

Syntheses and Investigations on Coordination Compounds Having Oxygen and Nitrogen Donors

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Abstract

A bidentate ligand (L), {[3-hydroxy-1-methylbutyl)-2-en-1-ylidene]amino} hexanoic acid, derived from acetylacetone and 6-aminocaproic acid and its cobalt(II), nickel(II) and copper(II) complexes have been synthesized and characterized by metal analysis, molar conductances, magnetic moments, IR and electronic spectral measurements. The stoichiometric reaction between the metal(II) ion and the synthesized ligand in molar ratio of M:L (1:2) forms the metal complexes of type $[M(L)_2(H_2O)_2]$ (where M = Co(II), Ni(II) or Cu(II)), and of M:L (1:1) of type $[M(L)(H_2O)_2] Cl$ (where M = Ni(II) or Cu(II) and Co:L (1:1) of type $[Co(L)(H_2O)_4] Cl$. Infrared spectra of all the complexes agree that the complexes with the coordination to the central metal ion through the nitrogen of azomethine group and the negative oxygen atom of the carboxylate group. The magnetic moment data suggested for the complexes with metal : ligand ratio as 1:2 and of Co:L (1:1) to have an octahedral geometry around the central metal ion and a square planar configuration for nickel and copper complexes with the metal : ligand ratio as 1:1. The electronic spectral data also agree with their proposed structures.

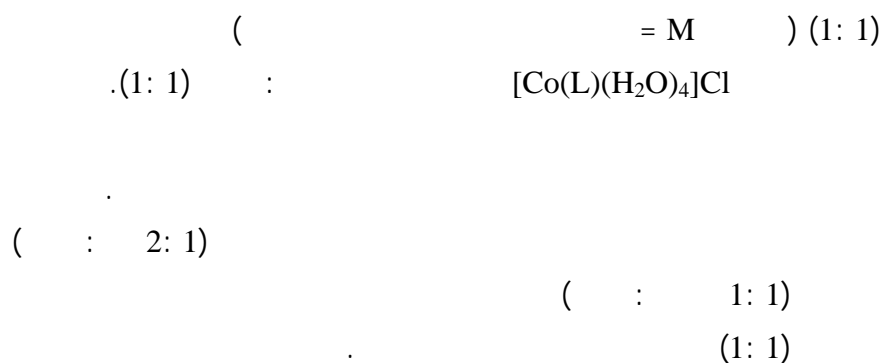
-2-(-1- -3)]} (L)

{ [-1-
-6

$[M(L)_2(H_2O)_2]$

= M) (2: 1) :

: $[M(L)(H_2O)_2]Cl$ (



Introduction

The study of the transition metal complexes of β -diketones have been known for many years and have been extensively studied⁽¹⁻⁴⁾. Several ligands derived from β -diketones are also known to form metal complexes⁽²⁾. These ligands derived from β -diketones have been employed for the preparation of new complexes⁽³⁾. The β -diketone ligands are considered as potential ligands due to their enol form. Schiff bases and the relevant transition metal complexes are still found to be of great interest in coordination chemistry⁽⁵⁻⁷⁾ although this subject has been extensively studied⁽⁸⁻¹¹⁾. Chemists have reported on the chemical, structural and biological properties of Schiff bases and their complexes because they are an important class of ligands in coordination chemistry and find extensive applications in different spheres⁽¹²⁻¹⁷⁾. Bidentate Schiff bases with a NO donor atom set are well known to coordinate with various metal ions, and this has attracted the interest of many authors⁽¹⁸⁻²⁰⁾. Nitrogen and oxygen, the first members of the respective groups have simple properties. The ligand bonding through nitrogen and oxygen to the central metal ions form an important class of biologically active ligands⁽²¹⁾, and

provide models for metal-ligand binding sites in several enzymes⁽²²⁾. It is believed that ligands containing NO type form more stable complexes than either OO or NN types⁽²³⁾.

Keeping this in view, and the variety of possible Schiff base metal complexes with wide choice of ligands, and coordination environments, has prompted us to undertake research in this area. In the present study, a Schiff base has been synthesized using acetylacetone and 6-aminocaproic acid. This bidentate ligand forms 1:2 and 1:1 complexes with Co(II), Ni(II) and Cu(II) ions (Figures 1,2 and 3).

