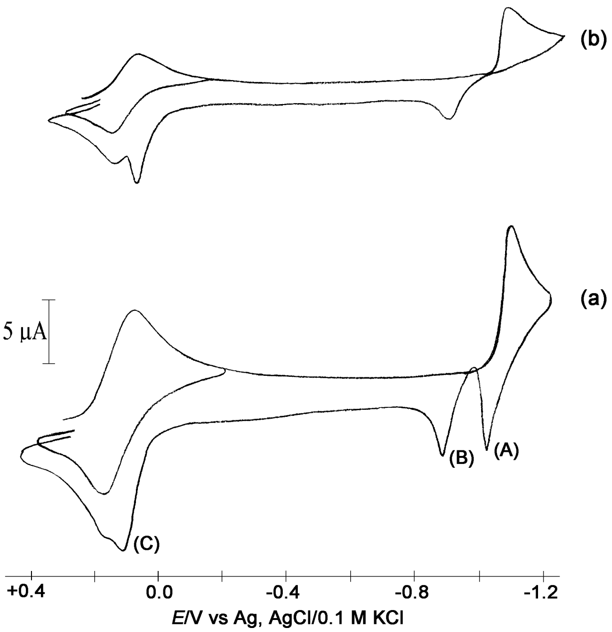

Figure 5. Cyclic voltammograms of a Co(dipy)$_3$(ClO$_4$)$_3$ solution (2 × 10^{-3} M) in a DMSO−H$_2$O (20 vol %)/0.1 M NaClO$_4$/1 × 10^{-2} M Tris system with potential scan rates of 100 mV s^{-1} (a) and 20 mV s^{-1} (b).

Table 2. E_{pc} and I of Co(III)/Co(II) and Co(II)/Co(I) Waves of **3** in Aqueous−DMSO Solutions and in the Presence of Receptors **1** and **2**

complex	E_{pc} (Co(III)/Co(II)), V	E_{pc} (Co(II)/Co(I)), V	I, μA
3	0.09	−1.08	8.8
3 + **2** (1/6)[a]	0.09	−1.12	6.5
3 + **1** (1/3)	0.02	−1.13	4.5

[a] 1/6 is the concentration ratio of [Co(dipy)$_3$]$^{3+}$ and receptor **2**.

Another very important property of cobalt(III) tris(diimine) complexes is the DNA-induced change of their electrochemical properties. According to the above mentioned data, the main peculiarity of the ion-pairing of **3** with both cyclophanic receptors is the inclusion of the dipy fragment into the calixarene cavity. That is the reason it is interesting to compare the effect of cyclophanic counterions on the electrochemical properties of **3** with the effect of DNA. The presence of DNA results in a pronounced decrease of the peak current and shifts in $E_{1/2}$ to less negative CV values of [Co(diimine)$_3$]$^{3+}$ in aqueous solution in the presence of Tris-buffer at pH 7.2.[1] These pH conditions are rather convenient because receptor **2** is kept in the **2**$^{4-}$ form and receptor **1** in the **1**$^{5-}$ form. Thus, CVs of **3** in the absence and presence of various amounts of receptors **1** and **2** were obtained in aqueous−DMSO media in the presence of Tris. The reduction of **3** without **1** and **2** results in two waves corresponding to Co(III)/Co(II) and Co(II)/Co(I) couples.[31,32] The second wave is sharper, but according to the polaragraphic study, both waves are produced by a one-electron transfer. The wave corresponding to the Co(III)/Co(II) couple is reversible; the reverse from the potential of the second reduction peak shows three maximums (Figure 5). These maximums indicate that cobalt complexes in lower oxidation states exhibit poor solubility in aqueous−DMSO medium and thus deposit on

