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The electrochemical behaviour and electrooxidative polymerization of tetraazaannulenic alkyl– and aryl–cobalt complexes

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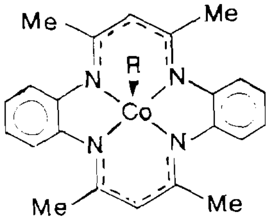
Abstract

Three σ-bonded tetraazaannulenic complexes of Co(III), [tetramethyltetraaza[14]annulene(R–Co)] (R = CH_3, C_2H_5 or C_6H_5), have been synthesized. The complexes have been studied by cyclic voltammetry. Two anodic waves, imputable to monoelectronic, ligand-centered, oxidative processes are found at about +0.7 and +1.1 V, only moderately influenced by the R group. The cathodic region exhibits two waves around −1.3 and −1.6 V. Growth of thin films by 6–6′ σ polymerization of the monomers on Pt surface in CH_3CN/0.1 M [TBA][BF_4] by consecutive potential scans in the range +1.40→ −1.80 V (versus NHE) is observed. Electrochemical evidence for the absence of Co–C bond cleavage during electropolymerization is reported.

Introduction

Deposition of polymers by different techniques on metallic or semiconducting surfaces received a considerable attention during the past ten years [1]. A large number of papers concerns the polymers obtained from organometallic (like vinyl-ferrocene [2]) or coordination (like bis(vinylterpyridine)cobalt(II) [3]) complexes, due to their interesting charge transport properties and to their capability of providing efficient electrocatalyzing sites. More recently the interest of many researchers has been attracted by the study of electropolymerized tetraazaannulene [4, 5] macrocycles owing to their good capability to undergo electrooxidative polymerization coupled with potentially wide tunability of redox and chemical properties. However, the optimization of some parameters like solubility in organic solvents, stability in aqueous solution and crystallinity degree, in view of suitable application of these systems, is still an open question. Therefore having in mind these considerations, we decided to investigate by electrochemical techniques the versatile Co–tetraazaannulenes complexes having the Co atom functionalized with a σ-bonded alkyl or aryl group. The ligand in these species shows the well known property of conjugated systems, like porphyrins analogues, which are able to stabilize the cobalt atom in various formal oxidation states (i.e. d^6Co(III), d^7Co(II) and d^8Co(I)) and in different coordination geometries.

In this paper we report the synthesis and electrochemical characterization of (R–Co)tetramethyltetraaza[14]annulene, [(R–Co)TMTAA] (**a**) complexes (R = CH_3, **1a**; R = C_2H_5, **2a**; R = C_6H_5, **3a**).



Electropolymerization studies of **1a**, **2a** and **3a**, carried out by cyclic voltammetry, are also reported in order to understand the influence of the R group on the properties of the modified electrodes.

Experimental

^1H NMR spectra were carried out on a 300 MHz Bruker spectrometer. UV–Vis spectra were run using a Varian-Cary 2300 spectrophotometer; UV–Vis spectra of the electropolymerized species were recorded after their deposition on highly (F^-) doped SnO_2 glass plates [1, 6]. Infrared spectra were recorded with a Perkin-Elmer model 883 spectrophotometer. Voltammograms were carried out on a EG & G 273 PAR potentiostat-galvanostat equipped

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with a computerized data acquisition system by using a locally manufactured two compartments – three electrodes H cell. The working electrode was 0.07 cm^2 platinum disk, the counter was platinum wire and an Ag/AgCl, 3 M NaCl electrode was used as reference. The ferrocene/ferrocenium couple, to which the experimental potentials are referred, was used as internal standard, and this allows a rescaling to NHE [7]. The sweep rate was 200 mV/s when not differently stated. No *IR* compensation was used. Acetonitrile, for electrochemical experiments, was distilled over CaH_2; DMF was stirred 48 h over 4 Å molecular sieves before use. The solutions were degased by bubbling prepurified argon for 10 min before measurements. Electrodes were polished prior to use with 1 μm diamond paste (Buehler) and rinsed thoroughly with water and acetone. The experimental error on the values reported for the potentials is ±0.01 V.

Tetramethyldibenzotetraaza[14]annulene (H_2-TMTAA) was obtained as previously described [8] by template condensation of 1,2-diaminobenzene and 2,4-pentanedione on Ni^{2+} ions and subsequently stripping of the metal by gaseous HCl.

