

Synthesis and characterization of some transition metal complexes with new mixed-donor schiff base ligands derived from 2-hydroxynaphthaldehyde

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ABSTRACT: 2-[3-(2-Formyl-naphthoxy)-2-hydroxypropoxy] naphthaldehyde (1) have been prepared by reaction of 2-hydroxynaphthaldehyde with 1,3-dichloro-2-propanol. New N_2O_3 macro-acyclic ligands (L^1 , L^2) synthesized from the reaction of (1) with aniline or cyclohexylamine. Ni (II), Co (II) and Cu (II) complexes was prepared from reaction of Schiff-bases with metal chloride and nitrate salts. All of these compounds characterized by FT-IR, 1H and ^{13}C NMR, mass spectroscopy, elemental analysis, DSC and TGA techniques. Electrochemical behaviors, spectroscopic measurements and conductivity studies of the complexes were reported.

Keywords: Copper complex; 2-Hydroxy naphthaldehyde; Schiff base; Synthesis; Thermogravimetry.

INTRODUCTION

Schiff bases have been playing an important role in the development of coordination chemistry although this subject has been extensively studied (Karaoğlu, *et al.*, 2011). The imine group present in such compounds has been critical to their biological activities as anti-viral (De Clercq, 2003) antifungal (Guo, *et al.*, 2007) antibacterial (De Souza, *et al.*, 2007) and anticancer (Invidiata, *et al.*, 1991). Naphthalene derivatives have found application in a number of areas including coloration of polymers (Ding, *et al.*, 2007) potential pho-

tosensitive biologically units (Tao and Qian, 1999) and photo induced electron transfer sensors (Grabchev, *et al.*, 2003) In recent report, Schiff bases are also used as fluorescent chemo sensor (Azadbakht, *et al.*, 2012). Many Schiff bases derived from 2-hydroxynaphthaldehyde have been studied by NMR spectroscopy and X-ray analysis in the solid-state (Rozwadowski, *et al.*, 2005, Sivagamasundari and Ramesh, 2007, Alarcon, 2004, Ambroziak, *et al.*, 2002, Popovic, *et al.*, 2001, Rao, *et al.*, 2003). There is no reported macro-acyclic Schiff base ligand derived from 2-hydroxynaphthalde-

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hyde incorporating pendant alcohol function. The hydroxyl group at the C-backbone in these compounds has been chosen because it is easily transformed to amines or another fundamental group (Khandar and Hosseini-Yazdi, 2003). We report the synthesis and characterization of the Ni, Co, and Cu complexes prepared from reaction of Schiff bases with metal chloride and nitrate salts.

MATERIALS AND METHODS

Physical measurements

CHN analyses were carried out using Eager-300 CHNS elemental analyzer instrument. ^1H and ^{13}C NMR spectra were taken on a Bruker 400 MHz ultra-shield spectrometer using CDCl_3 and DMSO-d_6 as solvent. Proton chemical shifts are reported in ppm unit relative to TMS as internal standard. Infrared spectra were recorded on a shimadzu prestige-21 FT-IR spectrophotometer using KBr pellets ($4000\text{--}400\text{ cm}^{-1}$). Conductance measurements were performed using an ETD instruments BA380 conductivity meter. A Shimadzu 1601-PC UV/Vis spectrophotometer was used to record the electronic spectra. Cyclic voltammetry was performed by using an autolab cyclic voltammogram instrument (ECO Chemic, The Netherlands). The three-electrode system consisted of glassy carbon electrode as a working electrode, an Ag/AgCl (3M KCl) as reference electrode and a platinum wire as auxiliary electrode was used. Measurements were carried out at room temperature under nitrogen with 0.1 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ as supporting electrolyte. The DSC thermograms of the compounds were obtained on a Mettler-Toledo DSC 822e module, which was calibrated with indium metal ($T = 156.6 \pm 0.3$, $\Delta H = 28.45 \pm 0.6\text{ J g}^{-1}$). TGA were carried out on a Mettler-Toledo TGA 851e at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. Materials Solvents were dried and purified according to published procedures (Furniss, et al., 1989, Perrin, et al., 1988). 2-hydroxynaphthaldehyde purchased from Alfa aesar, all other reagents were obtained from Merck and used without further purification.

