

Synthesis and Characterization of Cobalt (II), Nickel (II) and Copper (II) Complexes with Schiff Base Derived from 9,10-phenanthrenquinon

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Abstract

In this paper, a Schiff base ligand derived from 9,10-phenanthrenquinon and 2-aminothiophenol was synthesized in 1:2 molar ratio respectively. The complexes of this ligand with some metal ions such as cobalt (II), nickel (II) and copper (II) were synthesized also. The production of the ligand was carried out by refluxing 9,10-phenanthrenquinon with 2-aminothiophenol in the presence of hydrochloric acid as a catalyst for four hours. While the ligand complexes were prepared by reacting the ligand with the mentioned metal ion salts in ethanol in 1:1 L:M ratio to produce the related metal complex. IR spectroscopy, UV-Visible, conductivity measurements, magnetic susceptibility and thermogravimetric analysis techniques were used to characterize the produced compounds. According to the obtained IR spectroscopy results, the coordination between the metal ions and the ligand occurs through the imine group of Schiff base and the thione group of 2-aminothiophenol. Conductance measurements shows the electrolytic nature of the three complexes. While, the magnetic susceptibility measurements were found to be 1.51, 0.0 and 1.48 BM for Co (II), Ni (II) and Cu(II) complexes respectively. By the available results from UV-Visible, conductivity measurements, magnetic susceptibility and thermogravimetric analysis the square planar structure is suggested for the complexes and their suggested general chemical formula is $[M(L)] Cl_2 \cdot nH_2O$.

Keywords: MetalComplexes, SchiffBase, 9, 10phenanthrenequinone, 2-Aminothiophenol

1. Introduction

In chemistry, one of the common ways to synthesize Schiff bases is the condensation reaction between aldehydes or ketones with primary amines. The resulted Schiff base compound contains the characteristic azomethine or imine group ($-C=N-$) where the carbonyl group in the aldehyde or ketone chemical structure will be replaced by the azomethine or imine group by the Schiff base synthesis^{1,2}.

This type of compounds (Schiff bases) reacts with different metal ions, produce their complexes through the coordination between these ions and the azomethine group. This coordination becomes more interesting with the presence of some substituted donor atoms in the skeleton of Schiff base ligands, such as O, S and N which are adjacent to the azomethine group³⁻⁵.

Furthermore, research deals with Schiff bases and their metal complexes have grown rapidly and received more attention because they are easy to prepare and they play an important role in various applications, such as in biology and industry^{6,7}. In the biological fields Schiff bases have been used to treat cancer, viruses, bacteria and inflammations⁸⁻¹⁴. While in industry they can be used as catalysts for hydrogenation and polymerization of alkenes and oxidation of organic compounds¹⁵⁻¹⁸.

In this work, a Schiff base ligand was prepared from the reaction between 9,10-phenanthrenquinon and 2-aminothiophenol. Cobalt (II), nickel (II) and copper

(II) complexes with this Schiff base ligand were prepared and characterized.

2. Experimental part

2.1 Chemicals

9,10-phenanthrenquinon and 2-Aminothiophenol were purchased from Shanghai Macklin biochemical. Metal chlorides were purchased from Merck and C.D.H. Ethanol was purchased from ECHO CHEM, DCM was supplied from CHEM-SUPPLY-PTY.LTD. and DMSO and hydrochloric acid were supplied from Thomas Baker for chemicals.

2.2 Instruments

The infrared spectra was measured using Fourier transform infrared spectrophotometer (FT-IR – 8400S) ($4000-400\text{ cm}^{-1}$) from shimadzo using KBr disk. The electronic transitions were measured by UV-Visible spectrophotometer (UV – 1700) from shimadzo. ¹H NMR spectra were measured using NMR Innova 5 Concole with an oxford 500 Magnet device. Thermal analysis was measured by differential thermal gravimeter (DTG-160-FC-60A), while conductivity was measured by WTW SERIES, cond 722. Magnetic susceptibilities were recorded by Auto Balance Magnetic Susceptibility Balance Sherwood Scientific. Melting points were measured using melting point / SMP30 Stuart apparatus.

2.3 Synthesis of Schiff base ligand

9,10-phenanthrenquinon (1gm, 4.803 mmol) in 20 ml

absolute ethanol was mixed with 2-aminothiopenol (1.20gm, 9.61mmol) and three drops of hydrochloric acid were added to this mixture. The solution was refluxed for four hours. A green precipitate of Schiff base ligand was collected by filtration, washed with water and ethanol and recrystallized from ethanol.

