

## Synthesis and study of complexes of tetradentate Schiff base and bridging ligand of thiocyanate with transition metals of Fe, Cr and Co

Ali Javadi Zare\* and Peyman Ataieinia

Department of Inorganic Chemistry, Ardabil branch, Islamic Azad University, Ardabil, Iran

**ABSTRACT:** A group of combinations which have more importance in biological studies, biochemistry and also catalytic applications, are schiff base complexes. They have been considered by the chemists. In this research, Schiff base ligand was provided by means of 2,3-diaminopyridine and salicylaldehyde in absolute ethanol solvent with reflux method. Then the complexes of transition metals Fe, Cr and Co with the supplied ligand to being determined synthesized bridging thiocyanate and using FT-IR, cyclic voltammetry (CV) and UV-Vis spectroscopy. The information obtained from cyclic voltammograms of the complexes showed that the electrochemical behavior of the synthesized combinations indicates reversible the state of the complexes. Electronic spectra in the complexes accompanied by axial ligand with due attention to central electron giving ligand feature has decreased or increased transfers intensity which can be confirmed in complex formation.

[Ali Javadi Zare\* and Peyman Ataieinia. **Synthesis and study of complexes of tetradentate Schiff base and bridging ligand of thiocyanate with transition metals of Fe, Cr and Co.** *Life Sci J* 2012;9(4):2396-2405]. (ISSN: 1097-8135). <http://www.lifesciencesite.com>. 356

**Keywords:** Bridging thiocyanate, Schiff base, Transition metals, 2,3-Diaminopyridine and salicylaldehyde

## INTRODUCTION

Schiff bases are very important in development of coordination chemistry. These compounds have a lot of uses. For example, dye industries, plastic, agriculture, biochemistry, physiology and providing liquid crystal [1,2]. Aliye Altundas and associates (2010) reported that pathogene structure in the field of medical has made in Cr(III), Zn(II) complex. All these elements have examined in order to antibacterial activity against pathogenic strains compounds like *Listeria monocytogenes* 4b (ATCC-19115), *Staphylococcus aureus* (ATCC25923), *Proteus* OX2 Wrah (ETS.40-A-4), *Escherichia coli* (ATCC-1280), *Salmonella typhi* H (NCTC-901.8394), *Pseudomonas putida* sp., *Brucella abortus* (A.99, UK-1995) RSKK-03026. *Sh. boydii* type 11 (Pasteur51.6), *Sh. boydii* type 16 (cHe 67.11), *Sh. boydii* type 6 (RSKK-96043), and antifungal activity against *Candida albicans* (Y-1200-NIH, Tokyo). Some of the compounds exhibited activity comparable to ampicillin ofloxacin, nystatin, kanamycin, sulphamethoxazol, amoxycillin, and chloroamphenicol [3]. The new Co(II), Cu(II), Ni(II) and Zn(II) complexes of

potentially N<sub>2</sub>O<sub>2</sub> schiff base ligand [N,N'-bis(salicylaldehyde)-1,4-bis-(*o*-aminophenoxy)butane] (H<sub>2</sub>L) prepared from 1,4-bis-(*o*-aminophenoxy)butane and salicylaldehyde in DMF. Obtained data from microanalysis, elemental analysis, magnetic measurements, <sup>1</sup>HNMR, <sup>13</sup>CNMR, UV-Visible and IR spectrum indicated that they cause amplification of structure like as conductivity's measurement. In all complexes, H<sub>2</sub>L functions as a tetradentate ligand [4]. Ismet kaya and associates (2008) reported that a new schiff base polymer has made as a compound (PHMPMDAP) by spectroscopy, elemental analysis and thermal analysis. This azomethine polymer, easily complexes with transitions elements Co(II), Zn(II), Fe(II), Cu(II) and Pb(II). By using the study of IR, UV-Vis phenol oxygen and safety nitrogen indicated that ligand has a configuration. Data Thermogravimetric analysis (TGA) indicates that polymer has as stability as monomer. Obtained polymer structure by using FT-IR, UV-Vis, <sup>13</sup>CNMR, <sup>1</sup>HNMR has reinforced and detection has performed by TGA, SEC and solubility tests. Also,