2-[3-(2-Formylnaphthoxy)-2-hydroxypropoxy] naph-

thaldehyde

2-[3-(2-Formylnaphthoxy)-2-hydroxypropoxy] naphthaldehyde prepared by the method of Lindoy and Armstrong (Lindoy., 1975) with minor modification. 2-hydroxynaphthaldehyde (17.2 g, 0.1 mol) dissolved in hot ethanol (70 ml), then sodium hydroxide (4.0 g, 0.1 mol) in water (200 ml) added. The mixture warmed and 1,3-dichloro-2-propanol (6.45 g, 0.05 mol) added. Sufficient ethanol (100 ml) added to produce a homogeneous solution. The solution was refluxed under nitrogen for 76 h. The solid product was filtered off washed with water and recrystallized in THF. The obtained crystals were collected by filtration and dried in a vacuum desiccator over P_4O_{10} . Yield 8.5 g (42%), m.p. 216°C . Anal. Calc. (Found) for $\text{C}_{25}\text{H}_{20}\text{O}_5$: C, 74.99 (75.08); H, 5.03 (5.49) %. ^1H NMR (DMSO-d_6) δ 10.88 (s, 2H, 2ArCHO); 9.13 (d, 2H, 2ArH); 8.27 (d, 2H, 2ArH); 7.93 (d, 2H, 2ArH); 7.62 (d, 2H, 2ArH); 7.64 (t, 2H, 2ArH); 7.4 (t, 2H, 2ArH); 4.4-4.53 (m, 5H, $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$) ppm. ^{13}C NMR (DMSO-d_6) δ 192.31 (CHO); 164.02, 138.43, 131.13, 130.24, 129.09, 128.69, 125.18, 124.38, 116.30, 115.35 (Ar); 71.44 (OCH_2); 67.97 (CHOH) ppm. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3452s (OH), 3080w, 2949m, 2926m, 2868m, 2792w, 1667s (C=O), 1589s, 1246s, 1174m, 1064s, 758s. The Mass spectrum shows peak at 400 m/z. Macrocycle of L1A methanolic suspension (40 ml) of 2-[3-(2-Formylnaphthoxy)-2-hydroxypropoxy] naphthaldehyde (0.8g, 2 mmol) mixed with proportional amount of aniline (0.37g, 4mmol). Two drop glacial acetic acid added as catalyst. The mixture stirred at room temperature for 8h. Reaction monitored by TLC. Yellow precipitate filtered then washed with n-hexane several times and recrystallized in chloroform. The obtained crystals were collected by filtration and dried in a vacuum desiccator over P_4O_{10} . Yield 0.93 g (84%), m.p. 131°C . Anal. Calc. (Found) for $\text{C}_{37}\text{H}_{30}\text{N}_2\text{O}_3$: C, 80.70 (80.76); H, 5.49 (5.73); N, 5.09(4.71) %. ^1H NMR (CDCl_3) δ 9.28 (s, 2H, 2ArCHN); 8.95 (d, 2H, 2ArH); 7.92 (d, 2H, 2ArH); 7.87 (d, 2H, 2ArH); 7.62 (t, 2H, 2ArH); 7.45 (m, 7H, 7ArH); 7.31 (m, 7H, 7ArH); 4.46 (m, 5H, $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$) ppm. ^{13}C NMR (CDCl_3) δ 158.01 (CH=N); 152.06, 133.69, 132.47, 129.45, 129.32, 128.59, 128.30, 126.08, 124.64, 124.35, 121.05, 117.96, 115.73, 113.58 (Ar); 71.60 ($\text{CH}_2\text{CH}(\text{OH})$)

