

Role of Metal Complexes of Cu (II), Ni (II), Co (II) and Schiff Bases derived from Heterocyclic Amines

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ABSTRACT

Coordination compound plays a very significant role in our lives. Schiff base ligand are considered privileged ligand because they are easily prepared by the condensation between aldehyde and amines. The metal complexes formed by ligand containing sulphur, nitrogen and oxygen are of immense importance due to exhibiting anticancer, antiviral, anti-bacterial and antifungal properties. Schiff bases and their Co(II), Cu(II), and Ni(II) complexes have been synthesized and characterized on the basis of their conductance and magnetic measurement, elemental analysis, conductance and NMR, H-NMR and mass spectroscopy. The most significant changes that occur in the infrared spectra of the metal complexes as compared to free ligand. With the modern and fast studies made in practical applicability of complexes uncommon stereochemical and the unique pharmacological aspects of schiff base metal complexes have involved a considerable interest of chemists.

Keywords- coordination compound, complex, ligand, IR spectroscopy, magnetic susceptibility.

tuberculosis activity. The schiff bases derived by the condensation of P-substituted benzaldehyde and various amines have anti-tumour activity against leukemia in rats. Schiff bases are an important class of ligands in coordination chemistry and find extensive application (Hughes, Tarafder, Seitz). Schiff bases have played an important role as chelating ligands for a large variety of metal ions. In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance as catalysts in many reactions (Deepa, Chatterjee, Chohan and Ali). Also, Schiff base complexes derived from heterocyclic compounds have acquired more attention in the field of bioinorganic chemistry because of their biological activities. Some heterocyclic-ketone derived Schiff bases show antibacterial activity and some others can act as antibacterial agent. The present investigation deals with synthesis and characterization of complexes of Cu (II), Ni(II) and Co(II) by Schiff base ligand (L) derived from furan 3 carboxaldehyde and 3- amino pyridine using various techniques (Cohan, Zahid and Kausar). Schiff base ligands have shown a long range of biological activities (Zou, Liu, Gao, Rodriquez). In the last two decades there has been rapid advancement in the field of Schiff base transition metal complexes due to the diversity of their magnetic properties (Kanh,1993) building blocks of supra molecular architecture through intermolecular interaction (Lehn), as redox active sites in various processes in biosphere (Cotton, Wilkinson, Murillo, Bochman), their fascinating structure (Miller, Dearden, Fenske) and important physical properties (Ford, Yam, Brockman, Brechin, Muller). The well documented potential application of Schiff base and their metal complexes have attracted much attention over the years (Erxleben, Ghiladi, Biswas, Chakraborty). A large number of Schiff Bases are used as anti-helmintic (Gutmann, Ainscough), Anti-inflammatory (Jayashree, Rafique), Anti-pyretic, anti-covulsant and analgesic etc.

I. INTRODUCTION

The role of metal complexes with multi-dentate ligands having delocalised D-orbital such as schiff bases has recently gained more attention because of their numerous uses. Compounds having at least one ion formed by combination of ligand and metal ion is known as complex compound. The metal complexes of Schiff bases have been playing a major role in the development of coordination chemistry. It is due to their flexibility in synthesis, sensitivity and selectivity to the central metal atom. They have structural similarity with complexes occurring naturally in biological system. The azomethine group is of immense importance in elucidation of the mechanism of racemination and transformation in biological system. Various schiff bases and their transition metal complexes have also been used as catalyst, herbicides, perfumes and cosmetics. There have been a number of applications of schiff bases as plant growth inhibitor oxygen absorbent and tranquilizers. The carbonyl part of Schiff bases plays the key role in anti - tumour activity (Sommers et al. and Haggerty et al). The Schiff bases with an unsubstituted amino group like 4,5 di-bromo salicylanilide possess anti -

II. CHEMICALS AND APPARATUS USED

A number of techniques, instrument, and glassware are used in the process. All glasswares were used were pyrex or borosil make. All chemicals used

were AR/LR grade. Chemicals such as methanol, ethanol, chloroform, metal chloride etc. from Qualigens and Lancaster were used.

III. INSTRUMENTS USED

Systronic Conductivity meter with a dip type cell, Perkin Elmer Lambda 15 UV/VIS spectrophotometer, Shimadzu 8201 PC spectrophotometer (4000-400 cm^{-1}) was used for recording IR spectra (KBr pellets) Mass spectrometer-JEOL, JMADA 5000 mass and Gouy balance were used during the research work.

IV. SYNTHESIS OF SCHIFF BASES

4.1. Benzaldimine Thiophene

Benzaldehyde (0.01 mol) and Ortho amino thiophene (0.01 mol) were mixed in 50 ml of ethyl alcohol. The mixture was refluxed for 3-4 hours on a water bath. The resulting content was filtered to get white coloured crystal which were washed with ether and then recrystallized from ethanol. The crystal was then dried under reduced pressure over fused calcium chloride.

