

COMPLEXING BEHAVIOUR OF METAL(II) MIXED LIGAND COMPLEXES AND THEIR APPLICATION TO BIOLOGICAL FIELD

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ABSTRACT

In the present article, we have described the synthesis and characterization of mixed ligand complexes of Ni(II) and Cu(II) with benzoyl hydrazine. The characterization of the complexes was carried out by various techniques viz., elemental analyses, magnetic moment value, molar conductance, IR and electronic spectral studies. The antibacterial and antifungal activity's data show that the metal complexes have a promising biological activity comparable with the parent ligand against bacterial and fungal species.

Keywords: Benzoyl hydrazine, Ni(II) Chloride, Cu(II) Chloride, Oxalic Acid.

I. INTRODUCTION

Complexes of transition metal ions with multidentate organic ligands have been the subject of intensive research because they not only have interesting spectral and magnetic properties, but they also possess a diverse spectrum of biological activities “as discussed elsewhere[1-6]”. Transition metal complexes containing Schiff bases are used as catalysts and as biological models for the understanding of the structures of biomolecules. Also, the Schiff bases are widely studied because of increasing recognition of their role in biological systems, “as discussed elsewhere[7,8]”. The study of the coordination of transition metal ions with different types of ligands has been amplified by the recent developments in the field of bioinorganic chemistry and medicines, “as discussed by Yamet.al. [9]”. Thus, the bioinorganic chemistry of nickel is a topic of increasing interest, “as discussed elsewhere[10,11]” because the study of the interactions of Ni(II) with nucleotides offers an unique opportunity for understanding various properties of Ni(II) complexes such as the carcinogenicity of some nickel compounds “as discussed by Andonikashvili et.al.[12]”.

II. MATERIALS AND METHODS

All the chemicals used in the present investigations were of AR grade. Mixed ligand oxalate Ni(II) & Cu(II) benzoyl hydrazine complexes were synthesized by treating alcoholic solution of metal(II) chloride, benzoyl hydrazine and oxalic acid in 1:2:2 molar ratio, “as described earlier by Sharma et.al.[13]”. The complexes so obtained were characterised by physico-chemical techniques such as elemental analyses, solubility, electrical conductance and molecular weight determinations etc. IR and electronic spectra were recorded on Perkin Elmer Spectrophotometer at CDRI, Lucknow. Magnetic measurements were carried out at room temperature by

Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant, "as discussed by Dilworth[14]". The diamagnetic corrections were applied using Pascal's constant, "as discussed by Audreithet.al.[15]".

III. RESULTS AND DISCUSSION

The synthesized complexes were coloured, freely soluble in DMF and DMSO and quite stable at room temperature. The Ni(II) complex show a magnetic moment of 3.12 B.M. , which reveal octahedral stereochemistry of ligand around central metal ion, "as discussed elsewhere[16, 17]". The magnetic moment value for Cu(II) complex was found to be 1.81B.M., (Table-1), indicating a distorted octahedral geometry in terms of Jahn-Teller effect, "as discussed elsewhere[16, 17]".

In the IR spectra, the amide-I band shows a negative shift of $20\text{-}22\text{ cm}^{-1}$ (as comparing BH) in the spectra of the complexes, "as discussed elsewhere[18, 19]", suggesting the involvement of oxygen atom of $>\text{C}=\text{O}$ group and nitrogen atom of $-\text{NH}_2$ group in coordination. IR spectra of oxalato complexes show bands at 1700, 1645, 1470, 1670, 1365 and 1300 cm^{-1} . These bands are not observed in the spectra of BH, therefore identified as $\nu_{\text{as}}\text{C}=\text{O}$ and $\nu_{\text{s}}\text{C}=\text{O}$. In the complexes new bands observed in the far infrared region of the complexes at 545 & 550, 422 & 435, 350 & 375 cm^{-1} are probably due to the formation of $\nu\text{M-O}$, $\nu\text{M-N}$, and $\nu\text{M-O-C}$ bonds respectively, "as discussed by Manimekakaiet.al.[20]" (Table-2).

The diffused reflectance spectra of Ni(II) complex exhibited three bands in the regions 9875, 16300 and 25300 cm^{-1} , due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (ν_1), ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) (ν_2) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P) (ν_3) respectively in an octahedral geometry²¹⁻²³. The ν_2/ν_1 value of Ni(II) complex falling in the range reported for majority of octahedral Ni(II) complexes "as discussed elsewhere[21-23]". In Cu(II) complex a multi-structured band (13445 cm^{-1}) may be assigned due to combination of the transitions: ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ (ν_1), ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ (ν_2) and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ (ν_3) in a distorted octahedral geometry, "as discussed by Reddy et.al.[24]". From the spectral parameters values of 10Dq (Table-1), B , β , β^0 were also calculated. The value of 10Dq and LFSE clearly show the distorted octahedral geometry around central metal ion.

IV. BIOLOGICAL ACTIVITY OF THE COMPLEXES

It was demonstrated that, prepared metal complexes showed antimicrobial effect against *A. solani*. The experiments were conducted during crop season in randomized block design with three replications. The metal complexes in solution form were sprayed at 10-days interval. PDI & disease progress curve were also calculated. The minimum disease reduction was found in Cu(II) oxalate complex in terms of leaf blight and fruit rot.