electrical conductivities of PHMPMDAP and polymer-metal complexes are measured by four probe technique [5]. Novel zinc(II), copper(II), and cobalt(II) complexes of the Schiff base derived from 2-hydroxy-1-naphthaldehyde and D,L-selenomethionine were synthesized and characterized by elemental analysis, IR, electronic spectra, conductance measurements, magnetic measurements and powder XRD. The analytical data showed the composition of the metal complex to be  $ML(H_2O)$ , where L is the Schiff base ligand and  $M = Co(II)$ ,  $Cu(II)$  and  $Zn(II)$ . IR results confirmed the tridentate binding of the Schiff base ligand involving azomethine nitrogen, naphthol oxygen and carboxylato oxygen atoms.  $^1H$  NMR spectral data of lithium salt of the Schiff base ligand  $[Li(HL)]$  and  $ZnL(H_2O)$  agreed with the proposed structures. The conductivity values of complexes between  $12.50$  and  $15.45\text{ S cm}^2\text{ mol}^{-1}$  in DMF suggested the presence of non-electrolyte species. The powder XRD studies indicated that  $Co(II)$  complex is amorphous, whereas  $Cu(II)$  and  $Zn(II)$  complexes are crystalline. The results of antibacterial and antifungal screening studies indicated that  $Li(HL)$  and its metal complexes are active, but  $CuL(H_2O)$  is most active among them [6].

## MATERIALS AND METHODS

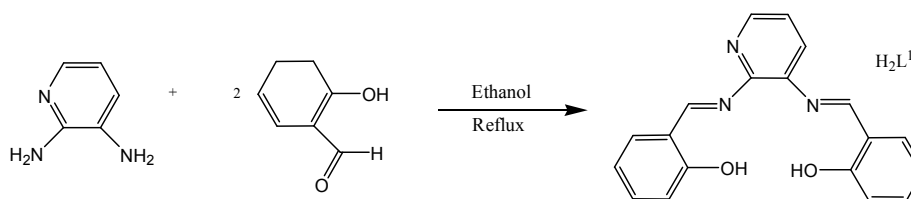
### Ligand synthesis (2,3-diaminopyridine and salicylaldehyde)

In a 250 ml ballon we solved 1 mol 2,3-diaminopyridine (1 mmol and 0.109 g) in 30 ml absolute ethanol and refluxed it for half an hour. Then we added 2 mol salicylaldehyde (2 mmol and 0.2 cc) and refluxed it for 3 to 4 hours on a magnetic mixer and we continued refluxion until refluxion sediment formed. When a dark brown sediment formed we filtrated the sediment. To make sure that the sample is pure, we did TLC test during the experiment. First, we solved a little amount of the sample in ethanol and with a capillary tube we put the sample on TLC paper and we put it in hexane and ethyl acetate (1:1) solvent. Blemish went up in the solvent. Because it has capillary feature and it is made sure of sample purity by seeing just one blemish in the tank. Also sample electrical conduction in ethanol solvent with  $10^{-3}\text{ M}$  concentration was measured and it was  $0.11\text{ }\mu\text{S/cm}$  in  $16\text{ }^\circ\text{C}$  figure (1).

