Comparative electrochemical study of some cobalt(III) and cobalt(II) complexes with azamacrocycles and β-diketonato ligands

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Abstract. The electrochemical properties of eight mixed-ligand cobalt(III) and cobalt(II) complexes of the general formulas $[Co^{III}(Rac)cyclam](ClO_4)_2$ (**1**)–(**4**) and $[Co_2^{II}(Rac)tpmc](ClO_4)_3$ (**5**)–(**8**) were studied. The substances were investigated in aqueous $NaClO_4$ solution and non-aqueous $LiClO_4/CH_3CN$ solution by cyclic voltammetry at a glassy carbon electrode. In aqueous solution, *cyclam* and *Rac* ligands being soluble in water undergo anodic oxidation. Coordination to Co(III) in complexes **1**–**4**, stabilizes these ligands but reversible peaks in catohodic region indicate the redox reaction Co^{III}/Co^{II} ion. In the case of the binuclear Co(II) complexes **5**–**8**, peaks recorded on the CVs represent oxidation of the bridged *Rac* ligand. The complexes examined influence the cathodic reaction of hydrogen evolution in aqueous solutions by shifting its potential to more negative values and its current is increased. In non-aqueous solution the CVs of the ligands show irreversible anodic peaks for *cyclam*, *tpmc* and for the *Rac* ligands soluble in acetonitrile. The absence of any peaks in the case of the investigated complexes **1**–**4** indicates that coordination to Co(III) stabilizes both the *cyclam* and *Rac* ligands. Cyclic voltammograms of the complexes **5**–**8** show oxidation processes of the *Rac* ligand and Co(II) ions but the absence of a highly anodic peak of the coordinated macrocycle *tpmc* shows its stabilization. Contrary to in aqueous solution, the redox reaction Co(III)/Co(II) does not occur in acetonitrate indicating a higher stability of the complexes **1**–**4** in this media in comparison with the binuclear cobalt(II)-*tpmc* complexes **5**–**8**.

Keywords: cobalt(III) and cobalt(II) complexes, azamacrocycles and β-diketonato ligands, cyclic voltammetry, glassy carbon.

INTRODUCTION

Complexes with macrocyclic polyamines might serve as convenient building blocks for the construction of mixed-ligand mono- and polynuclear complexes.[1] Tetraamine [14]and-N_4 *cyclam* (1,4,8,11-tetraazacyclotetradecane) as a macro-

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cyclic flexible ring can exist in the *cis* and *trans* configurations[2] but only *cis* complexes have been observed in the presence of additional bidentate co-ligands.[3–7] The N_4-2-pyridylmethyl-substituted octaamine ligand *tpmc* (N,N',N'',N'''-tetra-kis(2-pyridyl methyl)-1,4,8,11-tetraazacyclotetradecane) through coordination provides interesting structural and chemical properties, *i.e.*, invariable formation of binuclear molecules with strong affinity towards various anions to form bridged complexes[8–10] and unusual stabilization of the divalent state of cobalt ion against oxidation to the trivalent state.[10] Macrocyclic ligands such as *cyclam* and *tpmc* are very useful to form and stabilize mixed-ligand complexes with additional exo-cyclic ligand(s).

In this context, β-diketones are suitable to combine with other ligands of comparable ligating ability, especially because of their ability to form keto-enolate structures and a few different coordination modes.[11] The chelating "pseudoaromatic" ring of β-diketones have found extensive application in the study of the formation of various types of metal complexes,[12] as well as giving the opportunity to investigate them in terms of different β-diketones R-groups.[7]

Therefore, these types of complexes could be interesting not only from aspects of molecular structures but from the electrochemical point of view as well, because structural and electronic factors may simultaneously affect the multi-redox peak potentials and catalytic features of the complexes.[3,8,13] For example, cyclic voltametric data for the cobalt(III)-*cyclam* oxalato complex[3] suggest large electrochemical stability, as well as its possible catalytic effect on the electrochemical reduction of CO_2. In the case of the binuclear cobalt(II)-*tpmc* oxalato complex[8] mulit-redox reactions of the metal centers and high electrochemical stability up to the potential of cobalt reduction were observed. The fact that the potential of hydrogen evolution is shifted to the anodic side in the presence of the complex indicates possible catalytic properties as well.[8] Electrochemical examination of mixed-ligand cobalt(III)-*cyclam* complexes with heterocyclic dithiocarbamates (*Rdtc*)[13] show redox reactions of the Co(III) ion at potentials the position of which are influenced by the presence of different heterocyclic rings in the *Rdtc* ligand, while the preliminary results in acidic media show their inhibition of iron corrosion and influence on hydrogen evolution in acidic media.