[(R–Co)TMTAA] was prepared by modification of the method used by Costa *et al.* [9] for the preparation of the analog [(R–Co)Salen] compounds starting from $[Co(TMTAA)(C_5H_5N)Br]H_2O$.

$[Co(TMTAA)(C_5H_5N)Br]H_2O$. This compound was prepared by air refluxing a mixture of $CoBr_2 \cdot 6H_2O$ (6.5 g) and stoichiometric amount of H_2TMTAA in methanol (100 ml) containing 10 ml of pyridine. After 3 h the solvent was evaporated and the solid formed, dissolved in ethanol, was crystallized as red needles after addition of ether.

[(R–Co)TMTAA] ($R=CH_3$, **1a**; $R=C_2H_5$, **2a**; $R=C_6H_5$, **3a**). The alkylated species were obtained by adding, dropwise at −60 °C, RMgBr (7.5 mmol) in anhydrous (accurately degassed) tetrahydrofuran to 2.5 mmol of $[Co(TMTAA)(C_5H_5N)Br]H_2O$ suspended in 50 ml of tetrahydrofuran. After stirring for 4 h at room temperature in N_2 atmosphere the reaction mixture was neutralized with 2 N HCl and the solvent removed by distillation under vacuum. The obtained red–brown powders of $[(R–Co)TMTAA]H_2O$ were exposed to vacuum (10^{-3} atm) to give dark-green air stable powders of [(R–Co)TMTAA]. *Anal.* Calc. for **1a**:C, 66.35; H, 6.01; N, 13.46. Found: C, 65.80; H, 5.7; N, 13.05%. Calc. for **2a**: C, 66.98; H, 6.28; N, 13.02. Found: C, 66.10; H, 5.8; N, 12,65%. Calc. for **3a**: C, 70.29; H, 5.65; N, 11.71. Found: C, 68.90; H, 5.1; N, 11.05%. Relevant characterization data are reported in Table 1.

Results and discussion

Monomer characterization

The three R–Co σ-bonded tetraazaannulenic complexes of Co(III), [(R–Co)TMTAA], **1a**, **2a** and **3a**, have been studied by cyclic voltammetry. Voltammograms of **1a**, **2a** and **3a** obtained in anhydrous CH_3CN by using 0.1 M $[TBA][BF_4]$ (TBA = tetrabutylammonium) as supporting electrolyte are reported in Fig. 1. The scans were run from 0.00 to +1.40 V and from 0.00 to −1.80 V (versus NHE), respectively. Scans in the whole range +1.40 to −1.80 V starting from 0.00 V and cycling in the positive direction were not significantly different. Moreover the dependence on the scanning rate in the range 0.05 ÷ 1.00, on the solvent polarity (CH_3CN versus DMF) and on the counterion nature (BF_4^-, ClO_4^-) was also investigated. In all cases no significant difference was found and the most relevant features of the voltammograms were retained along the whole series of the complexes under study.

The anodic region consists of two irreversible or quasi-reversible ($\delta E_p = 0.10 \div 0.15$ V) waves, Nernstian in appearance, centered at values reported in Table 2. Both oxidative processes lack a non-negligible reductive component, this fact being more evident for **3a**. It has been clearly shown in recent electrochemical and spectroscopic works on M(II)TMTAA (M(II) = Ni(II), Cu(II) and Co(II)) [5], where similar shapes of the voltammograms were found in the anodic region, that the consecutive waves occurring between +0.40 and +1.20 V (versus SSCE) are fairly independent of the central metal atom and are imputable to monoelectronic ligand centered processes. Thus, the oxidations localized at $E_{pa1} = +0.60$ to $+0.79$ and $E_{pa2} = +1.03$ to $+1.22$, produce radical cationic or bicationic, respectively. As already found for Ni(II) and Cu(II) TMTAA derivatives [10–12], these radicals are susceptible to dimerization or polymerization by carbon–carbon σ bond formation between the C(6)–C(6)′ atoms of the propanediimine backbone, as shown in Fig. 2. Assuming these consideration the two waves correspond to the monoelectronic removal of two π-electrons from the delocalized system of the ligand. In appearance E_{pa1} and E_{pa2} are moderately influenced by the R group. The E_{pa} values depend on the donor capability of the R group: shifts towards more positive values are observed for **1a**. Moreover, within experimental error, $E_{pa2} - E_{pa1}$ has a constant value for the three complexes which amounts to 0.43 V.

