



Synthesis and characterization of salen and thiocyanate complexes with Co^{2+} , Fe^{3+} , Cu^{2+} , and Mn^{2+} transition metal cations

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ABSTRACT

In this research we synthesized yellow colored salen ligand from the condensation reaction of ethylenediamine and salicylaldehyde in absolute ethanol. After this, we synthesized salen and thiocyanate bridging ligand complexes of transition metals including Co(II), Fe(III), Cu(II) and Mn(II). Synthesized compounds were characterized with application of IR, UV/Vis spectroscopy and cyclic voltammetry and conductivity. Presence of a sharp pick near to 2000cm^{-1} supports coordination of thiocyanate ligand to metal center. Shifts in IR spectra of complexes compared with free ligand refers to coordination on salen ligand to metals via O and N dentates. As a result of ligand coordination to metals, shifts and absorption magnitude in UV/Vis spectra of complexes in the comparison with ligand can be observed. Conductivity measurements revealed that some complexes are ionic compounds. CV characterizations showed that the compounds have reversible and irreversible behaviors.

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Introduction

Schiff bases are organic molecules which are containing imine or azomityne groups that are still among the most interesting compounds in research of coordination chemistry [1]. These types of molecules have shown that they are good ligands for transition metals to form complexes have the broad applications ranging from pharmaceutical and industrial materials such as catalysts [2]. Undoubtedly, Schiff base ligands, such as salen ligands, have attracted most attention due to their specific structure (planar molecule with four connectable teeth to the metals) [3]. The classified ligands in this category have four teeth that composed of two iminonitrogen and two donors of phenolic oxygen which form stable complexes with most of metals due to chelate effect [4]. Various categories of diamines could be selected for preparation of this ligands beside of (non substituted or substituted) salicylaldehyde [5].

Four teeth salen ligand which obtained by condensation reaction with ethylene diamine [4] can form four-coordinated complexes with most of transition metals [5]. Transition metal complexes such as Cobalt with salen in oxidative reactions of Olefin have catalytic characteristic [9].

Another characteristic of the salen-type ligands, which is less studied, is their potential to form multiple nuclear complexes [6]. This feature is due to their connection with more than one metallic ion [7]. Transition metal complexes with salen ligands are used in catalytic reactions. Such salen complexes are used to catalyze the epoxidation reaction of olefins [9]. For example, Mn^{2+} salen complex has been used for chiral epoxidation [8].

The objective of this present work is synthesizing of transition metals complexes with four teeth salen ligands and thiocyanate bridging ligand. Beside of four teeth salen ligand, in addition to five-coordinated complexes formation with different geometries, thiocyanate which is a two-ended teeth ligand, has been used for enable connection between metallic centers for obtaining complexes with two or more nucleus.

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Experimental

Consumed materials: salicylate aldehyde, ethanol, ethylene diamine, potassium thiocyanate, manganese sulfate (II) $\text{Mn}(\text{SO}_4)_2$, iron nitrate (III) $\text{Fe}(\text{NO}_3)_3$, copper sulfate (II) $\text{Cu}(\text{SO}_4)_2$, cobalt nitrate (II) $\text{Co}(\text{NO}_3)_2$. All of used chemicals were of analysis grade and are commercially available and were used without purification.

Synthesis of Salen ligand (N-N bis Salicyliden-1,2Ethylene diamine) $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$:

Ethylene diamine and salicyl aldehyde mixed together with 1:2 ratios. Salicyl aldehyde should be mixed in 50 ml and reflux ethanol solvent for 30 minutes. After addition of 1 mol ethylene diamine, the color of solution became yellow and reflux process was continued for another half an hour, then ligand was dried in laboratory temperature.

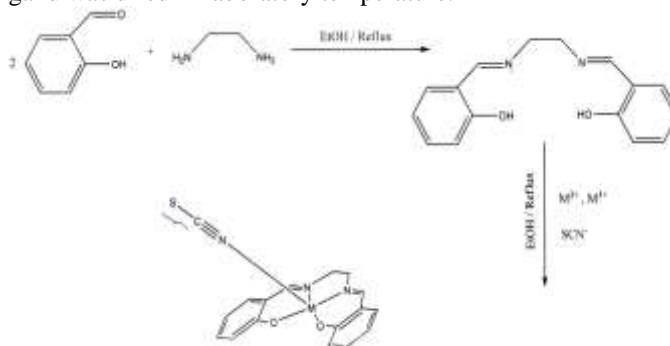


Figure 1: Synthesis process of salen ligand and metals complexes with thiocyanate ligand

