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Synthesis and Electrochemical Properties of New Derivatives of Dibenzo(perhydrotriazino)-aza-crown Ethers and Their Cobalt(II) Complexes

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Four novel dibenzo(perhydrotriazino)-aza-crown ethers, L_1, L_2, L_3 and L_4 have been synthesized in good yield by petrenko-kritchenko condensation of bisaldehydes (**a-d**) with thiourea in the presence of ammonium acetate in the mixture of ethanol and acetic acid. Subsequently, crown ethers L_1 and L_2 were used as a precursor to synthesize cobalt complexes $[Co(L_1)_2Cl_2]$ and $[Co(L_2)_2Cl_2]$, respectively. The newly synthesized crown ethers have been characterized with the elemental analyses, melting point, IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. The cobalt complexes of crown ethers have been characterized by IR spectra and elemental analyses. Also, electrochemical behaviour of these crown ethers and their cobalt(II) complexes was studied by cyclic voltammetry. The results showed that the electrochemical properties of the synthesized Co(II) complexes revealed the irreversible two electron transfer redox process.

Keywords: Crown ethers, Cobalt complexes, Cyclic voltammetry.

INTRODUCTION

The synthesis and the structural investigations of crown ether type macrocycles are essential for the organic and analytical chemistry, since crown ethers are useful in removing undesired metal cations [1]. Macrocyclic compounds containing oxygen, sulfur and nitrogen as donor atoms ligands that form a large, continuous ring around a metal ion and form extremely stable complexes with ions within their central cavity [2,3]. The synthesis of new aza-crown ethers as well as their metal complexes represents an active area of research due to their wide spread applications in biology, supra-molecular chemistry, new materials, medicine and the chemical industry [4,5]. Also, macrocyclic metal complexes have been of particular importance in coordination chemistry because of various application in biological processes such as photosynthesis and dioxygen transport [6]. Among macrocyclic ligands, nitrogen-oxygen mixed donor macrocycles have a strong tendency to form stable complexes with both alkali and transition metal ions [1]. For the reason, enormous progress in macrocyclic chemistry of aza compounds has been made in the past decade [7,8]. The synthesis of macrocyclic complexes of new aza ligands have resulted in a large number and variety of compounds. Therefore, the preparation of new macrocyclic ligands with more elaborate structures is a vital area of research [9]. In this paper, we report the synthesis, characterization and electrochemical properties of four new aza crown ethers, L_1, L_2, L_3 and L_4 as well as two Co(II) complexes $[Co(L_1)_2Cl_2]$ and $[Co(L_2)_2Cl_2]$. Aza crown macrocycles, L_1, L_2, L_3 and L_4 were synthesized by petrenko-kritchenko condensation of bisaldehydes **a-d** and thiourea in the presence of ammonium acetate in the mixture of ethanol and acetic acid. The synthesized macrocycles L_1 and L_2 were reacted with cobalt chloride to from their cobalt complexes. Electrochemical properties of these aza-crown ethers and related complexes were studied by cyclic voltammetry. The results showed that the synthesized aza crown macrocycles fully stable and for a long time can be stored at room temperature.

EXPERIMENTAL

All organic reagents and solvents used in this study were supplied by Merck chemical and were used without further purification. Melting points were measured on a Electrothermal digital 9200 melting point apparatus and the results were uncorrected. Thin layer chromatography (TLC) was carried out on silica gel-G plates using chloroform (merck) as solvent system. IR spectra were recorded in the region 4000-400 cm^{-1} on a Shimadzu Varian Model-4300 FT-IR spectrophotometer using KBr discs. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker-Avance DRX-300 and 75 spectrometer using TMS as an internal standard. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. Mass spectra were recorded on a GC-MS Shimadzu QP1000PX Mass spectro-

meter. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer. Cyclic voltammetric measurements for all aza crown macrocycles as well as two Co(II) complexes were done using a VA measurements were carried out in acetonitrile and N,N-dimethyl formamide solution, with a three electrode assembly comprising a glassy carbon disk working electrode, a platinum auxiliary electrode and an aqueous Ag/AgCl reference electrode, the latter of which was connected with the solution through a salt bridge (tetrabutylammonium perchlorate). The concentration of the supporting electrolyte, tetrabutylammonium perchlorate was 0.1 M, while that of the aza crown ethers and complexes were 0.05 g (0.1 mM).

