

Preparation and Characterization of new benzyl -2- [phenyl(pyridin-4 yl) methylidene] hydrazinecarbodithioate Schiff base and its Cu(II) and Ni(II) metal complexesAbeer Khalid Yaseen

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Abstract

A novel tridentate Schiff base has been prepared from the condensation of phenyl(pyridin-4-yl)methanone, the Schiff base was then reacted with transition metal salts Cu(II) and Ni(II) to form coordinated complexes. The novel Schiff base benzyl -2-[phenyl(pyridin-4-yl)methylidene]hydrazinecarbodithioate and the new metal complexes were characterized *via* various physico-chemical and spectroscopic techniques. The metal complexes are expected to be octahedral in geometry based on physico-chemical and spectroscopic analyses.

Introduction

There has been an increasing growth in the preparation, reactivity and structure of the Schiff bases because of their wide and potential applications in catalysis, ligand modeling, material chemistry and biological activity ^[1-3]. Beside, Schiff bases were largely used as a ligands in coordination with metal ion due to their electron donor and chelating ability ^[4-8].

New Schiff base benzyl -2-[phenyl(pyridin-4-yl)methylidene] hydrazinecarbodithioate (L4) was synthesized from the condensation reaction of phenyl(pyridin-4-yl)methanone with benzyl hydrazinecarbodithioate, also two metal complexes were prepared by reacting L4 with copper(II) acetate and nickel(II) acetate.

Experimental

Materials

Chemicals that have been used in this research are: phenyl(pyridin-4-yl)methanone (BDH), benzyl chloride (Acros), potassium hydroxide (BDH), hydrazine hydrate (Fluka), carbon disulphide (BDH), Cupper(II) acetate trihydrate (BDH), Cobalt (II)acetate hexahydrate (fluka). All chemicals were of analytical grade and were used as supplied without any further purification. Absolute ethanol (99.99%, BDH), dimethyl sulphoxide (DMSO) (99% BDH),

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Diethyl ether (fluka). All chemicals were of analytical grade and were used as supplied without any further purification.

Physical measurements

The infrared spectra of the prepared compounds were recorded using FT-IR-8300-Shimadzu, in the wave length range of (4000-400) cm^{-1} . Carbon, hydrogen, nitrogen and sulfur analyses were carried out using a Leco CHNS-932 analyzer. The electronic spectra obtained using (UV-Vis-160A) Shimadzu Spectrophotometer, in the range of wave-length (200-1100 nm). The magnetic susceptibility values using (Magnetic Susceptibility Balance), of Johnson mattey catalytic system division using atomic absorption technique by Perkin-Elmer-5000 to (Cu^{+2} , Ni^{+2}) metal ions. The molar conductivity measurements were carried out using Wissenschaftlich-Technisch Werk- -statten 8120 Weilheim I.O.B, Drucker-Printer. Melting point apparatus of Gallen kamp M.F.B 600.01 was used to measure the melting points of all prepared compounds.

Preparation of benzyl hydrazinecarbodithioate, (Ali and Tarafder, 1976)

Firstly (0.2mol) of KOH pellets was dissolved in 70 ml of absolute ethanol, 10 ml of hydrazine hydrate (0.2mol) was added slowly to the solution. The mixture was cooled down in ice-salt bath to $\sim 0^\circ \text{C}$. 12.0 ml of carbon disulphide was added drop wise during this time, two layers formed. The bottom layer which is light-brown color was separated and dissolved in 40ml of 50% ethanol. 23.0 ml of benzyl chloride was added drop wise. The white precipitate formed was filtered off and washed it with small amount of ethanol. The white product was SBDTC After drying, the product was recrystallized and dried over silica gel with a melting point around 124°C and percentage yield is 87.0%

Preparation of Schiff base by condensation reaction

(0.01 mole) of was dissolved in 95% ethanol by heating. An equimolar of 4-benzoylpyridine was dissolved in ethanol 95% by heating, the two solutions were mixed together and heated until the light yellow color crystals formed which were filtered off and washed with ethanol dried in room temperature. The Schiff base obtained has a melting point around 186°C .