4.2. Benzaldimine Furan

Benzaldehyde (0.01 mol) and Ortho amino Furan (0.01 mol) were mixed in 50 ml of ethyl alcohol. The mixture was refluxed for 3-7 hours on a water bath. The resulting content was filtered to get white coloured crystal which were washed with ether and then recrystallized from ethanol. The crystals were then dried under reduced pressure over fused calcium chloride.

4.3. Naphthaldimine Thiophene

Naphthaldehyde (0.01 mol) and Ortho amino thiophene (0.01 mol) were mixed in 50 ml of ethyl alcohol. The mixture was refluxed for 6-7 hours on a water bath. The resulting content was filtered to get yellow coloured crystal which were washed with ether and then recrystallized from ethanol. The crystal were then dried under reduced pressure over fused calcium chloride.

4.4. Naphthaldimine Furan

Naphthaldehyde (0.01 mol) and Ortho amino Furan (0.01 mol) were mixed in 50 ml of ethyl alcohol. The mixture was refluxed for 6-7 hours on a water bath. The resulting content was filtered to get yellow coloured crystal which were washed with ether and then recrystallized from ethanol. The crystal was then dried under reduced pressure over fused calcium chloride.

V. SYNTHESIS OF COMPLEXES

5.1. Benzaldimine Thiophene Cu(II), Ni(II) and Co(II) complex

Benzaldehyde (0.01 mol) dissolved in 20 ml of ethanol and Benzaldimine thiophene (0.01 mol) in 20 ml of ethanol and copper chloride (0.01 mol) in 10 ml of

water and ethanol were taken together in flask. The content was refluxed for 8-10 hours on a water bath and the solution was reduced to 1/3 volume. Blue, green and Brown coloured crystalline solid so obtained was filtered, washed with ether and then recrystallized with ethanol and dried in desiccator over fused calcium chloride.

Table 5.1: Value of molar conductance of Cu(II), Ni(II) and Co(II) Schiff base complexes derived from Benzaldehyde and Thiophene

S. No	Name of complex	Molecular Formula	Colour	Molar Conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
1.	Cu(BT) ₂ (H ₂ O) ₂ Cl ₂	C ₂₂ H ₁₈ N ₂ S ₂ Cu(H ₂ O) ₂ Cl ₂	Blue	4.1
2.	Ni(BT) ₂ (H ₂ O) ₂ Cl ₂	C ₂₂ H ₁₈ N ₂ S ₂ Ni(H ₂ O) ₂ Cl ₂	Green	5.1
3.	Co(BT) ₂ (H ₂ O) ₂ Cl ₂	C ₂₂ H ₁₈ N ₂ S ₂ Co(H ₂ O) ₂ Cl ₂	Brown	6.2

5.2. Benzaldimine Furan Cu(II), Ni(II) and Co(II) complex

Benzaldehyde (0.01 mol) dissolved in 20 ml of ethanol and Benzaldimine Furan (0.01 mol) in 20 ml of ethanol and copper chloride (0.01 mol) in 10 ml of water and ethanol were taken together in flask. The content was refluxed for 8-10 hours on a water bath and the solution was reduced to 1/3 volume. Blue, green and Brown colored crystalline solid so obtained was filtered, washed with ether and then recrystallized with ethanol and dried in desiccator over fused calcium chloride.

Table 5.2: Value of molar conductance of Cu(II), Ni(II) and Co(II) Schiff base complexes derived from Benzaldehyde and Furan

S. No	Name of complex	Molecular Formula	Colour	Molar Conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
1.	Cu(BF) ₂ (H ₂ O) ₂ Cl ₂	C ₂₂ H ₁₈ N ₂ O ₂ Cu(H ₂ O) ₂ Cl ₂	Blue	4.2
2.	Ni(BF) ₂ (H ₂ O) ₂ Cl ₂	C ₂₂ H ₁₈ N ₂ O ₂ Ni(H ₂ O) ₂ Cl ₂	Green	5.2
3.	Co(BF) ₂ (H ₂ O) ₂ Cl ₂	C ₂₂ H ₁₈ N ₂ O ₂ Co(H ₂ O) ₂ Cl ₂	Brown	6.1

5.3. Naphthaldimine Thiophene Cu(II), Ni(II) and Co(II) complex

Naphthaldehyde (0.01 mol) dissolved in 20 ml of ethanol and Naphthaldimine thiophene (0.01 mol) in 20 ml of ethanol and copper chloride (0.01 mol) in 10 ml of water and ethanol were taken together in flask. The

content was refluxed for 8-10 hours on a water bath and the solution was reduced to 1/3 volume. Blue, green and Brown coloured crystalline solid so obtained was filtered, washed with ether and then recrystallized with ethanol and dried in desiccator over fused calcium chloride.