CH₂); 68.59 (CH₂CH(OH)CH₂) ppm. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3473m (OH), 2958m, 1624s (C=N), 1587s, 1246s, 1159m, 1080m, 750s, 694s, 621m, 505m, 489m. The Mass spectrum shows peak at 550 m/z. Macrocycle of L2A methanolic suspension (40ml) of 2-[3-(2-Formylnaphthoxy)-2-hydroxypropoxy] naphthaldehyde (0.8g, 2 mmol) was mixed with proportional amount of cyclohexylamine (0.39g, 4mmol). Two drop glacial acetic acid was added as catalyst. The mixture was stirred at room temperature for 24h. Reaction was monitored by TLC. Solution filtered off and solvent was removed by using a rotary evaporator. Obtained product recrystallized in chloroform-diethyl ether and dried in a vacuum desiccator over P₄O₁₀. Yield 1g (89%), m.p. 72°C. Anal. Calc. (Found) for C₃₇H₃₀N₂O₃·(CH₃CH₂)₂O: C, 77.32 (77.78); H, 8.23 (8.70); N, 4.4(4.67) %. ¹H NMR (CDCl₃) δ 9.04 (s, 2H, 2ArCHN); 8.59 (d, 2H, 2ArH); 7.887 (d, 2H, 2ArH); 7.821 (d, 2H, 2ArH); 7.553 (t, 2H, 2ArH); 7.423 (t, 2H, 2ArH); 7.320 (d, 2H, 2ArH); 4.412 (m, 5H, CH₂CH(OH)CH₂); 3.350 (quintet, 2H, 2CycloCHN); 1.285-1.903 (m, 20H, 20CycloH₂) ppm. ¹³C NMR (CDCl₃) δ 156.26 (CH=N); 155.78, 132.01, 129.44, 128.39, 127.64, 124.95, 124.31, 123.97, 118.76, 115.88 (Ar); 71.60 (CH₂CH(OH)CH₂); 68.59 (CH₂CH(OH)CH₂); 68.42 (CycloCHN); 34.59, 25.56, 24.90 (Cyclo) ppm. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3371m (OH), 2926s, 1635s (C=N), 1591s, 1244s, 1145m, 1087m, 748s, 650m. The Mass spectrum shows peak at 562 m/z.

Synthesis of metal complexes Preparation of [ML²X_n]X_{2-n}·mH₂O, (M= Ni, Co, Cu; X= Cl or NO₃)

a) Nickel complex synthesized by adding Ni (NO₃)₂·6H₂O (0.5 mmol, in 10 ml n-butyl alcohol) solution of L1 (0.5 mmol, in 5 ml chloroform). Resulting solution stirred at room temperature for 24 h. The volume reduced to half by using a rotary evaporator. The obtain dark yellow solid collected by filtration and washed with cold ethanol and diethyl ether respectively and dried in a vacuum desiccator over P₄O₁₀. Yield 0.218 g (52%). It decomposes above 140°C. Anal. Calc. (Found) for C₃₇H₃₀N₄NiO₉·4H₂O: C, 55.18 (55); H, 4.76 (4.43); N, 6.96(6.67) %. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3329m, 2956m, 1635s (C=N), 1589s, 1483m, 1382m, 1296s, 1153s, 1020s, 752s, 696s, 559m, 489m.

b) Cobalt complex synthesized by similar procedure described above. CoCl₂·6H₂O (0.5 mmol, in 10 ml n-butyl alcohol) added to solution of L¹ (0.5 mmol, in 5 ml chloroform). Obtained mixture stirred at room temperature for 24 h. The obtained lime solid collected by filtration and washed with cold ethanol and diethyl ether respectively and dried in a vacuum desiccator over P₄O₁₀. Yield 0.24 g (61%). It decomposes above 225°C. Anal. Calc. (Found) for C₃₇H₃₀Cl₂CoN₂O₃·5H₂O: C, 57.67 (57.67); H, 5.23 (5.57); N, 3.64(3.49) %. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3552s, 3170w, 3064m, 2991m, 1633s (C=N), 1587s, 1280s, 1192s, 1157s, 1045m, 761s, 690s, 565m, 478m.

