

Synthesis, characterization and electro-spectroelectrochemical studies of four macrocyclic Schiff-base Co(II) complexes having N₂O₂ set of donor atoms

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Abstract Four macrocyclic Schiff-base cobalt complexes, [CoL¹][NO₃]₂ · 3H₂O, [CoL²][NO₃]₂ · 4H₂O, [CoL³][NO₃]₂ · 4H₂O and [CoL⁴][NO₃]₂ · 2H₂O, were synthesized by reaction of salicylaldehyde derivatives with 1,4-bis(3-aminopropoxy)butane or (±)-*trans*-1,2-diaminocyclohexane and Co(NO₃)₂ · 6H₂O by template effect in methanol. The metals to ligand ratio of the complexes were found to be 1:1. The Co(II) complexes are proposed to be tetrahedral geometry. The macrocyclic Co(II) complexes are 1:2 electrolytes as shown by their molar conductivities (Λ_M) in DMF (dimethyl formamide) at 10⁻³ M. The structure of Co(II) complexes is proposed from elemental analysis, Ft-IR, UV–visible spectra, magnetic susceptibility, molar conductivity measurements and mass spectra. Electrochemical and thin-layer spectroelectrochemical studies of the complexes were comparatively studied in the same experimental conditions. The electrochemical results revealed that all complexes displayed irreversible one reduction processes and their cathodic peak potential values

(*E*_{pc}) were observed in around of -1.14 to 0.95 V. It was also seen that [CoL¹][NO₃]₂ · 3H₂O and [CoL²][NO₃]₂ · 4H₂O exhibited one cathodic wave without corresponding anodic wave but, [CoL³][NO₃]₂ · 4H₂O and [CoL⁴][NO₃]₂ · 2H₂O showed one cathodic wave with corresponding anodic wave, probably due to the presence of different ligand nature even if the complexes have the same N₂O₂ donor set. In view of spectroelectrochemical studies [CoL³][NO₃]₂ · 4H₂O showed distinctive spectral changes in which the intensity of the band (λ = at 316 nm, assigned to n → π* transitions) decreased and a new broad band in a low intensity about 391 nm appeared as a result of the reduction process based on the cobalt center in the complex.

Keywords Macrocyclic Schiff bases · Salicylaldehyde derivatives · 1,4-bis(3-Aminopropoxy)butane · (±)-*trans*-1,2-Diaminocyclohexane · Electrochemistry

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Introduction

Schiff bases and their metal complexes play a key role in understanding the coordination chemistry of transition metal ions [1]. The chemistry of macrocyclic complexes has received much attention in recent years on account of its various applications in bioinorganic chemistry. Many tetradentate Schiff bases are known to stabilize unusual oxidation states of the coordinated metal [2]. Synthesis of these Schiff-base complexes is achieved through the template reaction or transmetallation reactions which are used when the transition metal cations are ineffective as templates [3, 4]. The cobalt(II) complexes play important roles as catalysts in the activation of small molecules. [5]. Thus, there has been a strong interest in determining

thermodynamically meaningful redox potentials of Schiff-base metal complexes and in understanding the relationship between these potentials and the detailed structure of the Schiff-base ligand [6]. In view of the above applications, in this article we report the synthesis and characterization of four cobalt(II) complexes by template effect by reaction of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 1,4-bis(3-aminopropoxy)butane or (\pm)-*trans*-1,2-diaminocyclohexane and salicylaldehyde derivatives. Spectral, magnetic properties and comparative electrochemical studies of the complexes were studied in detail.

Experimental

Materials

Dialdehydes, 1,2-bis(2-formylphenyl)ethane and 1,3-bis(2-formylphenyl)propane, used in the synthesis were prepared by the reaction of salicylaldehyde and 1,2-dibromoethane or 1,3-dibromopropane in the presence of K_2CO_3 at 155 °C according to the literature [7]. Dimethyl sulfoxide (DMSO) was dried over molecular sieve of 4 Å. Electrochemical grade tetrabutylammonium perchlorate (TBAP, Fluka Chemical Co.) was recrystallized from ethyl alcohol and dried in a vacuum oven at 40 °C for at least 1 week prior to use. The other chemicals and solvents were of analytical grade and used as received.