The synthesized combination has the following formula:

Chemical formula:  $C_{19}H_{15}N_3O_2$

Molecular weight:  $317.33\text{ g. mol}^{-1}$



**figure (1)** Ligand 2,3-diaminopyridine and salicylaldehyde synthesis

### Fe(III) chloride, Cr(III) chloride and Co(II) acetate synthesis respectively and separately with 2,3-diaminopyridine Schiff base ligand and salicylaldehyde with thiocyanate axial ligand

In a 250 ml ballon, we solved the ligand obtained (1 mmol and 0.31 g) in 30 ml absolute ethanol and they were refluxed for half an hour. Then to the same proportion of stoichiometry for the Fe

sample, iron salt (III) chloride (1 mmol and 0.27 g), for Cr sample, chromium salt (III) chloride (1 mmol and 0.26 g) and for Co sample, cobalt salt (II) acetate (1 mmol and 0.24 g) were added. It was refluxed on a magnetic mixer for an hour. Finally thiocyanate salt was added as axial ligand to the mixture of Fe, Cr and Co samples reactions respectively and separately in a stoichiometry proportion (6 mmol and 0.58 g). Refluxion

continued for 3 more hours until sediment formed. Samples sediment became brown after becoming dry. To make sure of the sample purity, during the experiment, TLC test was done. Sample melting point was about 205°C for Fe, 120 °C for Cr and 89 °C for Co. Complexes electric conduction in ethanol solvent with a  $10^{-3}$ M concentration was measured and its amount was 0.96  $\mu\text{S}/\text{cm}$  for Fe, 0.12  $\mu\text{S}/\text{cm}$  for Cr and 0.11  $\mu\text{S}/\text{cm}$  for Co in 16 °C. Fe, Cr and Co samples in ethanol, acetonitrile,

methanol, DMF and DMSO can be easily solved figure (2,3,4).

The synthesized combinations has the following formula:

Chemical formula(Fe):  $\text{C}_{20}\text{H}_{13}\text{N}_4\text{O}_2\text{SFe}$

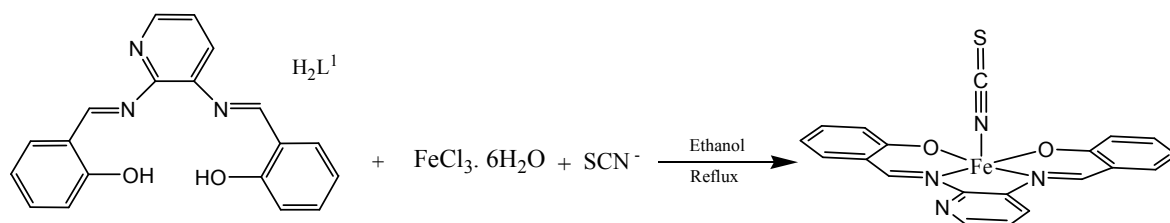
Molecular weight(Fe): 429.25 g.  $\text{mol}^{-1}$

Chemical formula(Cr):  $\text{C}_{20}\text{H}_{13}\text{N}_4\text{O}_2\text{SCr}$

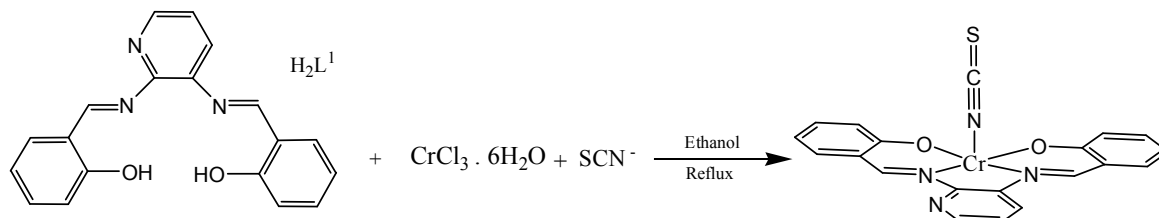
Molecular weight(Cr): 425.40 g.  $\text{mol}^{-1}$

Chemical formula(Co):  $\text{C}_{20}\text{H}_{13}\text{N}_4\text{O}_2\text{SCo}$