Preparing of metals complexes with Salen ligand Schiff base with thiocyanate ligand: first, 0.266 gr salen ligand had been weighted and added to 30 ml ethanol and the mixture had been reflux for 10 minutes. then, the salts of Co(II), Fe(III), Cu(II) and Mn(II) had been weighted separately and added to ligand and ethanol solution and the mixture had been reflux for an hour. Then, potassium thiocyanate salt had been poured into the solution and reflux process was continued for another 60

minutes. In the total period of experiment, solution was taken constant heat. Then the sediment had been filtered and eventually the all of complexes were dried in the room temperature (Fig.1).

Results and Discussion

Salen ligand is achieved by salicyldehyde reaction with ethylene diamine. This ligand were synthesized by adding of Co^{2+} , Fe^{3+} , Cu^{2+} , and Mn^{2+} metal salts with equal molar ratios in associated complexes' ethanol solvent in the presence of potassium thiocyanate.

Structural information of provided complexes was obtained by using of infrared spectroscopy (IR) and UV/Visible. Cyclic Voltammetry (CV) enables us to obtain electronic characteristics of complexes information in addition to electronic spectrum and to evaluate the application of those as reduction- oxidation reactions. Oxygen and nitrogen teeth coordination with central metal was shown by displacements observation in the infrared absorption of complexes in relation to ligand. The presence of a sharp peak in the range of 2000 cm^{-1} in complexes with thiocyanate ligands proves the thiocyanate coordination with the central metal in the complex structure (Table 1). The presence of axial ligand in UV/Vis spectrum (electronic spectrum) of complexes, by considering of electron-donoring of ligands to central metal, decreases or increases transitions intensity and this effect is a confirmation reason for complex formation (Table 2). Ionic or non-ionic characteristics of complexes would be shown by measuring of electrical conductivity of solution (Table 3).

Table (1): infrared spectroscopy data of salen ligand and metals complexes with thiocyanate ligand

IR vibration s	Salen: $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$	Co^{2+} : $\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Co}$	Fe^{3+} : $\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Fe}$	Cu^{2+} : $\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Cu}$	Mn^{2+} : $\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Mn}$
C=N	1636.40	1648.79	1626.91	1635.06	1632.48
C=C	1498.40	1600.77	1544.71	1443.71	1495.58
C=O	1150.20	1206.71	1151.09	1115.65	1111.98
M-O	-	595.78	795.63	756.98	853.77
M-N	-	470.49	533.51	460.43	290.01
OH	3051.77	3434.38	3433.76	3434.63	3417.62
SCN	-	2127.69	2047.85	2084.70	2083.06

The presence of iminic bond band for salen ligand in the frequency of 1636.40 cm^{-1} confirms the formation ligand. Comparing the infrared spectra of complexes with ligands shows the reduction in peak frequency of iminic bond. Also, the presences of peaks with the frequency of 2127.69 cm^{-1} of Cobalt metallic complex, the frequency of 2047.85 cm^{-1} of Iron metallic complex, the frequency of 2083.06 cm^{-1} of Manganese metallic complex and the frequency of 2084.70 cm^{-1} of Copper metallic complex are indication the presence of thiocyanate.

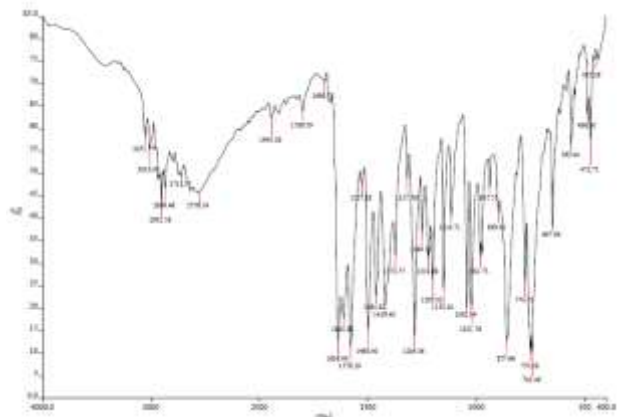


Figure 2: Salen ligand (N-N bis Salicyliden-1,2Ethylene diamine) $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$

