

The electrochemical behaviour of $[\text{Co}(\text{sep})]^{3+}$ bound with *p*-sulfonatothiacalix[4]arene and tetracarboxy-*p*-sulfonatocalix[4]arene in correlation with inclusive and non-inclusive binding modes

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Abstract The comparative study of the ion-pairing of Co(III) sepulchrate ($[\text{Co}(\text{sep})]^{3+}$) with *p*-sulfonatothiacalix[4]arene and *p*-sulfonatocalix[4]arene tetracarboxylic acid by ^1H NMR and pH-metric data in solution and X-ray data in solid state elucidates pH dependent effect of carboxylate groups on the stoichiometry and the mode of the ion pairing. The electrochemical data of $[\text{Co}(\text{sep})]^{3+}$ bound with both calix[4]arenes have been analyzed in the correlation with stoichiometry and the mode of their binding. The pH-dependent effect of tetracarboxy-*p*-sulfonatocalix[4]arene on the electrochemical behavior of $[\text{Co}(\text{sep})]^{3+}$ has been found to correlate with the participation of carboxylate groups in the host–guest binding.

Keywords *p*-Sulfonatothiacalix[4]arene · *p*-Sulfonatocalix[4]arene tetracarboxylic acid · Co(III) sepulchrate · Binding mode

Introduction

The properties of transition metal complexes are widely exploited in the design of molecular machines and devices [1–4]. Calix[n]arenes have gained an enhanced attention as inner and outer sphere ligands in the design of

such complexes [5–7]. The unique binding ability of calix[n]arenes towards metal ions and complexes results from their cyclophanic structure [8–11]. Both the inner and outer sphere complexation ability of calixarenes also has got great attention in a design of redox switches [12–16]. The redox switching of the outer sphere ion pairing between Co(II) and Fe(II) complexes with sulfonate derivatives of calix[n]arenes should be mentioned as fine example [13–15]. The preferable inclusion of the oxidized form of the complex versus its reduced form is the main reason of the redox induced molecular motion in such systems. Therefore metal complexes, capable of a reversible crossing from the reduced to oxidized forms are of great importance as metal-containing building blocks of supramolecular systems. As it has been mentioned above the development of the active response of the supramolecular system on the redox input greatly depends on the difference between the host–guest binding constants of the oxidized versus reduced forms of the guest. Though the ion pairing is the main driving force of the binding of a charged metal complex with sulfonate derivatives of calix[n]arenes, the cooperative effect of weak interactions, such as van der Waals is also important due to an inclusive mode of a host–guest binding. The inclusive binding mode is of particular importance for sulfonated derivatives of calix[4]arene and their thiocounterparts [17–21]. Therefore the correlation between the binding efficiency of the oxidized versus reduced form of metal complex with sulfonated calix[4]arene derivatives and the host–guest binding mode is of enhanced interest. Clathrochelates of transition metal ions have gained much attention due to their kinetic and thermodynamic stability in the oxidized and reduced forms [22]. Co(III) sepulchrate is well known for its unique redox activity [23–27] and as a good building block of supramolecular architectures based on sulfonated derivatives of calix[n]arenes [21, 28].

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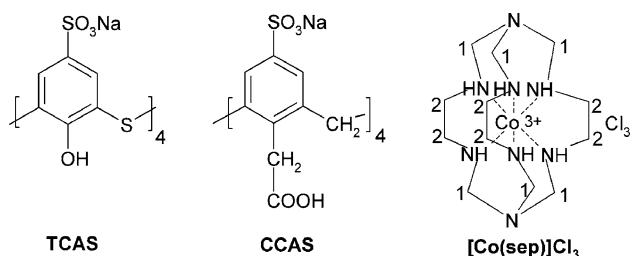
The choice of *p*-sulfonatothiacalix[4]arene (TCAS) and tetracarboxy-*p*-sulfonatocalix[4]arene (CCAS) (Scheme 1) as the outer sphere ligands for Co(III) sepulchrate (Scheme 1) is conditioned by their various structure, which in turn can result in the versatility of host–guest binding modes. Though CCAS is multifunctional receptor with donor groups on the upper and lower rims, the results represented in previous reports of Arena [29] highlight only 1:1 inclusive binding of CCAS with organic cations. At the moment it is well established that the inclusion capacity of TCAS is different from that of its classical counterpart [10, 11]. Therefore the comparison of the electrochemical behavior of [Co(sep)]³⁺ bound with TCAS and CCAS in the correlation with the corresponding binding modes is aided in understanding the effects of inclusive and non-inclusive calixarene-[Co(sep)]³⁺ interactions on the redox activity of Co(III) complex. The present work represents the binding modes of [Co(sep)]³⁺ with CCAS and TCAS both in solid state and solution. The effects of TCAS and CCAS on the electrochemical behavior of [Co(sep)]³⁺ are analyzed in the correlation with the modes of the ion pairing of [Co(sep)]³⁺ with both macrocycles.

Experimental section

TCAS and CCAS were synthesized using the well-known procedures [30–32]. [Co(sep)]Cl₃ was used as commercially available from Aldrich without purification.

Crystallographic study

Data set for single crystal (CCAS⁶⁻)[Co(sep)]³⁺₂(H₂O)₁₆ was collected with a Nonius KappaCCD diffractometer equipped with a molybdenum fine-focus sealed tube. Programs used: data collection COLLECT [33], cell refinement Dirax/lsq [34], data reduction EvalCCD [35], empirical absorption correction SADABS [36], structure solution SHELXS-97 [37], structure refinement SHELXL-97 [38], implemented in the WINGX package [39], graphics Mercury [40].