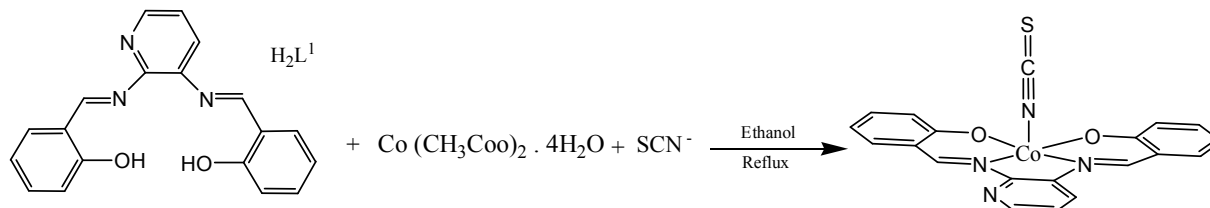
Molecular weight(Co): 432.34 g.  $\text{mol}^{-1}$



**figure (2)**  $\text{H}_2\text{L}^1$  with bridging thiocyanate



**figure (3)**  $\text{H}_2\text{L}^1$  with bridging thiocyanate



**figure (4)**  $\text{H}_2\text{L}^1$  with bridging thiocyanate

## RESULTS AND DISCUSSION

### FT-IR spectra features of ligand combination

There is an absorption band in  $3411.78\text{ cm}^{-1}$  range that is related to phenol OH stretch vibration. There are bands of aromatic stretch CH in  $2925.44\text{ cm}^{-1}$  range and aromatic bending CH band

in  $665.95\text{ cm}^{-1}$ . There is a strong absorption band in  $1610.95\text{ cm}^{-1}$  that is related to stretch vibration of safety group  $\text{C}=\text{N}$  and an absorption band in  $1397.06\text{ cm}^{-1}$  that is related to phenol C-O group figure (5).

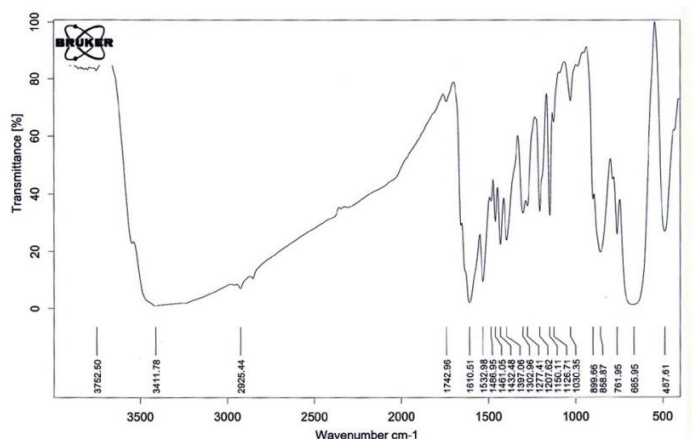


figure (5) FT-IR spectra ligand combination

### Cyclic voltammetry features of ligand combination

Synthesized ligand cyclic voltammogram had investigated with scanning rate  $0.1\text{ Vs}^{-1}$  and in 1 to -2 volt range in DMSO solvent. In high range of diagram, ie, in oxidation part, there is a short peak in  $E_a = -0.78\text{ V}$ , also there is another peak in  $E_a = 0.21\text{ V}$ . In low range of diagram, ie, in the

reduction part, there is a short peak in  $E_c = 0.19\text{ V}$  range and there are two peaks with low height respectively  $E_c = -0.42\text{ V}$  and  $E_c = -1.7\text{ V}$ . With a comparison of oxidation and reduction peaks, it can be resulted that there is a peak in reduction region like as a peak in oxidation region. Thus, its electrochemical behavior shows reversibility of ligand figure (6).