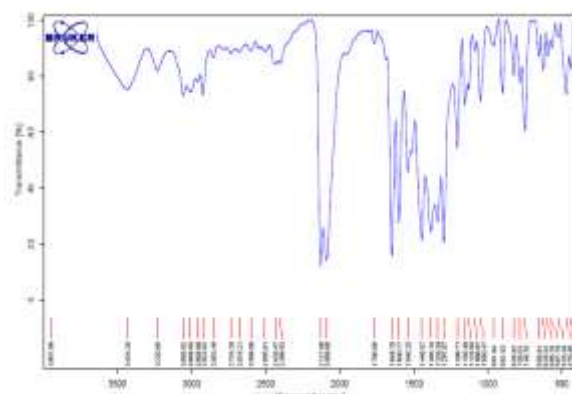


Figure 3: The complex of Co^{2+} : ($\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Co}$)

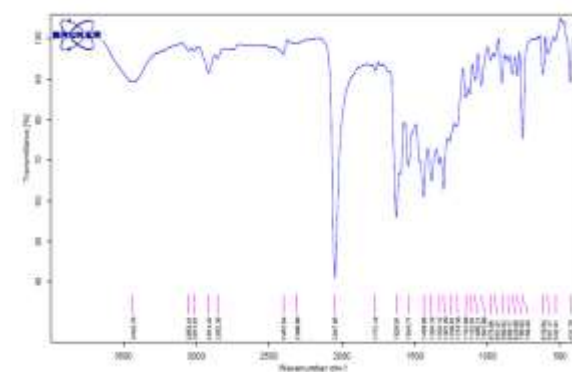


Figure 4: The complex of Fe^{3+} : ($\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Fe}$)

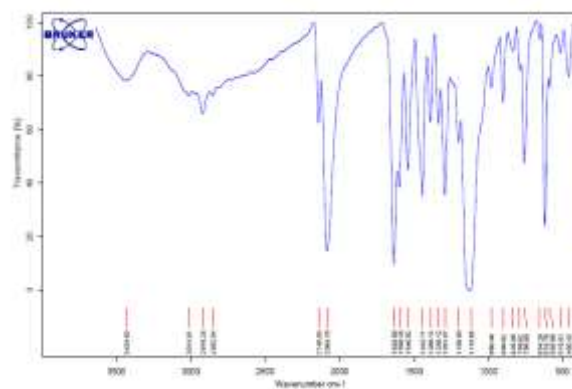


Figure 5: The complex of Cu^{2+} : ($\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Cu}$)

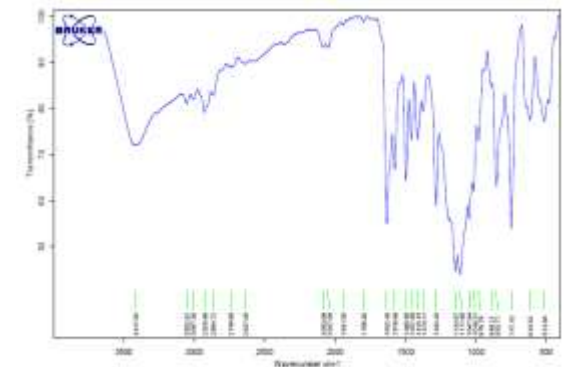


Figure 6: The complex of Mn^{2+} : ($\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Mn}$)
Table (2): UV spectral data of salen ligand and metals complexes with thiocyanate ligand

	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	d \rightarrow d
Salen: $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$	220 nm	320 nm	-
$\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Co}$	220 nm	370 nm	420 nm
$\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Fe}$	250 nm	390 nm	730 nm
$\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Cu}$	240 nm	360 nm	560 nm
$\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{S Mn}$	230 nm	330 nm	420 nm

In general, the wavelength of absorption bands shifts toward the red range as a result of ligand coordination with central metal cations. The obtained wavelengths in the ligand are in the range of 220 nm and 320 nm.

