ORIGINAL ARTICLE

The outer-sphere association of *p*-sulfonatothiacalix[4]arene with some Co(III) complexes: the effect on their redox activity in aqueous solutions

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Abstract The effect of the ion-pairing of Co(III) complexes with *p*-sulfonatothiacalix[4]arene (**STCA**) on Fe(II)–Co(III) electron transfer rate was evaluated from the analysis and comparison of kinetic data in double Co(III)–Fe(II) and triple Co(III)–Fe(II)—**STCA** systems at various concentration conditions. Complexes $[Co(en)_3]^{3+}$(**1**), $[Co(en)_2ox]^+$(**2**), $[Co(dipy)_3]^{3+}$ (**3**), $[Co(His)_2]^+$(**4**) and $[Fe(CN)_6]^{4-}$ were chosen as Co(III) and Fe(II) compounds. The effect of **STCA** was found to correlate with the association mode. The outer-sphere association with **STCA** was found to exhibit the insignificant effect on Fe(II)–Co(III) electron transfer k_{et} constants for complexes **3** and **4** with bulky and rigid chelate rings, while more sufficient inclusion of flexible ethylendiaminate rings of **1** and **2** into the cavity of **STCA** results in the unusual increase of k_{et}.

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Introduction

The outer-sphere electron transfer between transition metal complexes plays an essential role both in vivo [1] and in operation of molecular scale devices, such as molecular wires and logic gates [2–4]. The nature of the inner-sphere ligands is known to affect on a rate of metal-to-metal electron transfer [5]. The alteration of the outer-sphere environment of metal complex, caused by the variation of aqueous organic solvent mixtures, [6, 7] concentration of counter-ions [8] also has an influence on electron transfer reactions. The binding of one or both participants of redox reaction (donor or acceptor) by micellar pseudophase, [6, 7, 9–14] macromolecules, and macrocyclic compounds (DNA, cyclodextrines, peptides) [13–15] is in general referred to as restricted geometry conditions and is of great interest as a way of modification of redox processes. Macrocyclic compounds, such as cyclodextrins, antibiotics, cucurbiturils and calixarenes fill a special place among this list as they can serve as molecular containers for metal complexes [16–19]. Thus the encapsulation of metal complexes into various molecular containers should be regarded as a way of an alteration of metal complex redox activity. As it was discovered by Pina and Parola the outer-sphere environment of $[Fe(CN)_6]^{3-}$ provided by polyammonium macrocyclic receptor favors the intermolecular electron transfer from I^- to $[Fe(CN)_6]^{3-}$ in acidic media, thus underlying pH-controlled on/off switch [20].

Calix[n]arenes and thiacalix[n]arenes, bearing sulfonato-groups on their rims, belong to the class of promptly developing water-soluble artificial receptors, [21] which can modify optical [22] and redox properties of particles included [23–25]. As it was recently shown

p-sulfonatothiacalix[4]arene (**STCA**) binds some charged inert coordinatively saturated Co(III) complexes in the outer-sphere complexation mode. This binding results in the modification of spectropolarimetric and electrochemical properties of Co(III) complexes [26, 27]. Now it seems interesting to reveal the effect of **STCA** on redox activity of Co(III) complexes. So, the main goal of the work presented is to study the effect of *p*-sulfonatothiacalix[4]arene on the rate of Co(III)–Fe(II) electron transfer, where Co(III) complexes {$[Co(en)_3]^{3+}$(**1**), $[Co(en)_2ox]^+$ (**2**), $[Co(dipy)_3]^{3+}$ (**3**) and $[Co(His)_2]^+$ (**4**)} are bound with **STCA** and Fe(II) ($[Fe(CN)_6]^{4-}$) is not.

Experimental section

Materials

The receptor **STCA** and complexes $[Co(en)_3]Cl_3$, $[Co(en)_2ox]^+$, $[Co(dipy)_3](ClO_4)_3$, and $[Co(His)_2]ClO_4$ were synthesized by literature methods [28–32]. $K_4[Fe(CN)_6]$ ACS reagent grade, disodium ethylendiaminetetraacetate and NaCl were chemicals from "ICN Biochemicals & Reagents".

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 [33].