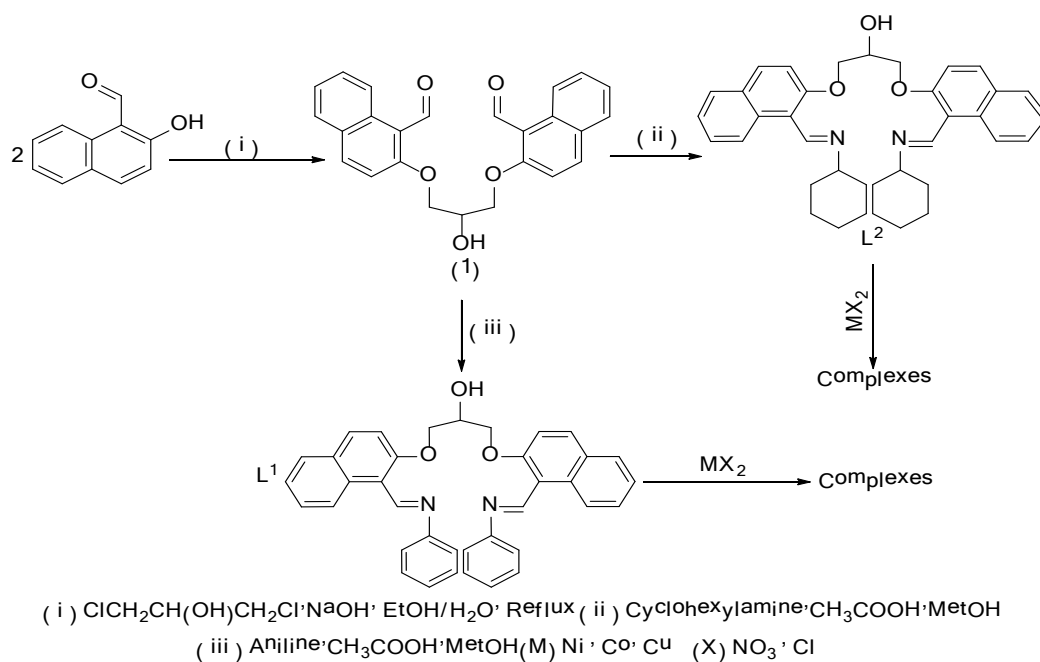
c) Copper complex synthesized following the same procedure adopted for cobalt complex using CuCl₂ instead of CoCl₂·6H₂O. Obtained olive green solid Yield 0.221 g (65%). It decomposes above 164°C. Anal. Calc. (Found) for C₃₇H₃₀Cl₂CuN₂O₃·H₂O: C, 63.20 (63.69); H, 4.59 (4.42); N, 3.98(3.77)%. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3446m, 2991m, 1633s (C=N), 1602m, 1591m, 1274s, 1244s, 1119s, 1155s, 1012s, 819s, 748s, 692s, 561m, 460m.

Preparation of [ML²X_n]X_{2-n}·mH₂O, (M= Ni, Co, Cu; X= Cl or NO₃)

Complexes e and f synthesized following the same procedure adopted for complex d using CoCl₂·6H₂O and CuCl₂ respectively instead of Ni (NO₃)₂·6H₂O.

d) An ethanol solution (10 ml) of Ni (NO₃)₂·6H₂O (0.291 g, 1mmol) added to stirring solution of L² (0.562 g, 1 mmol) in ethanol (5 ml). Resulting solution stirred at room temperature for 24 h. Obtained light green solid collected by filtration and washed with cold ethanol and diethyl ether respectively and dried in a vacuum desiccator over P₄O₁₀. Yield 0.426 g (50%). It decomposes above 215°C. Anal. Calc. (Found) for C₃₇H₄₂N₄NiO₉·4H₂O: C, 54.36 (54.67); H, 6.16 (5.59); N, 6.85(6.70) %. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3448m, 2935s, 1645s (C=N), 1589s, 1382s, 1363s, 1282m, 1246s, 1157s, 1064s, 1022s, 750s, 709m, 650sm, 561m.

e) Obtained Royal blue solid Yield 0.563 g (67%). It decomposes above 275°C. Anal. Calc. (Found) for C₃₇H₄₂Cl₂CoN₂O₃·5H₂O: C, 56.78 (57); H, 6.70 (6.93); N, 3.58(3.4) %. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3448m, 2927s, 1624s (C=N), 1573s, 1274s, 1249s,



Scheme 1

1153m, 1103s, 1022s, 754s, 669s, 613m, 543m, 466w.
 f) Obtained light green solid Yield 0.375 g (54%).
 It decomposes above 220°C . Anal. Calc. (Found) for $\text{C}_{37}\text{H}_{42}\text{Cl}_2\text{CuN}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$: C, 60.61 (60.38); H, 6.32 (6.49); N, 3.82 (3.54) %. Selected FT-IR data, $\nu(\text{cm}^{-1})$: 3446s, 2927s, 1625s (C=N), 1591m, 1273s, 1240s, 1153s, 1099m, 966m, 810s, 746s, 605m, 540w, 416m.