Experimental

All the chemicals used throughout investigation were of Analar, B.D.H., Aldrich and Fluka grade, used as supplied without further purification, all metal(II) were used as chloride salts.

Analysis and physical measurements :

The metal contents were determined according to the standard procedure⁽²⁴⁾. Melting points were determined by using Electrothermal 9300 digital melting point apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 0.001 M of the complexes in dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400 cm^{-1}

¹ range using KBr disc. Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in DMF at 25°C for 0.001 M solution of the compounds using a 1 cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined by the Faraday method at room temperature using a Bruker BM6 apparatus.

Synthesis of the ligand (L) :

An ethanolic solution of acetylacetone (0.01 mol.) was added to aqueous solution of 6-aminocaproic acid (0.01 mol.) and refluxed for 6 hours followed by concentration of the solution. The precipitate was separated by filtration, washed with ether and then dried in air.

Synthesis of the complexes :

A solution of the ligand in ethanol (50 mL) was added to a stirred solution of metal(II) chloride in ethanol (50 mL) having a required molar ratio of M:L (1:2 and 1:1). The mixture was

refluxed for 3 hours. The solid thus obtained was filtered, washed with ether and finally dried in air.

Results and discussion

All metal(II) complexes were prepared by using the respective metal salts as chloride with the ligand in two different molar ratios of metal:ligand as 1:2 and 1:1. All these complexes are colored and moisture stable solids. They are insoluble in common organic solvents and only soluble in DMF, except the nickel complex, $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$, is even very poor soluble in DMF. Molar conductance values of the soluble complexes in DMF indicated that complexes having molar ratio of metal:ligand as 1:2 have lower values (Table 1) indicating that they are all nonelectrolytic in nature. However, the complexes having molar ratio of metal:ligand as 1:1 showed higher values (Table 1) indicating them as electrolytic⁽²⁵⁾.

Table 1. Analytical and some physical properties of the compounds

Compound	m.p °C	Colour	Yield %	%Metal Calc. (Found)	$\Lambda_{\text{M}}(\text{DMF})$ $\text{cm}^2\text{ohm}^{-1}\text{mol}^{-1}$
L	252	Yellow	69	-----	-----
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$	382	Purple	73	11.35 (10.72)	19
$[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$	391	Beige	78	11.31 (11.91)	Very poor insoluble
$[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$	345	Olive	62	12.13 (11.75)	14
$[\text{Co}(\text{L})(\text{H}_2\text{O})_4]\text{Cl}$	299	Gray	77	15.57 (14.96)	88
$[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}$	270	Pale yellow	69	17.15 (17.78)	74
$[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}$	320	Brown	51	18.30 (17.41)	69

IR spectra

The IR spectrum of the Schiff base ligand shows the absence of bands at 3250 and 1709 cm^{-1} due to $\text{V}(\text{NH}_2)$ group of 6-aminocaproic acid and $\text{V}(\text{C}=\text{O})$ of acetylacetone, respectively. Instead, a new prominent band at 1629 cm^{-1} due to azomethine $\text{V}(\text{C}=\text{N})$ linkage appeared in the free ligand indicating that condensation between ketone moiety of acetylacetone and that of amino group of 6-aminocaproic acid has taken place resulting into formation of the Schiff base ligand⁽²⁶⁾. Also, the presence of bands at 3419 and 1540 cm^{-1} due to $\text{V}(\text{OH})$ and $\text{V}(\text{C}=\text{C})$ in the free ligand, respectively, clearly gave an evidence of establishing keto-enol tautomeric system in which this ligand behaves as enol⁽²⁷⁾. In the infrared spectra of the all complexes; the $\text{V}(\text{C}=\text{N})$ band suffers some sort of perturbation which shows a negative shift for the stretching vibration of azomethine group (Table 2). This perturbation in the spectra suggested coordination through the azomethine nitrogen atom with the metal(II) ion⁽²⁸⁾. In the ligand the asymmetric and symmetric stretching vibration of the carboxylate group, $\text{V}_s(\text{COO})$ and $\text{V}_a(\text{COO})$ appear at 1684 and 1438 cm^{-1} , respectively. In the complexes, these bands occur at (1616-1605) and (1416-1410) cm^{-1} , with difference $\Delta\text{V}(\text{COO})$ of (200-193) cm^{-1} and indicate the unidenticity of the carboxylate group (Table 2)⁽²⁹⁾. Also, the weak bands appear within the region (2774-2503) in the ligand spectrum are due to the hydroxyl stretching of the (COOH)