Kinetics

All kinetic measurements were performed under pseudo-first order conditions with $K_4[Fe(CN)_6]$ in at least ten fold excess over the cobalt complex. The concentrations of the Co(III) complexes were chosen $5 \cdot 10^{-4}$ M for **1**, **3**, and **4**. In order to avoid precipitation of Fe(III)–Co(III) and Fe(II)–Co(III) ionic pairs concentration of complex **2** was decreased up to $1.3 \cdot 10^{-4}$ M. The ionic force (*I*) was maintained at 0.15 M by NaCl, pH 5.8–6.1 was adjusted by Tris buffer (0.012 M) with the exception of kinetic data in ternary system Fe(II)-**3**-**STCA**, where the buffer capacity of Tris is not enough to prevent acidification of solutions up to pH 4.2 under the excess amounts of **STCA** (0.005–0.015 M) added. The pH decrease results in protonation of $[Fe(CN)_6]^{4-}$, which in turn can affect on the rate of the redox process studied [34]. The use of acetic-acetate buffer (0.012 M) was found to prevent acidification in this system. In the case of complex **1**

disodium ethylendiaminetetraacetate (Na₂EDTA, $c = 0.005$ M) was added to avoid a precipitation of $Co_3[Fe(CN)_6]_2$. For **1** the kinetic measurements were performed both in the presence and in the absence of Na₂EDTA. No difference was observed. Pseudo-first order rate constants k_{obs} were derived from the obtained absorbance (*A*) versus time (*t*) using a non-linear least squares regression to fit the experimental curve

$$(A_\infty - A) = (A_\infty - A_0) \exp(-k_{obs}t) \tag{1}$$

where A_∞ is infinite time absorbance. The calculations were performed with the help of ORIGIN 7.0 computer program. Each value of k_{obs} is the mean of at least three independent determinations differing by no more than 5%. When subsequent secondary reactions resulted in a drift in the absorbance at long times (in the case of complex **4**), as well as when precipitation restricts the accurate evaluation of A_∞ (for complex **3**), the latter was free parameter. Kinetic runs were followed at 423 nm where the appearance of $[Fe(CN)_6]^{3-}$ ($\varepsilon = 1023$ M⁻¹ cm⁻¹) can be well detected. All kinetic measurements were carried out in anaerobic conditions in order to avoid Fe(II) air oxidation. Kinetic runs were collected within 2–3 h. All measurements have been performed at least three times at 291 ± 0.1 K.

The values of A_∞ for redox processes Fe(II)-**1**(**2**, **4**) are within the range 0.53–0.55 ($c_{1(2,4)} = 5.0 \cdot 10^{-4}$ M, 10 mm cell), which is in good accordance with $\varepsilon = 1023$ M⁻¹ cm⁻¹ for $[Fe(CN)_6]^{3-}$. In the case of complex **3** with $c_3 = 1.3 \times 10^{-4}$ M the A_∞ values are within 0.60–0.65 at 423 nm (10 mm cell). Furthermore, after mixing solutions of Fe(II) and **3**, two absorption bands at 429 and 620 nm with intensity ratio of 1:3 are immediately apparent. These two bands can be assigned to metal-to-ligand charge transfer (MLCT), when the ion pair $[Co(dipy)_3]^{3+}$ $[Fe(CN)_6]^{4-}$ is formed. The charge transfer occurs from the Fe(II) t_{2g} orbitals to two first acceptor π^* orbitals of dipy, because the energy interval between these MLCT bands (7,180 cm⁻¹) is close to the energy difference between two first intra-ligand π–π^* transitions in dipy [35]. However, the fist MLCT bands (at 429 nm) may be partly overlapped with the band of metal-to-metal charge transfer (MMCT) Fe(II)–Co(III) in the same ion pair. Irrespective of the validity of the bands assignment, fast (not rate-determining) ion pair formation does not affect on the evaluation of kinetic parameters of Fe(II)–Co(III) electron transfer from the *A* versus *t* dependences.

Conductometric measurements

Conductometric measurements were performed on inoLab Cond Level 1 at constant concentration of **1** ($c = 5 \cdot 10^{-5}$ M) and various concentrations of **STCA** ($c = 2.5 \cdot 10^{-5}$–$2 \cdot 10^{-4}$ M). The $\Delta\chi$-value was calculated according to Eq. (2)

$$\Delta\chi = \chi_{STCA} + \chi_1 - \chi_{obs} \tag{2}$$

where χ_{obs} is the conductivity of aqueous solutions, containing **1** in the presence of definite concentration of **STCA**, χ_{STCA} and χ_1 are conductivities of **STCA** and **1** at the same concentrations correspondingly.

