

Copper (II) Complexes of Schiff Base derived from Vanilline and aminohydroxamic acid

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Abstract : Copper (II) complexes of Schiff base derived from Vanilline and 2-amino benzhydroxamin acid have been synthesized and characterized by elemental analysis, molar conductivity, magnetic moments, infrared and electronic spectra. All the complexes were found to be non electrolyte with general formula $[CuL_2B_2]$. Where L is amino acid Schiff base bidentate ligand i.e. 2 (4-hydroxy-3-methoxy benzidine) imino benz hydroxamic acid. B = Bases like water, ammonia, pyridine, quinoline, phenyl isocynaide etc. Suitable structures have been proposed for the complexes.

Keywords : 2-amino benz hydroxamic acid, vanilline, pyridine, quinoline etc.

I. INTRODUCTION

As a ligand with potential nitrogen donors Schiff base of amino hydroxamic acid is interesting and have gained special attention not only because of the structural chemistry of their co-ordination modes but also because of its importance in medicinal chemistry.¹

The ability of amino hydroxamic acid to form stable transition metal complexes is the basis of their usefulness as analytical reagent for the sensitive qualitative & quantitative determinations. Since it is readily associated with both carboxyl and hydroxylamine, it is reported to possess wide range of biological activities against bacteria, fungi & certain types of tumors.²

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II. MATERIAL & METHOD

All the chemicals used in the present work were either of E-Merck extrapure or BDH (AR) quality. The complexes were prepared by conventional method i.e. by treating ligand with Cu (II) salts in the presence of bases like water, ammonia, pyridine etc. in each case. The ligand & Cu (II) complexes were prepared as :

Preparation of Ligand

An alcoholic solution of Vanilline (0.2 mole) was mixed with the alcoholic (0.2 mole). The resulting solution was refluxed at water bath for two hours. After cooling in freezer, faint orange colour solid was obtained. The mp. of ligand was obtained to be 54⁰C.

Preparation of Cu (II) complex

The ethanolic solution of ligand was added to ethanolic solution of Cu (II) acetate chloride with regular and gradual shaking & stirring in the presence of bases like water, ammonia, pyridine etc. in each case. The resulting solution was then refluxed for an hour on water bath. After allowing the solution to stand overnight, crystals of different colours were separated out. The crystals were separated by filtration, washed with a small amount of acetone & then dried over KOH.

The ligand & Cu (II) complexes were characterised further by analytical method (Table-1) using standard procedure, IR spectra (on perking Elemer 577 spectrophotometer) electronic spectra (Hitachi 320 spectrophotometer) magnetic moment (Gouy's method using $\text{HgCO}(\text{SCN})_4$ as Calibrant) and conductivity measurement by conductivity meter bridge.

Table – 1

Analytical data of $[\text{Co}(\text{L})_2\text{B}_2]$ Complexes : Found (calculated)

Complexes	Metal	C	H	N
1. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$	8.76 (8.85)	54.08 (54.14)	4.55 (4.51)	8.45 (8.42)
2. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{NH}_3)_2]$	8.80 (8.88)	54.22 (54.30)	4.85 (4.82)	12.70 (12.67)
3. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{C}_6\text{H}_5\text{NC})_2]$ (Ph-isocynaide)	6.98 (7.05)	63.14 (63.24)	4.35 (4.31)	10.10 (10.06)
4. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{C}_9\text{H}_7\text{N})_2]$ (quinoline)	6.56 (6.64)	56.80 (64.94)	4.54 (4.51)	9.50 (9.47)
5. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{C}_5\text{H}_5\text{N})_2]$ (Pyridine)	7.40 (7.48)	60.85 (60.99)	4.60 (4.57)	10.70 (10.67)
6. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{C}_5\text{H}_4\text{NCH}_3)_2]$ (α -picoline)	7.15 (7.22)	61.74 (61.84)	4.92 (4.90)	10.32 (10.30)
7. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{C}_5\text{H}_4\text{NCH}_3)_2]$ (β -picoline)	7.14 (7.22)	61.76 (61.84)	4.95 (4.90)	10.35 (10.30)
8. $[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{C}_5\text{H}_4\text{NCH}_3)_2]$ (γ -picoline)	7.16 (7.22)	61.72 (61.84)	4.93 (4.90)	10.31 (10.30)

III. RESULTS AND DISCUSSION

Magnetic behaviour of Cu (II) complexes :

Cu (II) is a $3d^9$ system having one unpaired electron in 3d-orbital. Thus the expected value of magnetic moment in all the cases would be 1.73BM.

But the magnetic moment of CuL_2B_2 complexes were observed to in the range of 1.80 – 1.98 B.M. (Table-2).