Scheme 1 Schematic representation of *p*-sulfonatothiacalix[4]arene (TCAS), tetracarboxy-*p*-sulfonatocalix[4]arene (CCAS) and Co(III) sepulchrate chloride ([Co(sep)]³⁺)

Crystal data

C₃₆H₂₆O₂₄S₄ + 2(C₁₂H₃₀CoN₈) + 16H₂O, M = 1949.80, orange crystal 0.38 × 0.33 × 0.26 mm, triclinic, space group *P*-1, *a* = 12.088(1), *b* = 17.604(5), *c* = 20.548(3) Å, α = 89.46(2), β = 78.08(1), γ = 81.52(1)°, *V* = 4230.5(14) Å³, *Z* = 2, *D*_{calc} = 1.531 g cm⁻³, μ = 0.592 mm⁻¹, *T* = 198 K, λ = 0.71073 Å, 155115 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.64 Å⁻¹, 18384 independent (*R*_{int} = 0.117), 11465 observed reflections [*I* ≥ 2 σ(*I*)], 1,203 refined parameters, *R* = 0.065, *wR*₂ = 0.150, maximal residual electron density 1.16 (−0.59) e Å⁻³, hydrogens were calculated and refined as riding atoms, except two hydrogens in carboxy groups of the host molecule, hydrogens attached to nitrogens in Co sepulchrate and some water molecules, these being found from the difference Fourier map. Some peaks of electron density were modelled as disordered water molecules.

CCDC 763403 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

¹H NMR spectroscopy

The NMR experiments were performed on a Bruker DRX-500 spectrometer operating at 500.13 MHz (¹H). The spectrometer was equipped with a Bruker multinuclear z-gradient probe head. The experiments were carried out at 298 K. The NMR spectra were recorded in both aqueous (D₂O) and mixed D₂O–DMSO solutions (40 vol.% of DMSO-*d*₆). The chemical shifts were referred to the signals for the residual protons of the deuterated solvent D₂O (δ_H = 4.70 ppm) or DMSO-*d*₆ (δ_H = 2.50 ppm). The ¹H NMR-titration was carried out by the addition of the certain aliquots of TCAS solutions to solution of [Co(sep)]³⁺ with concentration of [Co(sep)]³⁺ varying from 3 × 10⁻³ to 1.5 × 10⁻³ M and concentrations of TCAS—from 5 × 10⁻⁴ to 1 × 10⁻² M at pH 4.8 (NaH₂PO₄) and 10 (Tris buffer). The logβ-values, as well as complexation induced shifts (CIS)-values of [Co(sep)]³⁺ were deduced by means of well-known Benesi–Hildebrandt procedure [41].

The phase-sensitive ROESY experiments were acquired with proton spectral widths of 4,000 Hz in both dimensions and 2 K data points in the *t*₂ domain. The spectra were obtained in the TPPI mode from 512 experiments in *t*₁, 32 scans in *t*₂, spinlock – τ_m(ROE) = 250 ms and relaxation delay 2.0 s.

One-dimensional DPFNOE spectra [42] were obtained for mixing time τ_m(NOE) = 400 ms using a spectral width of 20.03 ppm to give a digital resolution of 0.73 Hz per

point, an acquisition time of 1.36 s and an relaxation delay of 8.00 s. A Hermite-shaped pulse was used for selective irradiation.

Cyclic voltammograms

Cyclic voltammograms (CV) were recorded using a PI-50-1 potentiostat with a N307/2 XY-recorder at the varied potential scan rate (10, 20, 50, 100, 200 mV s^{-1}). A glassy carbon electrode ($d = 3.4 \text{ mm}$) pressed in Teflon served as a working electrode. The electrode was polished prior to each measurement. Pt wire was used as counter electrode. The potentials (E) were measured versus Ag, AgCl/0.1 M KCl at 295 K. $E_{1/2}$ -values were calculated as a half-sum of the reduction and re-oxidation peak potentials. The electrochemical measurements were performed for aqueous and aqueous DMSO solutions (40 vol.% of DMSO) of $[\text{Co}(\text{sep})]^{3+}$ ($C = 1.5 \times 10^{-3} \text{ M}$), mixture of $[\text{Co}(\text{sep})]^{3+}$ and TCAS at varied concentration ratio $[\text{Co}(\text{sep})]^{3+}$:TCAS at pH 2.8, 3.4, 5.0, 7.0. The pH-values were adjusted by acetic–acetate and Tris–HCl as buffer systems (0.1 M). The dissolved oxygen was removed by bubbling argon through the solutions.