The cathodic region of the voltammograms, when scanned up to −2.00 V, exhibits three waves; among these only the second, located around $E = -1.6$ V

TABLE 1. Relevant characterization data for [(R–Co)TMTAA] complexes

Species	UV–Vis[a] $\tilde{\nu}_{max}$ (cm^{-1}×10^{-3})	IR[b] $\tilde{\nu}$ (cm^{-1})	^{1}H NMR[c] δ (ppm)
1a	35.71(4.56) 34.25(4.52) 32.46(4.42) 30.48(4.26) 25.77(3.86) 20.16(3.41) 14.45(3.33)	280,s,Co–C stretching 740,m, benzenoid ring 1550,s,C=C stretching 1595,s,C=N stretching 2900–3000,s,C–H str.	7.8–7.1, arom. 5.45,bs,C–*H* 2.20,s,C–C*H*$_3$ 1.35,s,Co–C*H*$_3$
2a	37.03(4.59) 35.71(4.54) 34.72(4.46) 32.46(4.37) 27.02(4.03) 20.74(3.63) 14.70(3.48)	300,s,Co–C stretching 738,m, benzenoid ring 1550,s,C=C stretching 1585,s,C=N stretching 2900–3000,s,C–H str.	7.8–7.1, arom. 5.48,bs,C–*H* 2.45,q,C*H*$_2$CH$_3$ 2.20,s,C–C*H*$_3$ 1.20,t,CH$_2$C*H*$_3$
3a	38.46(4.55) 36.49(4.15) 35.71(3.93) 32.25(3.67) 26.66(2.59) 14.28(2.89)	280,s,Co–C stretching 738,m, benzenoid ring 1560,s,C=C stretching 1600,s,C=N stretching 2900–3000,s,C–H str.	

[a] Spectra in acetonitrile solutions; $C=3\times10^{-5}$ M; $T=20\pm0.5$ °C; 1 cm path length cell; log Σ in parentheses. [b] Spectra in KBr pellets; s = strong, m = medium. [c] Spectra in C_5D_5N solutions at room temperature; **3a** not soluble enough; s = singlet, t = triplet, q = quartet, m = multiplet, b = broad.

is reversible for **2a** and **3a**. The third wave, occurring at $E > -1.90$ V with very high i_{pc} values, is associated with reductive phenomena that produces deposition of insulating material on the electrode surface; the wave's shape is a looping form, as found in other polymerization processes [13]. In agreement with literature data [5, 14], that assume a remarkable stabilization of the R–Co(III)/R–Co(II) couple with respect to the Co(III)/Co(II) solvated couple, it is possible to relate the cathodic waves occurring around −1.3 V to the R–Co(III)/R–Co(II) couple. Bailey and coworkers report [5] for the [Co–TMTAA] complex a reversible process concerning the Co(III)/Co(II) reduction located at $E = 0.01$ V (versus SSCE) in acetonitrile solution. In our species we can evaluate the stabilizing ability in about 1.1 ÷ 1.3 V. Stabilization of the R–M(III)/R–M(II) couple is a well known process widely studied for L = SALEN, OEP, TPP (SALEN = *N*,*N*′-ethylenebis(salicylideniminato) dianion; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion) [14–16]. The resulting stabilizing ability falls in the range +1.00 to +1.40 V, and the same behaviour has been found for similar complexes of Fe [15]. In the present case the stabilizing effect on the Co(III) state is slightly dependent upon the nature of the R group; more negative potentials occur for the R–Co(III)/R–Co(II) couple on going from C_6H_5 to CH_3 and to C_2H_5. The second cathodic wave, centered at about −1.6 V is attributable to the R–Co(II)/R–Co(I) reduction. The reported results, in particular the shape of the oxidative waves, suggest that chemical reactions on the monomeric complexes occur after oxidation; in fact, in analogy with the reported behaviour of Ni(II) and Cu(II) TMTAA complexes [5], we found this reactivity leads to polymeric growth.

