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Synthesis and Characterization of Complexes of N_2O_2 Schiff Base and Bridging Ligands of Azide and Thiocyanate with Transition Metals of Co, Cr and Fe

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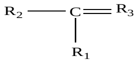
ABSTRACT

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 Co, Cr and Fe with the provided ligand were studied in the second stage with synthesized thiocyanate and using UV/Vis spectroscopy, cyclic voltammetry (CV). Electrone 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. Cyclic voltammetry makes it possible to be able to get information not only about electronic spectra, but also about electronic features of the complexes and evaluate the possibility of their usage as a catalyst in oxidation–reduction reactions.

KEY WORDS: Axial ligand, complex, schiff base, synthesis.

INTRODUCTION

Schiff base ligands are defined by the combinations that contain azomethine groups  $R_2-\underset{R_1}{\underset{|}{C}}=R_3$ in their structure. These combinations are obtained by means of a kind one amines concentration with a one carbonyl group contained molecule. Schiff base ligands can make stable complexes with many metal ions. These combinations have many applications. Some applications of Schiff bases are in paint and plastic Industry, Agriculture, biochemistry, liquid crystal provision and physiology [1, 2]. The other application of these compounds is in sensors and analytic studies [3, 4]. In order to be able to increase choosing and sensibility of the new industrial methods in analytic systems, Schiff base are used as analytic indicators [5]. New cobalt(II), copper(II) and zinc(II) complexes of Schiff base derived from D,L-selenomethionine and salicylaldehyde were synthesized and characterized by elemental analysis, IR, electronic spectra, conductance measurements, magnetic measurements and biological activity. The analytical data showed that the Schiff base ligand acts as tridentate towards divalent metal ions (cobalt, copper, zinc) via the azomethine-N, carboxylate oxygen and phenolato oxygen by a stoichiometric reaction of M: L (1:1) to form metal complexes [ML (H2O)], where L is the Schiff base ligand derived from D, L-selenomethionine and salicylaldehyde and M = Co (II), Cu (II) and Zn (II). 1H NMR spectral data of the ligand and Zn (II) complex agree with proposed structures. The conductivity values between 12.87 and 15.63 S cm2 mol-1 in DMF imply the presence of non-electrolyte species. Antibacterial and antifungal results indicate that the metal complexes are more active than the ligand [6]. 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(H2O), 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, naphtol oxygen and carboxylate oxygen atoms. 1H NMR spectral data of lithium salt of the Schiff base ligand [Li (HL)] and ZnL(H2O) agreed with the proposed structures. The conductivity values of complexes between 12.50 and 15.45 S cm2 mol-1 in DMF suggested the presence of non-electrolyte species. Survey indicated that the powder XRD The complex Co (II) non-crystalline (irregular) is, 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 (H2O) is most active among them [7].

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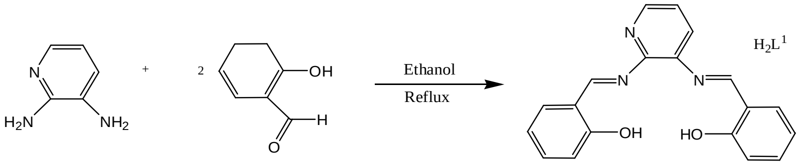
MATERIALS AND METHODS

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 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. Marking 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 M concentration was measured and it was 0.11 μs/cm in 16 °C. The synthesized combination has the following formula:

Chemical formula: C19H15N3O2 Molecular weight: 317.33 g. mol-1

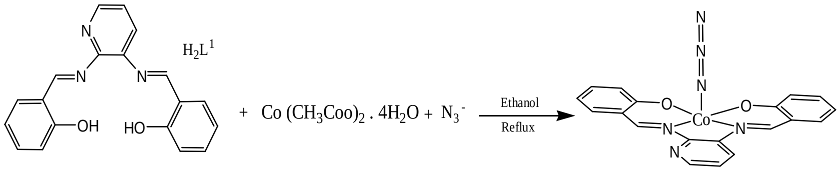


Ligand 2,3-diaminopyridine and salicylaldehyde synthesis

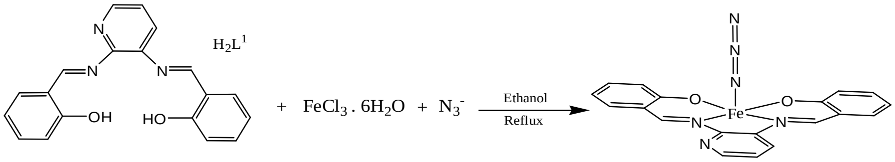
Co (II) acetate and Fe (III) chloride synthesis respectively and separately with Schiff base ligand 2, 3-diaminopyridine and salicylaldehyde with azide axial ligand