Results and discussions

The solid state structure

The X-ray diffraction analysis of the single-crystal grown from the aqueous solution of CCAS and $[\text{Co}(\text{sep})]\text{Cl}_3$ at $\text{pH} \sim 3.5$ reveals molecular host:guest 1:2 complex with 16 co-crystallized water molecules. The host calixarene molecule in crystal adopts a pinched cone conformation of approximate C_{2v} symmetry with the dihedral angles between the opposite aromatic rings being equal to 77 and 32°. One of the $[\text{Co}(\text{sep})]^{3+}$ guests is included into the cavity of the host molecule, while the second guest molecule is bound via $\text{N-H}\cdots\text{OOC}^-$ hydrogen bonds with the deprotonated carboxy groups in the outer-sphere mode (Fig. 1). The inclusion mode in more details is evident from Fig. 2. It is also worth noting that the inclusion of $[\text{Co}(\text{sep})]^{3+}$ is facilitated by host–guest (via $\text{N-H}\cdots\text{O}_3\text{S}^-$) hydrogen bonding. Moreover one Co(III) sepulchrate cation links two host calixarene molecules, while the latter also binds two cations, thus a zigzag chain is formed. Water molecules fill the space between the anions to provide close packing (Fig. 1). One should note that two of four carboxy groups at the lower rim of calixarene are deprotonated. The two residuary carboxylic hydrogens are participating in the hydrogen bonding: one $-\text{COOH}$ group participates in the intramolecular hydrogen bonding with

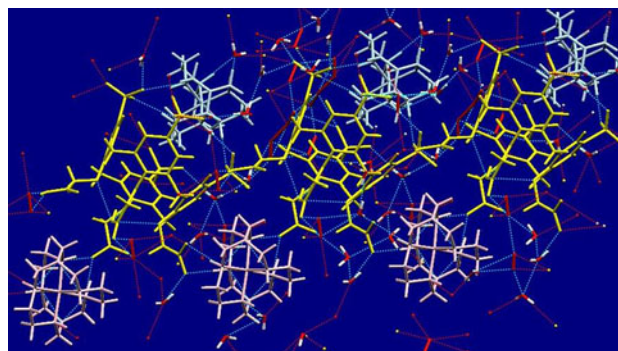


Fig. 1 A fragment of crystal packing showing intermolecular interactions between host CCAS and both included and lower-rim bound guests ($[\text{Co}(\text{sep})]^{3+}$), short contacts shown by *dashed lines*

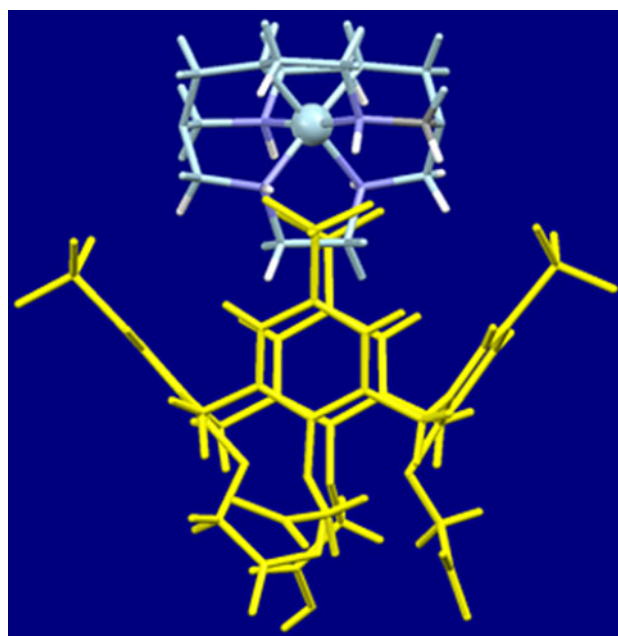


Fig. 2 Inclusion complex of $[\text{Co}(\text{sep})]^{3+}$ with CCAS

the adjacent carboxylate groups, the second one is bound with the neighbouring water molecules through the intermolecular H-bonds. The calixarene molecules form one-dimensional chain along the a -axis via weak interactions between the sulfonate group of one calixarene and two methylene groups of the adjacent calixarene molecule, one of which is the methylene bridge and the second one is the methylene carboxylate group. Thus X-ray single diffraction indicates that the binding ability of CCAS is not limited to 1:1 inclusion mode of host–guest binding, but the 1:2 (CCAS: $[\text{Co}(\text{sep})]^{3+}$) stoichiometry is also possible. It is worth noting that the binding of the second $[\text{Co}(\text{sep})]^{3+}$ is facilitated by the electrostatic attraction between complex cation and deprotonated carboxylate group of CCAS. This in turn indicate the particular role of the deprotonated

carboxylate groups in the formation of 1:2 complexes. Unfortunately no successful crystal growth was obtained in more acidic media, where the deprotonation of carboxy groups is not possible. Thus the effect of carboxylate versus carboxy groups should be elucidated in solution. Though X-ray data elucidate hydrogen bonding and electrostatic attraction as main driving forces of 1:2 complex formation, it is still unclear whether 1:2 complex is stable enough to be detected in solution or its formation is the result of crystal packing. To answer this questions the binding modes of $[\text{Co}(\text{sep})]^{3+}$ with CCAS should be studied in solution at various pHs. According to the published data complex ability of *p*-sulfonatocalix[4]arene and its thia-counterpart in most cases is restricted by 1:1 inclusion binding of complex cations [21, 28]. Thus the analysis of the binding modes of $[\text{Co}(\text{sep})]^{3+}$ with CCAS should be done in comparison with TCAS in order to reveal the difference between these calix[4]arene derivatives.

