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Synthesis, characterization and electrochemical behavior of some Ni(II), Cu(II), Co(II) and Cd(II) complexes of ONS type tridentate Schiff base ligand

Sefa Durmus [a,*], Alparslan Atahan [a], Mustafa Zengin [b]

[a] Department of Chemistry, Faculty of Arts and Science, Duzce University, 81100 Duzce, Turkey
[b] Department of Chemistry, Faculty of Arts and Science, Sakarya University, 54100 Sakarya, Turkey

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ABSTRACT

Tridentate Schiff base (H_2L) ligand was synthesized via condensation of o-hydroxybenzaldehyde and 2-aminothiophenol. The metal complexes were prepared from reaction of the ligand with corresponding metal salts presence of substituted pyridine in two different solvents (MeOH or MeCN). The ligand and metal complexes were then characterized by using FTIR, TGA, ^{1}H NMR and ^{13}C NMR spectroscopies. The FTIR spectra showed that H_2L was coordinated to the metal ions in tridentate manner with ONS donor sites of the azomethine N, deprotonated phenolic-OH and phenolic-SH. Furthermore, substituted pyridine was coordinated to the central metal atoms. The thermal behavior of the complexes was investigated by using TGA method and dissociations indicated that substituted pyridine and ligand were leaved from coordination. This coordination of the metal complexes was correlated by ^{1}H NMR and ^{13}C NMR. Finally, electrochemical behavior of the ligand and a Ni(II) complex were investigated.

1. Introduction

A large number of Schiff bases and their metal complexes have been synthesized for their interesting properties e.g. light emittion diode (LED) [1], corrosion inhibitor [2], potentiometric sensor [3,4], intermediates to obtain of some heterocyclic compounds [5], to synthesize of conjugate polymers containing azomethine bond [6] and their wide spectrum biological activities [7–9].

In addition, Schiff bases containing nitrogen, oxygen and sulphur chelating groups in their structures have received much attention and for further studies during the past few years because of their specific properties e.g. electrochemically active compounds [10] catalytically active materials in asymmetric catalysis [11], photochromism [12], complexing towards heavy metals [13], determining of some cations [14], intermediates for heterocyclic compounds containing sulphur and nitrogen atoms [15] and antimicrobial activities [16].

In this paper, we describe the preparation, structures, spectroscopic, thermal and electrochemical properties of ONS type tridentate Schiff base containing nitrogen, oxygen and sulphur donor atoms and its several complexes obtaining in presence of pyridine, 4-methylpyridine or 3,5-dimethyllutidine were described.

2. Experimental

2.1. Analytical methods and physical measurements

The reagents 2-hydroxybenzaldehyde (Merck), 2-aminothiophenol (Merck) and all solvents were purchased commercially and were used as received. 2-((2-Mercaptophenylimino)methyl)phenol was prepared as described previously [17]. All the reagents used were of AR grade and the solvents used were dried, distilled and purified by the standard methods. IR spectras were acquired using a Mattson 1000 FTIR Spectrophotometer by preparing KBr disc of the samples (5–10%). TG–DTA curves were obtained using a Schimatzu DTG-60H instrument. Platinum pans were used for thermograms obtained between room temperature and 850 °C. The curves were obtained under nitrogen atmosphere with a flow rate of 100 mL min^{-1}. The heating rate was 10 °C/min. NMR studies were carried out with 300 MHz Oxford Varian NMR Spectrometer. Chemical shifts are reported in ppm (δ) from internal $(CH_3)_4Si$ for hydrogen and carbon ($CDCl_3$).

Voltammetric measurements were carried out according to the literature [18–20] with BAS100 B/W Electrochemical Analyzer. Glassy Carbon Electrode (BAS MF-2012, 3.0 mm diameter) was used as working electrode with a silver wire in contact with 0.01 M $AgNO_3$ as the reference electrode. The solution part of the reference electrode was prepared in DMF with 0.1 M TBATFB supporting electrolyte. The counter electrode was a platinum wire (BAS MW-1032). The whole system was deaerated for 10 min for by purging pure argon before use. All the measurements were taken at room

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* Corresponding author. Tel.: +90 380 541 2404; fax: +90 380 541 2403.
E-mail address: sefadurmus@duzce.edu.tr (S. Durmus).