Bisaldehydes (**a-d**) was prepared by the method of refluxing in alcoholic solution under nitrogen atmosphere [10]. To stirred solution of 2-hydroxy-3-methoxy benzaldehyde (15.21 g, 0.1 mol) in hot ethanol (10 mL) was added sodium hydroxide (4.0 g, 0.1 mol) in water (200 mL). The mixture was warmed and 1,3-dibromo propanol or 1,4-dibromo butane (10.1 g, 0.5 mol) was added. Sufficient ethanol (150 mL) to produce a homogeneous solution was then added. The progress of reaction was monitored by thin layer chromatography (TLC). The solution was refluxed under nitrogen for 100 h and then cooled and let stand at 0 °C. The cream coloured crystals produced were washed with water. Recrystallization was performed using an ethanol-water mixture to give bisaldehydes **c** and **d** in 73.31 and 86.41 % yield, respectively. The resulting crystals were collected by filtration and dried in vacuum desiccators over P_4O_{10}.

Synthesis of aza crown ethers: A solution of freshly prepared aromatic bialdehyde **a-d** (0.3 g, 1 mmol), thiourea (0.076 g, 0.1 mmol) and ammonium acetate (0.1 g, 1.3 mmol) in a mixture of alcohol (3 mL) and acetic acid (0.2 mL) was stirred at 20 °C for 13 h. The progress of reaction was monitored by thin layer chromatography (TLC). The separated white precipitate were filtered off, washed with ethanol and recrystallized from hot chloroform.

$C_{18}H_{19}O_2N_3S$ (L_1): Yield: 81 %; m.p.: 167 °C; IR (KBr, ν_{max}, cm^{-1}): 3404, 3329 and 3176- (N-H), 1114 (C-O), 1056 (C=S); ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 7.3-7.49 (m, 2H, H-5), 7.2 (s, 2H, H-3), 6.83-6.99 (dd, 4H, H-4, 2), 5.-4 (t, 2H, H-7), 3.9 (t, 4H,O*CH*$_2$CH$_2$), 2.13 (m, 2H, O*CH*$_2$CH$_2$), 1.-7 (s, 3H, NH) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ: 175.63 (C, C-8), 156.74 (C, C-1), 130.7 (CH, C-5), 130.71 (CH, C-3), 130.16 (C, C-6), 120.81 (CH, C-4), 111.43 (CH, C-2),69.31 (OCH_2, O*CH*$_2$CH$_2$), 67.41 (CH, C-7), 29.11 (CH_2, O*CH*$_2$CH$_2$) ppm; MS (*m/z*) = 341[M^+]; Elemental analysis calcd. (%) for $C_{18}H_{19}O_2N_3S$: C, 63.22-; H, 5.8; N, 12.10; found (%): C, 63.32, H, 5.61; N, 12.31.

