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Synthesis and characterization of aldazine ligands containing sulfur and nitrogen donor atoms and its cobalt, nickel and iron complexes

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ABSTRACT

A linking ligands containing sulfur and nitrogen donor atoms in the terminal thiophene and pyrrole rings, 1,2-bis(thiophene-2-ylmethylene)hydrazine (L1) and 1,2-bis(pyrrolyle-2-ylmethylene)hydrazine (L2) were prepared by Schiff-base condensation. Some complexes have been prepared by salts of $CoCl_2$, $NiCl_2$ and $FeCl_3$ reacting with azine ligands dissolved in alcohol in the molar ratio of (1:2). The prepared complexes were characterized by using IR, UV-Visible and cyclic voltammetry. Conductivity of the powder samples were measured by two probe method. We report here the synthesis, characterization and electrochemical behavior of azines and its complexes. Measured electrical conductivities of Co(II), Fe(III) and Ni(II) complexes of azines are investigated in this study. It is found that at room temperature these complexes show insulator behavior.

KEYWORDS

Linking ligand containing sulfur and nitrogen donor atoms;
Metal ions;
Azines compounds;
Cyclic voltammetry.

INTRODUCTION

Azines containing the N, O donor system are an important class of ligands and have found wide application in various fields. Many studies have shown that azines are good synthones for obtaining heterocyclic compounds such as pyrazols, purines, pyrimidines and pyrroles. These compounds can be utilized for some useful synthetic transformations and they constitute an important class of compounds with unexpected biological activities[1-6]. Also Poly(azomethine)s exhibit interesting properties which are associated mainly with their conjugated backbone and the presence of imine sites[7]. Thus, they present good thermal stability, mechanical strength, non-linear optical properties, ability to form metal chelates, semiconducting properties, environmental stability and fiber-forming properties[8,9].

Azines have also been extensively used as ligands in coordination chemistry, since the flexibility of these compounds around the N–N bond offers different mononucleating and binucleating coordination modes[10-15]. On the other hand, azine compounds are conjugated systems and they have good potential for preparation of conducting polymers[16,17].

We report here the synthesis, characterization and electrochemical behavior azines derived from heterocyclic aldehydes, with thiophene- 2-aldehyde (L1) and pyrrole-2-aldehyde (L2). Then these linking ligands containing sulfur and nitrogen donor atoms in the terminal thiophene and pyrrole rings were used to prepare of Fe (III), Ni (II) and Co (II) complexes. Electrical and electrochemical properties of ligands and its complexes have been studied. Also electropolymerization behavior of conjugate ligands has been investigated.

EXPERIMENTAL

Materials

Thiophene-2-carboxaldehyde and pyrrole-2-carboxaldehyde were obtained from the Aldrich Chemical Co. and were used without further purification. All other chemicals were reagent grade. All other chemicals used as received. The FTIR spectra (500–4000 cm^{-1}) and UV-Vis spectrum were obtained from ABB (MB3000, Canada) spectrophotometer and PG T60, respectively. Scanning electron microscope (SEM) was used for investigated morphology of ligand and its complex. Cyclic voltammetry of ligands and its complexes were investigated with Parsatate instrument. Glassy carbon, Pt and Ag/AgCl were used as working electrode, counter electrode and reference electrode, respectively.

Preparation of 1,2-bis(thiophen-2-ylmethylene) hydrazine (L1)

To an ethanol solution (30 mL) containing hydrazine (35 wt% solution in H_2O) (0.916 mL, 10 mmol) and 2-thiophenecarboxaldehyde (1.836 g, 20 mmol) was added a dichloromethane solution (30 mL) containing formic acid (0.2 mL), and the solution was stirred for 4 h. The resulting brown slurry was filtered, washed with hexane (25 mL × 2), and dried under vacuum to give a yellow solid of (L1)[4].

Preparation of 1,2-bis(pyrrolyl-2-ylmethylene) hydrazine (L2)

To an ethanol solution (20 mL) containing 2-pyrrolecarboxaldehyde (0.38 g, 20 mmol) and acetic acid (0.2 ml) was added a ethanol solution (20 mL) containing hydrazine (0.2 ml), and the solution was refluxed for 4 h. Solvent was separated with rotary and dried for 24 h under vacuum to give a red solid of (L2).

Preparation of complexes

$FeCl_3,6H_2O$, $NiCl_2,6H_2O$, $CoCl_2,6H_2O$ and $Cd Cl_2, 6H_2O$ was dissolved in MeOH and an MeOH solution of the ligands was added to it in 1:2 molar ratios. The solution was refluxed for 1 h and, after concentrating, was kept overnight in a refrigerator. The precipitate obtained was washed repeatedly with C_6H_6 and then with cyclohexane and finally dried in vacuum.