RESULTS AND DISCUSSION

Synthesis and characterization Dialdehyde 1 was prepared by Williamson condensation reaction between 2-hydroxynaphthaldehyde and 1,3-dichloro-2-propanol as outlined in Scheme 1. The IR and NMR data are in accordance with the proposed structure. The in-

frared spectrum of dialdehyde shows a carbonyl mode at 1667 cm^{-1} and in ^1H NMR spectrum resonances attributable to aldehydic functions appear as a singlet at 10.88 ppm. Macro-acyclic Schiff bases (L^1 and L^2) were synthesized by the condensation of the dialdehyde 1 with aliphatic and aromatic primary amines in 1:2 molar ratio in the presence of acetic acid as catalyst, using the conditions described in Section 2, (see Scheme 1). The structures of Schiff bases were characterized by using elemental analysis (C, H, N), ^1H and ^{13}C NMR, FT-IR and mass spectral data.

Conversion of the aldehyde groups into Schiff base derivatives is indicated by the absence carbonyl absorption (1667 cm^{-1}) band and appearance of strong bands in 1624 and 1635 cm^{-1} for L^1 and L^2 respectively assignable to the $\nu(\text{C}=\text{N})$ imine groups (Karaoglu, *et al.*, 2009). In ^1H NMR spectrum, resonances attributed

Table 1. Molar conductance values of the complexes recorded in DMF solution

Compound	solvent	Λ_M	C(mol/Lit)	Electrolyte type
$\text{NiL}^1(\text{NO}_3)_2$	DMF	168	0/001	[1:2]
CoL^1Cl_2	DMF	84	0/001	[1:1]
CuL^1Cl_2	DMF	35	0/001	Non-Electrolyte
$\text{NiL}^2(\text{NO}_3)_2$	DMF	132	0/001	[1:2]
CoL^2Cl_2	DMF	18	0/001	Non-Electrolyte
CuL^2Cl_2	DMF	20	0/001	Non-Electrolyte

Table 2. Electronic absorption data of ligands and complexes recorded in DMF solution

Compound	λ_{max} (nm)	Band assignments
L ¹	266359, 317, 317	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N)
L ²	264342, 307, 307	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N)
NiL ¹ (NO ₃) ₂	266353, 316, 316 and 459620, 459620	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N) and d-d transitions
CoL ¹ Cl ₂	266356, 316, 316 and 606670, 606670	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N) and d-d transitions
CuL ¹ Cl ₂	265354, 316, 316 and 715-1050(broad), 715-1050(broad)	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N) and d-d transitions
NiL ² (NO ₃) ₂	265350, 316, 316 and 666(broad), 666(broad)	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N) and d-d transitions
CoL ² Cl ₂	266345, 310, 310 and 603661, 603661	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N) and d-d transitions
CuL ² Cl ₂	270346, 316, 316 and 720(broad), 720(broad)	$\pi \rightarrow \pi^*$ (Aromatic & C=N) & $n \rightarrow \pi^*$ (C=N) and d-d transitions

to aldehydic functions at 10.88 ppm are absent and imine resonances appear as a singlet at 9.29 ppm for L¹ and L². The IR spectra of metal complexes show that the stretching frequency of the C=N bond was shifted to lower or higher wavenumbers (cm⁻¹) in comparison to free ligand after coordination. The band at 1246-1244 cm⁻¹, assigned to ν (C–O–C) in the free ligands, was shifted toward lower or higher frequency, indicating the complexation of the ether oxygen atoms to the metal ions (Khandar, *et al.*, 2007) The yellow colour Schiff base (L¹) is soluble in CHCl₃, CH₂Cl₂, DMF, THF but insoluble in water, ethanol and butanol. On the other hand, light-yellow colour Schiff base (L²) is soluble in common organic solvents but insoluble in water.