Physical measurements

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. Ft-IR spectra were recorded on a Perkin Elmer Spectrum RX1 Ft-IR spectrophotometer on KBr pellets in the wave number range of 4000–400 cm^{-1} . Electronic spectral studies were conducted on a SHIMA-DZU model 160 UV–visible spectrophotometer in the wavelength 200–900 nm. Molar conductivity was measured with a WTW LF model 330 conductivity meters, using prepared solution of the complexes in DMF solvent. Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [8]. Mass spectra were recorded using a Agilent model 1100 MSD mass spectrometer. Cyclic voltammograms (CVs) were carried out using CV measurements with Princeton Applied Research Model 2263 potentiostat controlled by an external PC. A three electrode system (BAS model solid cell stand) was used for CV measurements in DMSO and consisted of a 2 mm sized platinum disc electrode as working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode.

The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as an internal standard but all potentials in the paper are referenced to the Ag/AgCl reference electrode. Solutions containing the complex were deoxygenated by a stream of high purity nitrogen for at least 5 min before running the experiment. The solution was protected from air by a blanket of nitrogen during the experiment. UV–visible spectroelectrochemical experiments were performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode [9]. Potentials were applied and monitored with a Princeton Applied Research Model 2263 potentiostat. Time- and potential-resolved UV–visible spectra were recorded on Agilent Model 8453 diode array spectrophotometer.

General procedure for preparation of Co(II) complexes

To a stirred solution of dialdehydes, 1,2-bis(2-formylphenyl)ethane and 1,3-bis(2-formylphenyl)propane (2 mmol), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol) in methanol (60 mL) was added dropwise 1,4-bis(3-aminopropoxy)butane or (\pm)-*trans*-1,2-diaminocyclohexane (2 mmol) in methanol (40 mL). After the addition was completed, the stirring was continued for 2 h. Then precipitate was filtered and washed with methanol. Then dried in air.

Characterization of $[\text{CoL}^1](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

Yield: 0.29 g (21.4%). Anal Calcd. for $\text{CoC}_{26}\text{H}_{34}\text{N}_4\text{O}_{10} \cdot 3\text{H}_2\text{O}$: C, 46.23; H, 5.97; N, 8.29. Found: C, 46.37; H, 6.16; N, 8.14. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3361 $\nu(\text{H}_2\text{O})$; 3076 $\nu(\text{Ar}-\text{CH})$; 2933, 2881 $\nu(\text{Alph.}-\text{CH})$; 1635 $\nu(\text{C}=\text{N})$; 1491, 1456 $\nu(\text{Ar}-\text{C}=\text{C})$; 1384, ionic $\nu(\text{NO}_3^-)$; 1292, 1247 $\nu(\text{Ar}-\text{O})$; 1162, 1043, $\nu(\text{R}-\text{O})$; 756 $\nu(\text{Substituted benzene})$; 522 $\nu(\text{Co}-\text{O})$ 501 $\nu(\text{Co}-\text{N})$. $\Lambda = 179 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in DMF). UV–VIS (λ_{max} , nm) in DMF: 238, 272, 307, 651. Mass spectrum (m/z): 559 $[[\text{CoL}^1](\text{NO}_3)]^+ \cdot \mu_{\text{eff}} = 3.96 \text{ B.M.}$

Characterization of $[\text{CoL}^2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