For the above-mentioned reasons, eight new mixed-ligand cobalt complexes were synthesized and characterized elsewhere,[6,7] *i.e.*, cobalt(III) complexes with macrocyclic ligand *cyclam* or *tpmc* in binuclear cobalt(II) complexes with R-symmetric bidentate β-diketones (*Rac*), *i.e.*, *acac* (2,4-pentanedionato), *dibzac* (1,3-diphenyl-1,3-propanedionato), *hfac* (1,1,1,5,5,5-dexafluoro-2,4-pentanedionato) or *tmhd* (2,2,6,6-tetramethyl-3,5-heptanedionato) ions, of the general formulas [Co^{III}(Rac)cyclam](ClO_4)$_2$ **(1)–(4)** and [Co_2^{II}(Rac)tpmc](ClO_4)$_3$ **(5)–(8)**, respectively. The aim of this work was a comparative study of the electrochemical behavior of these compounds and corresponding ligands in aqueous and non-aqueous solutions by
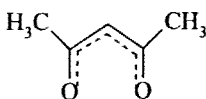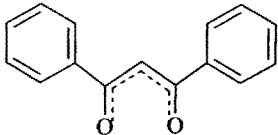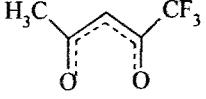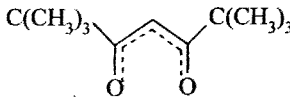
cyclic voltammetry (CV) and their possible influence on hydrogen evolution and oxygen reduction.

EXPERIMENTAL

A glassy carbon (GC) disc electrode (Sigardur-Sigri Electrographite, GmbH, Germany) was used as the working electrode. The electrode was mechanically refreshed with emery paper of decreasing grain size, polished with alumina ($0.5~\mu$ particle size) and cleaned in $18~M\Omega$ water in an ultrasonic bath. For each experiment, the prepared electrode was first examined in the basic electrolyte by CV before the substance was added to the solution. The counter electrode was a platinum wire. A saturated calomel electrode (SCE) was used as the reference in aqueous solution and a bridged SCE in CH_3CN.

All the complexes 1–8, macrocyclic *cyclam* and *tpmc* as well as the corresponding *Rac* ligands were examined in the concentration range of 10^{-6} to 10^{-4} M, in 0.1 M $NaClO_4$ aqueous solution and in 0.1 M $LiClO_4$ in CH_3CN. The solutions were prepared from analytical grade reagents and were maintained oxygen-free by purging with nitrogen.

TABLE I. β-Diketonato ligands in the complexes 1–8

Structure of *Rac* ion	Abbreviations and name of *Rac*	Coordinate d *Rac* in complexes
H_3C — CH$_3$ (O O)	*acac* 2,4-Pentanedionato ion	(1) (5)
(diphenyl, O O)	*dibzac* 1,3-Diphenyl-1,3-propanedionato ion	(2) (6)
H_3C — CF$_3$ (O O)	*hfac* 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato ion	(3) (7)
$C(CH_3)_3$ — $C(CH_3)_3$ (O O)	*tmhd* 2,2,6,6-Tetramethyl-3,5-heptanedionato ion	(4) (8)

Cyclic voltammetry was performed at sweep rates of 25, 50 and 100 mV/s. The potential range examined was between -0.5 V to 2.0 V in aqueous and -1.5 V to 1.5 V in non-aqueous solution. All the potentials are given *versus* the SCE electrode.

The $[Co^{III}(hfac)cyclam](ClO_4)_2$ complex (at a concentration of 10^{-4} M) was examined in 0.1 M $HClO_4$ solution by cyclic voltammetry (potential range from -1.2 V to 1.2 V *vs*. SCE, sweep rate 25, 50, 100 mV/s) as well. Also, the possible influence of this complex on the reduction of oxygen was tested in 0.1 M $HClO_4$ solution saturated with O_2 at a rotating GC electrode at a sweep rate of 5 mV/s in the potential range 0.2 V to -1.1 V *vs*. SCE.