$C_{19}H_{21}O_2N_3S$ (L_2): Yield: 70 %; m.p.: 173 °C; IR (KBr, ν_{max}, cm^{-1}): 3450, 3329 and 3170 (N-H), 1116 (C-O), 1045 (C=S); ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 7.3-7.4 (m, 2H, -H-5), 7.2 (s, 2H, H-3), 6.93-7.01 (dd, 4H, H-4, 2), 5.33 (s, 2H, H-7), 4.01 (t, 4H, O*CH*$_2$CH$_2$), 2.25 (s, 3H, NH), 1.97 (t, 4H, O*CH*$_2$CH$_2$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ: 176 (C, C-8), 157.57 (C, C-1), 130.57 (CH, C-5), 124.79 (CH, C-3), 120.93 (C, C-6), 112.68 (CH, C-4), 79.75 (CH, C-2), 71.17 (OCH_2, O*CH*$_2$CH$_2$), 68.29 (CH, C-7), 26.22 (CH_2, O*CH*$_2$CH$_2$) ppm; MS (*m/z*) = 355 [M^+]; Elemental analysis calcd. (%) for $C_{19}H_{21}O_2N_3S$: C, 63.95; H, 5.7; N, 12.06; found (%): C, 64.20, H, 5.95; N, 11.82.

$C_{20}H_{23}O_4N_3S$ (L_3): Yield: 66 %; m.p.: 175 °C; IR (KBr, ν_{max}, cm^{-1}): 3392, 3311 and 3184 (N-H), 1113 (C-O), 1072 (C=S); ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 7.2-7.35 (m, 4H, H-5, 3), 6.85-6.95 (m, 2H, H-4), 6.7 (s, 2H, H-2), 5.2 (s, 2H, H-7), 4.4 (t, 4H, O*CH*$_2$CH$_2$), 3.73 (s, OCH_3) 2.15 (m, 2H, O*CH*$_2$CH$_2$), 1.95 (s, 3H, NH) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ: 174.83 (C, C-8), 154.13 (CH, C-2), 146.07 (C, C-1), 130.56 (C, C-6), 124.79 (CH, C-5), 121.66 (CH, C-4), 114.11 (CH, C-3), 56.08 (CH, OCH_3), 76.73 (OCH_2, O*CH*$_2$CH$_2$), 70.19 (CH, C-7), 29.89 (CH_2, O*CH*$_2$CH$_2$) ppm; MS (*m/z*) = 401 [M^+]; Elemental analysis calcd. (%) for $C_{20}H_{23}O_4N_3S$: C, 54.44; H, 6.10; N, 10.70; found (%): C, 59.83, H, 5.77; N, 10.47.

$C_{21}H_{25}O_4N_3S$ (L_4): Yield: 93 %; m.p.: 178 °C; IR (KBr, ν_{max}, cm^{-1}): 3408, 3307 and 3163 (N-H), 1180 (C-O), 1010 (C=S); ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 7.35 (s, 2H, H-5, 3), 7.05-7.08 (t, 2H, H-4), 6.95 (t, 2H, H-2), 6 (s, 2H, H-7), 4.47 (t, 4H, O*CH*$_2$CH$_2$), 3.86 (s,OCH_3), 2.05 (s, 3H, NH), 1.7 (t, 2H, O*CH*$_2$CH$_2$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ: 180 (C, C-8), 153.32 (CH, C-2), 147.22 (C, C-1), 131.60 (C, C-6), 124.42 (CH, C-5), 116.86 (CH, C-4), 113.65 (CH, C-3), 72.37 (OCH_2, O*CH*$_2$CH$_2$), 64.75 (CH, C-7), 55.90 (CH, OCH_3), 25.21 (CH_2, O*CH*$_2$CH$_2$) ppm; MS (*m/z*) = 415 [M^+]; Elemental analysis calcd. (%) for $C_{21}H_{25}O_4N_3S$: C, 60.43, H, 6.20; N, 9.95; found (%): C, 60.70; H, 6.06; N, 10.11.

Synthesis of cobalt(II) complexes: A solution of $CoCl_2{\cdot}6H_2O$ (0.03 g, 0.1 mmol) in 2 mL acetone was added dropwise to a solution of the ligands (0.08 g, 0.2 mmol) in a minimum amount of choloroform at 20 °C. After 3 days, the blue coloured crystalline precipitate that formed was filtered off, washed with choloroform:acetone (1:1) and finally dried in room temperature to a constant weight.