Results and discussion

Host–guest complexation between Co(III) complexes and STCA

As mentioned above all Co(III) complexes studied form outer-sphere associates with **STCA** [26, 27]. Macrocycle **STCA** (Scheme 1) at conditions studied (pH 6.1) in aqueous solutions exists in the form of penta-anion with four charged sulfonate groups on the upper rim and one deprotonated phenolate group on the lower rim [36]. The ^{1}H NMR study of the ion-pairing of complexes **1**–**4** with **STCA** reveals only 1:1 binding, which is evident from sufficient shielding of guest protons as the result of their inclusion into the cavity and/or multiple electrostatic interactions with the charged rim of **STCA** [26, 27]. The values of the up-field shift of guest protons at saturation conditions or so-called CIS-values enable to evaluate the structure of a host–guest complex [37]. The Fig. 1 shows the structure of the outer-sphere associates derived from the ^{1}H NMR data [26]. In the case of **3** the binding mode was proved by X-ray data [27]. According to ^{1}H NMR data the most tight binding occurs for **1** and **3** with $\log\beta > 4.0$ (β is binding constant), while the
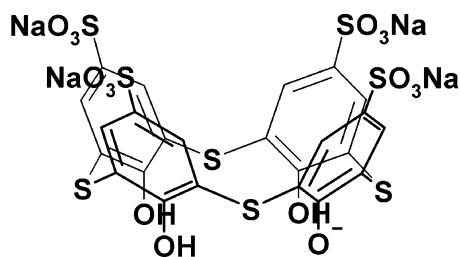
accurate determination of such constants is not available from NMR titration data. The less tight binding ($\log\beta = 4.05$) is observed for complex **2** due to the presence of oxalate anion in its inner-sphere [26]. Though, the outer-sphere associates with tris-chelates are inclusion-type, they are not similar. The rigid and bulky complex **3** is included via its fragment (Fig. 1(c), while the size of ethylendiamine ring is rather suitable for the complete inclusion into the cavity (Fig. 1(a)), which is confirmed by complexation induced shift data [26]. The CIS-values are the least for complex **4**, that can be attributed to the efficient ($\log\beta > 4.0$) ion-pairing with **STCA** without inclusion into its cavity (Fig. 1(d)) [26]. Thus some additional host–guest interactions at the excess of host (1:2 ion-pairing, for example) without inclusion of guest moieties into calixarene cavity can be NMR-silent. At the same time the conductivity method can indicate all types of the ion-pairing. The raising of $\Delta\chi$ (Eq. 2) versus **STCA:1** concentration ratio (Fig. 2) is practically linear and sharp up to definite concentration ratio (**STCA:1** = 1:1.5), while further increase of **STCA:1** ratio leads to very slight $\Delta\chi$ change, which is within experimental error. So it should be assumed that the 1:1 ion-pairing dominates within concentrations studied for complex **1**, the same should be true for complexes **2**–**4**. Thus the above-mentioned types of the outer-sphere 1:1 association with **STCA** provide various changes in the outer-sphere environment of complexes **1**–**4**, which can lead to different changes in their redox properties.

Binary Fe(II)–Co(III)–STCA redox systems

The redox process between $[Co(dm)_3]^{3+}$ (dm is diamine or diimine) and $[Fe(CN)_6]^{4-}$ undergoes in three steps [38–40]. An ion-pairing (Eq. (3) with equilibrium constant Q) is the first fast step. The second step is an electron transfer (Eq. (4)), which is slow enough to determine the rate of redox process. The third step (5) including a destruction of labile Co(II) complex is also fast.
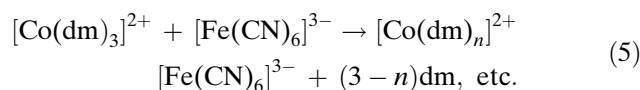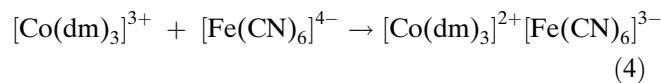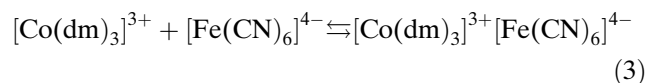
$$[Co(dm)_3]^{3+} + [Fe(CN)_6]^{4-} \leftrightarrows [Co(dm)_3]^{3+}[Fe(CN)_6]^{4-} \tag{3}$$

$$[Co(dm)_3]^{3+} + [Fe(CN)_6]^{4-} \rightarrow [Co(dm)_3]^{2+}[Fe(CN)_6]^{3-} \tag{4}$$

$$[Co(dm)_3]^{2+} + [Fe(CN)_6]^{3-} \rightarrow [Co(dm)_n]^{2+}$$
$$[Fe(CN)_6]^{3-} + (3-n)dm, \text{ etc.} \tag{5}$$