In a 250 ml ballon, the obtained ligand for Co(II) acetate and Fe(III) chloride were solved separately (1 mmol and 0.31 g) in 30 ml absolute ethanol and refluxion was done for 30 minutes. Then to the same proportion of stoichiometry for the Co sample, cobalt salt (II) acetate (1 mmol and 0.24 g) and for Fe sample, iron salt (III) chloride (1 mmol and 0.27 g) were added. They were refluxed on a magnetic mixer for 1 hour. Finally azide salt was added to both reaction mixtures separately with stoichiometry proportion (6 mmol and 0.39 g) as axial ligand, so that a green solution were obtained. Refluxion continued for 3 more hours until sediment formed. The sediment became brown for both of the samples when it became dry. To make sure that the samples are pure, during the experiment, TLC test was done. Sample melting point was about 81 °C and about 258 °C respectively for Co and Fe. Also electric conductivity of both samples complex was measured separately in ethanol solvent with a concentration of 10-3 M, and its amount was 0.21 μs/cm for Co and 0.71 μs/cm for Fe in 16 °C. The related sample to Co can be easily solved in ethanol, acetonitrile, methanol, DMF and DMSO and the sample related to Fe is solvable in ethanol, acetonitrile, methanol, DMF and DMSO. The synthesized combination for both samples has the following formula:

Chemical formula(Co): C19H13N6O2Co Molecular weight(Co): 416.27 g. mol-1
Chemical formula(Fe): C19H13N6O2Fe Molecular weight(Fe): 413.19 g. mol-1



H2L1 with azide bridging



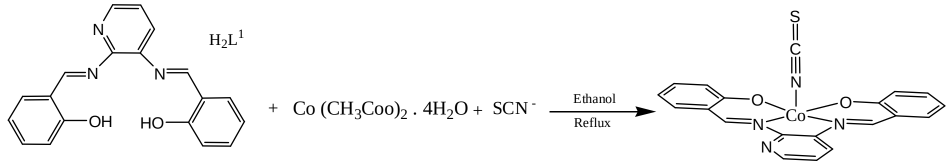
H2L1 with azide bridging

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

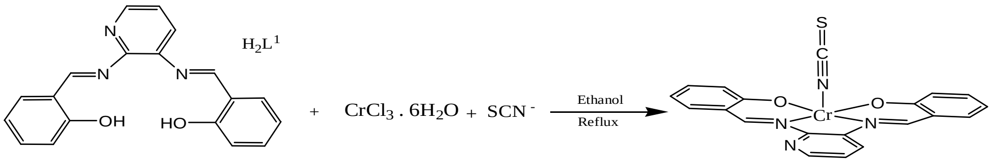
In a 250 ml ballon, we solved the ligand obtained for Co and Cr (1 mmol and 0.31 g) in 30 ml absolute ethanol and they were refluxed for half an hour. Then to the same stoichiometry proportion cobalt salt (II) acetate (1 mmol and 0.24 g) was added separately to cobalt sample and chromium salt (III) chloride (1 mmol and 0.26 g) was added to Cr sample. It was refluxed on a magnetic mixer for an hour. Finally thiocyanate salt was added as axial ligand to the mixture of Co and Cr samples reactions respectively and separately in a stoichiometry proportion (6 mmol and 0.58 g), (6 mmol and 0.58 g). A blue solution was obtained for cobalt and a purple solution was gotten for Cr. Refluxion continued for 3 more hours until sediment formed. Both 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 89 °C for Co and 120 °C for Cr. Complex electric conduction of both samples in ethanol solvent with a 10-3 M concentration was measured and its amount was 0.11 μs/cm for Co and 0.12 μs/cm for Cr in 16 °C. Co in ethanol, acetonitrile, methanol, DMF, DMSO and Cr in ethanol, acetonitrile, methanol, DMF and DMSO can be easily solved.