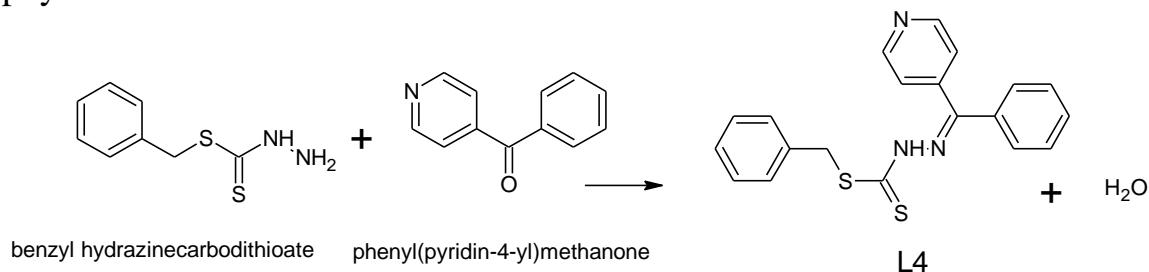
Preparation of metal complexes

0.5 g of Schiff base L4 was dissolved in 40 ml ethanol 95% and heated. A half molar of metal salt was dissolved in ethanol 95% and heated. Both solution were mixed together and heated. Then the mixture was allowed to cool and the precipitate formed was filtered off. The complex formed was dark in color and was then dried at room temperature. The metal complex obtained has a melting point higher than the from Schiff base.

Results and discussions

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The synthesis equation of new L4 Schiff base is shown in scheme 1. The percentage of carbon, hydrogen, nitrogen and sulfur of the compound and the physical data were listed in table 1.



Scheme 1: Preparation reaction of L4 ligand

The analytical results were found nearly same to the calculated value. The formula for Schiff base and the molecular formula of the metal complexes is as shown in Table 1. All the complexes have two ligands attached to metal center

Table 1: physical properties and CHNS of the synthesized compounds

Compound	Colour	Yield%	Melting point (°C) ± 1 °C	% Found(calculated)				
				%C	%H	% N	%S	%M
L4 C ₂₀ H ₁₇ N ₃ S ₂	Yellow	65.6	195.7	68.89 (66.08)	4.32 (4.71)	12.66 (11.56)	19.14 (17.64)	-
Cu(L4) ₂ C ₄₀ H ₃₆ CuN ₆ S ₄	Dark brown	48.5	225.4	54.38 (60.62)	4.76 (5.82)	7.97 (7.58)	14.07 (11.57)	8.12 (7.80)
Ni(L4) ₂ C ₄₀ H ₃₆ NiN ₆ S ₄	Yellowish brown	49.3	202.1	55.18 (60.62)	5.18 (4.58)	12.92 (10.60)	19.76 (16.18)	7.68 (8.02)

Fourier Transform Infrared Spectroscopy (FTIR)

The results of interpreted data from the spectrum of Fourier Transform Infrared Spectroscopy (FTIR) are as shown in table 2

In Schiff base, there is no peak assigned to C=S it's indicating that the Schiff bases appear in thiole form. There are peak at *ca*(1656 cm⁻¹) which attribute to C=N, from this observation, it is concluded that the Schiff bases are formed via condensation reaction in which the primary amine reacted with the carbonyl group to yield the respective product.

For complexes of nickel and copper, there are peak assigned at *ca.*, 972 cm⁻¹ 839 cm⁻¹, (bending) which attribute to C-S, This only can happen if ligand in thiole forms. It indicating that the ligand were undergoes deprotonated and acted as tridentate uni-negative (NNS-) chelating agents. In Schiff base C=N showed at peak (1656 cm⁻¹) but as we can see that in the metal complexes, it is shift to the lower frequency to 1560 cm⁻¹ and 1598 cm⁻¹) this indicating that the metal bonded through azomethine nitrogen atom, ν (N-N) was also shifted to lower due to complexation with central metal ion [9-11].

Table 2: Fourier Transform Infrared Spectroscopy (FT IR) data

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Compound	ν (C=N)	ν (C-S)	ν (N-N)
SB4BPY	1656	-	1054
Cu(L4) ₂	1560	972	1022
Ni(SB4BPY) ₂	1598	839	1028