Scheme 1

Fig. 1 Schematical representation of the outer-sphere associates of **STCA** with complexes **1** (**a**), **2** (**b**), **3** (**c**) and **4** (**d**)
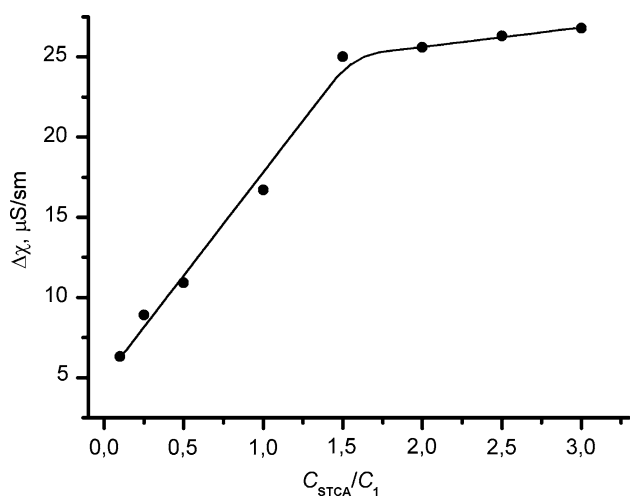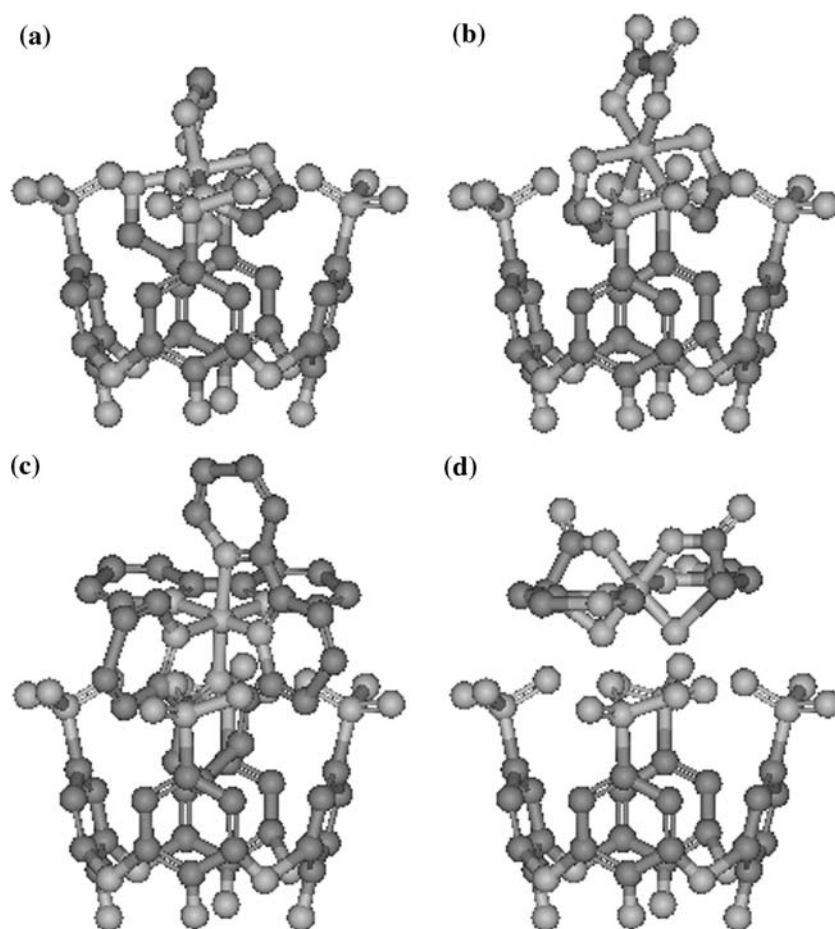