All of the experiments were performed at room temperature in a three electrodes – three-compartment electrochemical cell. The electronic equipment in all of the experiments consisted of a Pine Instrument, Model RDE4 Potentiostat and a Philips Model 8033 X-Y recorder.

RESULTS AND DISCUSSION

The series of eight complexes, with general formulas $[Co^{III}(Rac)cyclam](ClO_4)_2$ (1)–(4) (Fig. 1A) and $[Co^{II}(Rac)tmpc](ClO_4)_3$ (5)–(8) (Fig. 1B) and the corresponding

$R = CH_3$ *acac*

dibzac

CF_3 *hfac*

$C(CH_3)_3$ *tmhd*

1A   1B
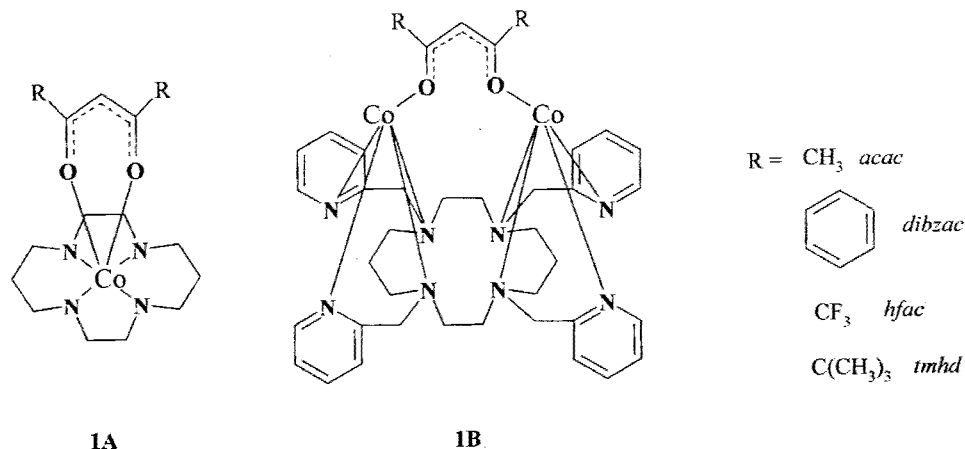
Fig. 1. Structures of the $[Co^{III}(Rac)cyclam](ClO_4)_2$ complexes 1–4 (1A) and of the $[Co_2^{II}(Rac)tpmc](ClO_4)_3$ complexes 5–8 (1B).

macrocyclic *cyclam* and *tpmc* as well as *Rac* (Table I) ligands were electrochemically characterized both in aqueous and non-aqueous solutions. The peak potentials for all of the ligands examined and for the complexes 1–8 are listed in Table II and the selected cyclic voltammograms are presented in Figs. 2–4.

Aqueous solution

The cyclic voltammogram of the GC electrode in aqueous ($NaClO_4$) solution in the absence of any compound shows no electron exchange occurred. With the addition of the macrocyclic ligands *cyclam* and *tpmc* one irreversible anodic peak appears at 0.95 V *vs.* SCE for the tetraaza amine only (Table II).[13,8] The CVs for the *Rac* ligands soluble in water (H*acac* and H*hfac* – Table II and Fig. 2A) indicate the existence of an irreversible anodic peak at 1.05 V and 1.40 V *vs.* SCE, respectively, which should correspond to oxidation processes of the organic species.