Table – 2

Analytical data of [Ni (L)₂ B₂] Complexes

Found (calculated) → %

Complexes	Metal	C	H	N
1. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) ₂ (H ₂ O) ₂]	8.75 (8.83)	54.08 (54.15)	4.54 (4.51)	8.45 (8.42)
2. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) ₂ (NH ₃) ₂]	8.74 (8.85)	54.30 (54.32)	4.86 (4.82)	12.72 (12.67)
3. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) (C ₆ H ₅ NC) ₂] (Ph-isocynaide)	6.98 (7.05)	63.14 (63.24)	4.35 (4.31)	10.12 (10.06)
4. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) (C ₉ H ₇ N) ₂] (quinoline)	6.56 (6.62)	64.81 (64.95)	4.56 (4.50)	9.52 (9.47)
4. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₅ N) ₂] (Pyridine)	7.38 (7.46)	60.90 (61.01)	4.62 (4.57)	10.74 (10.67)
6. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₄ NCH ₃) ₂] (β-picoline)	7.10 (7.20)	61.74 (61.86)	4.96 (4.90)	10.35 (10.31)
7. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₄ NCH ₃) ₂] (β-picoline)	7.06 (7.20)	61.77 (61.86)	4.94 (4.90)	10.38 (10.31)
8. [Ni (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₄ NCH ₃) ₂] (γ-picoline)	7.12 (7.20)	61.70 (61.86)	4.93 (4.90)	10.32 (10.31)

The slightly higher magnetic moments probably results from the spin – orbit coupling, negative value of λ and absence of spin- spin interaction in the complexes.³ This values suggest a distorted octahedral geometry for Cu (II) complexes⁴.

Electronic Spectra of Cu (II) complexes⁶ :

CuL₂B₂ complexes show an intense band at 25000cm⁻¹ and 26500cm⁻¹ respectively is assigned to charge transfer from Ligand to metal. Other two bands observed by each complex at (18500, 16800 Cm⁻¹) may be due to d-d transitions. These bands suggest a square planar geometry.⁵ The spectra of CuL₂B₂ complexes were observed at 16000–16400 (ε-15), 15000-15800 (ε-14), 15800–16000 (ε-15) and 15900–15800 (ε-14), 15800–16000 (ε-15) and 15900–16200 (ε-16) respectively which are indicative of their distorted octahedral structure. (Table-4)

Table – 4

Electronic spectral data of [Co (L)₂ B₂] Complexes

Found (calculated) → %

Complexes	ν_1 (cm ⁻¹)	ϵ	ν_2 (cm ⁻¹)	ϵ	ν_2 (cm ⁻¹)	ϵ	C.T. band
1. [Co (C ₁₅ H ₁₃ N ₂ O ₄) ₂ (H ₂ O) ₂]	8650	2.1	17800	0.0	21600	4.1	33000
2. [Co (C ₁₅ H ₁₃ N ₂ O ₄) ₂ (NH ₃) ₂]	8690	1.4	17400	0.4	20800	3.7	34000
3. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₆ H ₅ NC) ₂]	8750	1.6	16300	1.2	20600	2.9	33500
4. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₉ H ₇ N) ₂]	8690	1.7	17200	0.8	20900	2.8	33200
5. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₅ N) ₂]	8490	1.5	16800	1.0	21200	3.0	33100
6. [Co (C ₁₅ H ₁₃ N ₂ O ₄)(C ₅ H ₄ NCH ₃) ₂]	8650	1.3	16900	1.1	20500	2.6	33400
7. [Co (C ₁₅ H ₁₃ N ₂ O ₄)(C ₅ H ₄ NCH ₃) ₂]	8700	1.8	17500	1.2	20700	2.4	32500
8. [Co (C ₁₅ H ₁₃ N ₂ O ₄)(C ₅ H ₄ NCH ₃) ₂]	8560	1.9	17500	0.7	20200	2.7	33300

IR Spectra⁷

From the IR spectra of the complexes of Cu (II) Cations, it is found that the frequencies due to ν OH and ν OCH₃ vibrations of ligand and complex remain unchanged. This means that –OH & –OCH₃ groups of vanilline are not participating in bond formation with the metal cation indicating that these two groups are not the co-ordination sites of ligand. However, IR spectra of all the Cu (II) complexes show down ward shift of 30-35 cm⁻¹ in ν C=N frequency, 5–10 cm⁻¹ in ν C=N frequency, upward shift of 20-30 cm⁻¹ in ν N=O frequency indicating co-ordination of hydroximino nitrogen atom in the complex formation and deprotonation of hydrogen present in N–OH group.

The co-ordination of nitrogen atom of azomethine >C=N group and hydroximoto nitrogen atom is further confirmed due to the presence of a weak and sharp band in the region of 440-455 cm⁻¹ which was assigned due to ν M–N vibrations.