Molar conductivity

The complexes were dissolved in DMF and molar conductivities of 10⁻³ M of their solutions at 25°C were measured. The molar conductance values of the complexes were given in Table 1. It is concluded from the results that NiL¹ and NiL² chelate is found to have molar conductance values of 168 and 132 Ω⁻¹ cm² mol⁻¹ respectively. This value indicates 1:2 ionic

natures of these complexes. The CoL¹ complex has 84 Ω⁻¹ mol⁻¹ cm² molar conductance values, indicate that this complex is in 1:1 electrolyte type. On the other hand, molar conductivity values of CuL¹, CoL² and CuL² complexes have a small conductance values, indicating that they are non-electrolyte (Geary, 1971).

UV-Visible spectra

The electronic absorption spectral data for ligands were obtained in 25×10⁻⁶M DMF solutions and for complexes were obtained in 3×10⁻³ and 25×10⁻⁶M DMF solutions for 250-400nm and 400-1100nm region respectively. The electronic spectrum of L¹ and L² in DMF shows absorption bands 266 nm, 300 nm, 317nm, 350nm and 264 nm, 297 nm, 307 nm, 340 nm, respectively. The bands appearing at the low energy side are attributable to $n \rightarrow \pi^*$ transitions associated with the azomethine chromophores. The bands at higher energy arise from $\pi \rightarrow \pi^*$ transitions within the phenyl and naphthyl rings (Er, *et al.*,2008). The electronic spectrum of NiL¹ complexes shows a moderate-weak band in the regions 459 and 620 nm. Electronic spectrum of NiL₂ complexes shows a weak broad band centered at 665nm. The electronic absorption data of

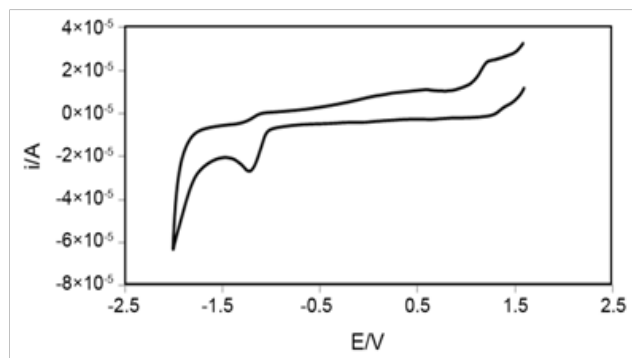


Fig. 1. Cyclic voltammogram of the L¹

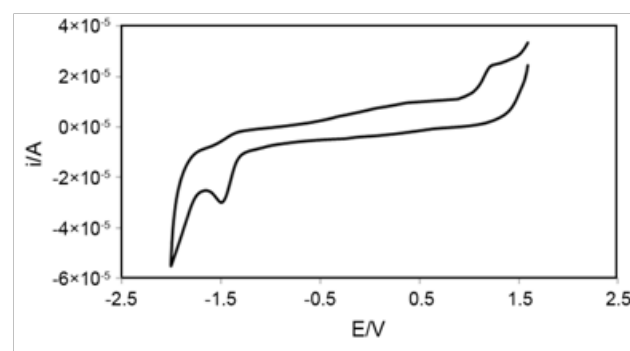
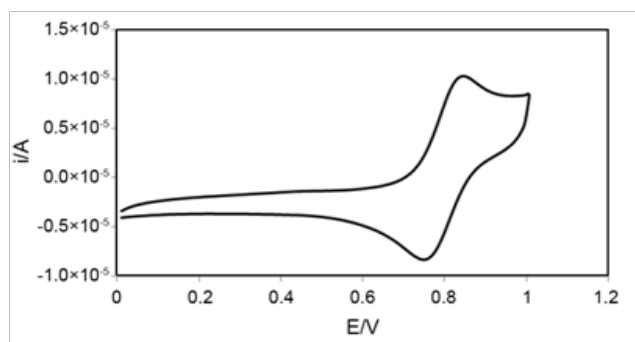


Fig. 2. Cyclic voltammogram of the L²

Fig. 3. Cyclic voltammogram of the CuL¹ Complex

ligands and Complexes are given in Table 2.