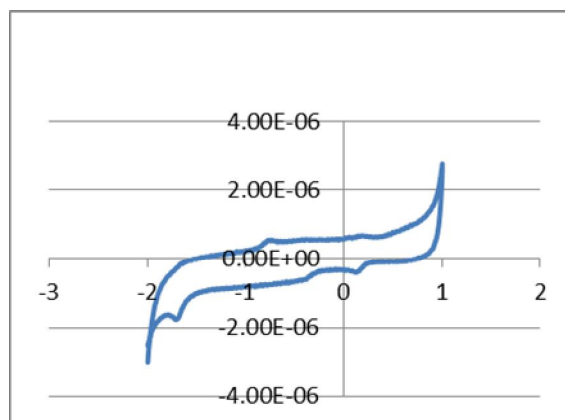


figure (6) Cyclic voltammogram ligand combination

### UV-Vis spectra features of ligand combination

There are transitions in synthesized ligand around 200-280 nm range that is related to aromatic ring  $\pi \rightarrow \pi^*$  transitions. 280-350 nm range is related to

$\pi \rightarrow \pi^*$  electron transition of safety bond system that it has a high peak. In 350-400 nm range, there are  $n \rightarrow \pi^*$  transitions with a sharp and high peak that is related to nonbond electrons on nitrogen atoms of azomethine bond figure (7).

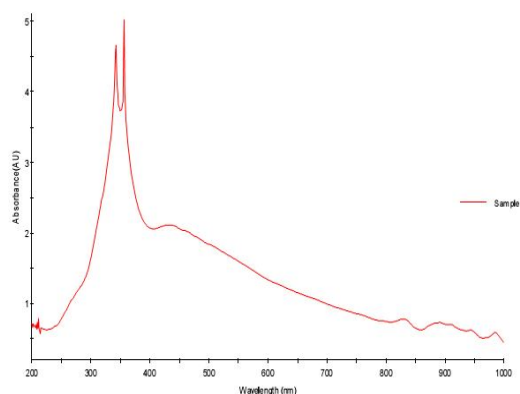
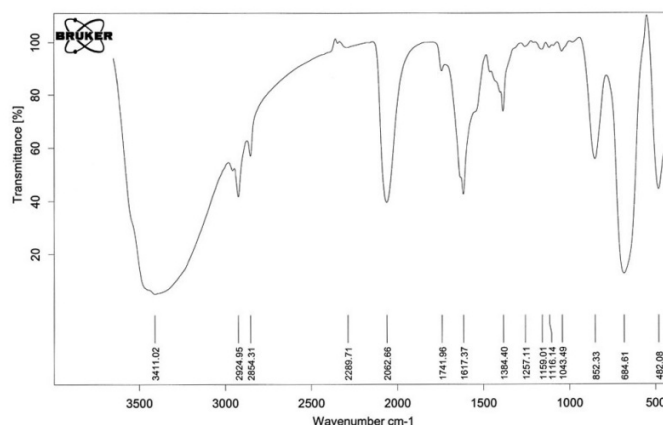


figure (7) UV-Vis spectra ligand combination

### FT-IR spectra features of Fe(III) chloride with bridging thiocyanate combination

In FT-IR spectra, there is an iron complex that has displaced in absorption band with regard to free ligand that indicates coordination of central metal atom to electron donation atoms in ligand structure. In this complex, there is a C=N bond in

$1617.37 \text{ cm}^{-1}$  frequency that it indicates coordination of central metal to ligand. Absorption band that has obtained in  $3411.02 \text{ cm}^{-1}$  range is related to phenol OH stretch vibration. There is CH vibration in  $684.61 \text{ cm}^{-1}$  that is related to aromatic bending and also CH vibration that is in  $2924.95 \text{ cm}^{-1}$  indicates aromatic stretch. There is phenol C-O vibration in  $1384.40 \text{ cm}^{-1}$  range figure (8).