Fig. 2 Plot of the $\Delta\chi$ ($\Delta\chi = \chi_{STCA} + \chi_1 - \chi_{obs}$) versus c_{STCA}/c_1, where c_{STCA} and c_1 are concentrations of **STCA** and **1**

Pseudo-first order rate constants k_{obs} were obtained in double Fe(II)–Co(III) systems under varied concentration of Fe(II). The increase of k_{obs} with $K_4[Fe(CN)_6]$ concentration followed coming on

plateau for cobalt tris-chelates **1**, **2**, **3**, and **4** is common for bimolecular redox reactions (Fig. 3). These data are described by Eq. (6) where k_{et} is the rate constant of Fe(II)–Co(III) electron transfer.

$$k_{obs} = (k_{et}Q[Fe(CN)_6^{4-}])/(1 + Q[Fe(CN)_6^{4-}]) \qquad (6)$$

Both k_{et} and Q values were calculated by a two-parameter least squares fit according to Eq. (6) and are given in Table 1. The Q value found for **1** at $I = 0.15$ M (NaCl) may be compared with $Q = 90 \pm 20$ M^{-1} at $I = 0.21$ M (NaClO$_4$) [41] and $Q = 78 \pm 5$ M^{-1} (4 M NaCl) [42]. The data obtained indicate that Q decreases in the following order **1 > 3>4 > 2**, which in general correlates with electrostatic efficiency of Co(III)-Fe(II) ion-pairing. The decrease of k_{et} values in the order **3 > 4>2 > 1** (Table 1) correlates well with the increase of electron pair donor capacity of the ligands [5].

Ternary Fe(II)–Co(III)–STCA redox systems

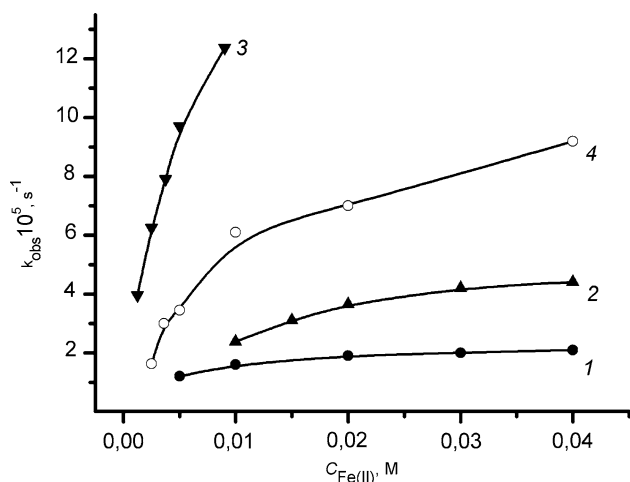To evaluate the effect of **STCA** on Fe(II)–Co(III) electron transfer, kinetic measurements were also

Fig. 3 Plots of pseudo-first order rate constants (k_{obs}) versus $K_4[Fe(CN)_6]$ concentration ($c_{Fe(II)}$) in binary Fe(II)—1(2–4) systems at $c_1 = 5 \cdot 10^{-4}$ M, $c_2 = 10^{-3}$ M, $c_3 = 1.3 \cdot 10^{-4}$ M, $c_4 = 5 \cdot 10^{-4}$ M

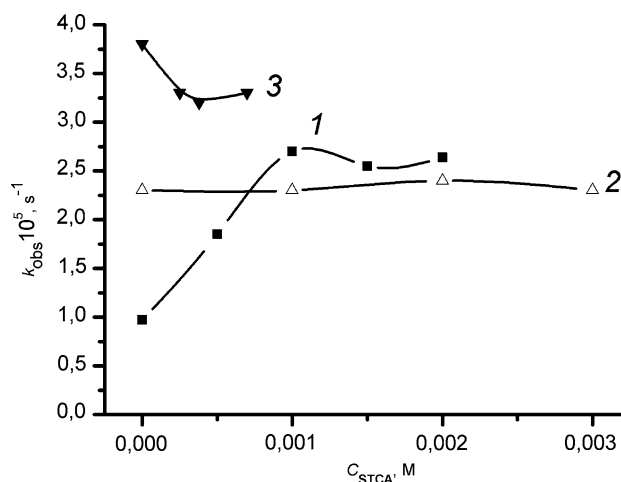**Fig. 4** Plots of pseudo-first order rate constants (k_{obs}) in ternary Fe(II)—1 (2, 3)—STCA systems versus concentration of STCA (c_{STCA}) at $c_1 = 5 \cdot 10^{-4}$ M, $c_2 = 1 \cdot 10^{-3}$ M, $c_3 = 1.3 \cdot 10^{-4}$ M at the ten fold excess of $K_4[Fe(CN)_6]$