The binding mode in solution

The ^1H NMR spectroscopy reveals both structural and thermodynamic features of calix[4]arene complexes due to the up-field shifting of the guest protons signals resulted from the ring current effect of calix[4]arene cavity [41]. Therefore ^1H NMR titration of $[\text{Co}(\text{sep})]^{3+}$ by both macrocycles (TCAS and CCAS) was performed to elucidate the interaction mode of CCAS with $[\text{Co}(\text{sep})]^{3+}$ in comparison with TCAS in aqueous and aqueous DMSO solutions. The use of D_2O – DMSO-d_6 mixtures is conditioned by the restricted solubility of the ion pairs between $[\text{Co}(\text{sep})]^{3+}$ and both macrocycles in aqueous solutions. Figure 2 represents the up-field shifts of $[\text{Co}(\text{sep})]^{3+}$ protons signals versus $C_{\text{TCAS}}/C_{\text{Co}}$, where C_{Co} and C_{TCAS} are the concentrations of $[\text{Co}(\text{sep})]^{3+}$ and TCAS in aqueous and aqueous DMSO solutions. These data indicate the inclusion of $[\text{Co}(\text{sep})]^{3+}$ into the TCAS cavity in both solvents (Fig. 3). The ^1H NMR titration profiles of $[\text{Co}(\text{sep})]^{3+}$ by TCAS at pH 4.8 and 10 in aqueous solutions are very close to each other, indicating that the binding of $[\text{Co}(\text{sep})]^{3+}$ with TCAS is not pH-dependent. The binding constant (β) is 3.6 ± 0.2 logarithmic units in aqueous DMSO solutions, while the similar value in aqueous solution is larger ($\log \beta = 4.5 \pm 0.1$). So, the binding of $[\text{Co}(\text{sep})]^{3+}$ with TCAS in D_2O – DMSO mixtures is less tight than that in pure aqueous solutions. The CIS-values exhibited by sepulchrate protons signals are close to each other without significant difference between the up-field shifts of H(1a,b) and H(2a,b) protons in aqueous and aqueous DMSO solutions (the assignment of protons is shown in Scheme 1).

It is worth noting that aromatic protons of TCAS in binary TCAS– $[\text{Co}(\text{sep})]^{3+}$ solutions are manifested in the ^1H NMR spectrum as a singlet, indicating that TCAS is in

cone conformation. The strong positive crosspeaks in ROESY spectrum obviously demonstrate the close proximity between aromatic protons of the calixarene-host and all methylene protons of the sepulchrate-guest (Fig. 4). Thus ROESY spectral data together with the similarity of the CIS-values for all types of protons of $[\text{Co}(\text{sep})]^{3+}$ indicate its free rotation within the cavity of TCAS, which is quick enough in the NMR time scale.

The NMR titration of $[\text{Co}(\text{sep})]^{3+}$ by CCAS was performed at pH 10 and 3 in D_2O – DMSO-d_6 in order to reveal the effect of carboxylate groups on the binding of $[\text{Co}(\text{sep})]^{3+}$ (Fig. 5). According to pH-metric data (Fig. 7) the step-wise deprotonation of CCAS occurs in aqueous solutions ($\text{p}K_{1,2} = 5.86$, $\text{p}K_3 = 4.67$, $\text{p}K_4 = 10.2$, where $K_{1,2}$ is total constant of deprotonation, $\text{p}K_{1,2} = \text{p}K_1 + \text{p}K_2$). Though pK values tend to increase on going from aqueous to aqueous DMSO solutions it is obvious that at least three of four carboxy groups are deprotonated at pH 10 in aqueous DMSO mixture, while only one of four carboxy groups is partially deprotonated at pH 3, thus their participation in the binding of $[\text{Co}(\text{sep})]^{3+}$ should be negligible in such acidic conditions. The profile of the NMR titration of $[\text{Co}(\text{sep})]^{3+}$ by CCAS indicates two steps of binding, while the similar titration curve at pH 3 is looking like one step binding. The up-field shifting is slowed down at the beginning of the titration curve with coming to plateau at $C_{\text{CCAS}}/C_{\text{Co}} = 0.5$ in alkaline conditions. Further increase of CCAS concentration leads to more rapid decrease of $\Delta\sigma$ -values with reaching another plateau at the excess amounts of CCAS. The X-ray data indicate the possibility of the binding of two $[\text{Co}(\text{sep})]^{3+}$ ions: one via the upper and another on the lower rim of CCAS $^{6-}$. It is naturally to

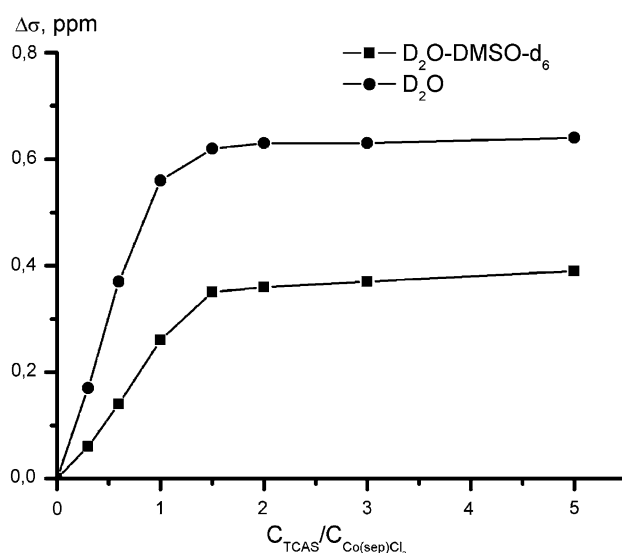


Fig. 3 The up-field shifts ($\Delta\sigma$) of $[\text{Co}(\text{sep})]^{3+}$ protons H(2b) as a function of $C_{\text{TCAS}}/C_{\text{Co}(\text{sep})\text{Cl}_3}$ in D_2O and D_2O – DMSO-d_6 mixture