Table 5.3: Value of molar conductance of Cu (II), Ni (II) and Co (II) Schiff base complexes derived from Naphthaldehyde and Thiophene

S. No	Name of complex	Molecular Formula	Color	Molar Conductance Ohm ⁻¹ cm ² mol ⁻¹
1.	Cu(NT) ₂ (H ₂ O) ₂ Cl ₂	C ₃₀ H ₂₂ N ₂ S ₂ Cu(H ₂ O) ₂ Cl ₂	Blue	5.2
2.	Ni(NT) ₂ (H ₂ O) ₂ Cl ₂	C ₃₀ H ₂₂ N ₂ S ₂ Ni(H ₂ O) ₂ Cl ₂	Green	5.4
3.	Co(NT) ₂ (H ₂ O) ₂ Cl ₂	C ₃₀ H ₂₂ N ₂ S ₂ Co(H ₂ O) ₂ Cl ₂	Brown	4.1

5.4. Naphthalimine Furan Cu(II), Ni(II) and Co(II) complex

Naphthaldehyde (0.01 mol) dissolved in 20 ml of ethanol and Naphthalimine Furan (0.01 mol) in 20 ml of ethanol and copper chloride (0.01 mol) in 10 ml of water and ethanol were taken together in flask. The content was refluxed for 8-10 hours on a water bath and the solution was reduced to 1/3 volume. Blue, green and Brown coloured crystalline solid so obtained was filtered, washed with ether and then recrystallized with ethanol and dried in desiccator over fused calcium chloride.

Table 5.4: Value of molar conductance of Cu(II), Ni(II) and Co(II) Schiff base complexes derived from Naphthaldehyde and Furan

S. No	Name of complex	Molecular Formula	Color	Molar Conductance Ohm ⁻¹ cm ² mol ⁻¹
1.	Cu(NF) ₂ (H ₂ O) ₂ Cl ₂	C ₃₀ H ₂₂ N ₂ O ₂ Cu(H ₂ O) ₂ Cl ₂	Blue	4.2
2.	Ni(NF) ₂ (H ₂ O) ₂ Cl ₂	C ₃₀ H ₂₂ N ₂ O ₂ Ni(H ₂ O) ₂ Cl ₂	Green	4.4
3.	Co(NF) ₂ (H ₂ O) ₂ Cl ₂	C ₃₀ H ₂₂ N ₂ O ₂ Co(H ₂ O) ₂ Cl ₂	Brown	5.5

VI. RESULTS AND DISCUSSION

IR spectra of the organic molecule are not easy to interpret. It is very complex in nature and therefore, a comparative study of infrared spectra of ligands and their metal complexes have been done to evaluate their

results. A study of spectra of the ligands and its metal complexes reveals that certain peaks were common in both the spectra. It is not always possible to explain all the peaks, hence only the important peaks have been chosen and explained. All their bands indicate the presence of ligand moiety and its coordination to the metal through donor atoms. The comparative band's position of ligands and their respective metal complexes. IR spectra of free ligands show a strong band region of 1630-1600 cm⁻¹ which may attributed to the stretching vibration of azomethine group (>C=N-). This band is shifted towards lower frequency region in the spectra of metal complexes suggesting thereby the participation of Imine =N- in coordination (Taylor, Pritz, Busch). A broad band a 3470 cm⁻¹ and another band of medium intensity appear in the region of 860-840 cm⁻¹ which may be assigned to stretching and rocking vibration of -OH group coordination water molecule in the complexes (Ansari, Rana). Some new bands appeared in the IR spectra of metal complexes in the region 550-500 and 450-400 cm⁻¹ may be attributed due to formation of M-N and M-O bond respectively, which further give evidence in favour of coordination of metal through azomethine and coordinated water (Kettle, Braibanti, Dassch).

Table 6.1: IR spectral Data of Benzaldimine Thiophene and its metal complexes

S.No	Functional Group	Ligands	Cu(II)	Ni(II)	Co(II)
1	>C=N-	1620	1600	1590	1595
2	M-O	-	510	500	520
3	M-N	-	425	435	435
4	M-Cl	-	360	370	370
5	Coordinated water	-	3460	3450	3455

Table 6.2: IR spectral Data of Benzaldimine Furan and its metal complexes

S.No	Functional Group	Ligands	Cu(II)	Ni(II)	Co(II)
1	>C=N-	1630	1610	1580	1585
2	M-O	-	520	510	510
3	M-N	-	420	425	430
4	M-Cl	-	370	380	360
5	Coordinated water	-	3450	3460	3465