$Co(L_1)_2Cl_2$: Yield: 87 %; m.p.: 180 °C; IR (KBr, ν_{max}, cm^{-1}): 3383 and 3331 (N-H), 1116 (C-O); 1046 (C=S); MS (*m/z*) = 815 [M^+]; Elemental analysis calcd. (%) for $C_{36}H_{40}N_6O_4S_2CoCl_2$: C, 47.64; H, 4.86; N, 8.78; found (%): C, 47.58; H, 4.42; N, 9.

$Co(L_2)_2Cl_2$: Yield: 80 %; m.p.: 185 °C; IR (KBr, ν_{max}, cm^{-1}): 3331 and 3215- (N-H), 1120 (C-O); 1035 (C=S); MS (*m/z*) = 843 [M^+]; Elemental analysis calcd. (%) for $C_{38}H_{44}N_6O_4S_2CoCl_2$: C, 54.68; H, 5.86; N, 9.48; found (%): C, 54.66; H, 5.59; N, 9.33.

RESULTS AND DISCUSSION

Preparation of aza crown macrocycles and their cobalt(II) complexes: Aza crown macrocycles, L_1, L_2, L_3 and L_4 were successfully synthesized by condensation reaction between bisaldehydes (**a-d**) and thiourea in the presence of ammonium acetate in the mixture of ethanol and acetic acid (**Scheme-I**). These aza crown ethers have been characterized by its elemental analyses, melting point, IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. All synthesized aza crown macrocycles are very stable at room temperature in the solid state. The syntheses of the Co(II) complexes of the aza crown ethers L_1 and L_2 are illustrated in **Scheme-I**. These complexes are readily obtained in high yield from the reaction of the macrocycles L_1 and L_2 with $CoCl_2{\cdot}6H_2O$. The synthesized complexes are very stable at room temperature in the solid state, are soluble in

$CHCl_3$, DMF and DMSO and insoluble in most common solvents, including water, ethanol, ethyl acetate and acetonitrile. The macrocyclic complexes were characterized by elemental analyses, melting point, IR, ^1H NMR, ^{13}C NMR and mass spectral data. Also, electrochemical behaviour of newly synthesized aza crown macrocycles and related complexes was studied by cyclic voltammetry.

Characterization of aza crown macrocycles and their cobalt(II) complexes

FT-IR spectra: The IR spectrum of the aza-crown ethers shows bands mainly in the regions 1050, 1116 and 3450-3163 cm^{-1}, which may be assigned to the stretching frequencies of (CS-NH), (C-O) and (N-H) bands, respectively, which confirms the formation of the aza crown macrocycles. In addition, the bands at 1600-1487, 3080-3050 cm^{-1} are corresponding to the C=C and C-H stretching of aromatic ring. Furthermore, the absence of (C=O) and (NH_2) stretching vibrations in the spectrum of the aza-crown ethers, related to bisaldehyde and thiourea, indicated the complete condensation between bisaldehydes and thiourea. The IR spectrum of the complexes shows the bands at 3383, 3331 cm^{-1} assigned to ν(N-H) stretching vibrations. The ν(C=C) bands of the aromatic rings are generally shifted to higher wave numbers than in the free ligands, suggesting the coordination to the metal ions. The broad bands within the range at 3370 cm^{-1} for complexes can be attributed to stretching vibrations of water molecule ν(H_2O).