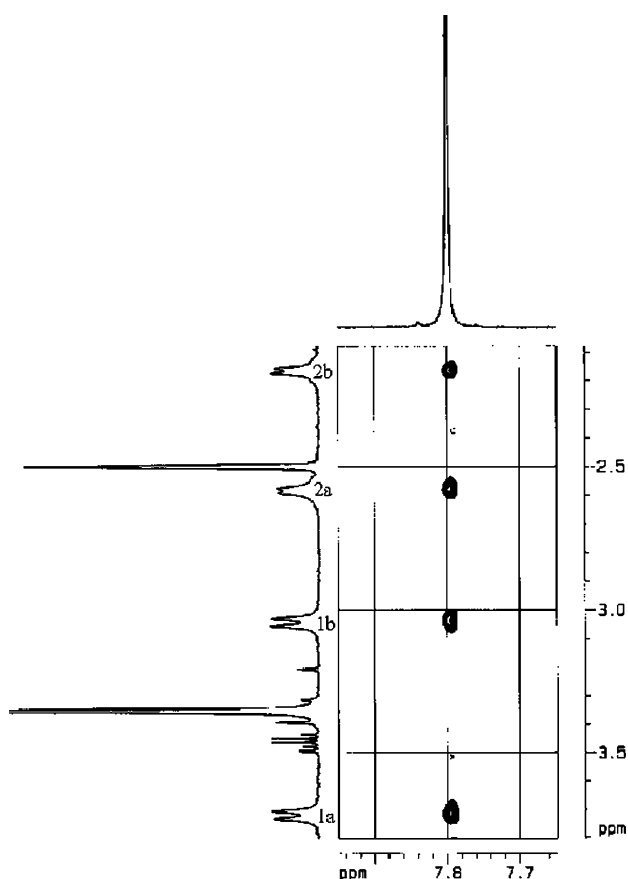


Fig. 4 ROESY spectrum of $[\text{Co}(\text{sep})]^{3+}$ with TCAS (1:1) in aqueous DMSO-d_6 solution

assume the similar binding in solution. Thus the first step most probably corresponds to the binding of two $[\text{Co}(\text{sep})]^{3+}$ by one CCAS (2:1 stoichiometry). According to the NMR titration data the CIS-values of $[\text{Co}(\text{sep})]^{3+}$ at the first step are much less than those derived from the 1:1 binding. This is rather awaited if one takes into account that only one of $[\text{Co}(\text{sep})]^{3+}$ is shielded by the cavity, while the protons signals of the second one bound through carboxylate groups of the lower rim should exhibit rather small if any up-field shift. To confirm these binding modes 1D NOESY measurements of $[\text{Co}(\text{sep})]^{3+}$ and CCAS at various concentration ratio have been performed in aqueous DMSO solutions. In all cases the intermolecular nuclear Overhauser effects (nOe's) are observed between aromatic protons of CCAS and methylene protons of $[\text{Co}(\text{sep})]^{3+}$. The particular case is the excess of $[\text{Co}(\text{sep})]^{3+}$, where the additional nOe's between carboxymethylene of CCAS and methylene protons of $[\text{Co}(\text{sep})]^{3+}$ are observed (Fig. 6).

The up-field shifts in aqueous DMSO solutions reveal the difference between the inclusion modes of $[\text{Co}(\text{sep})]^{3+}$ into CCAS and TCAS. The difference between CIS(1a,b) and CIS(2a,b) is insignificant when $[\text{Co}(\text{sep})]^{3+}$ is included into TCAS, while it is more pronounced in the case of