Electrochemical studies

Electrochemical properties of the complexes were studied on a ECO Chemic autolab Cyclic Voltammo-

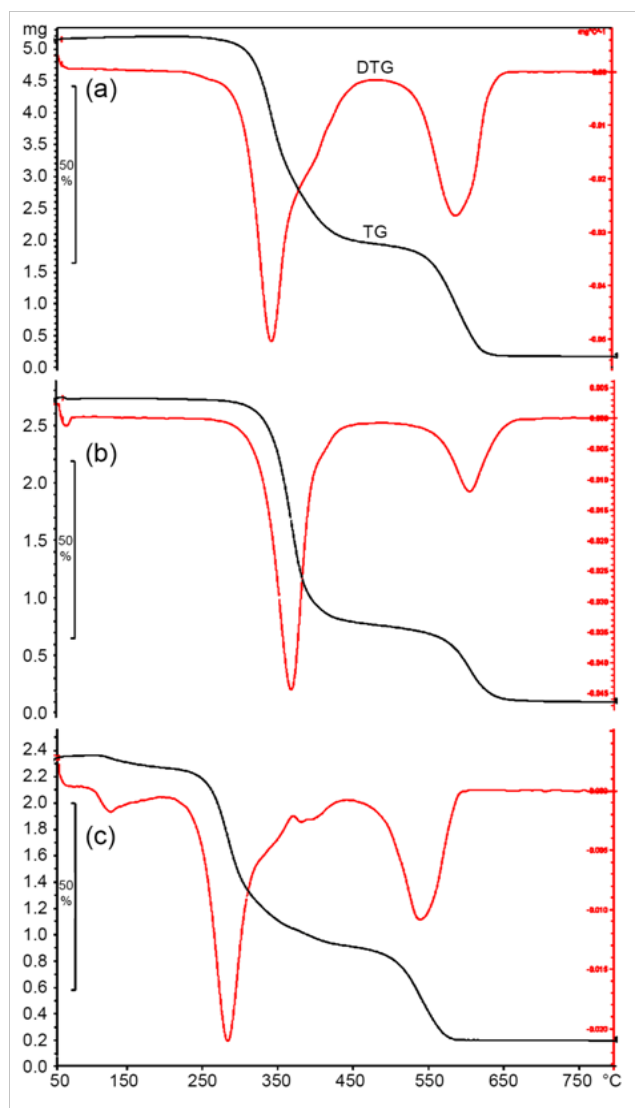


Fig. 4. TG and DTG curves: (a) dialdehyde, (b) L1, (c) L2, Sample mass: 5.1, 2.7 & 2.3 mg respectively