Yield: 0.30 g (21.2%). Anal Calcd. for $\text{CoC}_{27}\text{H}_{36}\text{N}_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$: C, 45.84; H, 6.27; N, 7.92. Found: C, 45.24; H, 5.96; N, 7.78. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3356 $\nu(\text{H}_2\text{O})$; 3125 $\nu(\text{Ar}-\text{CH})$; 2923, 2862 $\nu(\text{Alph.}-\text{CH})$; 1634 $\nu(\text{C}=\text{N})$; 1490, 1455 $\nu(\text{Ar}-\text{C}=\text{C})$; 1384, ionic $\nu(\text{NO}_3^-)$; 1311, 1239 $\nu(\text{Ar}-\text{O})$; 1092, 1038, $\nu(\text{R}-\text{O})$; 753 $\nu(\text{Substituted benzene})$; 535 $\nu(\text{Co}-\text{O})$ 502 $\nu(\text{Co}-\text{N})$. $\Lambda = 171 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in DMF). UV–VIS (λ_{max} , nm) in DMF: 238, 268, 322, 649. Mass spectrum (m/z): 636 $[[\text{CoL}^2](\text{NO}_3)_2+\text{H}]^+ \cdot \mu_{\text{eff}} = 3.78 \text{ B.M.}$

Characterization of $[\text{CoL}^3](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

Yield: 0.36 g (31.0%). Anal Calcd. for $\text{CoC}_{22}\text{H}_{24}\text{N}_4\text{O}_8 \cdot 4\text{H}_2\text{O}$: C, 43.78; H, 5.34; N, 9.28. Found: C, 44.14; H, 5.42; N, 9.31. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3369 $\nu(\text{H}_2\text{O})$; 3071 $\nu(\text{Ar}-\text{CH})$; 2939, 2886 $\nu(\text{Alph.}-\text{CH})$; 1636 $\nu(\text{C}=\text{N})$; 1384, ionic $\nu(\text{NO}_3^-)$; 1292, 1243 $\nu(\text{Ar}-\text{O})$; 1162, 1042, $\nu(\text{R}-\text{O})$; 752 $\nu(\text{Substituted benzene})$; 519 $\nu(\text{Co}-\text{O})$ 506 $\nu(\text{Co}-\text{N})$. $\Lambda = 142 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in DMF). UV-VIS (λ_{max} , nm) in DMF: 239, 270, 327, 655. Mass spectrum (m/z): 530 $[[\text{CoL}^3](\text{NO}_3)_2-\text{H}]^+ \cdot \mu_{\text{eff}} = 3.85 \text{ B.M.}$

Characterization of $[\text{CoL}^4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