Electropolymerization studies and polymer characterization

Representative voltammograms concerning the growth of thin polymeric films of **1a**, **2a** and **3a** on Pt surface in CH_3CN/0.1 M [TBA][BF_4] by consecutive potential scans in the range +1.40 to +1.80 V (versus Ag/AgCl) starting from 0.00 V in the positive direction are reported in Fig. 3. The voltammograms are similar for the three complexes and their shapes do not strongly depend on the kind of electrodes used: in fact we obtained similar waves both on Au and on glass-carbon electrodes. It may be easily recognized that only the first oxidative process exhibits a remarkable increase of i_{pa}; a noticeable increase of i_{pc1} and i_{pc2} is also observed, coupled with a complete absence of cathodic and

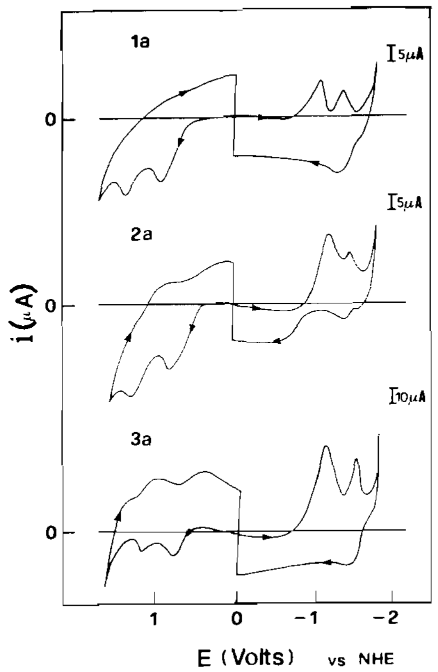

Fig. 1. Cyclic voltammograms of 10^{-4} M CH_3CN solutions of **1a**, **2a** and **3a**; experimental conditions: V = 200 mV/s, electrolyte = 0.1 M $[TBA][BF_4]/CH_3CN$, Pt electrode, E(V) vs. NHE, scans in the range $0.00 \rightarrow +1.40 \rightarrow 0.00$ and $0.00 \rightarrow -1.80 \rightarrow 0.00$.

anodic prewaves as found indeed for Ni(TMTAA) polymerization [10]. Polymers were grown also scanning the potential in the range $0.00 \rightarrow +1.40 \rightarrow 0.00$ V or potentiostating the solution at +1.40 V or at +1.00 V. However in the last case the polymer growth was very slow, likely indicating an appreciable difference in the kinetic stability between monocationic and dicationic monomeric species. The apparent aspect of each polymer, observed by optical microscope (60×) was independent of the route used during the electropolymerization process. The surface of the films was smooth with a perceptible disordered fibrous structure. The three polymers $(\mathbf{1a})_n$, $(\mathbf{2a})_n$ and $(\mathbf{3a})_n$ are different in colour being respectively lustrous-gold, silver and gold. Thin films of $(\mathbf{1a})_n$, $(\mathbf{2a})_n$ and $(\mathbf{3a})_n$ deposited on SnO_2 surface show, in the UV–Vis region, a large and intense absorption band centered at $\bar{\nu}_{max}$ = 28 570, 23 810 and 33 300 cm^{-1}, respectively and the absence of any band at lesser values of ν_{max} in the visible region. All three films are strongly stuck to the electrode surfaces irrespective of their composition (i.e. Pt, Au or SnO_2 surfaces) and are insoluble in most of organic solvents, in water or in aqueous HNO_3. The apparent surface coverage, Γ^{app}, was investigated at the same experimental condition for **1a**, **2a** and **3a**. It was determined by integrating the area under the anodic peaks in the positive region from +0.40 to +1.40 V and dividing by the monolayer coverage (2.43×10^{-11} mol/cm^2) as assumed for Ni(TMTAA) [4]; the results are reported in Fig. 4. We found that in the whole range $\Gamma_{3a}^{app} > \Gamma_{2a}^{app} > \Gamma_{1a}^{app}$. Moreover, in the case of the 10^{-4} M solution after one scan in the range 0.00 to +1.40 V the charge flow through the working electrode was 5.53×10^{-6} C for **1a**, 9.99×10^{-6} C for **2a** and 1.31×10^{-5} C for **3a**. Furthermore the number of 'monolayers' was 34, 61 and 80 for the three complexes, respectively. These data are comparable with values obtained for [Ni(R-TMTAA)] (R = Cl, CH_3CO, NO_2) [4] complexes. The different coverage capability might be imputable to the effect of the R group on the ability of $(\mathbf{1a})_n$, $(\mathbf{2a})_n$ and $(\mathbf{3a})_n$ to assume a coiled conformation on the Pt surface. The polymers obtained retain an electroactive response showing the same anodic and cathodic behaviour as the monomeric complexes after prolonged immersion (t > 2 h) in DMF, H_2O, acetone or benzene. However the