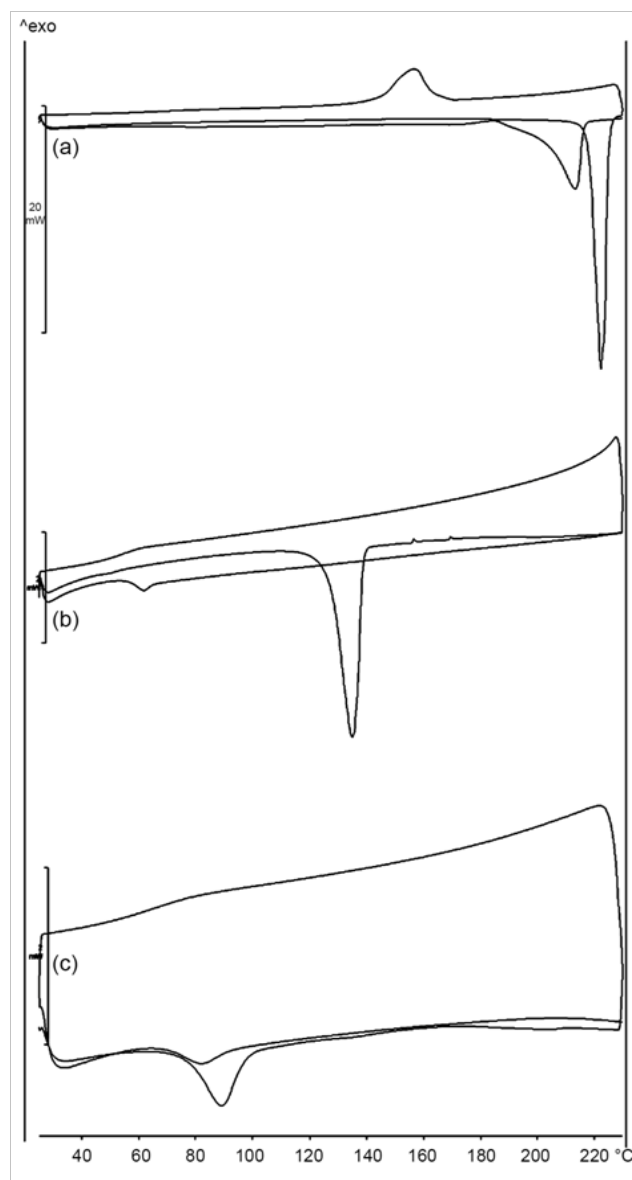


Fig. 5. DSC curves: (a) dialdehyde, (b) L1, (c) L²

gram instrument in *N,N*-dimethyl formamide (DMF) containing 0.1M LiClO₄ as the supporting electrolyte. The L1 exhibited irreversible reduction and oxidation waves at -1.16 V and $+1.68$ V and L2 exhibited irreversible reduction and oxidation waves at -1.46 V and $+1.19$ V Figs. 1 and 2. These processes may be due to the reduction of the azomethine nitrogen and oxidation of alcoholic function. The Nickel and Cobalt complexes don't exhibit remarkable Redox peaks respectively. As seen from Fig. 3, the CuL1 complex displays a reduction peak at $E_{pc} = 0.76$ V with corresponding oxidation peak at $E_{pa} = 0.82$ V. The most significant feature of the Cu(II) complex is the Cu(III)/Cu(II) couple which is a quasi-reversible one electron

Table 3. Thermogravimetric characteristics of the Compounds

Compound	Decomposition stage (°C)			
	First	Second	Third	Fourth
Dialdehyde				
Temperature interval (°C)	124-450	450-646	–	–
Mass losses (%)	63.73	34.05	–	–
L¹				
Temperature interval (°C)	118-397	397-606	–	–
Mass losses (%)	71.04	25.71	–	–
L²				
Temperature interval (°C)	134-213	213-371	371-450	450-609
Mass losses (%)	3.4	52.78	6.03	31.5

oxidation (Temel, *et al.*, 2012). A cyclic voltammogram of CuL2 complex displays a single oxidation peak at $E_{pa} = 0.65V$ without corresponding reduction peak.

Thermal properties

The thermal decomposition of the dialdehyde and Schiff base ligands, studied in this work presented characteristic pathways, depending on the nature of the ligands, as can be seen from the TG/DTG curves in Fig. 4 and DSC curves presented in Fig. 5. DSC curves presented a melting process in 217.83-224.95 °C, 127.03-138.84 °C and 46.68-55.21 °C region for dialdehyde, L1 and L2, respectively. The TG and DTG curves indicate that the dialdehyde and L1 decomposes at two steps, whereas L2 decomposes at four steps in which the pattern of 2, 4 destruction steps are similar to dialdehyde and L1 decomposition pattern. Temperature range and the percentage of loss weight for steps were collected in Table 3.

CONCLUSIONS

In this work, we have prepared a series of Schiff-bases derived from 2-[3-(2-Formyl-naphthoxy)-2-hydroxy-propoxy] naphthaldehyde and related Nickel, Cobalt and Copper complexes. FT-IR, ¹H and ¹³C NMR, Mass spectroscopy, elemental analysis confirms the structure of these compounds. The IR spectra of Nickel complexes show split pattern for nitrate ion bands indicate that the nitrate ion coordinated to Ni (II) atom. The Electrochemical studies show that Nickel and Cobalt complexes don't exhibit remarkable Redox peaks.

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