group. These several weak bands are absent in the all spectra of complexes, which were an evidence that the ligand loses a proton, and it is worthwhile mentioning here that 6-aminocaproic acid exists as zwitter ion, NH_3^+ AA. COO^- (AA means Amino Acid). These overall data suggest that the azomethine-N and carboxylate-O groups are involved in coordination with the metal(II) ion in complexes. In the low frequency region, spectra of the metal(II) complexes exhibit new bands which are not present in the spectra of the ligand. These bands are located at (515-511) and (477-422) cm^{-1} , which are attributed to $\text{V}(\text{M}-\text{O})$ and $\text{V}(\text{M}-\text{N})$ ⁽³⁰⁾, respectively. The broad band in the region (3551-3423) cm^{-1} was observed in all the complexes spectra, indicates the presence of coordinated water⁽³⁰⁾. Also the coordinated water in all the metal(II) complexes presents different peaks in the regions (934-840) and (743-656) cm^{-1} which could be assigned to rocking and wagging modes⁽³⁰⁾, respectively, support the presence of coordinated water. Finally, the $\text{V}(\text{C}=\text{N})$ band for the Ni(II) complex, $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$, is not observed in the IR spectrum since it is hidden under the strong band of $\text{V}_s(\text{COO})$ at 1605 cm^{-1} , also both the two bands of $\text{V}_s(\text{COO})$ for the complexes $[\text{Co}(\text{L})(\text{H}_2\text{O})_4]\text{Cl}$ and $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}$ are not observed in the IR spectra since they are hidden under the broad and strong bands of $\text{V}(\text{C}=\text{N})$.

Table 2. Important IR spectral bands (cm⁻¹)

Compound	$\nu(\text{C}=\text{N})$	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{H}_2\text{O})$ Rocking	$\nu(\text{H}_2\text{O})$ Wagging
L	1629	1684	1438	-----	-----	-----
[Co(L) ₂ (H ₂ O) ₂]	1593	1605	1412	3550	840	734
[Ni(L) ₂ (H ₂ O) ₂]	Hidden	1605	1411	3452	934	656
[Cu(L) ₂ (H ₂ O) ₂]	1556	1608	1415	3450	894	731
[Co(L)(H ₂ O) ₄]Cl	1556	Hidden	1410	3551	840	700
[Ni(L)(H ₂ O) ₂]Cl	1597	Hidden	1414	3423	872	670
[Cu(L)(H ₂ O) ₂]Cl	1557	1616	1416	3449	894	743

Electronic spectra and magnetic moments :