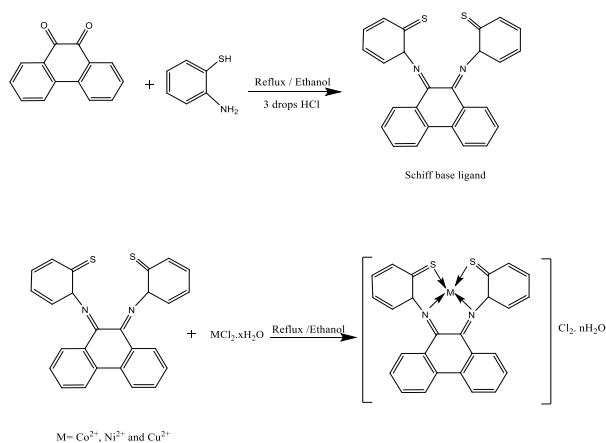
2.4 Synthesis of cobalt (II), nickel (II) and copper (II) complexes

All metal complexes were prepared by dissolving the prepared Schiff base ligand (0.4gm, 0.95mmol) in 20ml ethanol and mixing it with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2252gm, 0.95mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.225 gm, 0.95mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1614gm, 0.95mmol) in 1:1 L:M ratio. The mixture was refluxed for six hours. Blue precipitates were formed for all metal complexes which were filtered, washed with water and ethanol.

3. Results and Discussion

3.1 ligand and metal complexes synthesis

The Schiff base ligand was synthesized by the common used reaction to prepare such compounds, which relies on the condensation of a ketone (9,10-phenanthrenquinone) with an amine (2-aminothiopenol) in 1:2 ratio respectively. The former green ligand was then refluxed with cobalt (II), nickel (II) and copper (II) chlorides to produce their complexes. Scheme (1) shows steps to ligand synthesis and its metal complexes, while Table (1) shows some of the physical properties of the ligand and the complexes.



Scheme (1) Schiff base ligand synthesis with its cobalt (II), nickel (II) and copper (II) complexes

Compound	Yield (%)	Color	M.P.(°C)	Formula weight (g/mol)
Ligand (L)	49	Green	210-212	422.56
[Co(L)]	$\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	78Blue	>350	606.44
[Ni(L)]	$\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	67Blue	>350	606.20
[Cu(L)]	$\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	54Blue	>350	593.04

3.2 FT-IR Spectroscopy

The FT-IR spectra of Schiff base ligand shows a characteristic new band at 1510 cm^{-1} which is

assigned to imino group ($\text{C}=\text{N}$). The formation of this group was also confirmed by the absence of an adsorption band of the NH_2 - in the free 2-Aminothiopenol at 3446-3356 cm^{-1} with the absence of ν ($\text{C}=\text{O}$) group adsorption band at 1674 cm^{-1} in 9,10-phenanthrenquinone. The ν (S-H) vibration frequency in 2-Aminothiopenol which appears at 2522 cm^{-1} as a single band was disappeared in the ligand spectra which suggests its conversion to the thione form ($\text{C}=\text{S}$) at 1325 cm^{-1} . The two bands ($\text{C}=\text{N}$) and ($\text{C}=\text{S}$) were changed when the metal complexes are formed. The ν ($\text{C}=\text{N}$) frequency in all metal complexes was shifted to 1508 cm^{-1} which indicates the metal coordination with ligand through the nitrogen of imino group. While the ν ($\text{C}=\text{S}$) was shifted to 1338 cm^{-1} in Co^{2+} , Cu^{2+} complexes and to 1336 cm^{-1} in Ni^{2+} complex which suggests the metal coordination with ligand through the thione group. New bands appear at 400-600 cm^{-1} refer to M-N and M-S bonds. While a broad band at 3200-3600 cm^{-1} suggests the presence of hydrated water molecule in the complex chemical structure. Table (2) gives a summary of the characteristic bands in the FTIR spectrum of the ligand and how they were shifted upon complex formation.

Compound	ν ($\text{C}=\text{N}$) cm^{-1}	ν ($\text{C}=\text{S}$) cm^{-1}	ν (M-N) cm^{-1}	ν (M-S) cm^{-1}	ν (H_2O) cm^{-1} (hydrated)
Ligand (L)	1510	1325	----	----	----
[Co(L)]	$\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	1508	1338	549	480 3200-3600
[Ni(L)]	$\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	1508	1336	559	472 3200-3600
[Cu(L)]	$\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	1508	1338	507	451 3200-3600

3.3 $^1\text{H-NMR}$ spectrum

The ligand $^1\text{H-NMR}$ spectrum was recorded using DMSO-d_6 as a solvent. This spectrum shows signals in the range δ 6.5-9 ppm which are related to the aromatic protons. And signal between δ 3-4 ppm which was identified to S-H bond in the ligand structure.