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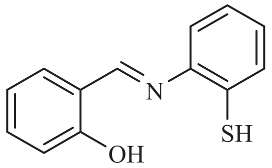


Scheme 1. General structure of the Schiff base ligand (H_2L).

temperature, 20 ± 1 °C. The working electrode were polished before each use with 1 μm, 0.3 μm and 0.05 μm alumina slurries made from dry Buehler alumina and ultra pure water (18 MΩ cm) on polishing microcloth.

Voltammetric working solutions were prepared by diluting the stock solutions to obtain the desired concentrations. The supporting electrolyte of tetrabutylammonium tetrafluoroborate (TBATFB) was purchased from Fluka (21796-4) and used without further purification. The DMF used was a dry (water ≤0.01%) batch of Fluka (40248) kept on beads of a molecular sieve. A potential range of +2000 to −2000 mV, with a scan rate of 100 mV s^{-1} was used.

2.2. *Preparation of the ligand (H_2L)*

The compound (Scheme 1) was synthesized using general condensation reaction [17,21,22]. A quantity of 0.050 mol (6.10 g) of salicylaldehyde was dissolved in 50 mL of ethanol. 2-Aminothiophenol (0.050 mol, 6.25 g) was added to this solution and the mixture was stirred for 4 h. The solvent was evaporated in vacuum and the resulting solid was recrystalized in ethanol. The yellow crystals were filtered and dried in air.

2.3. *Preparation of the complexes (LMPy)*

Mononuclear complexes of H_2L (Scheme 2) were obtained by the following general method: 1.15 g (0.005 mol) of the Schiff base (H_2L) and 0.40 g (0.005 mol) pyridine, 0.47 g (0.005 mol) 4-methylpyridine or 0.61 g (0.005 mol) 3,5-dimethylpyridine was dissolved in 30 mL of methanol. To this solution was added separately the solution of 1.24 g (0.005 mol) $Ni(CH_3COO)_2{\cdot}4H_2O$, 0.85 g (0.005 mol) $CuCl_2{\cdot}2H_2O$, 1.19 g (0.005 mol) $CoCl_2{\cdot}6H_2O$ or 1.10 g (0.005 mol) $(CdCl_2){\cdot}2H_2O$ in 10 mL of water. The resulting mixture was stirred for 2–3 h. The coloured precipitate was filtered, recrystalized in butanol/dichloromethane and dried in vacuo. For some complexes same procedure carried out in acetonitrile.

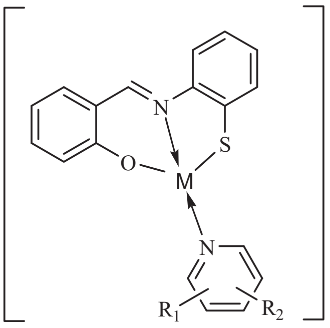
3. Results and discussion

3.1. *IR spectra*

The IR spectra of the ligands were compared with those of the metal complexes in order to confirm the binding mode of the Schiff base ligands to the corresponding metal ion in the complexes. IR spectral data (4000–400 cm^{-1}) of the H_2L and its corresponding complexes was shown in Table 1. The free Schiff base ligand (H_2L) showed a strong band in the region 1614 cm^{-1}, which is the characteristic frequency of the azomethine ν(C=N) group [23]. The ν(C=N) band is shifted to lower frequency in all the complexes 1606–1600 cm^{-1}, indicating coordination of the Schiff bases through the azomethine nitrogen atom. A band that appeared at 1280 cm^{-1} [23] due to phenolic C–O stretching in the free Schiff base ligand (H_2L) has been shifted to higher frequency in the range 1385–1430 cm^{-1} indicating the coordination through the phenolic oxygen atom in the complexes. The δ(OH) band 1463 cm^{-1} disappeared upon complexation showing deprotonation prior to coordination through the oxygen atom in all the complexes. Moreover the absorption due to ν(C–S) of H_2L at 754 cm^{-1} is shifted to 749–694 cm^{-1} in these complexes [Ni(L)(Py_1)] in MeOH, [Ni(L)(Py_2)] in MeCN, [Ni(L)(Py_2)] in MeOH, [Ni(L)(Py_3)] in MeOH, [Cu(L)(Py_3)] in MeCN, [Cu(L)(Py_3)] in MeOH, [Co(L)(Py_3)] in MeOH, [Cd(L)(Py_3)] in MeOH, indicating that another coordination site is a thiophenolic sulphur atom [23].