Table 6.3: IR spectral Data of Naphthalimine Thiophene and its metal complexes

S.No	Functional Group	Ligands	Cu(II)	Ni(II)	Co(II)
1	>C=N-	1640	1620	1570	1590
2	M-O	-	515	520	525
3	M-N	-	425	435	435
4	M-Cl	-	365	360	380
5	Coordinated	-	3450	3440	3465

water				
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Table 6.4: IR spectral Data of Naphthaldimine Furan and its metal complexes

S.No	Functional Group	Ligands	Cu(II)	Ni(II)	Co(II)
1	>C=N-	1620	1610	1560	1580
2	M-O	-	520	510	510
3	M-N	-	420	425	430
4	M-Cl	-	360	370	365
5	Coordinate d water	-	3460	3465	3470;ggggaaaaaa v

Magnetic Studies

It is very important to find the numbers of unpaired electron in a transition metal complexes. Magnetic susceptibility measurement is a useful method of proving, whether the constituent atoms, ions or molecule of a coordinated compound possess unpaired electrons or not. Transition metal atoms are paramagnetic in nature. Much of our understanding of transition metal compounds. Magnetic data give information about the oxidation state, bond type and stereochemistry of the metal atom in a particular compound.

Cu (II) Complexes

For Cu complexes, the observed value of magnetic moments lies between 1.70-2.10 B.M. The greater value of magnetic moment (1.91B.M.) can be attributed to the orbital contribution and to the distortion of octahedral structure leading to square planer geometry of the molecule. The subnormal value of magnetic moment of the Cu (II) complexes at room temperature indicated a partial spin. This could be attributed due to the partial spin pairing between metal ions and could be well interpreted in terms of Bleaney Bowers equation (Teotia)

Table 6.5: Magnetic Measurement of Copper complexes at 308 K

S.No	Name of complexes	Molar Susceptibility	Corrected Molar Susceptibility	Effective magnetic moments	No. Of unpaired electron
1	Cu(BT)2(H2O)2Cl2	1210.00	1220.00	1.75	1
2	Cu(BF)2(H2O)2Cl2	1310.00	1350.00	1.86	1
3	Cu(NT)2(H2O)2Cl2	1220.00	1250.00	1.85	1
4	Cu(NF)2(H2O)2Cl2	1310.00	1320.00	1.87	1

Ni(II) Complexes

The magnetic moment observed for the present

nickel (II) complex is 3.02B.M. Which is slightly higher than the spin-only value of 2.83 B.M. for high spin octahedral complexes (Nyholm) has discussed this increase in terms of mixing in upper energy states via spin orbit coupling.

Table 6.6: Magnetic Measurement of Nickel complexes at 308 K

S.No	Name of complexes	Molar Susceptibility	Corrected Molar Susceptibility	Effective magnetic moments	No. Of unpaired electron
1	Ni(BT)2(H2O)2Cl2	1270.45	1282.00	1.92	2
2	Ni(BF)2(H2O)2Cl2	3540.00	3550.00	3.00	2
3	Ni(NT)2(H2O)2Cl2	1270.00	1282.00	1.90	2
4	Ni(NF)2(H2O)2Cl2	3540.00	3550.00	3.02	2

Co(II) Complexes

The magnetic moment for most of the Co(II) complexes fall in the range of 1.91-2.09B/M. Which is consistent with low spin spectra coordinate Co(II), but lower than generally reported for square planer cobalt (II) (Rana, Gurtu, Beradar ,French).

Table 6.7: Magnetic Measurement of Cobalt complexes at 308 K

S.No	Name of complexes	Molar Susceptibility	Corrected Molar Susceptibility	Effective magnetic moments	No. Of unpaired electron
1	Co(BT)2(H2O)2Cl2	3860.00	3985.30	4.45	3
2	Co(BF)2(H2O)2Cl2	3648.00	3752.12	4.50	3
3	Co(NT)2(H2O)2Cl2	3870.00	3985.20	4.40	3
4	Co(NF)2(H2O)2Cl2	3648.00	3752.10	4.55	3

VII. CONCLUSION

In this paper, a schiff base derived from hetrocyclic amines was successfully synthesized. Schiff base transition metal complexes Cu (II), Ni (II) and Co (II) were synthesised from Benzaldehyde Thiophene , Furan and Naphthaldehyde Thiophene and Furan , characterized on the basis of analytical and spectral data. Elemental analysis shows the metal to ligand ratio is 1:2. Conductivity measurements show all complexes are non-

electrolytes. From SEM analysis crystalline nature of complexes is confirmed. Anti-bacterial study shows that all complexes are more active than ligand and an antifungal study indicates their inactivity towards fungi.

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