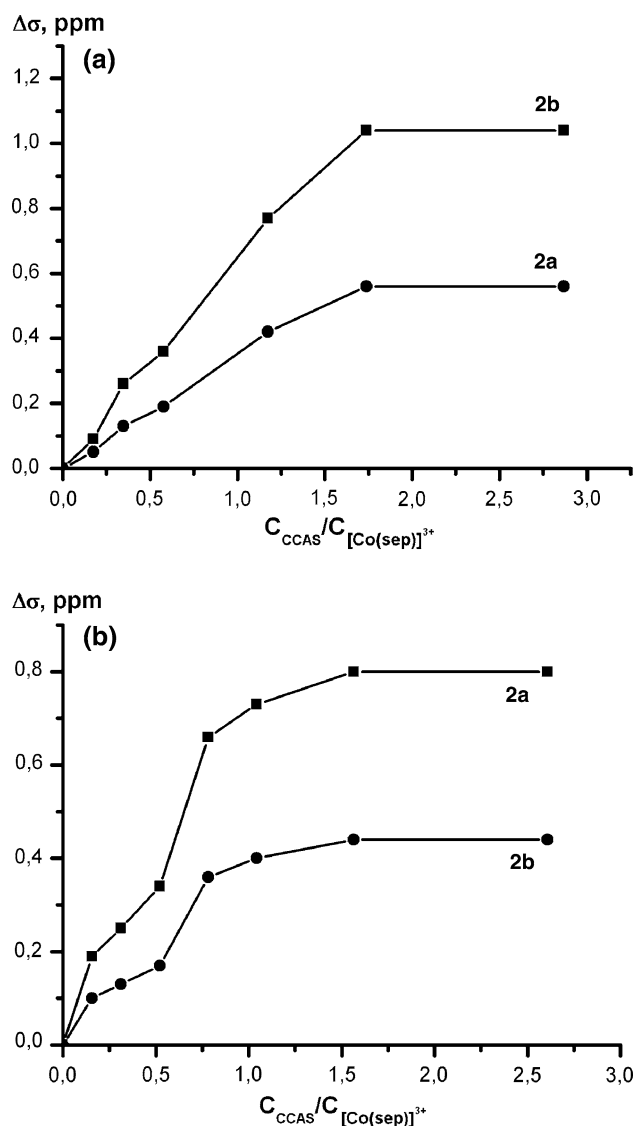


Fig. 5 The up-field shifts ($\Delta\sigma\text{H}$) of $[\text{Co}(\text{sep})]^{3+}$ protons H(2a, 2b) as a function of $C_{\text{CCAS}}/C_{[\text{Co}(\text{sep})]^{3+}}$ in $\text{D}_2\text{O-DMSO-d}_6$ mixture at pH 3 (a) and pH 10 (b)

CCAS (Table 1). The increased difference between CIS(1a,b) and CIS(2a,b) reveals their various shielding derived from the restricted rotation of $[\text{Co}(\text{sep})]^{3+}$ within the cavity of CCAS. The various mobility of the guest within the cavities of TCAS and CCAS reflects the difference in their size and shape [43, 44]. It is also worth noting that CIS-values are somewhat less for $[\text{Co}(\text{sep})]^{3+}$ bound with CCAS at pH 10 than those at pH 3. This results from the distribution of $[\text{Co}(\text{sep})]^{3+}$ between two binding centers, one of which is inclusive, while the other is non-inclusive. Though the inclusive binding mode is more efficient, the deviation between CIS-values at pH 3 and 10 (Table 1) indicates the participation of carboxylate groups in the binding of $[\text{Co}(\text{sep})]^{3+}$ at pH 10.

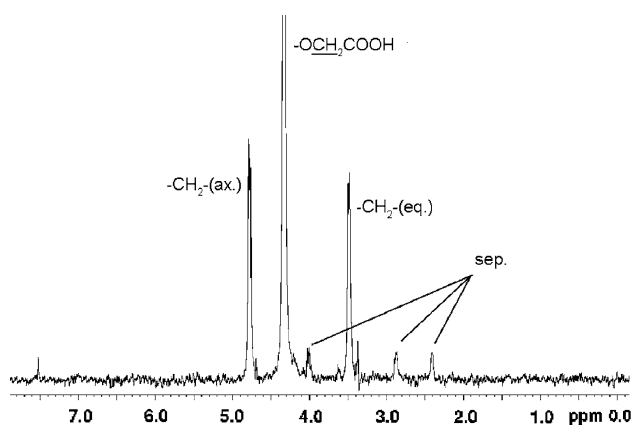


Fig. 6 DPGSE-NOE spectrum of the mixture of $[\text{Co}(\text{sep})]^{3+}$ and CCAS in the excess of $[\text{Co}(\text{sep})]^{3+}$ ($C_{[\text{Co}(\text{sep})]^{3+}} = 6 \times 10^{-3}$ M, $C_{\text{CCAS}} = 2 \times 10^{-3}$ M) in D_2O - DMSO-d_6 , $-\text{OCH}_2\text{COOH}$ irradiated

As it has been mentioned above the 1:1 inclusive binding of $[\text{Co}(\text{sep})]^{3+}$ by both macrocycles is pH independent, while the NMR titration reveals the pH dependent binding of $[\text{Co}(\text{sep})]^{3+}$ with CCAS via carboxylate groups. To confirm the participation of carboxy groups in the binding of $[\text{Co}(\text{sep})]^{3+}$ the pH-metric titration of CCAS without and in the presence of threefold excess of $[\text{Co}(\text{sep})]^{3+}$ has been performed. The comparison of the corresponding titration curves reveals the effect of $[\text{Co}(\text{sep})]^{3+}$ on the deprotonation of carboxy groups (Fig. 7). The titration profile observed for the “free” CCAS corresponds to the step-wise deprotonation of two carboxy groups with $\text{pK}_{1,2} = 5.86$, while the deprotonation of the third and fourth carboxylic groups is less easy with $\text{pK}_3 = 4.67$, $\text{pK}_4 = 10.2$. The pH-titration profile exhibits dramatic change when $[\text{Co}(\text{sep})]^{3+}$ is added, indicating the enhancement of the deprotonation of CCAS. The pH-metric titration at 1:3 ratio significantly deviates from the titration curve of CCAS. The obtained data reveal the pH dependent participation of carboxylate groups in the binding of $[\text{Co}(\text{sep})]^{3+}$, thus confirming the 1:2 host–guest binding at definite pH range.