The synthesized combination for both samples has the following formula:

Chemical formula(Co): C20H13N4O2Sco	Molecular weight(Co): 432.34 g. mol-1
Chemical formula(Cr): C20H13N4O2SCr	Molecular weight(Cr): 425.40 g. mol-1



H2L1 with thiocyanate bridging



H2L1 with thiocyanate bridging

RESULTS AND DISCUSSION

UV/Vis spectra features of ligand combination

In synthesized ligand, some transfers are observed around 200-280 nm zone which is mainly related to π→π* aromatic ring transfers. 280-350 nm zone is related to π→π* electronic transfer of the safety link system which has a high peak. In 350-400 nm zone n →π* transfer with high peak that is related to not linked electrones on nitrogen is azomethine and the related d-d transfer which is observed in 400-800 nm is related to complex transfers Figure (1).

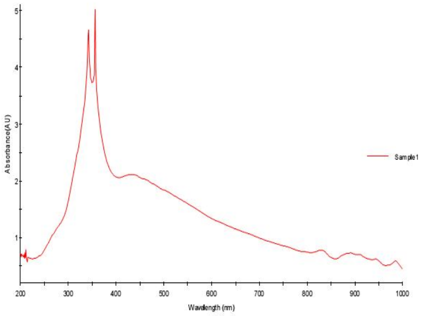


Figure (1): UV/Vis spectra (I) combination

Cyclic voltammetry features of ligand combination

Cyclic voltammogram synthesized ligand with 0.1 Vs-1 scan rate in 1 to - 2 volt was studied in DMSO solvent. It is observed in above graph a short peak in Ea = - 0.78 V zone. Also there is other peak in Ea = 0.22 V.

A short peak in Ec = 0.19 V and two other peaks with low height have appeared respectively in Ec = - 0.4 V and Ec = - 1.7 V. In a comparison of oxidation and reduction peaks in this graph, it can be concluded that the appeared peak has been observed in oxidation zone and also in reduction zone. So its electrochemical behavior shows the reversible state of the ligand Figure (2).

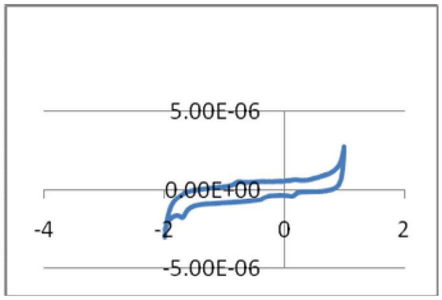


Figure (2): Cyclic voltammogram (I) combination

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

Cyclic voltammogram synthesized complex (II) with 0.1 Vs-1 scan rate in 1.2 to - 2 volt was studied in DMSO solvent. In comparing ligand graph with obtained complex in above graph a peak in Ea = - 1.25 V zone it is observed that it has moved, compared to ligand peak. Also a relatively high peak is seen in Ea = 0.77 V zone. In lower zone of the graph i.e in reduction zone two tiny peak Ec = 0.95 V and Ec = - 1.59 V are observed that has moved in reduction zone compared to ligand peak. In a comparison on oxidation and reduction peaks of this graph, it can be concluded that the appeared peak has been seen in oxidation and also reduction zones. So its electrochemical behavior shows reversible state of the complex. Since ligand and metal appear in a place close to each other, the peak of oxidation zone is relatively wide and high. Due to the movements which have been done in oxidation and reduction zones, the considered combination formation has been confirmed and the prepared complex is electroactive Figure (3).