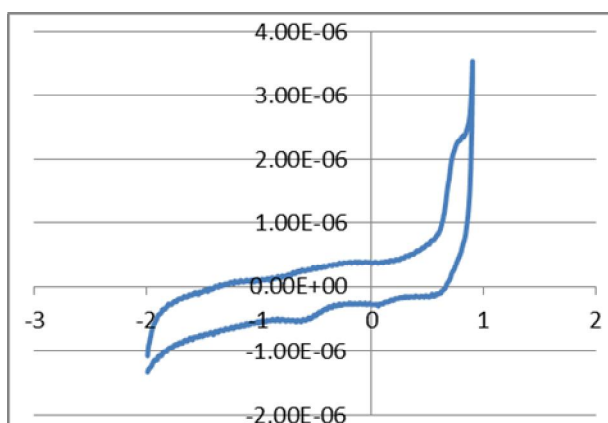


**figure (8)** FT-IR spectra Fe(III) chloride with bridging thiocyanate combination

#### Cyclic voltammetry features of Fe(III) chloride with bridging thiocyanate combination

Complex cyclic voltammogram Fe(III) that synthesized with scanning rate  $0.1 \text{ Vs}^{-1}$  had investigated in 0.9 to -2 volt range in DMSO solvent. In comparison of ligand diagram with obtained complex, there is a peak in  $E_a = -0.25 \text{ V}$  range in oxidation region and also there is a rather high peak in  $E_a = 0.76 \text{ V}$  range that has displaced with regard to a ligand peak. In low range of diagram, there are two peaks in  $E_c = 0.1 \text{ V}$  and  $E_c = -0.6 \text{ V}$  respectively that has displaced with regard

to a ligand peak in reduction range. With a comparison that obtained from oxidation and reduction of this diagram, it can be resulted that there are two peaks in oxidation range like as reduction range, thus its electrochemical behavior shows the reversibility of complex, ligand and metal are near together, for this reason a peak of oxidation range is rather full. Because of displacements that has taken both in oxidation and reduction ranges, it is an approval for formation of compound and supplied complex is an electroactive complex figure (9).

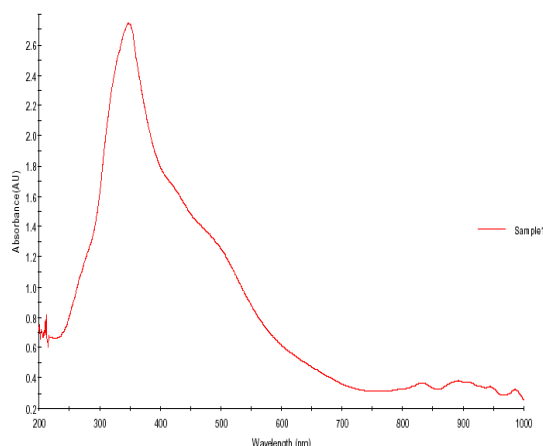


**figure (9)** Cyclic voltammogram Fe(III) chloride with bridging thiocyanate combination

### UV-Vis spectra features of Fe(III) chloride with bridging thiocyanate combination

In this complex, there is an absorption band in 200-280 nm that is related to aromatic  $\pi \rightarrow \pi^*$  transitions and there is a high peak in 280-400 nm that is related to  $\pi \rightarrow \pi^*$  transitions of C=N bond. There is a peak in 400-450 nm that is related to  $n \rightarrow \pi^*$  transition and also d-d complex transfers have appeared in 450-800 nm. Transfer rate has

influenced by axial ligand and electronical rate of this ligand to central metal that it is an approval for formation of this complex. Comparing electronic spectra of this combination with ligand spectra is an indicator of coordination of central metal into 2 nitrogen and phenol oxygen and the transfers in the above mentioned combination have moved towards red wavelength range figure (10).