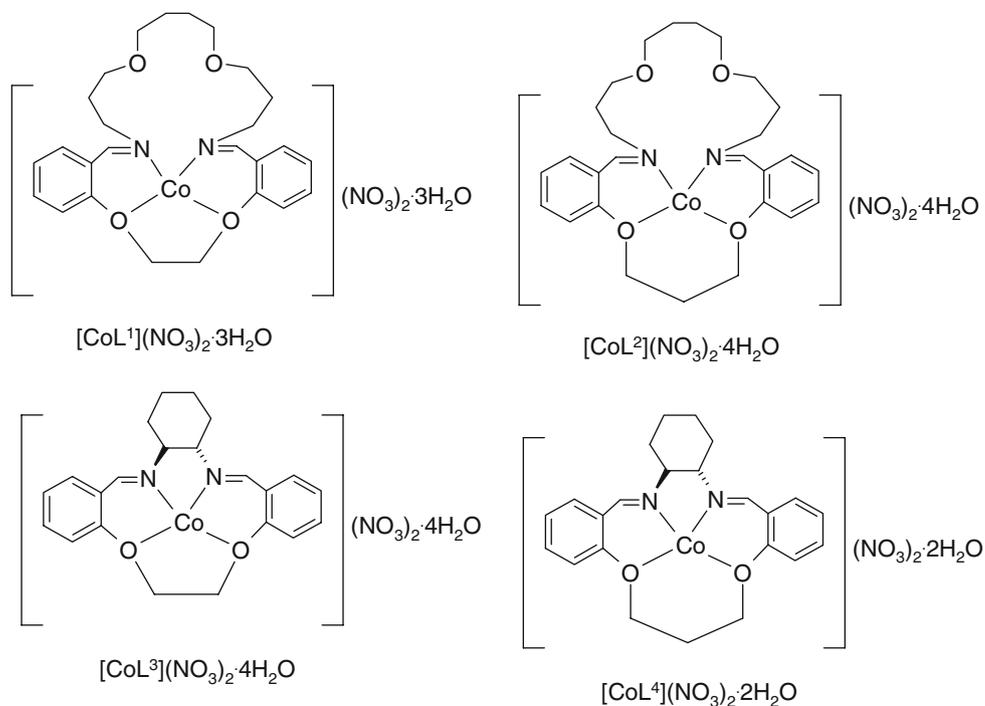
Yield: 0.44 g (39.4%). Anal Calcd. for $\text{CoC}_{23}\text{H}_{26}\text{N}_4\text{O}_8 \cdot 2\text{H}_2\text{O}$: C, 47.51; H, 5.16; N, 9.63. Found: C, 47.11; H, 5.07; N, 9.52. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3348 $\nu(\text{H}_2\text{O})$; 3119 $\nu(\text{Ar}-\text{CH})$; 2926, 2863 $\nu(\text{Alph.}-\text{CH})$; 1634 $\nu(\text{C}=\text{N})$; 1384, ionic $\nu(\text{NO}_3^-)$; 1311, 1238 $\nu(\text{Ar}-\text{O})$; 1091, 1039, $\nu(\text{R}-\text{O})$; 752 $\nu(\text{Substituted benzene})$; 531 $\nu(\text{Co}-\text{O})$ 496 $\nu(\text{Co}-\text{N})$. $\Lambda = 172 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in DMF). UV-VIS (λ_{max} , nm) in DMF: 239, 268, 321, 651. Mass spectrum (m/z): 483 $[[\text{CoL}^4](\text{NO}_3)_2]^+ \cdot \mu_{\text{eff}} = 3.88 \text{ B.M.}$

Result and discussion

Synthesis and characterization

In this work, [1+1] macrocyclic Schiff-base cobalt complexes are formed as the product by the reaction of 1,2-

Fig. 1 Supposed structure of the cobalt complexes



bis(2-formylphenyl)ethane or 1,3-bis(2-formylphenyl)propane and (\pm)-*trans*-1,2-diaminocyclohexane or 1,4-bis(3-aminopropoxy)butane with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in methanol. The proposed structures of the complexes are presented in Fig. 1. These macrocyclic complexes were characterized by the combination of elemental analysis, mass and IR spectrometry. The mass spectra of the complexes play an important role in confirming the monomeric [1+1] (dicarbonyl and diamine) nature of complexes. The complexes are insoluble in most common solvents, including water, ethanol, ethyl acetate and acetonitrile hence the suitable crystals could not be obtained for single-crystal X-ray structure determination. Analytical, molar conductance, magnetic susceptibility values and mass data of the complexes are listed in Table 1. The metal-ligand mole ratio was found to be 1:1, according to elemental analysis. Since all of the complexes are paramagnetic, their n.m.r. spectra could not be obtained.

IR analysis

The characteristic infrared spectrum data are given in the experimental section and Table 2. The infrared spectra of the metal complexes were recorded in KBr pellet from 4000 to 400 cm^{-1} . The broad bands within the range *ca.* 3350 cm^{-1} for all complexes can be attributed to stretching vibrations of water molecule $\nu(\text{H}_2\text{O})$ [10]. A medium band observed in the IR spectra of the complexes in the 1636–1634 cm^{-1} region is attributed to the $\nu(\text{C}=\text{N})$ stretch, indicating coordination of the azomethine nitrogen to metal ion [11]. The complexes are dominated by bands between

Table 1 Physical characterization, analytical, molar conductance and mass data of the complexes