Electrical measurement

The powdered complexes were palletized isostatistically in a steel disk of specific diameter under pressure of 5 – 6 tons per cm^2 with the help of hydraulic press; the pellet thus obtained was crack free and hard. These pellets were coated with silver paste to make good electrical contacts. The resistance of the pellets was measured on BPL – INDIA million mega meters R M 160 m K IIIA and D C micro voltmeter by voltage drop method[18].

RESULTS AND DISCUSSION

Preparation of ligands and its complexes

Figure 1 outlines the synthetic methods for the preparation of two ligands. Some physical properties of ligands and its complexes are shown in TABLE 1. It can be seen with introducing of metal ions into ligands, melting points is increased. Also scanning electron microscopy (SEM) was used to study the ligands and its metal complex morphology. Figure 2 shows that there is no drastic difference between morphology of ligand in comparison with its complex.

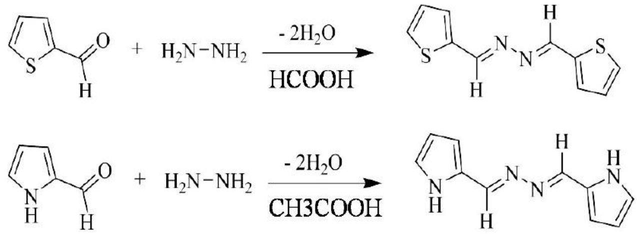

Figure 1 : Scheme of preparation of thiophene2- aldehyde azine (L1) and pyrrole-2- aldehyde azine (L2).

TABLE 1 : Physical properties data of ligands and its complexes.

Compounds	color	solvent	Melting point (°C)
Ligand L1	Yellow	Methanol- Chloroform	158
Ligand L1-Ni	Yellow	Methanol	304
Ligand L1-Co	Black	Methanol	214
Ligand L1-Fe	Yellow	Methanol	265
Ligand L2	Red	Methanol	133
Ligand L2-Ni	Yellow	Methanol	148
Ligand L2-Fe	green	Methanol	168
Ligand L2-Co	Black	Methanol	172

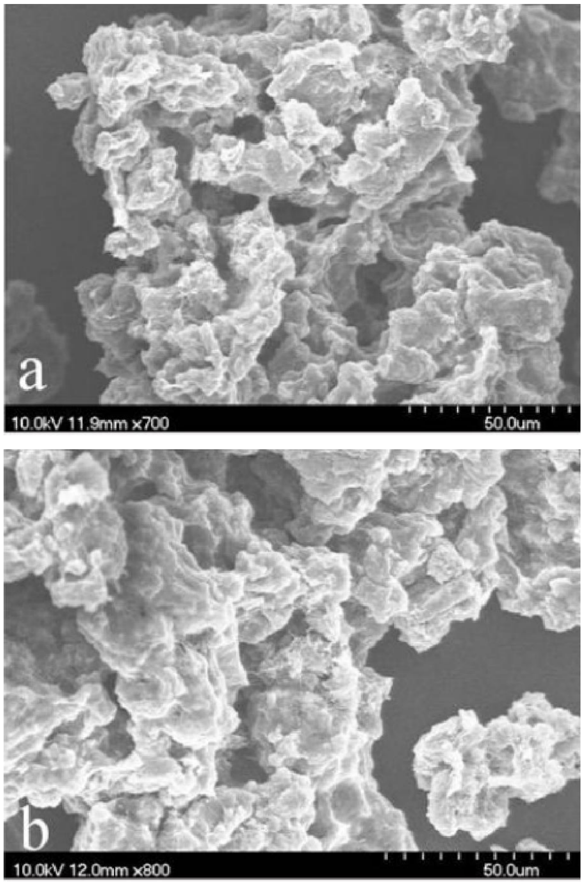

Figure 2 : SEM images of a) L1 and b) L1-Co.

TABLE 2. Absorption bands for two ligands and its complexes.

Compounds	L1	L1-Ni	L1-Co	L1-Fe	L2	L2-Ni	L2-Co	L2-Fe
Absorption bands (nm)	300, 400	320, 380	320, 380	300, 380	360, 400	285, 340	300, 340	280, 300

Analysis of FT-IR spectra

The infrared spectra of the ligands were recorded and some important features may be summarized as follows. The IR spectra of ligands exhibit at ca. 1630 cm $^{-1}$due to (C=N) stretching and at ca. 1050 cm^{-1} due to (N-N) stretching, respectively. The absence of C=O stretching band of 2-thiophenecarboxaldehyde and 2-pyrrolecarboxaldehyde in the FT-IR spectra of ligands confirmed azine compounds formation (Figure 3). In the infrared spectra of the corresponding complexes (Figure 4), the ∪(C-N) shifts by ca. 20cm^{-1} and ∪(N-N) by ca. 10 cm^{-1} due to the bonding through the azomethine nitrogen. This feature is further supported by the appearance of ∪(M-N) in the far IR spectra. In the spectra of the ligands, bands at ca. 3100 cm^{-1} and at ca. 1570 cm^{-1} are due to pyrrole or thiophene ring[19].