Two anodic peaks in the 0.65–0.90 V and 1.50–1.60 V *vs.* SCE regions for the cobalt(III)-*cyclam* complexes 1–3 can be identified only at the beginning of the cyclization (Fig. 2A – insert). During continued scanning, these anodic peaks are no longer observed, which might point to the low stability of the complex species. The number of cycles before the stabilization depends on the *Rac* ligand in the order of *hfac* > *acac* > *dibzac* in the complexes 1–3. In the case of complex 4 with a coordinated *tmhd* ligand (Fig. 2B), the steady state was established already at the first cycle, which can contribute to the higher stabilization of this complex ion. However, the steady-state CVs of the complexes 1–4 exhibit a reverse peak in the
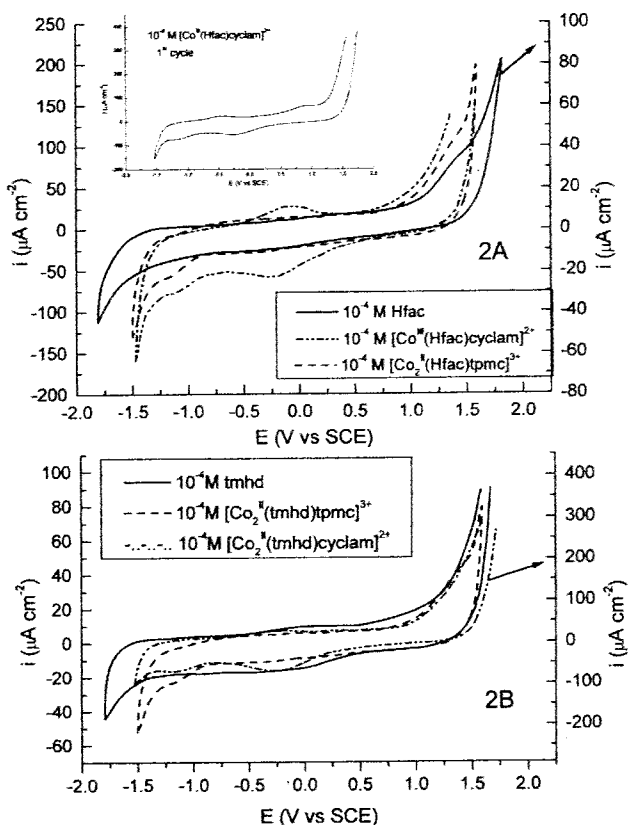
Fig. 2. Cyclic voltammograms at GC electrode in 0.1 M NaClO$_4$ and: A) 10^{-4} M *dibzac* ligand, 10^{-4} M [Co^{III}(dibzac)cyclam](ClO$_4$)$_2$ complex, 10^{-4} M [Co$_2$^{II}(dibzac)tpmc](ClO$_4$)$_3$ complex. B) 10^{-4} M *tmhd* ligand, 10^{-4} M [Co^{III}(tmhd)cyclam](ClO$_4$)$_2$ complex, 10^{-4} M [Co$_2$^{II}(tmhd)tpmc](ClO$_4$)$_3$ complex, (sweep rate 100 mV/s).

cathodic region (Table II and Fig. 2) in the region – 0.25 V to – 0.4 V depending on the *Rac* ligand. This pair of peaks probably indicates the redox reaction Co^{III}/Co^{II} from the complexes 1–4 as other previously characterized Co(III)-*cyclam* complexes (with dithiocarbamato and oxalato ligands) also display a similar redox pair at potentials influenced by the additional ligand.[3,13] In relation with these peaks, the highly cathodic peak at –1.15 V probably represent reduction to metal cobalt.

Peaks recorded on the CVs of the cobalt(II)-*tpmc* complex 5–8 between about 0.90 V to 1.40 V *vs*. SCE correspond to oxidation processes of the electroactive *Rac* ligands, exhibiting almost the same potential values for the free and coordinated β-diketonato ligands (Fig. 2A). The absence of any peak for the complex 6 with a coordinated *dibzac* ligand indicates its higher stability in aqueous media under the given electrochemical conditions. Only in the case of the complexes 5 and 8, with coordinated *acac* and *tmhd* ligand, respectively, a poorly defined cathodic peak at –1.15 V *vs*. SCE points to the reduction process to metal cobalt (Table II

and Fig. 2B).[8] The dependence of the peak current on the sweep rate indicates that all of the reactions are surface localized and not diffusion controlled, which should mean that the complexes are adsorbed on the electrode surface.