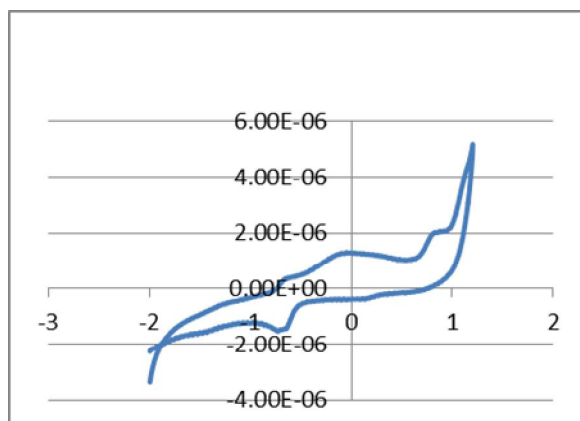


**figure (10)** UV-Vis spectra Fe(III) chloride with bridging thiocyanate combination

### Cyclic voltammetry features of Cr(III) chloride with bridging thiocyanate combination

Synthesized complex cyclic voltammogram Cr(III) with  $0.1 \text{ Vs}^{-1}$  scanning rate and in 1.2 to -2 volt range had investigated in DMSO solvent. With a comparison of a ligand diagram that obtained with complex, there has been a peak in  $E_a = -0.63 \text{ V}$  range and also there are two another peaks in  $E_a = -0.12 \text{ V}$  and  $E_a = 0.88 \text{ V}$  ranges that has displaced with regard to ligand peak. There are three peaks in  $E_c = 0.18 \text{ V}$ ,  $E_c = -0.61 \text{ V}$  and  $E_c = -0.75 \text{ V}$  ranges in reduction part that has displaced with regard to a

ligand peak in reduction range. With a comparison that obtained from oxidation and reduction peaks in this diagram, it can be resulted that there are three peaks in oxidation range like as reduction range, thus its electrochemical behavior shows its reversibility of complex and ligand and metal are near together, for this reason, a peak in oxidation region is rather full. Because of displacements that has taken both in oxidation and reduction ranges, it is an approval for formation of compound and supplied complex is an electroactive complex figure (11).

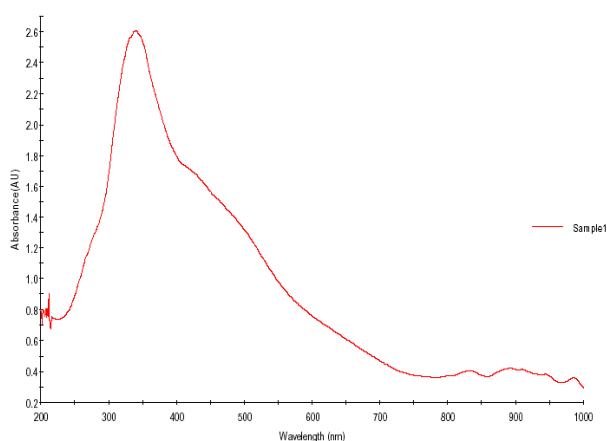


**figure (11)** Cyclic voltammogram Cr(III) chloride with bridging thiocyanate combination

#### UV-Vis spectra features of Cr(III) chloride with bridging thiocyanate combination

In this complex, there is an absorption band in 200-280 nm range that is related to aromatic  $\pi \rightarrow \pi^*$  transitions and there is a high peak in 280-410 nm range that is related to  $\pi \rightarrow \pi^*$  transitions of C=N bond. There is a peak in 410-450 nm range that is related to  $n \rightarrow \pi^*$  transition and also d-d complex transfers have appeared in 450-800 nm. Transfer

rates has influenced by the presence of axial ligand and electron donation rate of this ligand to central metal that it is an approval for formation of this complex. Comparing electronic spectra of this combination with ligand spectra is an indicator of coordination of central metal into 2 nitrogen and phenol oxygen and the transfers in the above mentioned combination have moved towards red wavelength range figure (12).

