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ELUCIDATION STRUCTURAL FEATURES OF SCHIFF BASE COMPLEXES OF AROMATIC ALDEHYDE AND AMINOTRIAZOLE

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ABSTRACT

Substituted benzaldehyde condensed with 3-amino-1,2,4-triazole under specific reaction condition resulted in formation of Schiff base. Schiff bases 4-[(nitro-benzylidene)-amino] -1,2,4- triazole (nbat) and 4-[(methoxy-benzylidene) –amino]-1,2,4-triazole (mbat) were synthesized. These Schiff bases were treated with acetates of Cu (II), CO (II), Ni (II) and Zn(II) in mole ratios 1:1 and 1:2 On the basis of analytical data, a mass spectra, ^{1}HNMR, F-T-IR, UV and magnetic moments value octahedral structure were obtained for Co(II), Ni (II) and Zn (II) complexes in both 1:1 and 1:2 mole ratio but for Cu(II) complexes both in 1:1 and 1:2 mole ratio square planar structure was obtained.

Keywords: Schiff Base, Triazole, Nbat, Mbat.

I INTRODUCTION

Compounds containing 1,2,4 –triazole rings are well known for drugs.[1] 1,2,4-triazoles are their derivatives are associated with various biological activities; such as anticonvulsant, antifungal, anticancer, anti-inflammatory and antibacterial properties [2-5].1,2,4- triazoles having amino groups as substituent are well known antimicrobial agent [6-7] .Coordination behavior of such legands with metal ions depend upon nature of substitutents present on the ligand, probable site of coordinations and pH of the reaction mixture as well as.

II EXPERIMENTAL

2.1 Synthesis of ligands

In the present investigation Schiff ligands have been synthesized by the condensation of 4-nitro /4-methoxy benzaldehyde with 3-amino 1,2,4 triazole. Ligands were synthesized under proper condition as reported in the literature [8] .

The molecular formula and structure of the ligands have been assigned on the basis of elemental analysis, IR, ^{1}HNMR and Mass spectral data.

2.2 Analytical data of ligands

2.2.1 4-[(nitro-benzylidene) –amino]-1,2,4-triazole (nbat) (HL^{1})

m.p 175-177^0 c (found : C, 49-57; H, 3.13; N, 32.08% Calcd. for $C_9 H_7 N_5 O_2$: C, 49.77; H, 3.23 ; N , 32.26%), MS : m/z (M+1) 219.8, (M-1) 217.8

4-[(Methoxy-benzylidene)- amino] -1,2,4-triazole (mbat) m.p. 252-257^{0}C (found:C, 59.65; H, 4.98; N, 27.68% . Calcd for $C_{10} H_{10} N_4O$: C, 59.41; H, 4.95; N,27.61%), MS: m/z (M+1) 203.4, (M-1) 201.3 exhibited

IP spectra (KBr, cm^{-1}) of the ligand (nbat) HL^1 a band at 1620,due to

(□ $_{H-C=N}$)^9 and 3415 cm^{-1} due to (NH_)^{10} observed. So, under this condition two Schiff ligands were synthesized (i) condensation of 4-nitrobenzaldehyde and 3-amino 1,2,4 triazole (ii) condensation of 4-methoxy benzaldehyde and 3-amino- 1,2,4 -triazole. Subsequently metal complexes were synthesized with these ligands. Similarly another ligand (mbat) HL^2 also exhibited band at 1630, (>C=N) and 3400 cm^{-1} (NH) respectively.

2.2.2 ^{1}HNMR of HL^1 (nbat) and HL ^{2} (mbat)

The resonance due to azomethine proton appears at 8.1 ppm. the peak due to NH of triazole ring appears at 11.2 ppm in the spectra of ligands.

The chemical shift due to aromatic ring protons appears at 7.0-7.5 ppm in the ligands. The streucture of The ligands is a follows.

III SYNTHESIS OF COMPLEXES

Metal complexes with ligands (nbat, mbat) have been synthesized by mixing aqueous hot ethanolic solution of acetates of Co(II),

Ni (II) , Cu(II) and Zn (II) with ethanolic solution of respective ligands in 1:1 and 1:2 mole ratios. The product formed were filtered and purified by washing throughly with warm water, with aqueous ethanol to remove unreacted metal acetates or ligands, and finally with acetone and dried. The molar conductivity of complexes (Measured in 10^{-3} DMF) are in the range 102-7 ohm^{-1} cm^2 mol$^{-1.}$ Indicating the non-electrolytic nature of complexes.[11] Analytical datas are incorporated in Table- 1. C.H.N-analysis was done on Perkin Elmer 2400. Electronic spectra of metal complexes were recorded in DMF at systronic 2203 double beam spectrophotomer. NMR spectra were recorded in DMSO-d_6 on Bruker ACE 300 spectrometer TMS as internal standard. IR spectra on MB-3000 ABB spectrometer in KBr was recorded.