TABLE II. The peak potentials of the ligands and the corresponding complexes in aqueous (NaClO$_4$) and non-aqueous (LiClO$_4$/CH$_3$CN) solutions vs SCE

Compound	Aqueous solution			Non-aqueous solution
	E_{pa}		E_{pc}	E_{pa}
tpmc	–		–	1.82
cyclam	0.95		–	1.75
acac	1.05		–	–
dibzac	–		–	1.30
hfac	1.40		–	1.40
tmhd	–		–	–
[Co(acac)cyclam]$^{2+}$ (1)	0.70*	1.50*	–1.15	–
	– 0.30		– 0.40	
[Co(dibzac)cyclam]$^{2+}$ (2)	0.65*	1.53*	–1.15	–
	– 0.25		– 0.30	
[Co(hfac)cyclam]$^{2+}$ (3)	0.90*	1.60*	–1.15	–
	– 0.25		– 0.30	
[Co(tmhd)cyclam]$^{2+}$ (4)	– 0.25		– 0.30	–1.15	–
[Co$_2$(acac)tpmc]$^{3+}$ (5)		0.95	–1.15	1.48
[Co$_2$(dibzac)tpmc]$^{3+}$ (6)		–		1.30
[Co$_2$(hfac)tpmc]$^{3+}$ (7)		1.4		1.30
[Co$_2$(tmhd)tpmc]$^{3+}$ (8)		0.9	–1.15	1.25

* Peaks recorded at the beginning of cyclization: E_{pa} = anodic peak: E_{pc} = cathodic peak

In aqueous NaClO$_4$ solutions, the CVs demonstrate that the presence of any of the Co(III)-*cyclam* and Co(II)-*tpmc* complexes **1–8** examined influence the cathodic reaction of hydrogen evolution by slightly shifting the potential to more negative values in the order coordinated *tmhd* > *acac* > *dibzac* > *hfac* ligands, increasing its current in the opposite order (Fig. 3a). The effect of the Co(III)-*cyclam* complexes **1–4**, regarding this reaction, is more pronounced, especially in the increase of the current, compared with the Co(II)-*tmpc* compounds **5–8**. Furthermore, the cathodic shift of potential occurred only in the presence of the complexes **6** and **8** characterized with cathodic peak at –1.15 V (possible reduction to Co), in which the current of the H$_2$ reduction slightly decreased. The other two Co(II)-*tmpc* complexes **5** and **7** negligibly affect the current of H$_2$ evolution and have practically no influence on the potential. Regarding the cathodic shift of hydrogen evolution, the Co(III)-*cyclam* complexes **1–4** are similar to Co(III)-*cyclam* oxalate complex[3] which, however, has
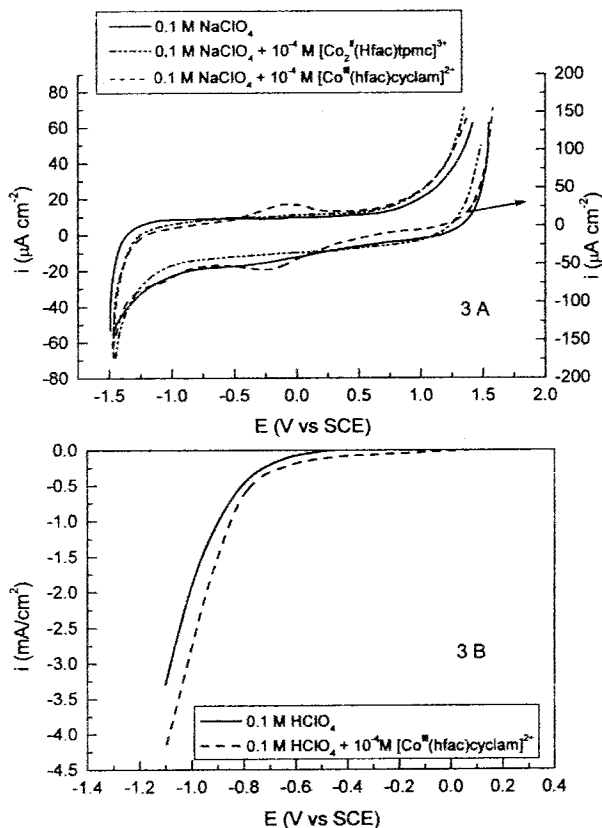
Fig. 3. A) Cyclic voltammograms at GC electrode in 0.1 M NaClO$_4$, 0.1 M NaClO$_4$ $-$ 10^{-4} M [Co^{III}(hfac)cyclam](ClO$_4$)$_2$ complex and 0.1 M NaClO$_4$ + 10^{-4} M [Co$_2^{II}$(hfac)tpmc](ClO$_4$)$_3$, (sweep rate 100 mV/s). B) Oxygen reduction curves for GC electrodes in 0.1 M HClO$_4$ saturated with O$_2$ and 0.1 M HClO$_4$ + 10^{-4} M [Co^{III}(hfac)cyclam](ClO$_4$)$_2$ complex saturated with O$_2$ (sweep rate 5 mV/s, 900 rpm).