Compound	Yield (%) (g)	(calcd)	Found	%C	%H	%N	λ_M (Ω^{-1} cm ² mol ⁻¹)	F. W.	MS/EI	Assignments	μ_{eff} (B.M)	
[CoL ¹][NO ₃] ₂ · 3H ₂ O	(21.4) 0.29	(46.23)	46.37	(5.97)	6.16	(8.29)	8.14	179	675	559	[[CoL ¹](NO ₃)] ⁺	3.96
[CoL ²][NO ₃] ₂ · 4H ₂ O	(21.2) 0.30	(45.84)	46.24	(6.27)	5.96	(7.92)	7.78	171	709	636	[[CoL ²](NO ₃) ₂ +H] ⁺	3.78
[CoL ³][NO ₃] ₂ · 4H ₂ O	(31.0) 0.36	(43.78)	44.14	(5.34)	5.42	(9.28)	9.31	142	603	530	[[CoL ³](NO ₃) ₂ -H] ⁺	3.85
[CoL ⁴][NO ₃] ₂ · 2H ₂ O	(39.4) 0.44	(47.51)	47.11	(5.16)	5.07	(9.63)	9.52	172	581	483	[[CoL ⁴](NO ₃)] ⁺	3.88

Table 2 IR (cm⁻¹) and UV–vis (nm) spectral data for the Co(II) complexes

Compound	$\nu(\text{H}_2\text{O})$ (s)	$\nu(\text{C}=\text{N})$ (m)	ionic $\nu(\text{NO}_3^-)$ (m)	$\nu(\text{M}-\text{O})$ (w)	$\nu(\text{M}-\text{N})$ (w)	$\pi \rightarrow \pi^*$ transition	$n \rightarrow \pi^*$ transition	${}^2E_g \rightarrow {}^2T_{2g}$ transition
[CoL ¹][NO ₃] ₂ · 3H ₂ O	3361	1635	1384	522	501	238,272	307	651
[CoL ²][NO ₃] ₂ · 4H ₂ O	3356	1636	1384	535	502	238,268	322	649
[CoL ³][NO ₃] ₂ · 4H ₂ O	3369	1636	1384	519	506	239,270	327	655
[CoL ⁴][NO ₃] ₂ · 2H ₂ O	3348	1634	1384	531	496	239,268	321	651

m: medium; s: strong; w: weak

2965 and 2855 cm⁻¹ due to $\nu(\text{Alph.}-\text{CH})$ groups. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra of the complexes appear at 552–515 cm⁻¹ and 511–471 cm⁻¹ assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretching vibrations [12]. The IR (cm⁻¹) spectral data for the metal complexes are given in Table 2.

UV–vis analysis

Electronic absorption spectral data of the complexes in dimethylformamide (DMF) at room temperature are presented in experimental section. The electronic spectra of cobalt(II) complexes in DMF show four peaks in the visible–ultraviolet region. The absorption bands below 300 nm are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine ($-\text{C}=\text{N}$) groups. The absorption bands observed within the 300–330 nm range are most probably due to the transitions of $n \rightarrow \pi^*$ of imine groups [13]. The general character of these spectra is very similar to that of the corresponding complexes of unsymmetrical disubstituted phenoxy groups. This is probably due to the fact that metal-to-ligand charge transfer and ligand-to-metal charge transfer transitions have similar energy differences [14]. The electronic spectrum of the Co(II) complexes shows an absorption band attributed to the ${}^2E_g \rightarrow {}^2T_{2g}$ transitions, characteristic for tetrahedral geometry [4]. The energy of the band assigned to $d \rightarrow d$ transitions can provide a rough estimate of the ligand field strength, since one of the electronic transitions comprised in the band envelope is dx^2-y^2-dxy and the energy associated with this transitions is 10Dq-C [14]. The electronic absorption bands of the presented Co(II)

complexes in the visible region exhibit solvent dependence behavior. The observed red shifts in the low-energy $d-d$ band of Co(II) metal complexes in DMF can be interpreted in terms of weakening of ligand field strength [14]. The UV–vis (nm) spectral data for the metal complexes are given in Table 2.