3.2. *Thermal analysis*

Fig. 1a–d shows the thermograms of H_2L Ni(II) complexes. It is seen two thermal reaction from thermograms for all complexes. The first thermal reaction is endothermic within 90–336 °C range.



LMPy

1= M:Ni, R_1:H, R_2:H, Solv.:MeOH
2= M:Ni, R_1:4-CH_3, R_2:H, Solv.:MeCN
3= M:Ni, R_1:4-CH_3, R_2:H, Solv.:MeOH
4= M:Ni, R_1:3-CH_3, R_2:5-CH_3, Solv.:MeOH
5= M:Cu, R_1:3-CH_3, R_2:5-CH_3, Solv.:MeCN
6= M:Cu, R_1:3-CH_3, R_2:5-CH_3, Solv.:MeOH
7= M:Co, R_1:3-CH_3, R_2:5-CH_3, Solv.:MeOH
8= M:Cd, R_1:3-CH_3, R_2:5-CH_3, Solv.:MeOH

Py_1 = Pyridine
Py_2 = 4-Methylpyridine
Py_3 = 3,5-Lutidine

Scheme 2. General structures of the Schiff base metal complexes.

Table 1
IR spectral data (4000–400 cm^{-1}) of the H_2L and its corresponding complexes.

Compound	ν(C=N)	ν(C–O)	δ(OH)	ν(CS)	ν(MO)	ν(MN)
H_2L	1614sh	1280sh	1463sh	754sh	–	–
$[Ni(L)(Py_1)]$ in MeOH	1606sh	1459sh	–	745sh	535m	460w
$[Ni(L)(Py_2)]$ in MeCN	1602sh	1460sh	–	749sh	556m	455w
$[Ni(L)(Py_2)]$ in MeOH	1602sh	1460sh	–	748sh	556m	460w
$[Ni(L)(Py_3)]$ in MeOH	1606sh	1459sh	–	744sh	560m	468w
$[Cu(L)(Py_3)]$ in MeCN	1606sh	1456sh	–	694sh	550s	435w
$[Cu(L)(Py_3)]$ in MeOH	1606sh	1456sh	–	695sh	554s	435w
$[Co(L)(Py_3)]$ in MeOH	1602sh	1456sh	–	704sh	544s	430w
$[Cd(L)(Py_3)]$ in MeOH	1600sh	1461sh	–	698sh	548s	432w

sh, sharp; m, medium; s, small; w, weak.

The mass loss at this stage corresponds approximately to the pyridine derivative present in the structure shown in Scheme 2. The first thermal reaction 90–336 °C corresponds the degradation of the complexes.

The second thermal degradation reaction is a two step degradation reaction for $[Cd(L)(Py_3)]$ in MeOH while it is three step reaction for other complexes between 156 and 735 °C. These degradation reactions correspond to the mass loss by the ligand molecule (L). Finally, injection of O_2 at 800 °C results in removal of the carbonated parts and formation of metal oxide.

Thermal gravimetric analyse results of H_2L and corresponding complexes was shown in Table 2. In summary, thermogravimetrical analyses have shown that the presence of a ligand molecule and a pyridine derivative per metal ion in all of the complexes and Co(II) complex is less stable than other metal complexes. The Ni(II) complexes are more stable than Cu(II), Co(II), Cd(II), complexes.

3.3. ^1H NMR and ^{13}C NMR spectra

Schiff base ligand (H_2L) and its nickel complexes have been characterized by ^1H NMR and ^{13}C NMR spectroscopies and the spectroscopic data was shown in Table 3. According to the ^1H NMR spectra, the Ar–OH proton of the ligand appears as a singlet at 12.85 ppm due to effect of phenolic OH and hydrogen bonding. The Ar–SH proton is not appeared in the spectra for ligand. The azomethine proton of H_2L appears as a singlet 8.60 ppm while, the azomethine protons of all complexes appear as a singlet between 8.38 and 8.40 ppm. Moreover Ar–OH and Ar–SH protons are not shown in the spectra for all complexes. The chemical shifts of