3.4 Electronic spectra

Figure (1) illustrates the UV-visible spectra from 200-1000 nm of the ligand and the metal complexes which was measured in dichloromethane as a solvent. While table 3 shows the electronic transitions of the ligand and the metal complexes, molar conductance, magnetic susceptibility and the suggested complexes structure.

The ligand spectra show bands in the range 227-392 nm and bands in the range 598-788 nm which are assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions respectively. In cobalt (II), nickel (II) and copper (II) complexes these bands are shifted which confirm the complexes formation. In cobalt (II) complex the absorption spectra shows a band at 360 nm which is related to INCT (intra-ligand charge transfer). While the four bands at 560, 602, 702 and 779 nm are related to the many transitions in square planar $\text{Co}(\text{II})$ complexes, such as $2\text{A}_1\text{g} \rightarrow 2\text{B}_1\text{g}$, $\text{E}_\text{g} \rightarrow 2\text{B}_1\text{g}$ and $\text{E}_\text{g} \rightarrow 2\text{A}_1\text{g}$.

The absorption spectra of the Ni (II) complex show also four bands. Two bands at 559 and 601 nm which are assigned to the $1A_{1g} \rightarrow 1B_{1g}$ and $1A_{1g} \rightarrow 1A_{2g}$ transitions in square planar complexes and they are characteristic for Ni²⁺ in square planar environment. While bands at 299 and 359 are related to INCT28. The absorption spectra of the Cu (II) complex also exhibit four bands. Two bands at 551 and 594 nm which are assigned to the $2B_{1g} \rightarrow 2B_{2g}$ and $2B_{1g} \rightarrow 2E_g$ transitions in square planar Cu²⁺ complexes. While bands at 293 and 308 are related to INCT29.

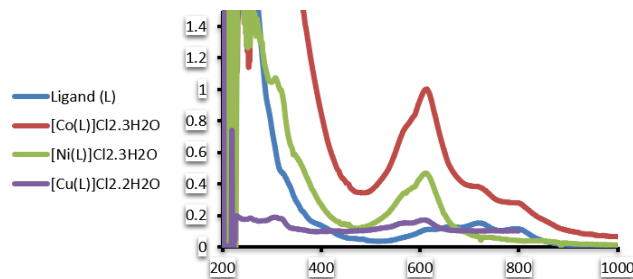


Figure (1) UV-visible spectra of L, Co (II), Ni (II) and Cu (II) complexes

Table (3) Electronic transitions with their wavelengths of the ligand and metal complexes, molar conductance, magnetic susceptibility and the suggested complex structure.

Compound	$\lambda_{max}(nm)$	Type of Transition	Molar conductance $\times 10^{-3}$ Ohm ⁻¹ cm ² mol ⁻¹ in DMSO	Magnetic Susceptibility (B.M)	Suggested complex structure
Ligand (L)	314, 392	$\pi \rightarrow \pi^*$	---	---	---
[Co(L)] Cl ₂ .3H ₂ O	598, 650, 712, 788	$n \rightarrow \pi^*$	360	1.51 (Para.)	square planar
[Ni(L)] Cl ₂ .3H ₂ O	299, 359	INCT	79	0.0 (Dia.)	square planar
[Cu(L)] Cl ₂ .2H ₂ O	293, 308	INCT	78	1.48 (Para.)	square planar

3.5 Molar Conductance measurements

As shown in table (3) the conductivity of the prepared complexes with the concentration 1×10^{-3} M were recorded in DMSO as a solvent. It's obvious from the conductance measurements (70-80) Ohm⁻¹ cm² mol⁻¹ that all three complexes are electrolytes and the complexes are considered to be 1:2 electrolyte type.

3.6 Magnetic Susceptibility

From the magnetic susceptibility values which are shown in table (3) it's clear that Co (II) complex is paramagnetic and it is found as a low spin complex with +2 oxidation state. The complex gives a magnetic susceptibility value equal to 1.51 B.M which agrees with the presence of one unpaired electron in d-orbital and the presence of Co (II) complex in square planar geometry. While Ni (II) complex gives a magnetic susceptibility value equal to zero which suggests the diamagnetic properties of nickel (II) complex and also supports the square planar geometry of it. For Cu (II) complex with a low $\mu_{eff} = 1.48$ B.M also suggests the paramagnetic properties of this ion and agrees with the square planar structure of Cu(II) complex.