performed in triple Fe(II)–Co(III)–STCA systems. The data obtained reveal the increase of k_{obs} with further coming on plateau for complex **1**, while the change of k_{obs} is within the experimental error for complexes **2** and **3** with the increase of STCA concentration. The accurate determination of the similar dependence in the case of complex **4** is restricted by the precipitation occurring with the increase of STCA concentration. Figure 4 illustrates the changes of k_{obs} for complexes **1–3** versus concentration of STCA at constant concentrations of Co(III) and Fe(II). Taking into account, that only one participant of redox process is bound by STCA, the analysis of kinetic data at various concentrations of STCA for complexes **1–4** can be made in the framework of pseudo-phase model according to Eq. (7), which is commonly used for analysis of kinetic data under restricted geometry [11–13]

$$k_{obs} = (k_w + k_c\beta[STCA])/(1 + \beta[STCA]) \qquad (7)$$

where k_w and k_c concern to complexes in aqua- and ion-paired with STCA forms correspondingly, β is the constant of the ion-pairing of Co(III) complex with

STCA. It is obvious that the data shown on Fig. 4 fit to pseudo-phase model for complex **1**, since k_{obs} values reach the plateau, while in the case of **2**, **3**, and **4** the change of k_{obs} is not enough pronounced within the concentrations of STCA studied, at the same time the precipitation restricts further increase of concentration. Thus the change of k_{obs} induced by STCA is the result of 1:1 binding between STCA and complex **1**. But the β value for complex **1** can be evaluated only roughly by two-parameter least squares fit procedure according to Eq. (7) from the data obtained: $\beta \approx 7,700$ M^{-1}. This value is somewhat less than the binding constant derived from NMR titration data in pure water. The difference observed most probably is conditioned by the difference in the ionic force.

To explain the effect of STCA on the redox reactions studied it is necessary to distinguish the change of Q and k_{et} in the presence of STCA. From the electrostatic point of view the ion-pairing with **1** should weaken the interaction with $[Fe(CN)_6]^{4-}$ and thus result in the decrease of Q. The two-parameter least squares fit according to Eq. (6) of the kinetic data in ternary Fe(II)—1(2, 3, 4)—STCA systems at

Table 1 The constants of the ion-pairing (Q) and electron transfer (k_{et}) for $[Fe(CN)_6]^{4-}$-**1**(2–4) redox systems both in the absence and in the presence of STCA at 291 K

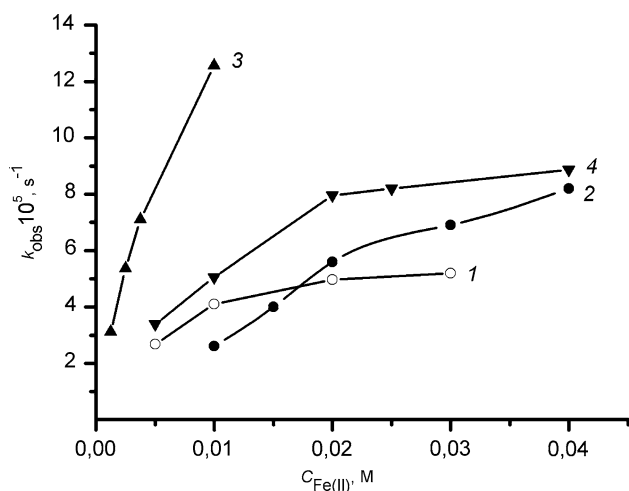| Complex	C_{STCA}, M	Q, M^{-1}	k_{et}, s^{-1}
$[Co(en)_3]^{3+}$(**1**)	0	211 ± 5	$(2.3 ± 0.2) \cdot 10^{-5}$
$[Co(en)_3]^{3+}$(**1**)	$1.0 \cdot 10^{-3}$	133 ± 21	$(6.8 ± 0.5) \cdot 10^{-5}$
$[Co(en)_2ox]^{+}$(**2**)	0	58 ± 7	$(6.6 ± 0.4) \cdot 10^{-5}$
$[Co(en)_2ox]^{+}$(**2**)	$2.0 \cdot 10^{-3}$	8 ± 3	$(3.7 ± 1.3) \cdot 10^{-4}$
$[Co(dipy)_3]^{3+}$(**3**)	0	194 ± 8	$(1.94 ± 0.6) \cdot 10^{-4}$
$[Co(dipy)_3]^{3+}$(**3**)	$2.5 \cdot 10^{-4}$	141 ± 10	$(2.08 ± 1.1) \cdot 10^{-4}$
$[Co(His)_2]^{+}$(**4**)	0	86 ± 6	$(1.25 ± 0.6) \cdot 10^{-4}$
$[Co(His)_2]^{+}$(**4**)	$1.0 \cdot 10^{-3}$	76 ± 10	$(1.23 ± 0.9) \cdot 10^{-4}$