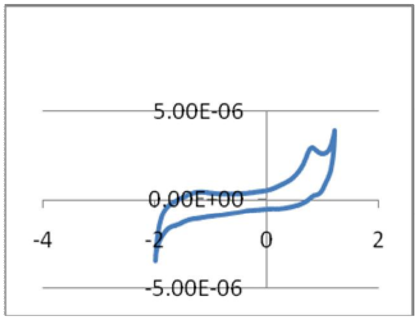


Figure (3): Cyclic voltammogram (II) combination

UV/Vis spectra features of Fe (III) chloride with azide bridging combination

In this complex an absorbing bond is observed in 200-280 nm zone that is related to aromatic $\pi\rightarrow\pi^*$ transfers and in 280-400 nm a high peak has appeared which is related to $\pi\rightarrow\pi^*$ transfers of C=N link. The peak related to n $\rightarrow\pi^*$ is seen in 400-460 nm and also d-d complex transfers have appeared in 460-800 nm. In spite of azide axial ligand and with due attention to the amount of electron giving by this ligand to the central metal, transfers intensity has been affected which can be confirmed in this complex formation. Comparing electronic spectra of this combination with ligand spectra is an indicator of coordination of central metal into 2 nitrogen and phenol oxygen and transfers in the above mentioned combination have moved towards red wavelength zones Figure (4).

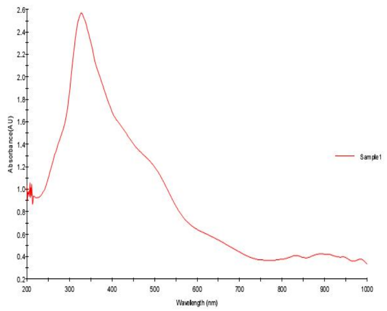


Figure (4): UV/Vis spectra (III) combination

UV/Vis spectra features of Co (II) acetate with thiocyanate bridging combination

In this complex an absorbing band is observed in 200-280 nm zone that is related to aromatic π→π* transfers and in 280-400 nm a high peak has appeared which is related to π→π* transfers of C=N link. The peak related to n →π* is seen in 400-460 nm and also d-d complex transfers have appeared in 460-800 nm. In spite of azide axial ligand and with due attention to the amount of electron giving by this ligand to the central metal, transfers intensity has been affected which can be confirmed in this complex formation. 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 zones Figure (5).

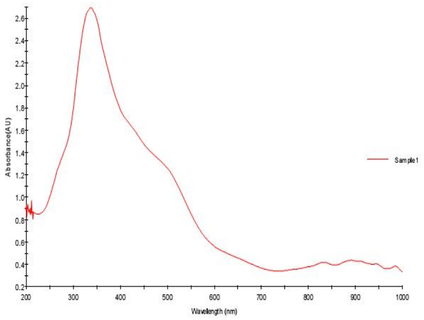


Figure (5): UV/Vis spectra (IV) combination

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

Cyclic voltammogram synthesized complex (VI) with 0.1 Vs-1 scan rate in 1.2 to - 2 volt was studied in DMSO solvent. In comparing ligand graph with obtained complex in above graph a peak in Ea = - 0.63 V zone it is observed and also there is an two other paeks in Ea = - 0.12 V and Ea = 0.88 V. It has moved compared to ligand peak. In the lower part of the graph i.e in reduction zone three tiny peak Ec = 0.18 V, Ec = - 0.61 V, Ec = - 0.75 V are seen which has moved in reduction zone compared to ligand peak. In a comparison between reduction and oxidation peaks of this graph, it can be concluded that all three appeared peaks in oxidation zone have been observed in reduction zone too. There fore, its electrochemical behavior shows reversible state of the complex. Oxidation zones peak is relatively wide because ligand and metal appear in a place close to each other. Due to the movements which have been done in oxidation and reduction zones, they can confirm the considered combinations formation and the prepared complex is electroactive Figure (6).

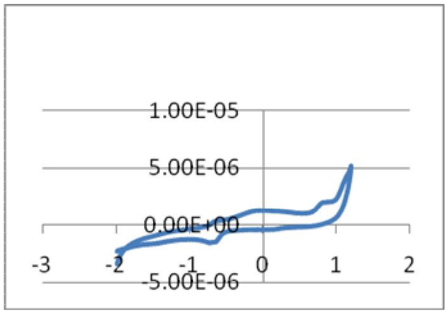


Figure (6): Cyclic voltammogram (VI) combination

CONCLUSION

The results obtained from UV/Vis spectra 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 azide bridging and thiocyanate combinations. 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. The information obtained from cyclic voltammograms of the complexes showed that the electrochemical behavior of the synthesized combinations indicates reversible the mood of the complexes.

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