3.7 Thermal Analysis

The thermal analysis was carried out under the nitrogen atmosphere at a rate of 20 °C/min with a temperature range 0-700 °C and 0-800 °C. Figure (2) shows the TG curves for the ligand and the metal complexes. While table (4) gives a summary for the decomposition temperature range and the mass loss from all the studied compounds. In Figure (2) the

early stages of ligand decomposition show the loss of moisture and the other volatile species in the temperature range 43-305 °C. while the other two decomposition steps refer to the loss of some of the ligand moiety in the range 305-771 °C. In Co (II) complex the TG curve shows the loss of one lattice water molecule from the outer sphere in the temperature range 64-198 °C with a mass loss of 2.890%. While the other two lattice water molecule and the two chloride ions from the outer sphere were lost in the temperature range 198-333 °C and 333-502 °C with a mass loss of 6.313% and 11.762% respectively. The last decomposition step leads to more of Co (II) complex decomposition when the temperature is between 502 and 639 and this shows the loss of some of the organic ligand molecule with a mass loss of 40.114%. The same explanation for Ni (II) and Cu (II) complex thermal decomposition is shown in table (4).

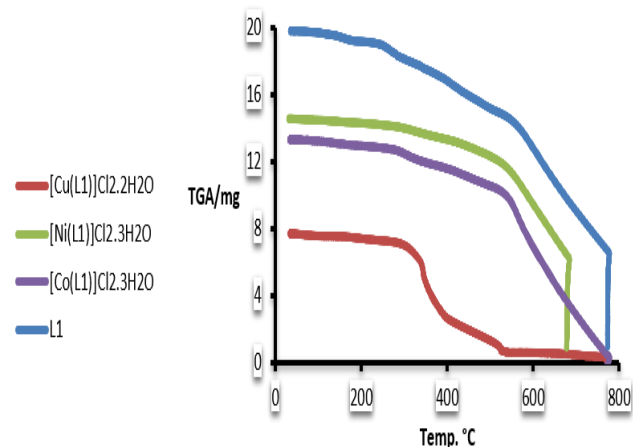


Figure (2) TG curves for L, Co (II), Ni (II) and Cu (II) complexes

Table (4) thermal decomposition data for L1, [Co(L1)] Cl₂. 3H₂O, [Ni(L1)] Cl₂. 3H₂O and [Cu(L1)] Cl₂. 2H₂O

Compound	Steps of Degradation	Temperature Range °C	Mass Loss %	Type of Lost Species
Ligand (L)	1	43-170	33.2	moisture
	2	170-305	5.664	-CN
	3	305-506	15.116	-2S
	4	506-771	42.300	-N + -2(C ₆ H ₆)
[Co(L)] Cl ₂ .3H ₂ O	1	64-198	2.890	-H ₂ O
	2	198-333	6.313	-2H ₂ O
	3	333-502	11.762	-2Cl-
	4	502-639	40.114	-2(C ₆ H ₅ S + N)
[Ni(L)] Cl ₂ .3H ₂ O	1	60-269	2.551	-H ₂ O
	2	269-410	5.096	-2H ₂ O
	3	410-544	11.828	-2Cl-
	4	544-633	37.464	-2(C ₆ H ₅ S)
[Cu(L)] Cl ₂ .2H ₂ O	1	38-178	2.105	-H ₂ O
	2	178-376	52	-H ₂ O + -2Cl+ -2 (C ₆ H ₅ S)
	3	376-526	39	-(C ₁₄ H ₈ N ₂)

4. Conclusion

A Schiff base ligand was synthesized from the condensation reaction between 9,10-phenanthrenequinone and 2-aminothiophenol in 1:2 molar ratio respectively. This ligand acts as tetradentate ligand and coordinates with cobalt (II), nickel (II) and copper (II) through its imine and thione groups. This coordination occurs in 1:1 molar ratio of ligand: metal respectively. The ligand was characterized by the ¹H-NMR and FTIR, while the three prepared complexes were characterized by FTIR, UV-visible, thermal analysis, molar conductance and magnetic susceptibility measurements. According to these available results the suggested structure of the prepared complexes is the square planar.

5. Acknowledgements

The authors would like to thank Department of Chemistry, College of Science for Women, University of Babylon for providing all the facilities to accomplish this work.

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