the opposite effect on the reaction current, namely increasing it. This difference could be ascribed to the structural factor of the enlarged chelate rings of the O,O'-β-diketone ligand in comparison with the oxalato one. On the other hand, the binuclear Co(II)-*tpmc* oxalato complex[8] when present in the solution leads to an anodic shift of hydrogen evolution and a remarkable increase of the reaction current, which is completely contrary to the Co(II)-*tpmc* β-diketone complexes 5–8.

Complexes of transition metals (like Co or Fe) of the MN$_4$ chromophore appear to be a promising class of materials for the reduction of oxygen.[14,15] According to Chang et al.,[16] *cis* and *trans* configuration of the complex favor different paths of oxygen reduction. Complexes with *cyclam*, as a macrocycle that can exist in both of these configurations, can be interesting from this point of view. Therefore, we were interested to test the influence of the [Co^{III}(*hfac*)cyclam](ClO$_4$)$_2$ complex on oxygen reduction in acidic solution. The complex was first examined in 0.1 M HClO$_4$ by cyclic voltammetry and the recorded CV displayed only the Co(III)/Co(II) redox peaks at the same potentials as in 0.1 M NaClO$_4$. The reduction of oxygen was examined at a GC rotating electrode in O$_2$ saturated 0.1 M HClO$_4$ in the potential range from 0.2 V to –1.1 V at a sweep rate of 5 mV/s and at 4 different rotation rates. As shown in Fig. 3B the pres-

ence of the $[Co^{III}(hfac)cyclam](ClO_4)_2$ complex caused a shift in of the potential of this reaction in the anodic direction and an increase of its current to some extent. Also, it can be seen that both curves for O_2 reduction are without a limiting current density plateau. Furthermore, the curve recorded for the GC electrode is similar to the one presented by Sundberg et al.[17] for the same material (GC Sigradur) in 0.1 M HCl and according to the authors shows the reduction of O_2 to H_2O_2 as the major final product. The rather small difference in the current of this reaction in the presence of the complex probably means that the same mechanism is operative as on a pure GC electrode. As this complex is in the cis conformation these results are contrary to the conclusion Chang et al.[16] that the cis conformation rather than the trans one favors the 4-electron path in the reduction of oxygen. However, more about the exact influence of the $[Co^{III}(Rac)cyclam](ClO_4)_2$ complex on the reduction of O_2 can be said after completion of the detailed examinations that are in progress.

Non-aqueous solution

Electrochemical characterization of the macrocyclic ligands cyclam and tmpc, β-diketonato ligands and all of the complexes 1–8 was also performed in non-aqu-

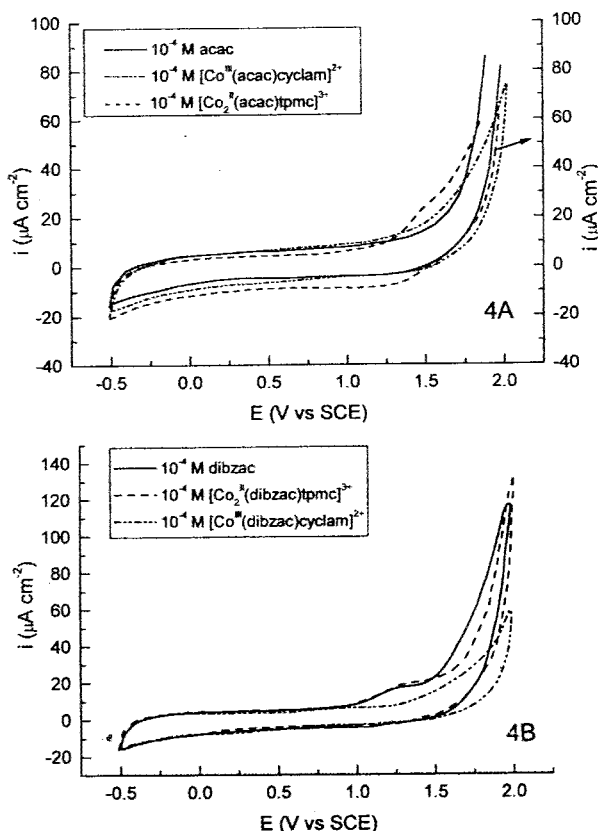Fig. 4. Cyclic voltammograms at GC electrode in 0.1 M LiClO$_4$/CH$_3$CN and: A) 10^{-4} M acac ligand, 10^{-4} M $[Co^{III}(acac)cyclam](ClO_4)_2$ complex, 10^{-4} M $[Co_2^{II}(acac)tpmc](ClO_4)_3$ complex. B) 10^{-4} M dibzac ligand, 10^{-4} M $[Co^{III}(dibzac)cyclam](ClO_4)_2$ complex, 10^{-4} M $[Co_2^{II}(dibzac)tpmc](ClO_4)_3$ complex. (sweep rate 100 mV/s).