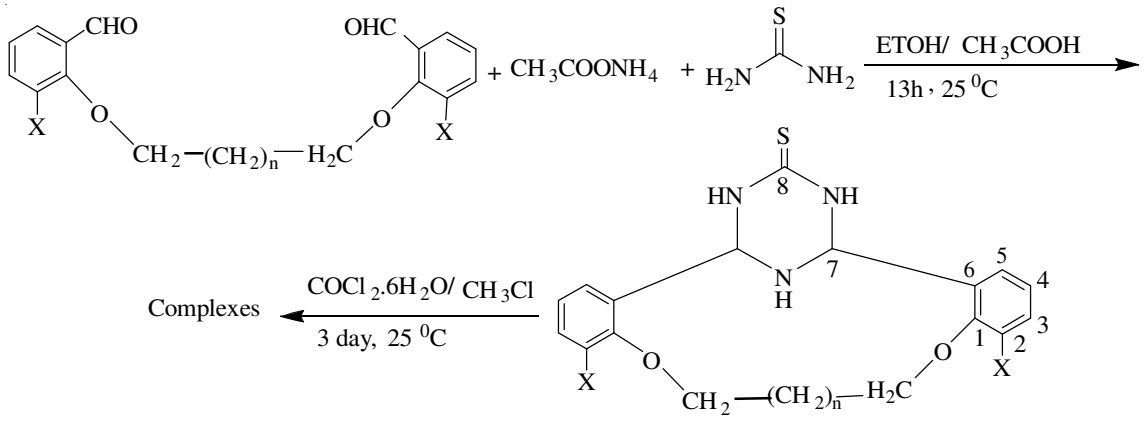
NMR spectra: ^1H and ^{13}C NMR spectra of the aza-crown ethers in $CDCl_3$ solvent confirmed the proposed structures. The ^1H NMR spectra of the aza crown macrocycles shows a band singlet in the range 1.7-2.15 ppm due to the protons of NH groups, another singlet at 3.7 ppm due to the protons of CH_3 groups and a singlet at 5.4 ppm due to C-7 protons. ^{13}C NMR spectra of the macrocycles shows the signals at 56.08 ppm corresponding to carbon atom of methoxy group, at 68.2 ppm due to carbon atom of C-7 group, at 131-114 ppm corresponding to aromatic ring carbon atoms and at 175 ppm due to C-8 carbon atom.

Mass spectra: The mass spectral of the- newly synthesized aza-crown ethers were studied in $CDCl_3$ solution. All the spectra exhibit parent peaks due to molecular ions (M^+). The proposed molecular formula of these compounds was confirmed by comparing their molecular formula weights with *m/z* values. The molecular ion (M^+) peaks obtained for various ligands are as follows (*m/z*): 341 (L_1), 355 (L_2), 401 (L_3) and 415 (L_4). This data is in good agreement with the proposed molecular formula for newly synthesized compounds.

Elemental analysis: The experimental elemental analyses results of the newly synthesized macrocyclic compounds and Co(II) complexes are in good agreement with the theoretical calculations.

Electrochemical studies: The electrochemical properties of the aza-crown ethers and Co(II) complexes were studied by cyclic voltammetric (CV) in acetonitrile and N,-N-dimethyl formamide at 25 °C under a nitrogen atmosphere using a glassy carbon electrode (GCE). Potential windows ranging from -1 to 2 V and an scan rate of 100 mV/s for the aza crown macrocycles, 20-0 mV/s for the complexes were employed. The cyclic voltammetric of all the macrocycles is shown in Fig. 1. It is known that in the negative potential range the electrochemical behaviour of aza crown macrocycles in the negative potential range is found to be sensitive to the electron-inductive nature of the substituent (methoxy) at the 2-position of the aromatic ring. For example, both the first and second reduction waves of the electron-releasing methoxy analogue are shifted to more negative potentials in comparison to the hydrogen (no substituent) analogue.

The cyclic voltammograms of complexes (L_1) and (L_2) have cathodic peaks in the range -0.23 to -0.45 V, corresponding to Co^{III}/Co^{II} reduction couple which is irreversible. These complexes have reversible one electron [$Co^{II} \rightarrow Co^{I}$] couple with $E_{1/2}$ in the range -1.12 to 1.17 V [11]. Complex



Complex	X	n
L_1	H	1
L_2	H	2

Bisaldehyde	Ligand	X	n
a	L_1	H	1
b	L_2	H	2
c	L_3	OCH_3	1
d	L_4	OCH_3	2

Scheme-I: Synthetic route for the preparation of aza crown ethers and the complexes $CoL_1(Cl_2)_2$ and $CoL_2(Cl_2)_2$