In case of aquo complexes, the frequency obtained in the range 700 – 800 cm⁻¹ may be attributed due to rocking mode of co-ordinated water. Similarly, the pyridine ring breathing vibrations located around 1000-1040 cm⁻¹ in the complexes have been taken to be characteristic vibrations of co-ordinated pyridine & picoline molecule. In case of phenyl isocyanide complexes, a band around 2090 cm⁻¹ is obtained indicating the participation of nitrogen atom of phenyl isocyanide in the complete formation. (Table 5-6)

Table – 5

Complexes	Colour	M_{eff} (B.M.)	Magnetic nature
1. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$	Light green	2.90	Paramagnetic
2. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{NH}_3)_2]$	Greenish White	2.92	Paramagnetic
3. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_6\text{H}_5\text{NC})_2]$	Faint green	2.96	Paramagnetic
4. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_9\text{H}_7\text{N})_2]$	Yellowish green	2.90	Paramagnetic
4. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_5\text{N})_2]$	Dirty green	2.92	Paramagnetic
6. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	Greenish White	2.94	Paramagnetic
7. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	Greenish White	2.95	Paramagnetic
8. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	Greenish White	2.93	Paramagnetic

Table – 6

Electronic spectral data of $[\text{Ni}(\text{L})_2\text{B}_2]$ Complexes

Found (calculated) → %

Complexes	ν_1 (cm^{-1})	ϵ	ν_2 (cm^{-1})	ϵ	ν_2 (cm^{-1})	ϵ
1. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$	9200	1.2	16200	2.98	24600	4.2
2. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)_2(\text{NH}_3)_2]$	9210	1.1	16100	3.2	24500	4.1
3. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_6\text{H}_5\text{NC})_2]$	9220	1.3	16150	3.0	24550	3.98
4. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_9\text{H}_7\text{N})_2]$	9190	1.4	16250	2.96	24650	4.3
4. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_5\text{N})_2]$	9180	1.3	16200	2.85	24520	4.1
6. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	9160	1.2	16100	2.80	24540	4.1
7. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	9170	1.3	16250	2.98	24580	3.96
8. $[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_4\text{NCH}_3)_2]$	9190	1.2	16100	2.94	24560	3.94

Molar Conductivity :-

Molar conductivity of solutions of complexes were measured by conductivity meter bridge manufactured by Wiss – Techen Wearch stathen type – LBR at room temp. in DMF. The Cell constant was measured at 30°C using N/10 and N/100 KCl solutions. Pure DMF & conductivity water were used as solvents (Table-3).

Table – 3
The magnetic moment data of [Co(L)₂B₂ complexes

Complexes	Colour	M _{eff} (B.M.)	Magnetic nature
1. [Co (C ₁₅ H ₁₃ N ₂ O ₄) ₂ (H ₂ O) ₂]	Faint brown	4.95	Paramagnetic
2. [Co (C ₁₅ H ₁₃ N ₂ O ₄) ₂ (NH ₃) ₂]	Light pink	4.92	Paramagnetic
3. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₆ H ₅ NC) ₂]	Yellowish brown	4.90	Paramagnetic
4. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₉ H ₇ N) ₂]	Pinkish brown	4.94	Paramagnetic
4. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₅ N) ₂]	Pinkish brown	4.86	Paramagnetic
6. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₄ NCH ₃) ₂]	Yellowish brown	4.90	Paramagnetic
7. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₄ NCH ₃) ₂]	Yellowish brown	4.88	Paramagnetic
8. [Co (C ₁₅ H ₁₃ N ₂ O ₄) (C ₅ H ₄ NCH ₃) ₂]	Yellowish brown	4.85	Paramagnetic

Thus on the basis of the elemental analysis, magnetic moment, molar conductance and spectral studies structure of the Cu (II) complexes are proposed to be octahedral in nature.

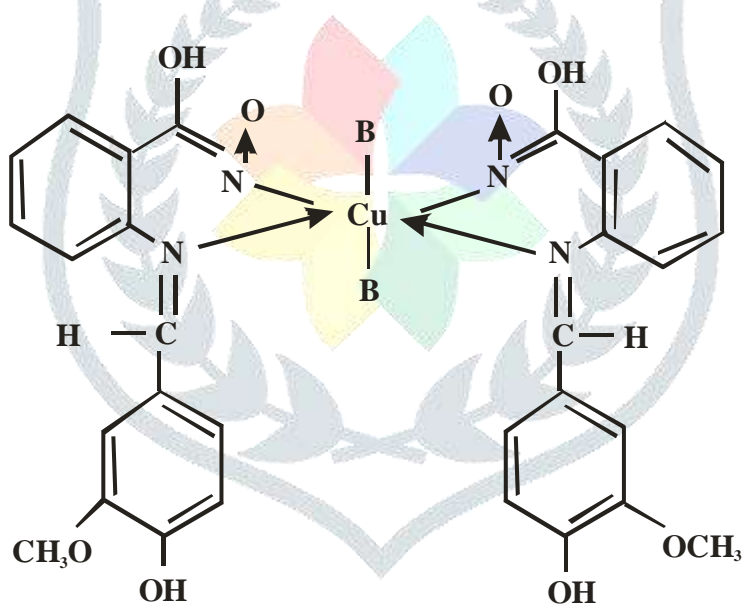


Fig.

B=Water, ammonia, pyridine, quinoline etc.

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