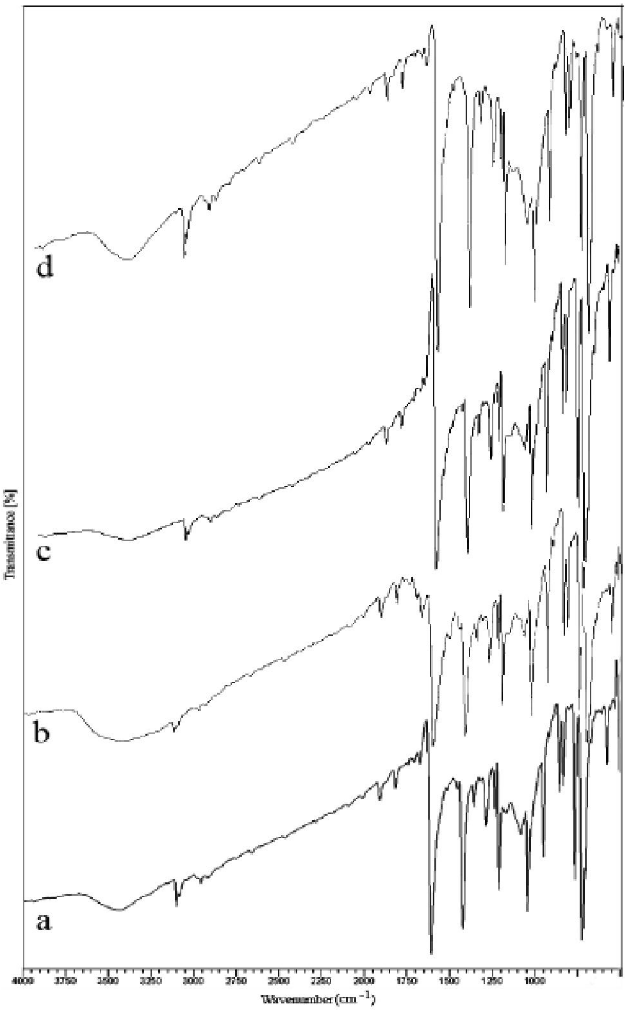

Figure 3 : FT-IR spectra of a) L1 b) L1-Co C) L1-Fe and d) L1-Ni.

Electronic spectra

When the carbonyl group reacts with amine, the imine group is formed and it shows some adsorption bands at UV-Vis spectra. Figure 5a, b represented UV-Vis spectra of ligands and its complexes. Two bands were observed at the range of 300 to 400 nm in the spectra of all ligands. The band at ~320 nm is due to the n – π* transition within the aromatic ring. Another band due to π–π* transition within the –C=N chromospheres of the ligands at ~ 400 nm shifts to a shorter wavelength in the complexes and appears at ~ 340 nm. This indicates the coordination of the azomethine nitrogen to the metal ions.

Cyclic voltammetry

Figure 6a shows a typical cyclic voltammograms of the electropolymerization of L1. During the electropolymerization of L1, an anodic peak is observed due to the oxidation of L1 in the first scan at *ca*. 1450 mV *vs*. Ag/AgCl. As the electropolymerization proceeds, an anodic peak current appears due to the oxidation of poly L1 in the second scan at *ca*. 40 mV *vs*. Ag/AgCl, during which the peak current also increases and the polymer film forms on the electrode surface. After 15 scans and washing the GC electrode containing the polymer film, cyclic voltammograms of the resulting polymer in the range of -1000 to 1200 mV *vs*. Ag/AgCl at various scan rates demonstrate semi-reversible behavior (Figure 6b). As an example, the loss of activity of the homolog polyL1 has been attributed to a decrease in the conductivity of the film as a consequence of overoxidation reactions, which lead to a loss of conjugation and electroactivity of the polymer film[20].