eous (LiClO$_4$ in CH$_3$CN) solution. Selected cyclic voltammograms are presented in Fig. 4 and the peak potentials are listed in Table II.CVs of macrocyclic ligands[8,13] show their irreversibly oxidation at potentials of 1.75 V for *cyclam* and 1.82 V for *tmpc* vs. SCE. One irreversible anodic peak at 1.30 V and 1.40 V vs. SCE (Table II and Fig. 4) were recorded on each CVs of β-diketonato ligands soluble in acetonitrile (H*dibzac* and H*hfac*).

The absence of any peaks of the investigated Co(III)-*cyclam* **1–4** complexes ruled out the redox reactions, indicating the stabilization both of *cyclam* and *Rac* ligands through the coordination to cobalt(III) (Fig. 4). Electrochemical inactivity of acetylacetonate ligand being in coordination sphere of Co(III) was found in other non-aqueous solutions too.[18] The solvent polarities might have a strong influence on forming intermolecular hydrogen bonds, due to electronic properties of both ligands, thus producing the corresponding diference in the bond stability between cobalt ion and nitrogen/oxygen atoms of the respecitve ligands.[19]

The absence of highly anodic peak of coordinated macrocycle *tpmc* in the Co(II)-*tpmc* **5–8** complexes means stabilization of this ligand in non-aqueous solution. It is probably due to the fact that the *tpmc* is very flexible ligand, adapting itself to both cobalt(II) ions with the bridging ligand. Anodic peaks at high positive potentials recorded on CVs of the binuclear **5–8** complexes (Table II and Fig. 4) correspond to oxidation processes of bidentate *Rac* ligand as well as metal ions. Actually, if the β-diketonato ligand is electrochemically non-acitve (as H*acac* and H*tmhd*) the anodic peak in 1.25–1.48 V region origins only from Co(II) ions oxidation (Fig. 4A), contrary to electroactive *Rac* ligands (as H*dibzac* and H*hfac*) where in the same range the process of oxidation both for the metal and *Rac* ligand probably proceeds simultaneously (Fig. 4B). Therefore, potential values are in correlation with combined electronic and steric effects of coordinated β-diketones and they are characteristic for the binuclear penta-coordinated cobalt(II) complexes.[20]

Correlation with IR and NMR/EPR data

All of the ligands as well as their **1–8** complexes were also examined by spectroscopy methods. According to the earlier results[6,7] R-groups on the β-diketone largely influence the frequencies shifting v(C∴C) and v(C∴O) bands in IR spectra of the all complexes, as a consequence of different resonance and inductive effects along conjugated double bonds through the *Rac* anion. Influence of R-groups exhibits movement of important bands in ^{13}C-NMR spectra of the **1–4** complexes as well as *g* factor values in EPR spectra of the **5–8** complexes, following from much positive to high negative inductive effect, in order of complexes with coordinated *tmhd* > *acac* > *dibzac* > *hfac* ligands.

The powerful efficacy of six fluorine atoms, of the *hfac* ligand in the **3** and **7** complexes, is especially expressed in all spectral characteristics through movement to higher wave numbers of important IR bands. In NMR[7] and EPR spectra (at

temperatures of 4 K and 11 K) the effect is quite opposite. In both series of complexes, electrochemical examinations in aqueous and non-aqueous solutions, display the anodic peaks at higher potential values for the corresponding **3** and **7** complexes with coordinated *hfac* ligand. On the other side, opposite electronic effect of $-C(CH_3)_3$ groups of *tmhd* ligand in **4** and **8** complexes gave anodic peaks at lowest potential values.