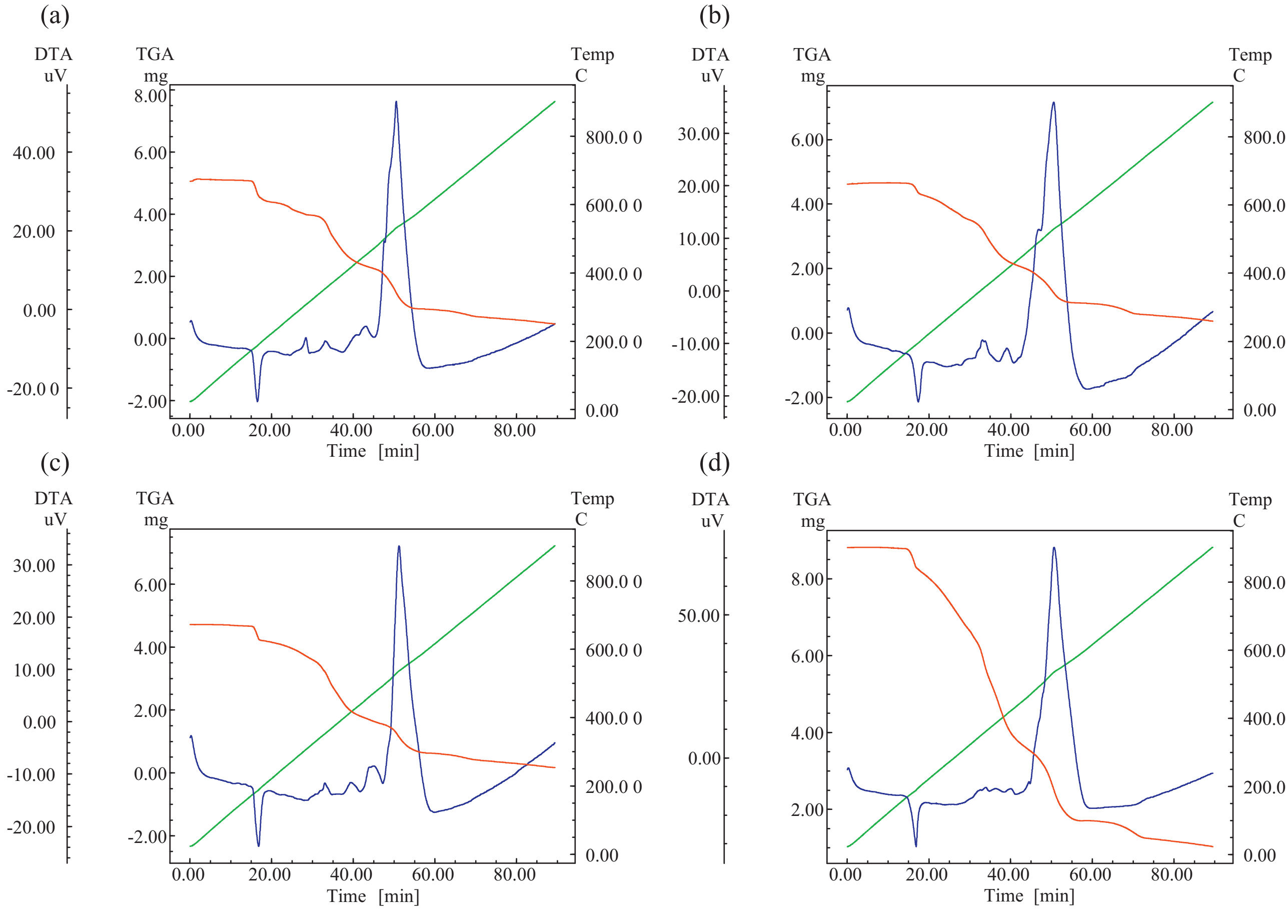


Fig. 1. (a) TG and DTA thermograms of $[Ni(L)(Py_1)]$ in MeCN. (b) TG and DTA thermograms of $[Ni(L)(Py_2)]$ in MeCN. (c) TG and DTA thermograms of $[Ni(L)(Py_2)]$ in MeOH. (d) TG and DTA thermograms of $[Ni(L)(Py_3)]$ in MeOH.

Table 2
Thermal gravimetric analyse results of H_2L and corresponding complexes.