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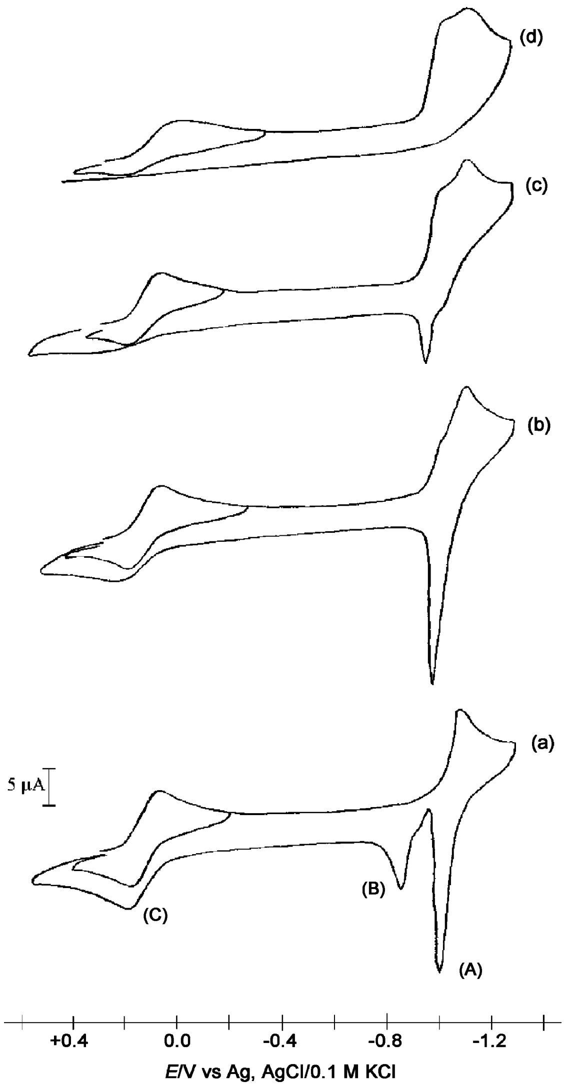

Figure 6. Cyclic voltammograms of a Co(dipy)$_3$(ClO$_4$)$_3$ solution (2×10^{-3} M) in a DMSO−H$_2$O (20 vol %)/0.1 M NaClO$_4$/1×10^{-2} M Tris system in the presence of **1** with concentration ratios for 3/1 of (a) 5/1, (b) 2/1, (c) 1/1, and (d) 1/2.

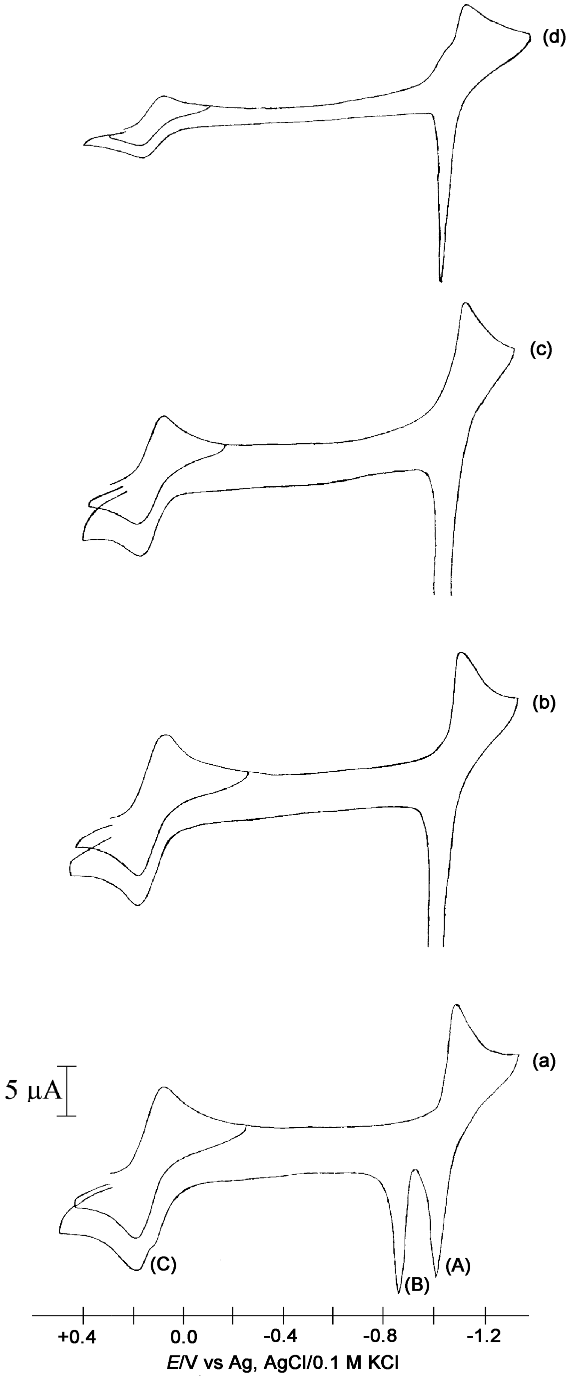

Figure 7. Cyclic voltammograms of a Co(dipy)$_3$(ClO$_4$)$_3$ solution (2×10^{-3} M^{-1}) in a DMSO−H$_2$O (20 vol %)/0.1 M NaClO$_4$/1×10^{-2} M Tris system in the presence of **2** with concentration ratios for 3/2 of (a) 5/1, (b) 1/1, (c) 1/3, and (d) 1/6.