Mass spectra

The mass spectrum of the [CoL⁴][NO₃]₂ · 2H₂O was given in Fig. 2. The values of the molecular ions (m/z) observed in the mass spectra of the complexes are also listed in Table 1.

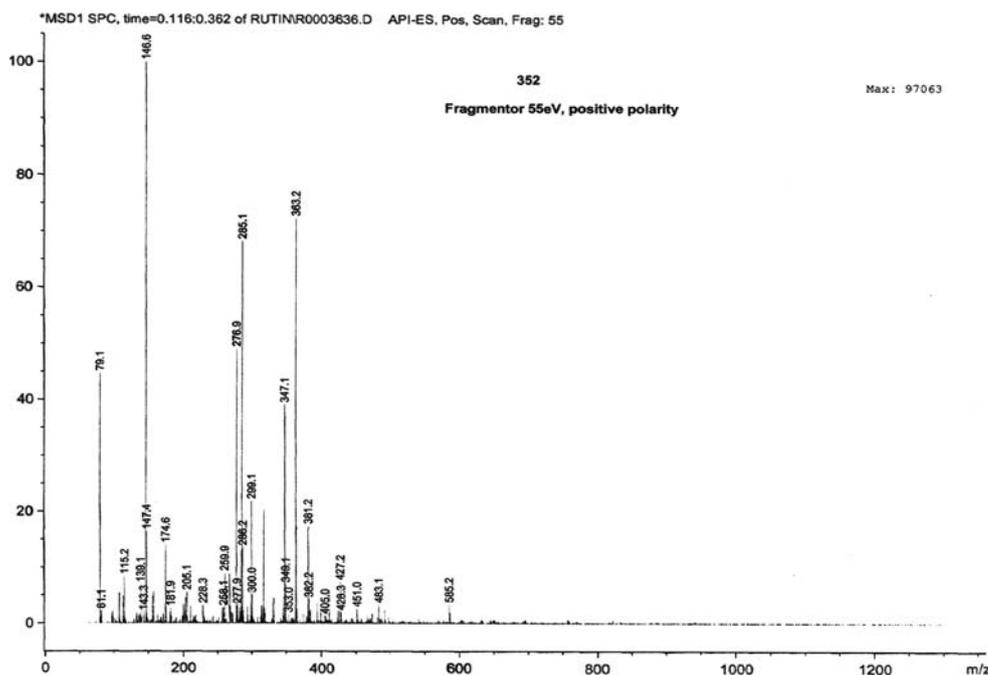
Magnetic susceptibility

Magnetic susceptibility measurements provide sufficient data to characterize the structure of the Co(II) complexes. The room temperature magnetic moment of between 3.78 and 3.96 B.M determined for Co(II) complexes, are close to the spin-only magnetic moments ($\mu = 3.87$ B.M) for three unpaired electrons. This results and the absorption bands observed for the electronic spectra of Co(II) complexes also support the tetrahedral geometry for Co(II) metal complexes [14].

Conductivity measurements

The Co(II) complexes are 1:2 electrolytes as shown by their molar conductivities (Λ_M) in DMF (dimethyl formamide) at 10⁻³ M, which are in the range 140–200 Ω^{-1} cm² mol⁻¹. The molar conductivities of the compounds in DMF are the range reported for 1:2

Fig. 2 The mass spectrum of the $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$



electrolytes [15, 16] The corresponding values are given in Table 1.