TABLE 2. Redox parameters of [(R–Co)TMTAA] complexes and $[(R\text{–}Co)TMTAA]_n$ polymers[a]

Species	Oxidation potential (V)[b, c]		Reduction potential (V)[b, c]	
	RCo(III)L/ RCo(III)L$^+$	RCo(III)L$^+$/ RCo(III)L^{2+}	RCo(III)L/ RCo(II)L	RCo(II)L/ RCo(I)L
1a	+0.79	+1.22	−1.24	−1.49
2a	+0.60(150)	+1.03(100)	−1.42	−1.71(60)
3a	+0.72(145)	+1.14(100)	−1.21	−1.65(60)
$(\mathbf{1a})_n$	+0.65	+1.11	−1.12	−1.40
$(\mathbf{2a})_n$	+0.55	+0.95	−1.35(55)	−1.65(55)
$(\mathbf{3a})_n$	+0.65	+1.00	−1.15(55)	−1.55(55)

[a] Data obtained in 0.1 M $[TBA][BF_4]$ acetonitrile solutions. Monomer concentration 10^{-4} to 5×10^{-5} M, $T = 20 \pm 0.5$ °C. [b] Volts, vs. NHE, ±0.01; scan rate = 200 mV/s. [c] Numbers in parentheses refer to δE_p values. Absence of any value indicates an irreversible process.

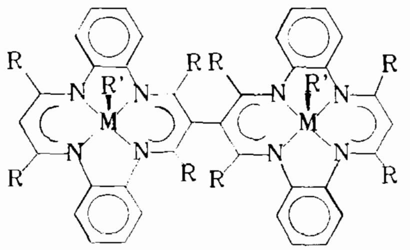

Fig. 2. Proposed dimeric species formed upon oxidation of [R–Co(III)TMTAA], showing the C(6)–C(6)′ σ bond formation between TMTAA macrocycles.

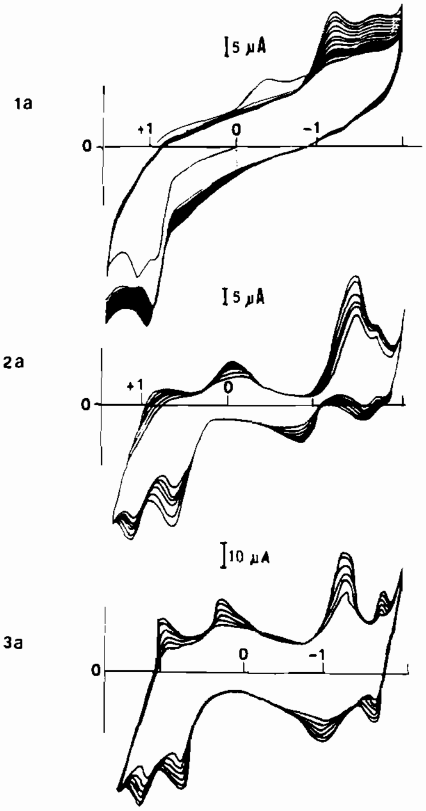

Fig. 3. Voltammograms of 10^{-4} M CH_3CN solutions of **1a**, **2a** and **3a** showing the electropolymerization process. Conditions: $v = 200$ mV/s, electrolyte = 0.1 M [TBA][BF_4], Pt electrode, in abscissa E(V) vs. NHE is reported, scan range from 1.40 to −1.80 V starting from 0.00 in the negative direction. Scans 2–12, in increments of 2 unrecorded scans, are reported for **2a** and **3a**; scans 1–12 for **1a**.

waves become irreversible and slightly shift towards less positive and less negative potentials, respectively (see Table 2 and Fig. 5(a) for $(\mathbf{2a})_n$). The stability of the films obtained scanning the modified electrodes in neat electrolyte in the region 0.00 to +1.40 and in the whole range +1.40 to −1.90 V was also tested by calculating the area drop under the oxidative waves. The results indicate a small loss of electroactivity of about 10% after 40 scans, irrespective of the potential range scanned.