Fig. 5 Plots of pseudo-first order rate constants (k_{obs}) versus K$_4$[Fe(CN)$_6$] concentration ($c_{Fe(II)}$) in ternary Fe(II)—**1**(**2–4**)—**STCA** systems at $c_1 = 5 \cdot 10^{-4}$ M, $c_2 = 1 \cdot 10^{-3}$ M, $c_3 = 1.3 \cdot 10^{-4}$ M, $c_4 = 5 \cdot 10^{-4}$ M at the two fold excess of **STCA**

two-fold excess of **STCA** and various [Fe(CN)$_6$]$^{4-}$ concentrations (Fig. 5) was used to evaluate both Q and k_{et} values and to compare them with those obtained in binary systems (Table 1). According to the data obtained (Table 1) the effect of **STCA** on both Q and k_{et} depends on the structure of Co(III) complex. In particular the least decrease of Q occurs for **4**. The effect of **STCA** on Q is more pronounced for complexes **1** and **3** and the most for the complex **2**. These regularities are well confirmed with the Co(III)–**STCA** binding mode (Fig. 1). The **STCA** induced weakening the ion-pairing with [Fe(CN)$_6$]$^{4-}$ is the least for bulky complexes **3** and **4**. Indeed their ion-pairing with STCA still retains the ability to binding with [Fe(CN)$_6$]$^{4-}$. Less bulky complex **1** loses the ability for the ion-pairing with STCA in much more extent. Since complex **2** is included into the cavity through its ethylendiaminate rings, the oxalate anion should look outward of cavity towards [Fe(CN)$_6$]$^{4-}$, thus resulting in the enhanced weakening of Co(III)–Fe(II) ion-pairing.

The effect of **STCA** on k_{et} also greatly depends on the nature of the Co(III) complex. In particular, k_{et} stays practically unchanged for **3** and **4**, while increases for complexes **1** and **2** (Table 1). The increase of k_{et} is more pronounced for **2**. It is worth noting that in the case of complex **2** the permanency of k_{obs} at various concentrations of **STCA** is conditioned by two oppositely affecting factors: the increase of k_{et} and decrease of Q. Taking into account that various size and shape of Co(III) complexes results in different outer-sphere association mode, it is interesting to correlate the effect

of **STCA** on the redox activity of Co(III) complexes with their outer-sphere association mode. First of all, no effect on k_{et} is observed for non-inclusively bound **4**, as well as **3**. The binding of **3** with **STCA** does not disturb the inner-sphere ligand environment, because 2,2′-dipyridyl ligand is rigid and only partly inserted into the cavity of **STCA**. The ethylendiaminate ring of **1** and **2** very probably can be inserted as a whole into the cavity of **STCA** [26], moreover the inclusion of ethylendiaminate ring of complexes **1** and **2** into **STCA** results in its conformation shift towards the less thermodynamically stable *ob* conformation, which is evident from the **STCA** induced changes in CD spectra [26]. Thus, the unusual acceleration observed for complexes **1** and **2** can be attributed to their deep inclusion, accompanied with conformational shift of chelate ring.

Summary

Summarizing the data obtained it should be concluded that the ion-pairing of complexes **1**–**4** with macrocycle **STCA** stays unchanged or accelerates Fe(II)–Co(III) electron transfer, depending on the Co(III) complex structure. The effect of **STCA** is conditioned by both Q decrease and k_{et} staying unchanged for complexes **3** and **4** and k_{et} increase for complexes **1** and **2**. The Q and k_{et} changes are more pronounced for **2**. To elucidate for true reasons of such unusual k_{et} increase for **1** and **2** at complexation with **STCA** we continue to carry out extensive studies which results will be reported elsewhere

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