Compound	Molar mass	TG range (°C)	n^*	Mass loss found (calc.%)	Assignment	Metallic residue
H_2L	229	–	–	–	–	–
$[Ni(L)(Py_1)]$ in MeOH	364	164–308	2.0	21.7 (21.7)	Py_1	NiL
		339–700	3.0	62.5 (62.4)	L	NiO
$[Ni(L)(Py_2)]$ in MeCN	378	169–315	2.0	22.1 (22.2)	Py_2	NiL
		339–700	3.0	60.2 (60.1)	L	NiO
$[Ni(L)(Py_2)]$ in MeOH	378	169–315	2.0	22.1 (22.2)	Py_2	NiL
		339–700	3.0	60.5 (60.1)	L	NiO
$[Ni(L)(Py_3)]$ in MeOH	392	152–336	2.0	27.3 (27.3)	Py_3	NiL
		337–735	3.0	58.0 (57.9)	L	NiO
$[Cu(L)(Py_3)]$ in MeCN	382	161–220	1.0	31.1 (28.0)	Py_3	CuL
		230–540	3.0	60.4 (59.4)	L	CuO
$[Cu(L)(Py_3)]$ in MeOH	382	161–220	1.0	28.6 (28.0)	Py_3	CuL
		230–540	3.0	59.9 (59.4)	L	CuO
$[Co(L)(Py_3)]$ in MeOH	378	90–154	1.0	27.3 (28.3)	Py_3	CoL
		156–696	3.0	60.4 (60.0)	L	CoO
$[Cd(L)(Py_3)]$ in MeOH	446	181–231	1.0	25.1 (23.9)	Py_3	CdL
		317–580	2.0	53.4 (50.9)	L	CdO

n^* = number of decomposition steps.

Table 3
^1H NMR and ^{13}C NMR spectral data of the ligand (H_2L) and its corresponding complexes ($CDCl_3$).

Compounds	Proposed assignment of the protons (ppm)
H_2L	**^{1}H NMR**: δ = 12.85, s, 1H; δ = 8.60, s, 1H; δ = 7.66, dd (J = 8.0 Hz, J = 2.4 Hz), 1H; δ = 7.36–7.44, m, 2H; δ = 7.12–7.24, m, 3H; δ = 7.38, dd (J = 6 Hz, J = 2.4 Hz), 1H; δ = 6.96 t (J = 10.0 Hz), 1H. **^{13}C NMR**: δ = 169.38, 162.77, 161.21, 132.76, 132.64, 128.43, 126.70, 125.55, 122.17, 121.52, 119.54, 117.88, 117.49.
$[Ni(L)(Py_1)]$ in MeOH	**^{1}H NMR**: δ = 8.98, bd (J = 6 Hz), 2H; δ = 8.40, s, 1H, δ = 7.75, t (J = 11.6 Hz), 1H; δ = 7.53–7.25, m, 6H; δ = 7.06, t (J = 11.2 Hz), 1H; δ = 6.87–6.95, m, 2H; δ = 6.68, t (J = 11.6 Hz), 1H. **^{13}C NMR**: δ = 164.58, 156.02 (2C), 150.18, 149.61, 142.15, 140.01, 134.42, 134.31 (2C), 133.95, 127.98, 126.79, 122.05, 122.02, 121.09, 115.66, 115.23.
$[Ni(L)(Py_2)]$ in MeCN	**^{1}H NMR**: δ = 8.76, bd (J = 6 Hz), 2H; δ = 8.38, s, 1H, δ = 7.48, d (J = 11.6 Hz), 1H; δ = 7.36–7.44, m, 2H; δ = 7.29, t (J = 11.6 Hz), 1H; δ = 7.12, bd (J = 6 Hz), 2H; δ = 7.03, t (J = 9.2 Hz), 1H; δ = 6.95–6.87, m, 2H; δ = 6.68, t (J = 10.8 Hz), 1H; δ = 2.38, s, 3H. **^{13}C NMR**: δ = 164.49, 155.58 (2C), 151.55, 134.45 (2C), 133.82 (2C), 127.93, 126.89 (2C), 125.25, 122.02, 121.03, 120.01, 115.50 (2C), 115.10, 21.03.
$[Ni(L)(Py_2)]$ in MeOH	**^{1}H NMR**: δ = 8.76, bd (J = 6 Hz), 2H; δ = 8.38, s, 1H, δ = 7.48, d (J = 11.6 Hz), 1H; δ = 7.36–7.44, m, 2H; δ = 7.29, t (J = 11.6 Hz), 1H; δ = 7.12, bd (J = 6 Hz), 2H; δ = 7.03, t (J = 9.2 Hz), 1H; δ = 6.95–6.87, m, 2H; δ = 6.68, t (J = 10.8 Hz), 1H; δ = 2.39, s, 3H. **^{13}C NMR**: δ = 164.49, 155.58 (2C), 151.55, 134.45 (2C), 133.82 (2C), 127.93, 126.89 (2C), 125.25, 122.02, 121.03, 120.01, 115.50 (2C), 115.10, 21.03.
$[Ni(L)(Py_3)]$ in MeOH	**^{1}H NMR**: δ = 8.62, bd, 2H; δ = 8.38, s, 1H; δ = 7.48, d (J = 12.0 Hz), 1H; δ = 7.40–7.25, m, 4H; δ = 7.08, t (J = 9.6 Hz), 1H; δ = 6.96–6.88, m, 2H; δ = 6.67, t (J = 11.6 Hz), 1H; δ = 2.31, s, 6H. ^{13}C NMR: δ = 164.48, 155.57 (2C), 150.08, 149.60, 142.12, 139.26, 134.42, 133.91 (2C), 133.75, 127.89, 126.89, 122.05, 121.07, 120.02, 115.56, 115.17, 18.32 (2C).