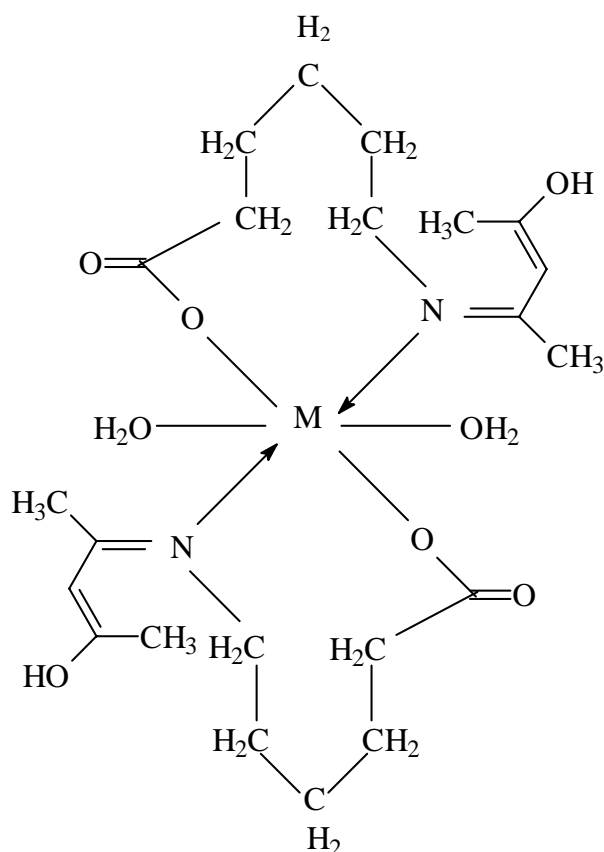
The [Co(L)₂(H₂O)₂] complex exhibits bands at 15151 cm⁻¹ and a band at 21097 cm⁻¹ (Table 3) are assigned to the transitions ⁴T_{1g}(F) → ⁴T_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) for a high spin octahedral geometry⁽³¹⁾. A band at 26315 cm⁻¹ was assigned to the metal to ligand charge transfer. The magnetic susceptibility measurement (4.81 B.M.) for the solid Co(II) complex is also indicative of three unpaired electrons per Co(II) ion suggesting consistency with their octahedral environment⁽³²⁾. The [Co(L)(H₂O)₄]Cl complex exhibits three bands were observed at 14836, 16447 and 25773 cm⁻¹, assigned to ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g} → ⁴T_{1g}(P) and the metal to ligand charge transfer⁽³¹⁾, respectively. The magnetic moment obtained for [Co(L)(H₂O)₄]Cl (Table 3) is in favor to infer the presence of high spin octahedral geometry around the central cobalt(II)⁽³²⁾. The electronic spectral study of the complex [Ni(L)₂(H₂O)₂] was unsuccessful due to its poor solubility in common organic solvents such as DMF and actually it shows a band at 26178 cm⁻¹ may be assigned to the metal to ligand charge transfer. The magnetic

measurement (3.11 B.M.) showed two unpaired electrons for Ni(II) ion suggesting an octahedral geometry⁽³³⁾. The electronic spectrum of [Ni(L)(H₂O)₂]Cl shows a band at 23364

cm⁻¹, which is attributed to ¹A_{1g} → ¹A_{2g} transition⁽³⁴⁾, supporting the square planar structure of nickel complex. Also the nickel complex is diamagnetic, suggesting square planar geometry for the metal ion⁽³⁵⁾. The electronic spectrum of [Cu(L)₂(H₂O)₂] shows a low energy band at 15015 cm⁻¹ and a strong high energy band at 28409 cm⁻¹. The low energy band in this position typically is expected for an octahedral configuration, corresponding to the transition ²E_g → ²T_{2g}⁽³¹⁾. The strong high energy band is assigned to metal → ligand charge transfer. Also, the magnetic moment value (2.27 B.M.) for this complex showed one unpaired electron for Cu(II) suggesting an octahedral geometry (Table 3)⁽³⁵⁾. [Cu(L)(H₂O)₂]Cl shows a d-d band at 23041 cm⁻¹ due to ²B_{1g} → ²A_{1g} transition, which supports square planar geometry⁽³⁴⁾. The magnetic moment (1.71 B.M.) lies in the region expected for square planar complexes⁽³⁵⁾.

Table 3. Electronic spectral data (cm⁻¹) and magnetic moments (B.M) of the complexes