From available results for the **1–8** complexes, it is evident that the same effects *i.e.*, structural and electronic, affect on spectral and electrochemical behavior, which were transmitted due to delocalised bands of coordinated *Rac* as a bidentate ligand in the Co(III)-*cyclam* **1–4** (Fig. 1A) or bridged bidentate ligand in the Co(II)-*tpmc* **5–8** complexes (Fig. 1B).

CONCLUSION

Based on the data obtained, some conclusions and comparison can be made about the influence of the structure of the **1–8** complexes and their electrochemical characteristics. Furthermore, the ability to influence these behavior seems to be related closely to the electronic properties of the *Rac* ligand as a whole, not just the oxygen atoms bonded to cobalt ions.

Consequently, Co(III) ions from the **1–4** and Co(II) ions from the **5–8** complexes undergo redox reactions in aqueous solution at the potentials, which are affected by the presence of different *Rac* ligands. The peak potentials of the mononuclear complexes **1–4** demonstrate reactions, which continuously proceed from Co^{III}/Co^{II} to Co^0 reduction while in the binuclear **5–8** complex species in aqueous solution only reduction to metal Co occurs. Those behaviors could indicate different influence of coordinated *Rac* ligand besides folded tetraamine (*cyclam*) than in the presence of macrocyclic octamine (*tpmc*) in *boat* conformation. On the other side, in correlation to the former binuclear Co(II)-*tpmc* oxalato complex[8] where electronic exchange – antiferromagnetic coupling between the two metal ions is presented, in the case of the complexes **5–8** particularly pronounced electronic effect of the *Rac* bridging unit subsists to produce additional stabilization.

Preliminary examinations of oxygen reduction in the presence of [$Co^{III}(hfac)$cyclam]$(ClO_4)_2$ complex shows possible catalytic effect on the reaction in acidic media.

Contrary to the aqueous solution, in acetonitrile, Co(III) redox reaction does not occur, indicating a higher stability of the complexes **1–4** in this media as well as their greater electrochemical stability in comparison with the binuclear cobalt(II)-*tpmc* complexes **5–8**. The influence of solvent polarities might be of importance on different redox behavior of the complexes in aqueous and non-aqueous solutions.[15]

ИЗВОД

КОМПАРАТИВНО ЕЛЕКТРОХЕМИЈСКО ИСПИТИВАЊЕ НЕКИХ КОБАЛТ(III) И КОБАЛТ(II) КОМПЛЕКСА СА АЗАМАКРОЦИКЛИЧНИМ И β-ДИКЕТОНАТО ЛИГАНДИМА

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Цикличном волтаметријом испитано је осам комплекса кобалта(III) и кобалта(II) са мешовитим лигандима, опште формуле [Co^{III}(Rac)cyclam](ClO$_4$)$_2$ (1)–(4) и [Co^{II}(Rac)tpmc](ClO$_4$)$_3$ (5)–(8), у воденој (NaClO$_4$) и неводеној (LiClO$_4$/CH$_3$CN) средини. У воденој средини *cyclam* и *Rac* лиганди подлежу анодној оксидацији. Координација са Co(III) у комплексима (1)–(4) стабилизује ове лиганде али долази до редокс реакције Co(III)/Co(II). У случају бинукеларних Co(II) комплекса (5)–(8) долази до оксидације *Rac* лиганада. Испитивани комплекси у воденом раствору утичу на реакцију издвајања водоника катодно померајући потенцијал и повећавајући струју. У неводеним растворима анодно се оксидују оба макроциклична (*cyclam* и *tpmc*) и *Rac* лиганди растворни у ацетонитрилу. Међутим, у овим растворима Co(III) комплекса не долази до електрохемијских реакција што значи не само да и овде координација са кобалтом стабилизује лиганде већ нема ни редокс реакције за кобалт. Са друге стране, у Co(II) комплесима стабилизован је *tpmc* али се оксидују *Rac* лиганди и Co(II) па су тако у неводеним растворима комплекси Co(III) стабилнији од бинукеларних Co(II)-*tpmc* комплекса.

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