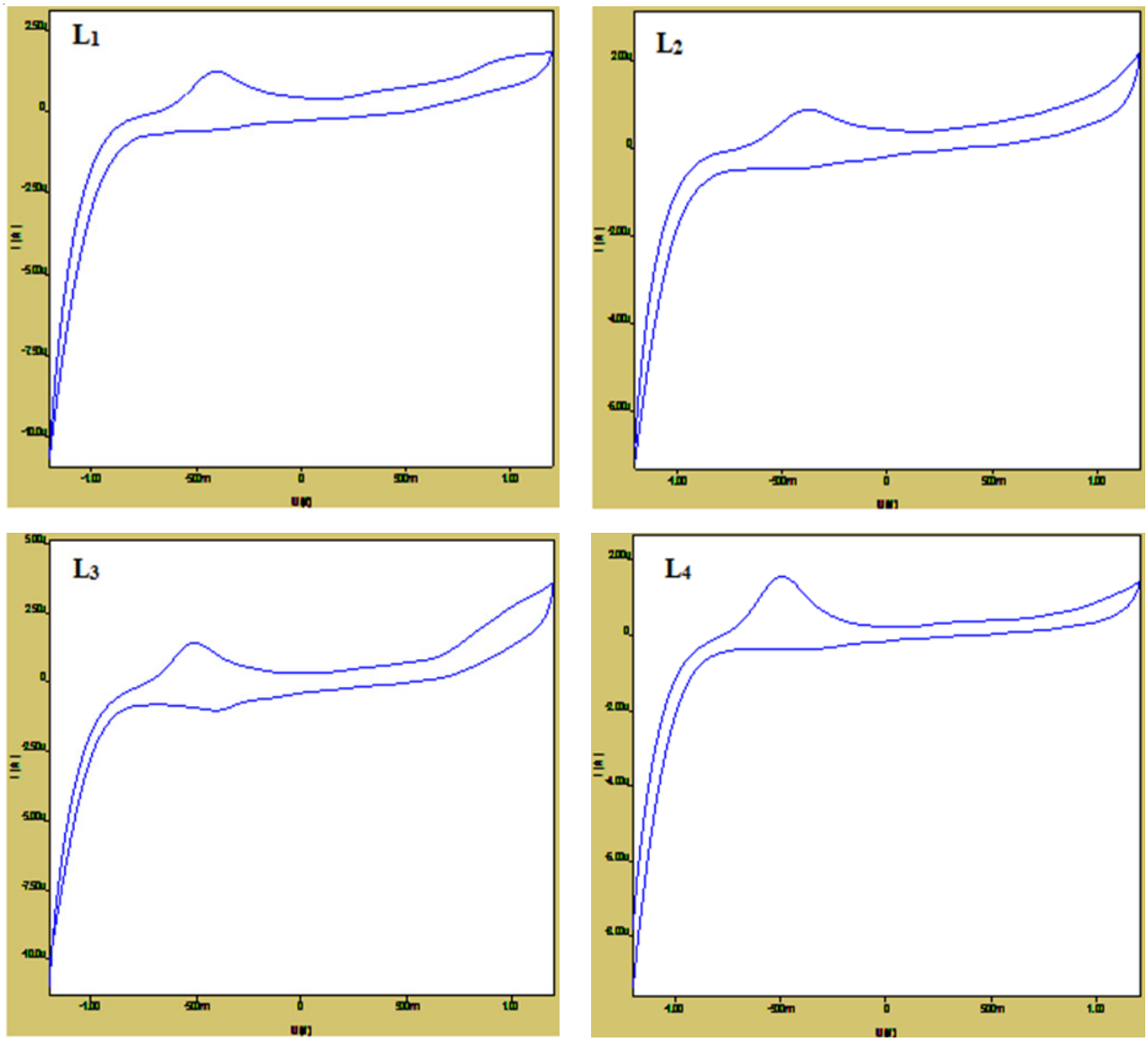


Fig. 1. Cyclic voltammograms of the aza crown macrocycles L_1, L_2, L_3 and L_4 at scan rate 100 mV/s