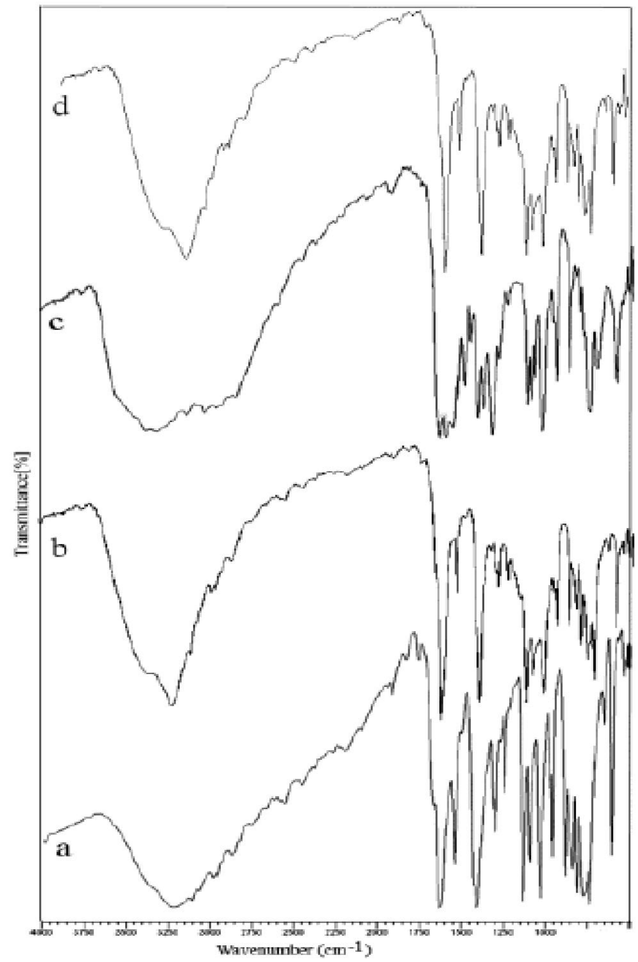

Figure 4 : FT-IR spectra of a) L2 b) L2-Ni C) L2-Co and d) L2-Fe.

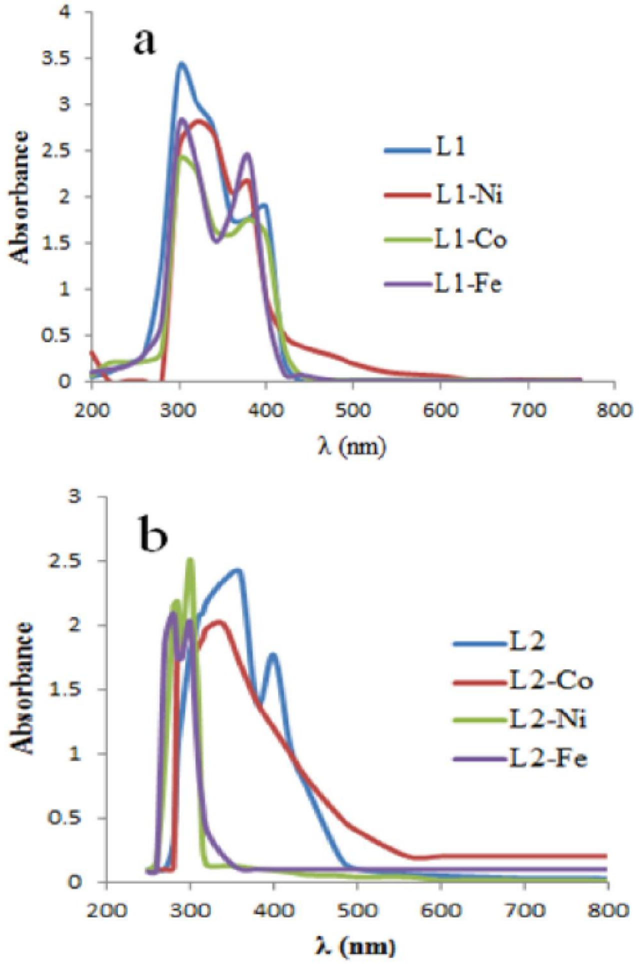

Figure 5 : Uv-Vis spectra of a) L1 and its complexes and b) L2 and its complexes.

The electrochemical oxidation of L2 with a potential scan range of -1000 to 1500 mV *vs*. Ag/AgCl is shown in Figure 7a. During the first scan, we see two maxima for Ep_a, 950 and 1100 mV *vs*. Ag/AgCl resulting from the oxidation of L2. However, from 1500 to 400 mV *vs*. Ag/AgCl, no maxima are observed, indicating an irreversible reaction. The build-up of the electroactive polymeric product, polyL2, from the oxidation process on the surface of the electrode, is observed to have an ionic structure. In Figure 7b, the repetitive cyclic voltammograms of polyL2 at various scan rates are illustrated with no fluctuation in the anodic and cathodic peak currents (*ip_a and ip_c*, respectively) of the polymer. Figure 8 shows that the variation of the anodic peaks for polyL2 *vs*. the scan rate is linear, although this behavior is not observed for polyL1. The relatively high voltage required for polymerization produces in the long run degradation of the polymer. For this reason deposits thick enough, e.g., for in situ conductivity could not be obtained.