Electrochemistry

The electrochemical behaviors of $[\text{CoL}^1][\text{NO}_3]_2 \cdot 3\text{H}_2\text{O}$, $[\text{CoL}^2][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$, $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ and $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$, were investigated using cyclic voltammetric technique in DMSO containing 0.1 M TBAP. Fig. 3 represents the CVs of $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ and $[\text{CoL}^2][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ in DMSO solution containing 0.1 M TBAP at the scan rate of 0.100 V s^{-1} . As seen from Fig. 3a, $[\text{CoL}^4][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ showed one irreversible reduction process, probably based on the cobalt center ($\text{Co}(2+)/\text{Co}(+)$ couples). The cathodic peak potential of this reduction process was observed at $E_{\text{pc}} = -0.91 \text{ V}$ versus Ag/AgCl . The value of the cathodic-to-anodic peak separation for the reduction process was calculated as 0.82 V in the scan rate of 0.010 V s^{-1} in DMSO, indicating an irreversible nature of the reduction process [17]. No any wave was recorded during the cathodic sweep range 0.40 to -0.50 V , which confirms that the wave observed at $E_{\text{pa}} = -0.91 \text{ V}$ belongs to the cathodic peak of the reduction process. This irreversible character of the reduction process with the large peak separation is probably caused by a low electron transfer on the electrode surface once the complex reduces [18]. The electrochemical behavior of $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ is almost the same with that of $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ in the same experimental conditions. The cathodic peak potential of $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ was observed at $E_{\text{pc}} = -1.14 \text{ V}$

versus Ag/AgCl , which appeared in the more negative potential compared to that of $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$. Fig. 3b indicates CV of $[\text{CoL}^2][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$. As seen, the complex exhibited a cathodic wave without a corresponding anodic wave which assigns to an irreversible cobalt-based reduction process. The cathodic peak potential of the process was appeared at $E_{\text{pc}} = -0.95 \text{ V}$. The electrochemical behavior of $[\text{CoL}^1][\text{NO}_3]_2 \cdot 3\text{H}_2\text{O}$ is similar to that of $[\text{CoL}^2][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ in the same experimental conditions with the exception that the cathodic peak (E_{pc}) potential of $[\text{CoL}^1][\text{NO}_3]_2 \cdot 3\text{H}_2\text{O}$ shifts toward more negative value compared with that of $[\text{CoL}^2][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ as observed for the $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ and $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$. When compared electrochemical behavior of the macrocyclic Schiff-base cobalt complexes, it is seen that $[\text{CoL}^1][\text{NO}_3]_2 \cdot 3\text{H}_2\text{O}$ and $[\text{CoL}^2][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ exhibited one cathodic wave without corresponding anodic wave but, $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ and $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ showed one cathodic wave with corresponding anodic wave. It is probably due to the presence of different ligand nature even if the complexes have the same N_2O_2 donor set [19].

Spectroelectrochemistry

The spectroelectrochemical behavior of $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ was investigated using an in situ spectroelectrochemical technique including chronoamperometry and UV–VIS spectroscopy in DMSO solution containing 0.2 M TBAP. The UV–VIS spectral changes or the reduced species of $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ were obtained in a thin-layer

cell during an applied potential. The convenient applied potential value for in situ spectroelectrochemical experiment was determined as $E_{\text{app}} = -1.44$ V for the reduction process by taking CVs of $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ in the thin-layer cell. The complex $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ showed well defined UV–VIS spectral changes during the reduction process ($E_{\text{app}} = -1.44$ V) while the other complexes did not exhibited well defined electronic spectra during the reduction, probably due their fast chemical decomposition or coupling during time scale of the spectroelectrochemical measurements. Fig. 4 shows the UV–VIS spectral changes of $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$, that is accompanied by the reduction process in the thin-layer cell. As seen, the spectra of the reduced species showed an isosbestic points at $\lambda = 357$ nm, confirming that the electrode reaction proceeds in a quantitative fashion and therefore the absence of any coupled chemistry [20, 21]. The complex showed distinctive spectral changes that the intensity of the band ($\lambda =$ at 316 nm, assigned to $n \rightarrow \pi^*$ transitions) decreased