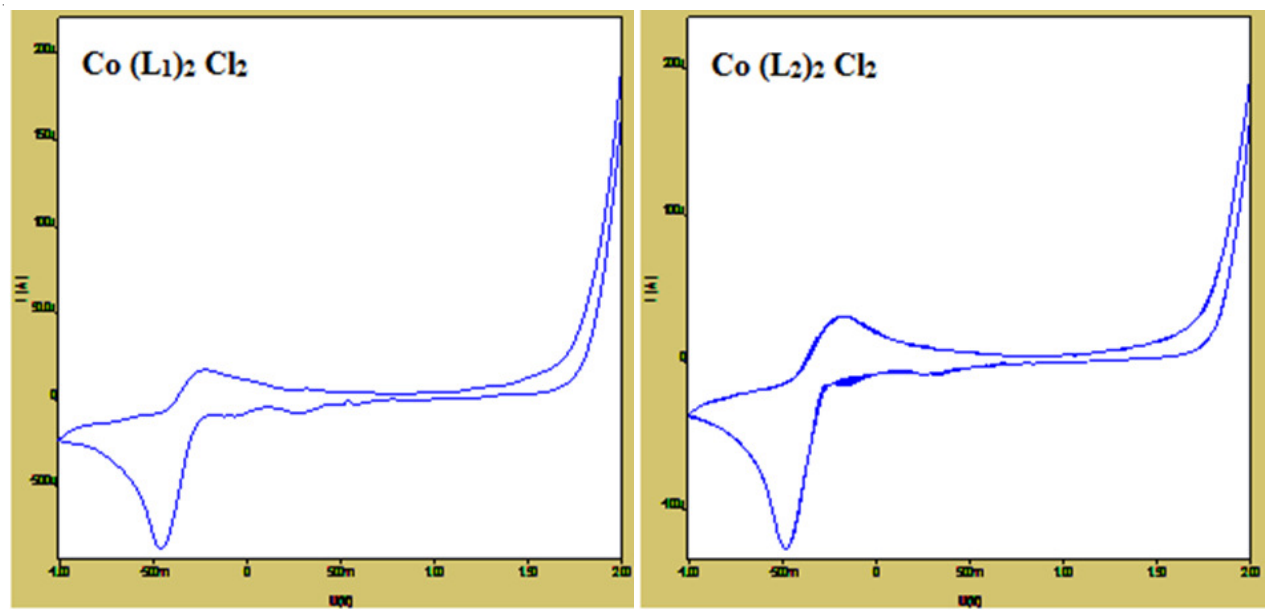


Fig. 2. Cyclic voltammograms of $Co(L_1)_2Cl_2$ and $Co(L_2)_2Cl_2$ at scan rate 200 mV/s

(L_2) has aza crown macrocycles containing an additional methylene group in internal chain. It is reduced at more negative potentials in comparison with complex (L_1). This suggests that the complexes with longer internal chain have more negative $E_{1/2}$ values than those of macrocycles with less internal chain. The electrochemical responses of the complexes $Co(L_1)_2Cl_2$ and $Co(L_2)_2Cl_2$- are shown in Fig. 2.

Conclusion

In this research paper, synthesis, characterization and electrochemical properties of a new series of aza crown ethers and some of its Co(II) complexes [($Co(L_1)_2Cl_2$ and $Co(L_2)_2Cl_2$)] are reported. The physico-chemical and spectroscopic data confirmed the structure of the newly obtained compounds. Electrochemical propertiesof Co(II) complexes the revealed irreversible two electron transfer redox process.

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