the electrode. The first peaks (A and B) correspond to the Co(I)/Co(II) couple, but only one of them (A) can be the result of the oxidation of [Co(dipy)$_3$]$^+$ (Figure 5). The second peak (B) corresponds to the oxidation of Co(I) in another ligand environment which is the result of chemical transformations of unstable [Co(dipy)$_3$]$^+$. Both peaks have nearly the same intensity under a potential scan rate of 100 mV s^{-1}. With a scan rate of 20 mV s^{-1}, peak A disappears indicating that [Co(dipy)$_3$]$^+$ eventually transforms into the complex providing peak B (Figure 5). The maximum, C, is quite different from that of the reversed wave of the Co(III)/Co(II) couple of [Co(dipy)$_3$]$^{3+}$ and thus also corresponds to the oxidation of Co(II) in another ligand environment. Receptors **1** and **2** as well as DNA induce the decrease of the peak current from 8.8 to 6.5 and 4.5 μA during ion-pairing with **2** and **1**, respectively, indicating that the ion-pairing with cyclophanic counterions restricts the mobility of the cobalt complex (Table 2).

Both receptors shift the potential of the second Co(II)/Co(I) wave toward more negative values (Table 2). The effect on the potential of the Co(III)/Co(II) wave is not the same for both receptors. Thiacalixarene **1** shifts the potential of the Co(III)/Co(II) wave from 0.09 to 0.02 V, while **2** does not shift the potential of the Co(III)/Co(II) wave. The presence of both receptors also affects the reversed curve (Figures 6 and 7). Maximum A becomes more intensive, while B and C decrease and entirely disappear at a 1/1 calixarene/[Co(dipy)$_3$]$^{3+}$ concentration ratio indicating that both receptors stabilize [Co(dipy)$_3$]$^+$ preventing its destruction. The effect of **1** on the reversed curve is masked because of the deposition of the reduced thiacalixarene **1** on the electrode (Figure 6).

Conclusions

By summarizing the data obtained, we concluded that the ion-pairing between $[Co(dipy)_3]^{3+}$ and cyclophanic anions *p*-sulfonatothiacalix[4]arene and tetrasulfonatomethylated calix[4]resorcinarene in aqueous and aqueous−DMSO solutions is accompanied by the inclusion of the dipyridyl moiety of $[Co(dipy)_3]^{3+}$ into the cavities of calixarenes. The inclusion mode of $[Co(dipy)_3]^{3+}$ as well as the efficiency of binding is not changed during the first-step dissociation of the *p*-sulfonatothiacalix[4]arene lower phenolic rim in aqueous solutions; the inclusion is shollower in aqueous−DMSO solutions than in aqueous solutions, and the depth of the inclusion decreases with increasing DMSO content. The invariability of the inclusion mode under the first-step dissociation of *p*-sulfonatothiacalix[4]arene was also revealed by X-ray data. The electrochemical property changes of $[Co(dipy)_3]^{3+}$ during ion-pairing with *p*-sulfonatothiacalix[4]arene and tetrasulfonatomethylated calix[4]resorcinarene indicate that this ion-pairing results in the stabilization of the unstable $[Co(dipy)_3]^{+}$. More efficient binding of *p*-sulfonatothiacalix[4]arene with $[Co(dipy)_3]^{3+}$ results in a more pronounced effect on the cyclic voltammograms of the latter. The effect of the ion-pairing with both receptors on the spectral properties of $[Co(dipy)_3]^{3+}$ is insignificant, masked or both by the absorbance of calixarenes.

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Supporting Information Available: X-ray crystallographic file in CIF format for **4** and two 2D NOESY spectra of mixtures of **1** and **3** in D_2O and **2** and **3** in a D_2O−DMSO-d_6 mixture with 20 vol % DMSO-d_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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