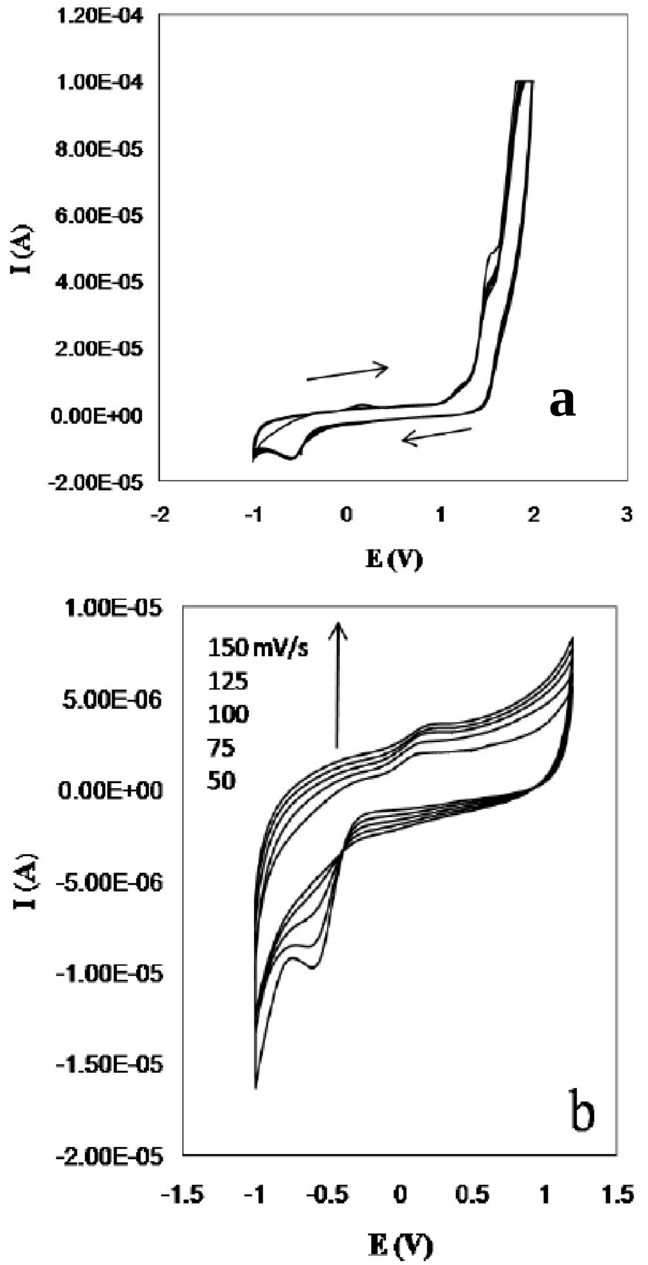

Figure 6 : Cyclic voltammograms of 0.01 M L1 in 0.1 M $LiClO_4/CH_3OH$ electrolyte at a scan rate of 50 mV s^{-1} *vs.* Ag/AgCl and b) Cyclic voltammograms of polyL1 in 0.1 M $LiClO_4/CH_3OH$ electrolyte at various scan rates.

In the presence of metal ions such as Fe, Co, and Ni, We observed some changing in the oxidation and reduction peaks (Figure 9 and 10). The one new reduction peak appeared in the presence of metal ions. Also two oxidation peak depend on metal ions are changed so that the coordination metal ions with ligand caused these changing. For detail, the oxidation and reduction potential of two ligands and its complexes are shown in TABLE 3.