α-hydrogen atoms of pyridine, 4-methylpyridine and 3,5-lutidine were recorded between 8.98 and 8.62 ppm for those complexes.

In addition, CH_3 hydrogen atoms of 4-methylpyridine and 3,5-lutidine appear as a singlet between 2.39 and 2.31 ppm for these complexes. The aromatic region is a set of doublets, triplets and multiplets in the range 7.75–6.67 ppm for the complexes while it is 7.67–6.92 ppm for the Schiff base ligand. Furthermore, the ^{13}C NMR data confirmed the structures as formulated in Scheme 2. $[Cu(L)(Py_3)]$ in MeCN, $[Cu(L)(Py_3)]$ in MeOH, $[Co(L)(Py_3)]$ in MeOH, $[Cd(L)(Py_3)]$ in MeOH not solved in $CDCl_3$ and DMSO D-6.

3.4. Electrochemical studies

The electrochemical behavior of H_2L and its Ni(II) complex were investigated in DMF with a scan rate of 100 mV s^{-1} (Fig. 2). The cyclic voltammogram of the free ligand (H_2L) displayed three cathodic peaks and one anodic peak. Three well-defined cathodic peaks at about +355 mV, −1168 V and −1775 mV and one anodic peak at about +743 mV were observed. The cathodic peaks which occurred at Epc = +355 mV, −1168 and −1775 were assigned to the reduction of the azomethine group. The cyclic voltammogram of nickel complex shows two cathodic and two anodic peaks. The first and second reduction peaks were very close to each other. Therefore, it can be said that making separate investigations on these peaks is impossible.

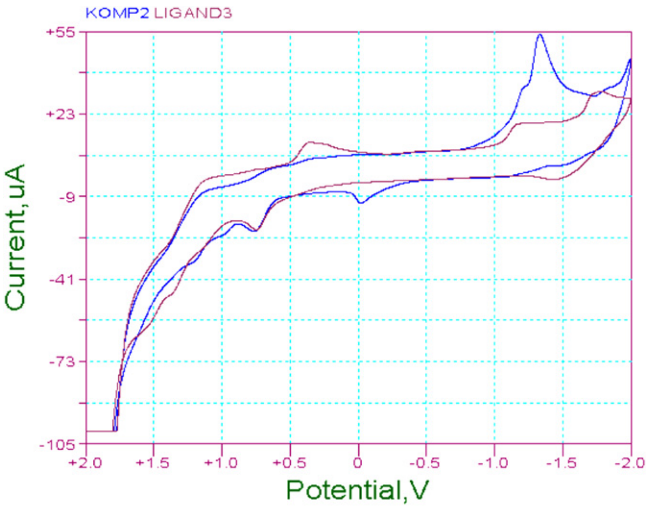


Fig. 2. The cyclic voltammograms of H_2L and Ni(II) complex in DMF.

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