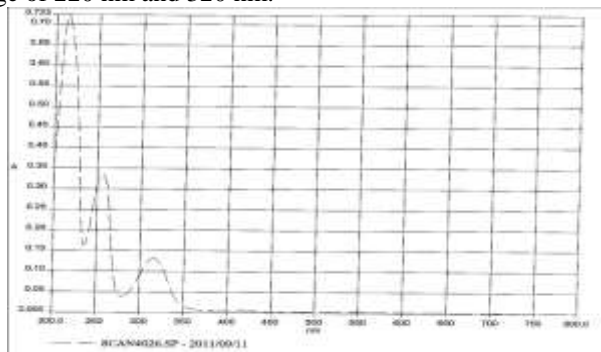


Figure 7: Uv spectrum of Salen ligand (N-N bis Salicyliden-1,2Ethylene diamine) $C_{16}H_{14}N_2O_2$

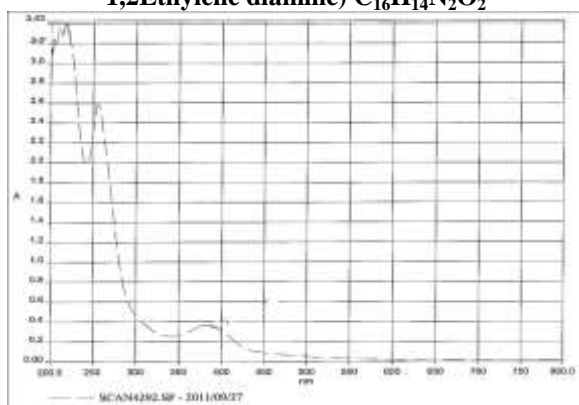


Figure 8: Uv spectrum of $Co^{2+}:(C_{17}H_{12}N_3O_2 S Co)$

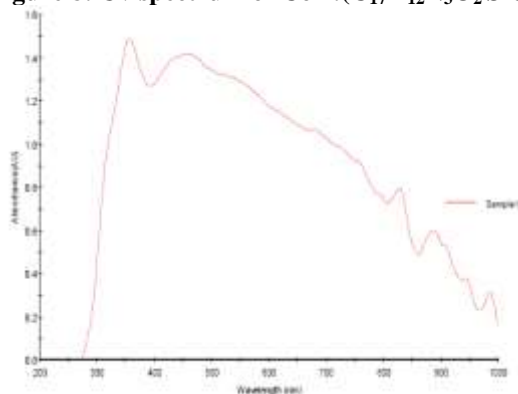


Figure 9: DRS spectrum of $Fe^{3+}:(C_{17}H_{12}N_3O_2 S Fe)$



Figure 10: Uv spectrum of $Cu^{2+}:(C_{17}H_{12}N_3O_2 S Cu)$

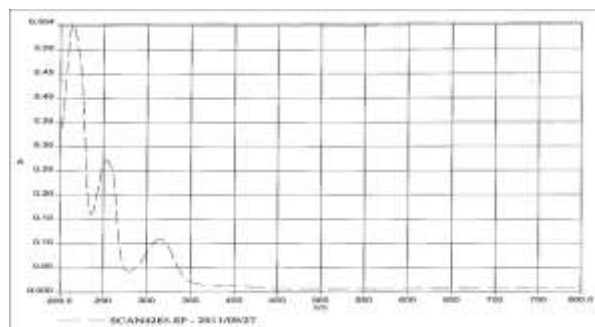


Figure 11: Uv spectrum of $Mn^{2+}:(C_{17}H_{12}N_3O_2 S Mn)$

Table (3): Electrical conductivity data of salen ligand and complexes

	Conductivity	Temperature ($^{\circ}C$)
Distilled water	6.88	19.3
Salen: $C_{16}H_{14}N_2O_2$	0.830	21.4
$C_{17}H_{12}N_3O_2 S Co$	187.5	20.7
$C_{17}H_{12}N_3O_2 S Fe$	0.202	20.6
$C_{17}H_{12}N_3O_2 S Cu$	54.8	20.6
$C_{17}H_{12}N_3O_2 S Mn$	21.8	20.0

Conclusion

Salen ligand is achieved by salicylic aldehyde reaction with ethylene diamine. This ligand was synthesized by adding of Co^{2+} , Fe^{3+} , Cu^{2+} , and Mn^{2+} metal salts with equal molar ratios in associated complexes' ethanol solvent in the presence of potassium thiocyanate.

Structural information of provided complexes was obtained by using of infrared spectroscopy (IR) and UV/Visible. Cyclic Voltammetry (CV) enables us to obtain electronic characteristics of complexes information in addition to electronic spectrum and to evaluate the application of those as reduction-oxidation reactions.

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