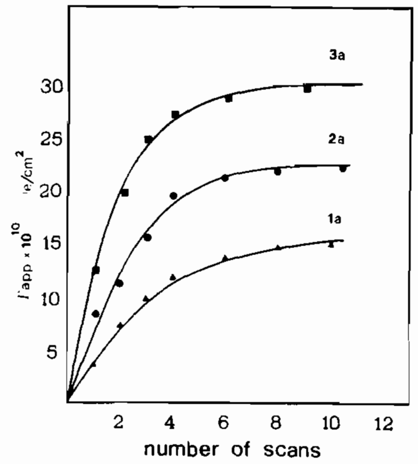

Fig. 4. Apparent surface coverage (Γ_{app}) as a function of the number of polymerization scans for 10^{-4} M solutions of **1a**, **2a** and **3a**. Conditions: $v = 200$ mV/s, electrolyte = 0.1 M [TBA][BF_4], Pt electrode, scan in the range 0.00 → +1.40 V (vs. NHE); the integrated area under oxidative peaks was measured between +0.40 and +1.40 V.

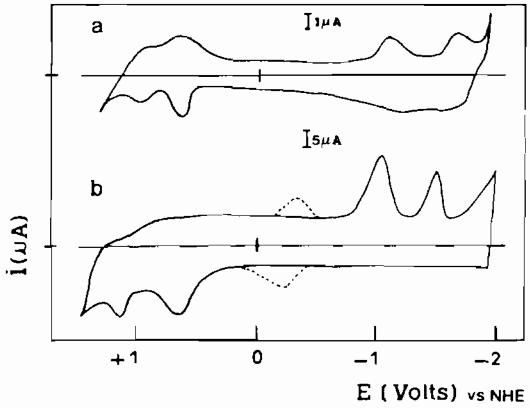

Fig. 5. (a) Voltammetric response of $(\mathbf{2a})_n$ in CH_3CN containing 0.1 M [TBA][BF_4] as supporting electrolyte in the range +1.40 to −1.85 V (vs. NHE); $v = 200$ mV/s. (b) Cyclic voltammograms of 10^{-4} M solution of **1a** containing 0.1 M [TBA][BF_4] (scan rate = 100 mV/s); scanning from −1.85 to +1.40 V after holding for 10 min at +1.40 V (——) and after holding for 10 min at −1.80 V (– – –).

Furthermore in order to detect the possible cleavage of the Co–C bond during the electropolymerization process, bulk electrolysis of **1a**, **2a**, **3a** 10^{-4} M solutions in acetonitrile/0.1 M [TBA][BF_4] was carried out, locking the working electrode potential at +1.40 V for 10 min. Taking care to avoid oxygen contamination of the solution, a new polished working Pt disk was submerged in the solution. After scanning the potential in the range −1.85 → +1.40 V in the positive direction starting from −1.85 V, we are unable to detect in the voltammogram, as shown in Fig. 5(b) for **1a**, any anodic wave, at $E° = +0.01$ V (versus SSCE) [5], which is characteristic of the Co(II)/Co(III) solvated couple. The same evidence for the absence of this couple can be obtained scanning the potential from +1.40 V in the negative direction.

Besides, the appearance of the mentioned couple occurred, as can be expected, as a consequence of strongly reductive bulk electrolysis. In fact we held the working electrode at −1.85 V (versus NHE) for 10 min, and we registered the potential scanning in the range $-1.80 \rightarrow +1.40$ V (starting from −1.80 V). As reported in Fig. 5(b), the voltammogram of a solution of **1a** exhibits an anodic peak located at around +0.15 V with a cathodic counterpart at −0.30 V. This wave is very close to that of the solvated Co(II)TMTAA/Co(III)TMTAA couple indicating the homolytic Co–C bond cleavage in these experimental conditions. Similar behaviour has already been reported for the analogous σ-bonded metallorganic complexes of cobalt [14].

Conclusions

The main electrochemical properties of [(CH_3–Co)TMTAA], [(C_2H_5–Co)TMTAA] and [(C_6H_5–Co)TMTAA] may be summarized as follows: (i) the induced electrochemical stabilization of R–Co(III)/R–Co(II) matches with the behaviour of the analogous organometallic complexes of Co(III); (ii) the oxidative processes centered on the macrocycle ligand become irreversible and polymerization phenomena occur; (iii) the apparent coverage capability of monomers is strongly influenced by the R group and, although to a lesser extent, the optical properties of polymers as well.

This suggests, owing to the large variety of R groups which can be bonded to the Co atom, a valid strategy to build a new class of electropolymerized compounds. Further studies in this direction are in progress.

Acknowledgements

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