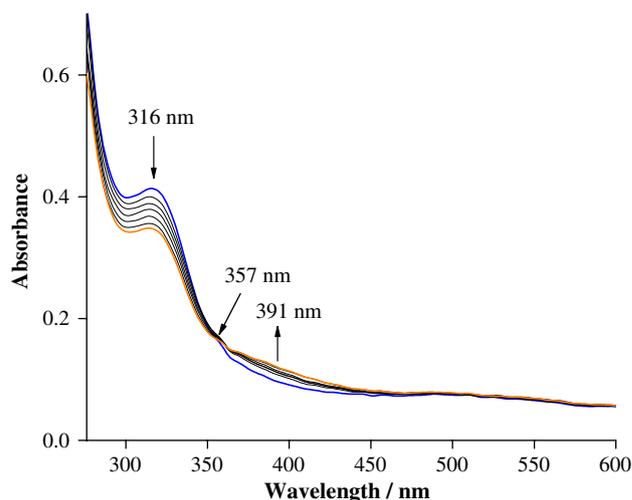


Fig. 4 Time-resolved UV–vis spectral changes of $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ during the reduction at $E_{\text{app}} = -1.44$ V in DMSO solution containing 0.2 M TBAP

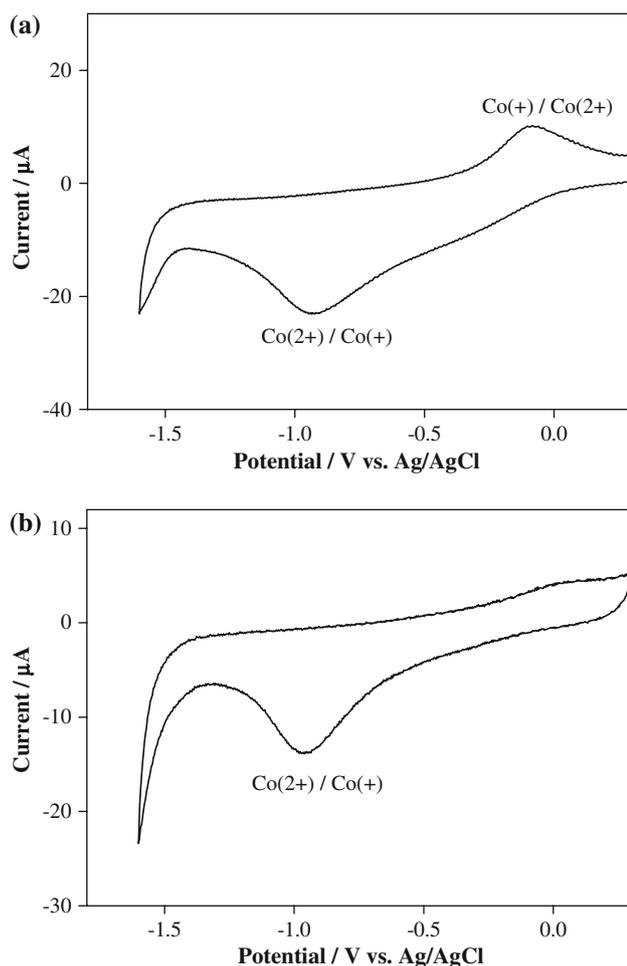


Fig. 3 Cyclic voltammograms of $[\text{CoL}^4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ (a); $[\text{CoL}^2][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ (b) in DMSO solution containing 0.1 M TBAP. Scan rates = 0.100 V s^{-1}

and a new broad band in a low intensity about 391 nm appeared as a result of the reduction process based on the cobalt center in the complex. The original spectrum of the neutral complex was recovered when the potential was applied $E_{\text{app}} = 0.30$ V in the thin-layer cell, indicates that the reduced species remain stable within the spectroelectrochemical measurements.

Conclusion

In this study, four new macrocyclic Schiff-base cobalt complexes, $[\text{CoL}^1](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $[\text{CoL}^2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $[\text{CoL}^3](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $[\text{CoL}^4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, were synthesized and characterized by the combination of elemental analysis, Ft-IR, UV–vis spectra, magnetic susceptibility, molar conductivity measurements and mass spectra. By this way, the Co(II) complexes are proposed to be tetrahedral geometry. Electrochemistry of the complexes and thin-layer spectroelectrochemical behavior of $[\text{CoL}^3][\text{NO}_3]_2 \cdot 4\text{H}_2\text{O}$ were also studied in the same experimental conditions.

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