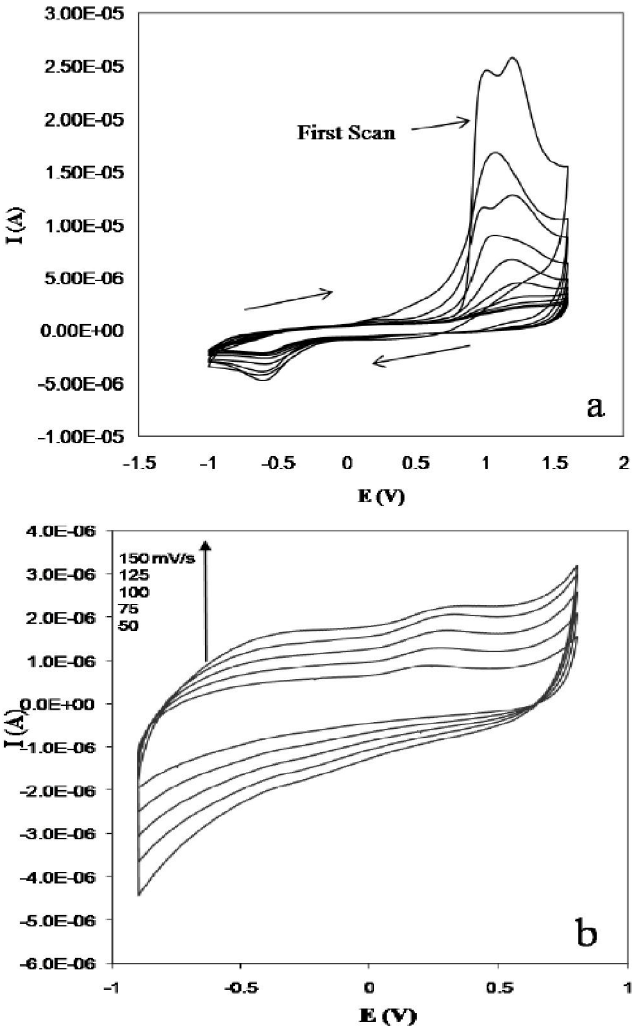

Figure 7 : a) Cyclic voltammograms of 0.01 M L2 in 0.1 M $LiClO_4/CH_3OH$ electrolyte at a scan rate of 50 mV s^{-1} *vs.* Ag/AgCl and b) Cyclic voltammograms of polyL2 in 0.1 M $LiClO_4/CH_3OH$ electrolyte at various scan rates.

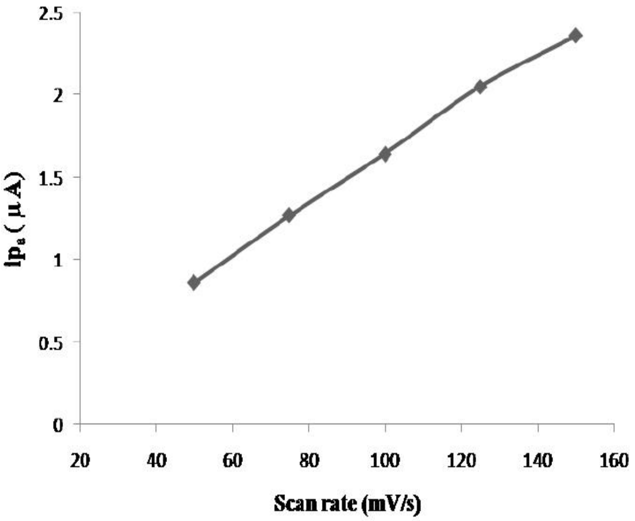

Figure 8 : Plots of anodic peak currents *vs.* scan rates of poly L2.