Electrochemical behavior

So, both CCAS and TCAS form inclusive complexes with $[\text{Co}(\text{sep})]^{3+}$, though the difference between their binding modes also has been revealed. Thus it is interesting to elucidate the correlation of the binding mode of $[\text{Co}(\text{sep})]^{3+}$ with its electrochemical behavior. The binding mode of CCAS with $[\text{Co}(\text{sep})]^{3+}$ is pH dependent, therefore the electrochemical behaviour of $[\text{Co}(\text{sep})]^{3+}$ itself and ion-paired with TCAS and CCAS has been studied at various pHs in aqueous solutions. The CV data reveal reversible one-electron reduction peak of $[\text{Co}(\text{sep})]^{3+}$ to $[\text{Co}(\text{sep})]^{2+}$ in aqueous solutions at various Co(III):TCAS(CCAS) concentration ratio (from 4:1 to 1:3) in the wide range of pH (Table 2). For all studied systems peak current was controlled by diffusion which was confirmed by linear dependence of peak current square root versus scan rate ($i_p^{\text{red}} \sim v^{1/2}$). According to literature data the ion pairing with sulfonated calix[n]arenes commonly leads to the extra stabilization of the oxidized forms of complex cations, thus resulting in the cathodic shift of potentials for Co(III)/Co(II) and Fe(III)/Fe(II) couples [13–15]. Therefore it is rather unexpected that the potential of Co(III)/Co(II) couple for $[\text{Co}(\text{sep})]^{3+}$ does not exhibit cathodic shift at the ion-pairing with TCAS, while the decreased peak current indicates the restricted mobility of metal complex due to its ion-pairing with bulky macrocycle. The lack of the cathodic shift indicates that the ion-pairing of $[\text{Co}(\text{sep})]^{3+}$ with TCAS does not provide the extra stabilization of Co(III) relative to Co(II) sepulchrates. Though the decreased peak current is evident for both calixarenes, the analysis of peak current changes reveals the difference between two calixarenes. In particular no effect on peak current is observed when TCAS is in deficiency at 4:1 and 2:1 ratio. The detectable decrease of the peak current appears only at equimolar amounts of TCAS, while CCAS provides the similar effect at 2:1 concentration ratio (Table 2). This is in good agreement with the binding of two $[\text{Co}(\text{sep})]^{3+}$ cations with both rims of CCAS. The effect of CCAS on the potential of Co(III)/Co(II) couple is also pH-dependent, while the effect of

Table 1 CIS-values of Co(III) sepulchrates protons from the ^1H NMR titration data by TCAS and CCAS at various solvents and pH

Proton number	CIS			
	TCAS		CCAS	
	D_2O	D_2O - DMSO-d_6	D_2O - DMSO-d_6 , pH = 3	D_2O - DMSO-d_6 , pH = 10
1a	-0.65	-0.4	-0.24	-0.14
1b	-0.72	-0.53	-0.27	-0.16
2a	-0.69	-0.54	-1.04	-0.44
2b	-0.63	-0.4	-0.56	-0.8

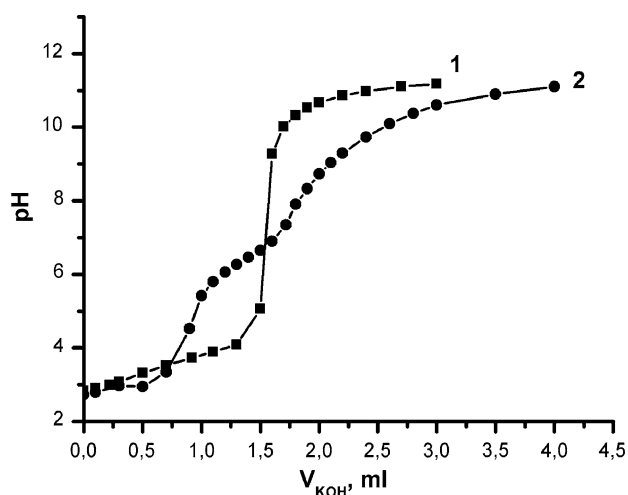


Fig. 7 pH-metric titration curves of CCAS (1) and the mixture of CCAS with $[\text{Co}(\text{sep})]^{3+}$ at threefold excess of cobalt complex (2) in aqueous solutions ($[\text{CCAS}] = 2 \times 10^{-3} \text{ M}$, $[\text{Co}(\text{sep})]^{3+} = 6 \times 10^{-3} \text{ M}$)

TCAS is not. No difference between two calix[4]arenes and no effect on the potential of Co(III)/Co(II) couple ($E_{1/2}$) is observed at pH 2.8 and 3.4, where only one of four carboxy groups is partially deprotonated (Table 2). The detectable (30 mV) cathodic shift of $E_{1/2}$, which is becoming more pronounced (50 mV) at twofold excess of CCAS is observed at pH 5 (Table 2). Thus the effect of CCAS on the electrochemical behavior of $[\text{Co}(\text{sep})]^{3+}$ correlates with the deprotonation of carboxy groups of CCAS. According to the above mentioned structural data the deprotonated carboxylate groups on the lower rim of CCAS provide the

competitive binding seat for $[\text{Co}(\text{sep})]^{3+}$. Thus the binding of $[\text{Co}(\text{sep})]^{3+}$ with carboxylate groups of CCAS at pH 5 is very probable reason of the extra stabilization of Co(III) versus Co(II) sepulchrate.