"Table-1": Characterization of Metal (II) Mixed Ligand Complexes

S.N.	COMPLEX	M% calc (found)	N% calc (found)	C% calc (found)	H% calc (found)	μ_{eff} B.M.	10Dq cm^{-1}
1-	[Ni(OX)(BH) ₂]	15.17 (15.01)	7.24 (7.19)	27.92 (28.02)	2.08 (2.01)	3.12	9825
2-	[Cu(OX)(BH) ₂]	16.22 (16.02)	7.15 (7.21)	25.57 (27.49)	2.06 (1.99)	1.81	14990

"Table-2": Ir Spectral Bands (Cm^{-1}) Of The Complexes

S.N.	COMPLEX	$\nu(\text{N-H})$	$\nu_{\text{s}}(\text{C=O})$	$\nu_{\text{as}}(\text{C=O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-O-C})$
1-	[Ni(OX)(BH) ₂]	3250 s,br	1470m	1700m 1645m	422w	550m	375w
2-	[Cu(OX)(BH) ₂]	3375m,br	1365m 1300s	1670s	435m	545m	350w

V. CONCLUSION

Both the complexes described here, i.e. Ni(II) oxalate benzoylhydrazine and Cu(II) oxalate benzoylhydrazine complexes were found to be insoluble in water but fairly soluble in DMF & DMSO. The ligands used in the present investigation were found to be bidentate in nature. The ν_2/ν_1 value of Ni(II) complex indicates the octahedral geometry of the complex. Spectral parameters values of Cu(II) complex clearly show the distorted octahedral geometry around central metal ion.

REFERENCES

- [1] Y.L. Angeliq and J.M. Thomas, Metal complexes as enzyme inhibitors, Chem. Rev., 99(9),1999,2711-2734.
- [2] D.R. Richardson and P.V. Bernhardt, Crystal and molecular structure of 2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone (NIH) and its iron(III) complex: an iron chelator with anti-tumour activity., J.B.I.C., 4, 1999, 2662.

- [3] Y. Zheng-Yin, Y. Ru-Dong, L. Fa-Shen and Y. Kai-Bei, Crystal structure and antitumour activity of some rare earth metal complexes with Schiff base, *Polyhedron*, 19,2000, 2599-2604 .
- [4] J.L. Buss, J. Neuzil and P. Ponk, Oxidative stress mediates toxicity of pyridoxalisonicotinoylhydrazone analogs, *Archives of Biochemistry and Biophysics*, 421,2004, 1-9.
- [5] L. Sommer, W.P. Maung-Gyeeand D.E. Ryan, Heterocyclic hydrazones of o-hydroxyaldehydes as analytical reagents, *Ser. Fac. Sci. Natur. Univ. Purkyniana*, 2(6), 1972, 115-128.
- [6] H. Shargi and M.A. Nasser, Schiff base metal(II) complexes as new catalysts in the efficient, mild and regioselective conversion of 1,2-epoxyethans to 2-hydroxy-ethyl thiocyanates with ammonium thiocyanate., *Bull. Chem. Soc. (JPN)*, 76, 2003, 137-142 .
- [7] J.A. McClevertyand T.J. Meyer, *Comprehensive coordination chemistryII from Biology to Nanotechnology*, (Elsevier Amsterdam), 1, 2004, .411.
- [8] A. Mederos, S. Dominguez, R. Hernandez-Molina, J. Sanchiz and F. Brito, *Coord. Chem. Rev.*, 1999,193.
- [9] V.W.W. Yam and K.K.W. Lo, Recent advances in utilization of transition metal complexes and lanthanides as diagnostic tools, *Coord. Chem. Rev.*, 184, 1999, 158-240.
- [10] H. Sigel and A. Sigel, Eds., *Metal ions in biological systems*, Marcel Dekker, Inc: New York, 1988, 23.
- [11] J.R. Lancaster, *The bioinorganic chemistry of nickel*: VCH Publishers: New York 1988.
- [12] E.L. Andronikashvili, V.G. Bregadgand J.R. Monaselidge, Interactions between nickel and DNA considerations about the role of nickel in carcinogenesis, *Met. Ions Biol. Syst.*, 23,1988, 331-357.
- [13] S. Sharma, A. Misra, S. Sajid S, *Jour. P.A.S.(Chem. Sci.)*, 16,2010, 18-22.
- [14] J.R. Dilworth, *Coardination Chem. Rev.*, 21, 1979, 129.
- [15] L.F. Audreith and B.A. Ogg, *The Chemistry of Hydrazine*, Wiley NewYork , 1951.
- [16] P.P. Hankare, S.R. Naravane, V. M. Bhuse, S.D. Delekarand A.H. Jagtap, *Ind. J. Chem.*, 43A,2004, 1464.
- [17] Raman N., Thangaraja C. and Johnsonraja S., *Ind. J. Chem.*, 44A,2005, 693.
- [18] J.F. Alcock, R.J. Baker and A.A. Diamantis, *Aust. J. Chem.*, 25, 1972, 289.
- [19] M.F. Iskander, S.E. Zayan, M.A. Khalifa and L El-Syed., *J. Inorg. Nucl. Chem.*, 36, 1974, 551.
- [20] A. Manimekakaiand B.S. Sivakumar, *Ind. J. Chem.*, 45A,2006, 1362.
- [21] A. Syamaland M.M. Singh, *J.Polym. Mater.*, 9,1992, 105.
- [22] A. Syamal and M.M. Singh, *Ind. J. Chem.*, 31A, 1992, 110.
- [23] A. Syamal, M. M. Singh, A.K. Singh, P.K. Gupta, Jaipal and L.K. Sharma, *Ind. J. Chem.*, 41A, 2002, 1385.
- [24] S. Reddy, Susheela and Jayatyagaraju, *Ind. J. Chem.*, 43A, 2004, 341.