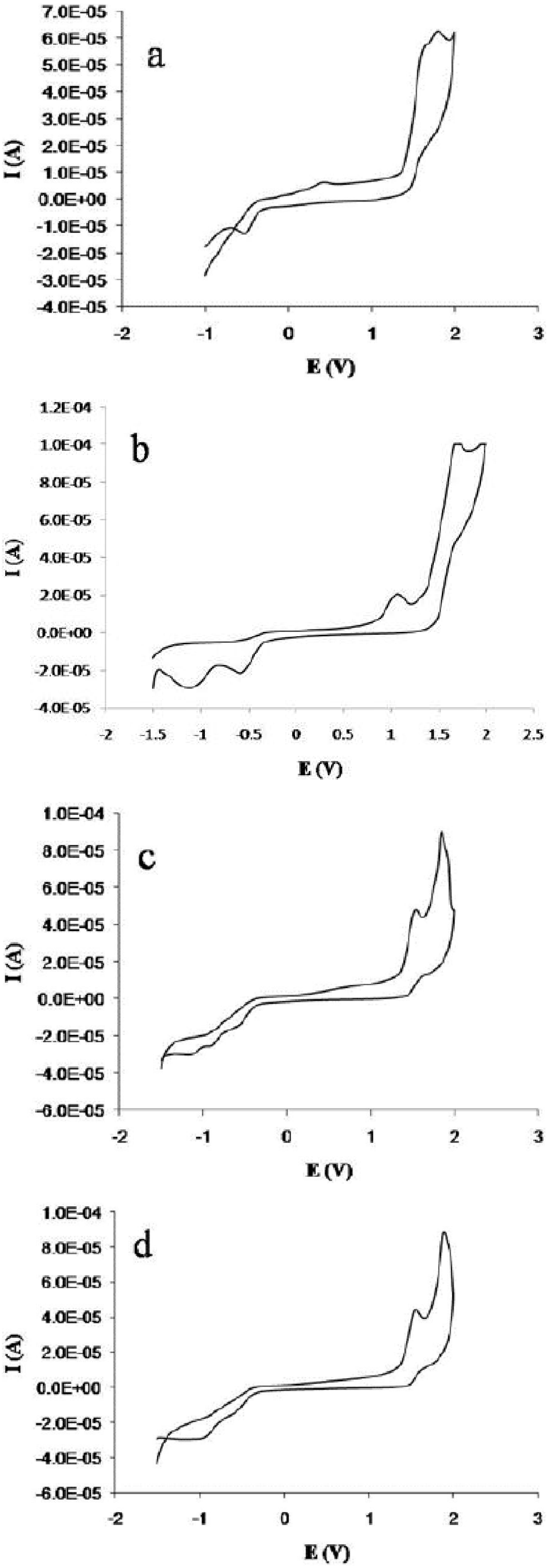

Figure 9 : Cyclic voltammograms of a) L2 b) L2-Co C) L2-Fe and d) L2-Ni in 0.1M $LiClO_4/CH_3OH$ electrolyte at scan rate 50 mV/s.

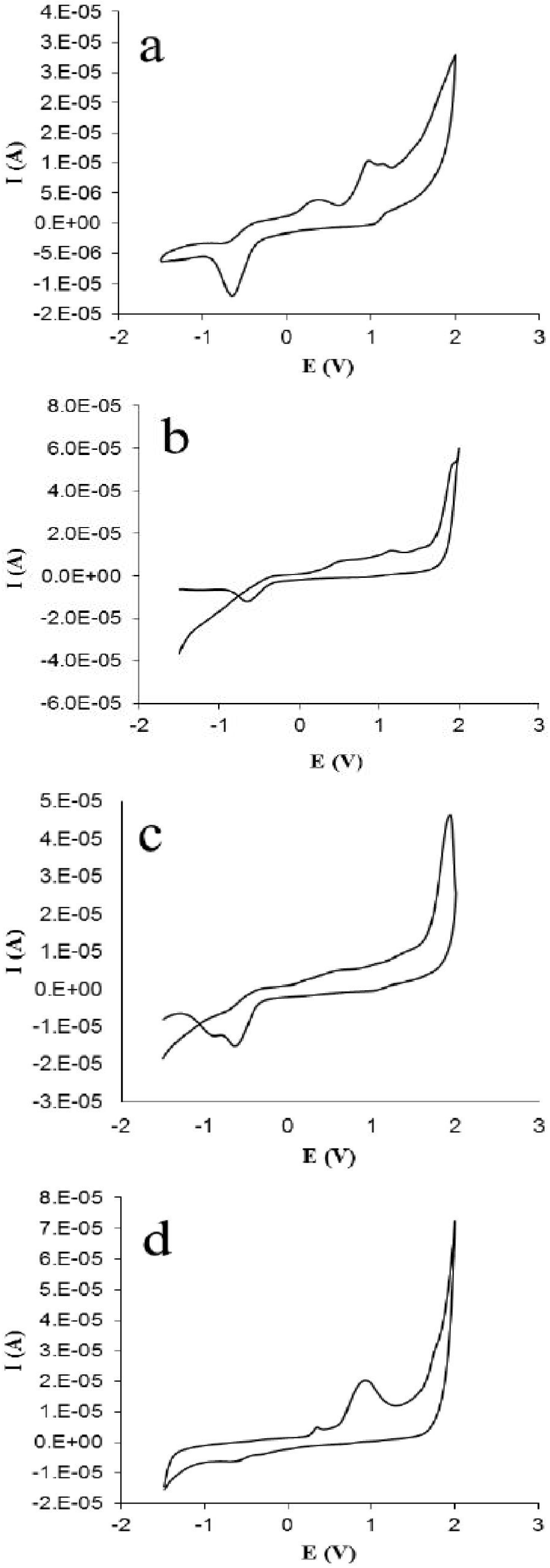

Figure 10 : Cyclic voltammograms of a) L2 b) L2-Ni C) L2-Co and d) L2-Ni in 0.1M $LiClO_4/CH_3OH$ electrolyte at scan rate 50 mV/s.