So, TCAS does not provide any effect on the potential of Co(III)/Co(II) couple of $[\text{Co}(\text{sep})]^{3+}$, while in the case of $[\text{Co}(\text{dipy})_3]^{3+}$ the detectable stabilization of the oxidized versus reduced form is observed in the presence of TCAS [20]. To explain this fact two points are worth noting. The first point is the unique cage-like structure of $[\text{Co}(\text{sep})]^{3+}$, which restricts the lengthening of Co–N bonds on going from the low spin Co(III) complexes to high spin Co(II) ones. It is well known that stability of sulfonatocalix[4]arenes based inclusion complexes decreases with the increase of bulkiness of a guest cation [6, 7, 41]. Since $[\text{Co}(\text{dipy})_3]^{2+}$ is more bulky than its oxidized form, both the charge decrease and the size increase are the reasons of the decreased binding constant of $[\text{Co}(\text{dipy})_3]^{2+}$ in comparison with the similar value for $[\text{Co}(\text{dipy})_3]^{3+}$. The size difference between the oxidized and reduced forms should be less pronounced for cage-like $[\text{Co}(\text{sep})]^{3+}$, where more rigid structure of ligand restricts the lengthening of coordination bonds. The second point is connected with the contribution of electrostatic interactions into the Gibbs energy of calixarene-guest binding. It is worth noting that the simple Coulomb relationship is not valid for the interaction of bulky charged metal complexes with calixarene cavity. Moreover our previous work [45] indicates no direct correlation between the charge of metal complex and binding constant. The presence of host–guest hydrogen bonding in the case of $[\text{Co}(\text{sep})]^{3+}$, but not in the case of

Table 2 $E_{1/2}$, I and $(I_0 - I)/I_0\%$ for complexes $[\text{Co}(\text{sep})]^{3+}$ with TCAS and CCAS at various pH and concentration ratio resulted from CV data

Complex	pH	$E_{1/2}^a$, V	I, μA	$(I_0 - I)/I_0\%$	Complex	$E_{1/2}^a$, V	I, μA	$(I_0 - I)/I_0\%$
$[\text{Co}(\text{sep})]^{3+}$	2.8	−0.55	57	–	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:1.3	−0.56	32
$[\text{Co}(\text{sep})]^{3+}/\text{TCAS}$	1:1.3	−0.55	57	0	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:1.3	−0.56	32
$[\text{Co}(\text{sep})]^{3+}$	3.4	−0.55	57	–	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:1.3	−0.56	32
$[\text{Co}(\text{sep})]^{3+}/\text{TCAS}$	1:1.3	−0.55	56	2	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	4:1	−0.58	40
$[\text{Co}(\text{sep})]^{3+}$	5	−0.56	47	–	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	2:1	−0.58	38
$[\text{Co}(\text{sep})]^{3+}/\text{TCAS}$	4:1	−0.57	46	2	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:1	−0.59	35
	2:1	−0.56	45	4	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:2	−0.61	29
	1:1	−0.57	36	2	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:3	−0.61	29
	1:2	−0.57	31	34				
	1:3	−0.58	29	39				
$[\text{Co}(\text{sep})]^{3+}$	7	−0.55	46	–	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:1	−0.59	27
$[\text{Co}(\text{sep})]^{3+}/\text{TCAS}$	1:1	−0.55	46	0	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:2	−0.58	26
	1:2	−0.55	39	15	$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	1:3	−0.58	26
					$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	2:1	−0.56	27
					$[\text{Co}(\text{sep})]^{3+}/\text{CCAS}$	4:1	−0.55	27

^a Maximum standard deviation is 0.01 V

$[\text{Co}(\text{dipy})_3]^{3+}$ is also worth noting. So, both the cage-like structure of $[\text{Co}(\text{sep})]^{3+}$ and hydrogen bonding with calixarene are the most sufficient factors differentiating the inclusion mode of $[\text{Co}(\text{sep})]^{3+}$ versus $[\text{Co}(\text{dipy})_3]^{3+}$. Thus the pH-dependent effect of CCAS on the electrochemical behaviour of $[\text{Co}(\text{sep})]^{3+}$ indicates that the electrostatic interactions with carboxylate groups provide more pronounced effect on the electrochemical behaviour of $[\text{Co}(\text{sep})]^{3+}$ than its inclusive binding with the upper rim of calix[4]arene.

Conclusions

The comparative study of the binding of $[\text{Co}(\text{sep})]^{3+}$ with two watersoluble calix[4]arenes TCAS and CCAS reveal that the inclusion of $[\text{Co}(\text{sep})]^{3+}$ into the cavities of both macrocycles is the predominant binding mode at pH 3. The participation of the carboxylate groups in the binding of $[\text{Co}(\text{sep})]^{3+}$ is the reason of 1:2 (CCAS: $[\text{Co}(\text{sep})]^{3+}$) along with 1:1 binding modes at pH 11. The electrochemical behavior of $[\text{Co}(\text{sep})]^{3+}$ ion paired with both calixarenes has been analyzed in the correlation with the binding modes. It is worth noting that the inclusion of $[\text{Co}(\text{sep})]^{3+}$ into the cavities of CCAS in acidic media and TCAS at the wide range of pH results in the insignificant effect on the electrochemical behavior of $[\text{Co}(\text{sep})]^{3+}$. Thus the inclusion of the reduced ($[\text{Co}(\text{sep})]^{2+}$) and the oxidized ($[\text{Co}(\text{sep})]^{3+}$) forms into host cavity occurs with the similar efficiency, which highlights the factors besides electrostatic attraction affecting the inclusion of the charged metal complex into the cavities of both calix[4]arenes. The pH-dependent effect of CCAS on the electrochemical behavior of $[\text{Co}(\text{sep})]^{3+}$ correlates with the deprotonation of carboxylic groups on the lower rim of calixarene. Thus the electrostatic interactions with carboxylate groups results in more pronounced effect on the electrochemical behaviour of $[\text{Co}(\text{sep})]^{3+}$ than its inclusive binding.

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