Complexes	Absorption region (cm ⁻¹)	Possible assignments	μ_{eff} (B.M)	Geometry
[Co(L) ₂ (H ₂ O) ₂]	26315	Charge transfer	4.81	Octahedral
	21097	⁴ T _{1g} (F) → ⁴ T _{1g} (P)		
	15151	⁴ T _{1g} (F) → ⁴ T _{2g} (F)		
[Ni(L) ₂ (H ₂ O) ₂]	26178	Charge transfer	3.11	Octahedral
[Cu(L) ₂ (H ₂ O) ₂]	28409	Charge transfer	2.27	Octahedral
	15015	² E _g → ² T _{2g}		
[Co(L)(H ₂ O) ₄]Cl	25773	Charge transfer	4.72	Octahedral
	16447	⁴ T _{1g} (F) → ⁴ T _{1g} (P)		
	14836	⁴ T _{1g} (F) → ⁴ T _{2g} (F)		
[Ni(L)(H ₂ O) ₂]Cl	23364	¹ A _{1g} → ¹ A _{2g}	Diamagnetic	Square planar
[Cu(L)(H ₂ O) ₂]Cl	23041	² B _{1g} → ² A _{1g}	1.71	Square planar



**Figure 1. The proposed structure of [M(L)₂(H₂O)₂]
M=Co(II) , Ni(II) or Cu(II)**

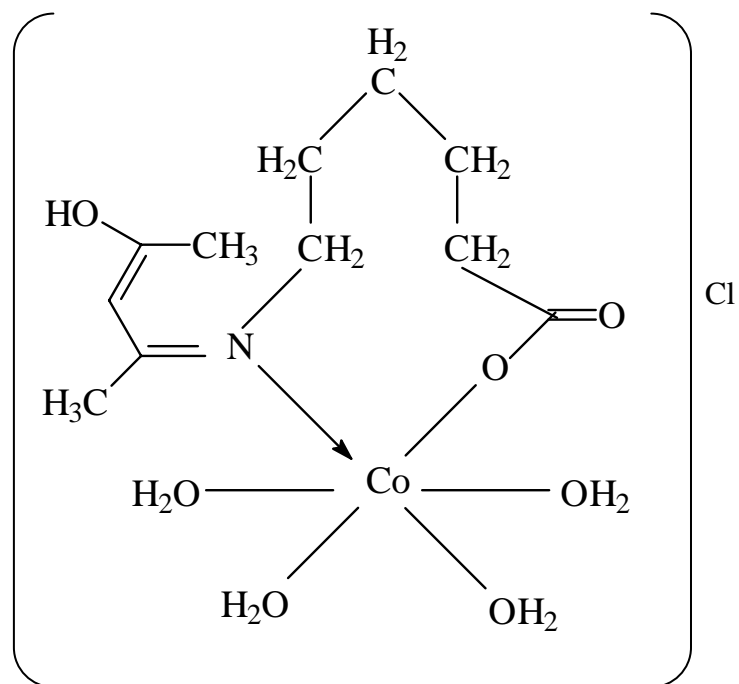


Figure 2. The proposed structure of $[\text{Co}(\text{L})(\text{H}_2\text{O})_4]\text{Cl}$

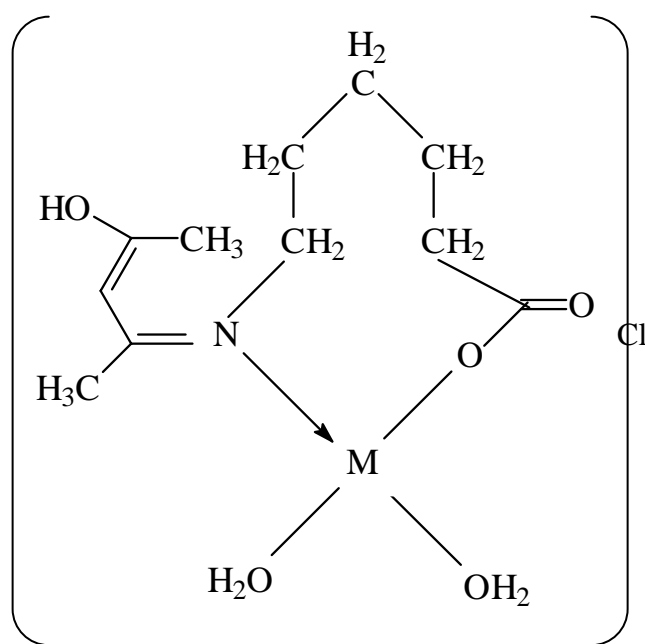


Figure 3. The proposed structure of $[\text{M}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}$

M=Ni(II) or Cu(II)

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