TABLE 3 : Cathodic and anodic potentials of two ligands and its complexes.

compounds	E_{1OX}	E_{2OX}	E_{1RED}	E_{2RED}
L1	0.26	1.72	-0.42	-
L1-Ni	-	1.5	-0.48	-0.86
L1-Co	0.97	1.64	-0.49	-0.97
L1-Fe	1.49	1.83	-0.49	-0.83
L2	0.23	0.94	-0.57	-
L2-Ni	0.39	1.05	-0.58	-
L2-Co	0.51	1.29	-0.56	-
L2-Fe	0.44	0.79	-0.56	-

Electrical properties

Measured electrical conductivities of Co(II), Ni(II) and Fe(III) complexes of azines are studied in this paper. It is found that at room temperature these complexes show insulator behavior (Less than 5×10^{-6} Scm^{-1}). But semiconductor behavior was obtained for L1 and L2 ligands and electrical conductivities of L1 and L2 were 1.3×10^{-3} and 3.4×10^{-3} Scm^{-1}, respectively.

CONCLUSION

A linking ligands containing sulfur and nitrogen donor atoms in the terminal thiophene and pyrrole rings, 1,2-bis(thiophene-2-ylmethylene)hydrazine (L1) and 1,2-bis(pyrrolyle-2-ylmethylene)hydrazine (L2) were prepared by Schiff-base condensation. Cyclic voltammetry of two ligands were investigated in details. FT-IR and UV-Vis spectroscopies and cyclic voltammetry confirmed the presence of metal ions in complexes. The electrical Conductivity of ligands and its complexes were measured and it is found that at room temperature these complexes show insulator behavior.

REFERENCES

[1] R.P.Ortiz, H.Yan, A.Facchetti, T.J.Marks; Materials, **3**, 1533 **(2010)**.

[2] A.Azfali, T.L.Breen, C.R Kagan; Chem.Mater., **14**, 1742 **(2002)**.

[3] M.Turbiez, P.Frère, R.Roncali; J.Org.Chem., **68**, 5357 **(2003)**.

[4] S.H.Kim, Soon W.Lee; Inorganica Chimica Acta, **361**, 137 **(2008)**.

[5] M.Ahmad, I.M.Isa, B.L.Shaw, S.D.Perera; Jurnal Sains Dan Matematik, **1**, 11 **(2009)**.

[6] M.Godara, R.Maheshwari, S.Varshney, A.K.Varshney; J.Serb.Chem.Soc., **72**, 367 **(2007)**.

[7] M.Grigoras, C.O.Catanescu; J.Macromol.Sci.Part C-Polym.Rev., **44**, 1 **(2004)**.

[8] J.V.Grazulevicius, P.Strohriegl, J.Pielichowski, K.Pielichowski; Prog.Polym.Sci., **28**, 1297 **(2003)**.

[9] C.J.Yang, S.A.Jenekhe; Chem.Mater., **3**, 878 **(1991)**.

[10] E.Kleinpeter, B.A.Stamboliyska; Tetrahedron, **65**, 9211 **(2009)**.

[11] C.Y.Wu, Y.Chen, S.Y.Jing, C.S.Lee, J.Dinda, W.S.Hwang; Polyhedron, **25**, 3053 **(2006)**.

[12] S.Pal, S.Pal; Inorg.Chem., **40**, 4807 **(2001)**.

[13] Z.Xu, L.K.Thompson, V.A.Milway, L.Zhao, T.Kelly, D.O.Miller; Inorg.Chem., **42**, 2950 **(2003)**.

[14] P.Cucos, M.Pascu, R.Sessoli, N.Avarvari, F.Pointillar, M.Andruh; Inorg.Chem., **45**, 7035 **(2006)**.

[15] S.G.Sreerama, S.Pal; Inorg.Chem., **44**, 6299 **(2005)**.

[16] C.Pozo-Gonzalo, J.A.Pomposoa, J.Rodr´iguez, E.Y.Schmidt, A.M.Vasil'tsov, N.V.Zorina, A.V.Ivanov, B.A.Trofimov, A.I.Mikhaleva, A.B.Zaitsev; Synthetic Metals, **157**, 60 **(2007)**.

[17] C.Y.Wu, Y.Chen, S.Y.Jing, C.S.Lee, J.Dinda, W.S.Hwang; Polyhedron, **25**, 3053 **(2006)**.

[18] M.M.Patil, R.J.Manavalan; Macromol.Sci.Chem.A, **20**, 789 **(1984)**.

[19] N.Karaboek; Transition Met.Chem., **31**, 118 **(2006)**.

[20] C.I.Simionescu, M.Grovu-Ivanoiu, I.Cianga, M.Grigoras, A.Duca, I.Cocarla; Angew.Makromol. Chem., **239**, 1 **(1996)**.