Magnetic susceptibility and molar conductivity measurement

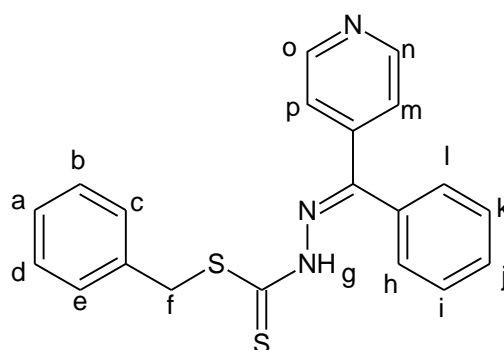
The magnetic susceptibility measurements of the two metal complexes at room temperature both are paramagnetic complexes. The conductivities in the range of 30-35 $\Omega^{-1}\text{cm}^2\text{mole}^{-1}$ are found 1:1 electrolyte type while 60-65 $\Omega^{-1}\text{cm}^2\text{mole}^{-1}$ are found 2:1 electrolyte type [12]. This indicates that both complexes are non-electrolytes and Schiff bases are still coordinated to the central metal ion in DMSO. Furthermore, the non-electrolytic nature of the complexes proves that the Schiff bases is coordinated to the metal ion as uninegatively charged bidentate species via the azomethine nitrogen atom and the mercapto sulphur atom [13-15].

Table 3: Magnetic moment and molar conductivity

Compound	μ_{eff}	λ_M ($\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$)
CuL _{A2}	1.42	12.78
NiL _{A2}	1.34	18.11

Nuclear Magnetic Resonance (NMR) Spectroscopic Analyses

For the NMR analysis, the products were dissolved in dimethyl sulphoxide. proton NMR and C-13 NMR were done. The result are shown in units of parts per million. Metal complexes were not analyzed using this method because the magnetic susceptibility measurements were not done for these complexes.



L4

Table 4a: Protocol of the ¹H assignment

Shift (ppm)	Node
8.7611	o
8.7496	n
8.5913	m

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7.4353	I
7.4169	h
7.3550	b
7.3344	c
4.4672	f

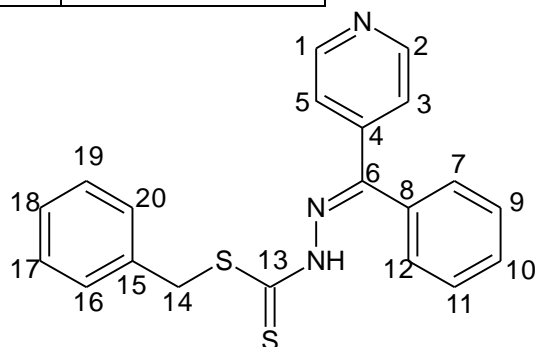


Table 4b: protocol of the ¹³C assignment

Shift (ppm)	Node
198.730	13
150.4105	1
150.2035	2
129.3205	12
128.9069	9
128.7804	11
128.5274	17
127.5155	18
127.3085	20
127.2510	16
123.7207	5

Based on the ¹H and ¹³C assignments of the structure of L4 ligand the peaks are satisfied with expected results. There are some peak does not appear in the spectrum because there were some overlapping due to the symmetrical structure. the carbon group 13 was a singlet group and it was a 198.6730 ppm because it was deshielded by two sulphur atom and a nitrogen atom ^[16-24].

Ultra Violet /Visible Analyses

The prepared solution from the compounds were run at UV/V is bands in the region 200-1000 nm. The compounds were dissolved in dimethyl sulfoxide (DMSO). In the Russell –Saunders states, the electronic states were splitting in the presence of crystal fields, The rise to the electronic absorption bands in the UV/V is spectra of the complexes are the results from the transition electrons between the levels .

As we see from Table 5 below, the Schiff base ligand shows the absorption on n-π* and π- π* which give band around (≈200 nm- 300 nm) he electronic spectra region which are attribute to charge transfer. While for copper

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(II) and nickel,(II) complexes, mostly gave bands at 623 nm and 641 nm respectively which attribute to d-d transition [25-27].

Table 5: Ultraviolet /Visible analysis data

Compound	$\lambda_{\max}(\text{nm})$
Schiff base ligand (L4)	257(4.5), 297(4.0), 339(4,0)
Cu(L4) ₂	251(4.57), 623(3.01)
NiL(4) ₂	262(4.44), 641(3.54)

CONCLUSION

New Schiff bases was successfully synthesized in alkaline medium through the Schiff bases condensation reaction. The FTIR results shows that the Schiff base exist in thione form because its contain functional group of –NH(C=S)SR, while the metal complexes contain two ligands. Based on the Ultraviolet / Visible analyses, its shows that the Schiff base have absorption on $n-\pi^*$ and $\pi-\pi^*$ while the metal complexes have absorption on the d-d transition. The result of the magnetic susceptibility measurement indicates the octahedral geometry for Cu(L4)₂ while Ni(L4)₂ tends to be square planner geometry.

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