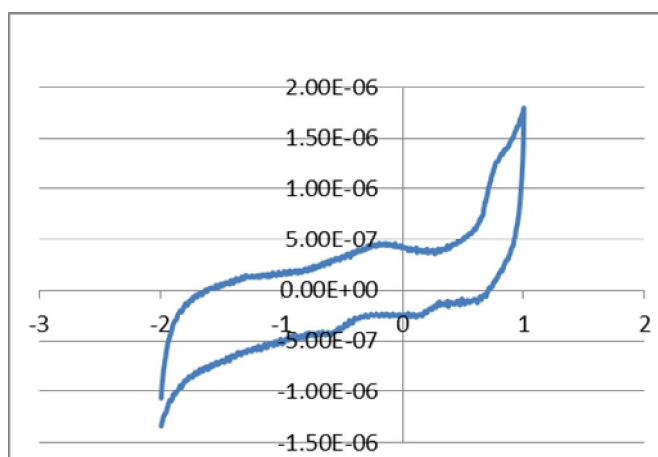


**figure (12)** UV-Vis spectra Cr(III) chloride with bridging thiocyanate combination

### Cyclic voltammetry features of Co(II) acetate with bridging thiocyanate combination

Synthesized complex cyclic voltammogram Co(II) with scanning rate  $0.1 \text{ Vs}^{-1}$  had investigated in 1 to -2 volt range in DMSO solvent. With a comparison of ligand diagram, there is a peak in high range of diagram, ie, in oxidation part in  $E_a = -0.24 \text{ V}$  and there is another peak in  $E_a = 0.76 \text{ V}$  range that has displaced with regard to ligand peak, in low range of diagram, ie, in reduction part, there are two very small peaks in  $E_c = 0.2 \text{ V}$ ,  $E_c = -0.6 \text{ V}$  respectively that has displaced with regard to ligand peak in

reduction range. With a comparison of oxidation and reduction peaks that obtained from this diagram, it can be resulted that there is a peak in oxidation region like as reduction region, thus its electrochemical behavior shows reversibility of complex and ligand and metal are near together, for this reason, the peak of oxidation range is rather full. For the reason of displacements that has performed both in oxidation and reduction ranges, it is an approval for formation of compound and supplied complex is an electroactive complex figure (13).



**figure (13)** Cyclic voltammogram Co(II) acetate with bridging thiocyanate combination

### CONCLUSION

The results obtained from UV-Vis spectra, FT-IR and also the information gotten from synthesized complexes cyclic voltammetry can confirm the considered complex formation. In this research, quite new structures were obtained due to using thiocyanate bridging combination. UV-Vis spectra of the complexes which shows  $\pi \rightarrow \pi^*$  transfers presence related to aromatic ring and absorbing band of  $n \rightarrow \pi^*$  safety link and d-d transfers of the center of metals is a reason for Schiff base formation and these bands movement in electronic spectra of the complexes, It is an indicator of Schiff base coordination with metal. Cyclic voltammetry makes it possible to be able to get

information not only about electronic spectrum, but also about electronic features of the complexes and evaluate the possibility of their usage as a catalyst in oxidation–reduction reactions.

### REFERENCE

- [1] M. A. Kamyabi, S. Shahabi, H. Hosseini-Monfared., J. chem. Eng. Data, 2008, 53, 2341–2345.

[2] J. Pacansky, A. D. McLean, M. D. Miller., J. Phys. Chem, 1990, 94, 1629–1632.

[3] A. Altundas, N. Sari, N. Colak, H. Ogutcu., Med. Chem. Res, 2010, 19, 576–588

[4] H. Temel, S. Ilhan., Russian journal of inorganic chemistry, 2009, 54, 543–547

[5] I. Kaya, A. Bilici, Murat. Gul., Polym. Adv. Technol, 2008, 19, 1154–1163

[6]. Xueguang Rana, Lingyun Wang, Yingcai Lin, Jie Hao and Derong Cao, Syntheses, characterization and biological studies of zinc(II), copper(II) and cobalt(II) complexes with Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and selenomethionine, (2010), 24, 741-747.

11/16/2012