IV RESULT AND DISCUSSION

All complexes are coloured and nonhygroscopic solids stable in air, insoluble in water and also in organic solvents except in DMF and DMSO.

Elemental analysis supports the formation of 1:1 and 1:2 metal complexes with HL^1 and HL^2 ligands with Co(II), Ni (II) , Cu(II) and Zn(II) metal ion.

Molar conductance of complexes measured in 10^{-3} M DMF are in the range 1.3-3.7 ohm^{-1} cm^2 mol^{-1} indicating the non-electrolytic nature of complexes. On comparision of IR spectra of ligands (HL^1, HL^2) with complexes, it has been observed that azomethine group frequency $\nu_{(N=CH)}$ has been observed in free ligands at 1620 cm^{-1} . This band is shifted to the lower[12] frequency by 5-20 cm^{-1} in the spectra of complexes indicating co-ordination through Nitrogen of azomethine group.

A new band at 480-520 cm^{-1} done to $\nu_{(M - N)}$ is further confirmed coordination of metal to azomethine group. In the spectra of metal complexes a broad band in the region 3200-3490 cm^{-1} appeared , indicatged the presence of coordinated water molecule. A strong band in the region 1740-1760 cm^{-1} has been assigned to $\nu_{(COOCCH3)}$ in 1:1 metal complexes .

$\nu_{(N-H)}$ band appeared both in free LH^1 and LH^2 ligands was found to be absent in all the complexes,indicating coordination through deprotonated Nitrogen.^{1}HNMR spectra have been recorded for Zn(II) complexes only. The ligands (HL^1 and HL^2) exhibited characteristic azomethine proton singlet at δ 10.20 and 10.45 ppm respectively. These characteristic signals , due to azomethine proton deshielded in the spectra of metal complexes, suggests coordination of metal ions to azomethine [13] nitrogen atom .

The aromatic protons of Schiff bases appeared as double of doublet and two doublets at δ 7.35, 7.52 and 8.08 ppm respectively . The aromatic protons signals show a slight downfield shift upon coordination. The proton signal of NH group of both ligands LH^1 and LH^2 are observed at 13.6-13.8 ppm. This signal was found absent in all the complexes; indicating deprotonation of NH group during coordination.

The magnetic moment measurement and electronic spectra of 1:1 and 1:2 Co(II) complexes with HL^1 and HL^2 ligands show magnetic moments (μ_{eff}) 4. 83-4.95 B.M./ well within expected range of octahedral complexes.

Co(II) complexes exhibit two absorption band in the region
10865-10950 cm^{-1} (ν_1) and
20120 – 20870 cm^{-1} ((ν_3) , which
is assigned to $^4T_{1g}$ (F) → $^4T_{2g}$ (F)
(ν_1) ; $^4T_{1g}$ (F) → $^4T_{1g}$ (P) (ν_3) transition . [14]

These are characteristic of high spin octahedral Co(II) complexes. ν_2 can be calculated by equation $\nu_2 = \nu_1 +$ 10Dq, the value of ν_2 is close to ν_3 . Dq (cm^{-1}) , B (cm^{-1}), ν_2 / ν_1, B and β % has been observed in the range 1199.9 – 1213.4 (cm^{-1}), B (683.9- 748.1) cm^{-1}, ν_2 / ν_1 = 2.09-2.11, β (.770-.703) and β % 29.6-22.2) are in accordance with high spin Octahedral Co(II) complex. less than one value of β indicates partial covalency in metal-ligand bond.

The nickel complexes show magnetic moment values in the range 3.38-3.49 B.M, indicative of octahedral structure of Nickel complexes. The three absorption bands in octahedral environment corresponding to $^3A_{2g}$ (F) → $^3T_{2g}$ (F), $^3A_{2g}$ (F) → $^3T_{1g}$ (F), (ν_2), and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) (ν_3) observed. The ligand field parameters Dq, B, β and β% has been calculated and found in the range (995.0-1012.0o) cm^{-1},
B (751.0- 783.0) cm-1, ν_2 / ν_1 = 1.60-1.70, B= .740 – 721 and β % = 25.3-31.5 respectively .
These parameters indicate significant covalent character of metal ligand band.

Cu(II) complexes have exhibited magnetic moment values 1.90-2.15 B.M. . The electronic spectra of Cu(II) complexes showed broad band around 18680 cm^{-1}, which can be assigned to $^2B_{1g}$ → $^2A_{1g}$ (ν_1) transition . It is a characteristic band of square planar geometry around the Cu(II).

REFERENCES

[1] O. Bekircan and H. Bektas, Molecule, 2006, 11, 469.

[2] B.S. Holla, B. Veerendra, M.K. Shivananda and B.Poojary, Eur. J.Med. Chem., 2003, 38, 759.

[3] T.S. Lobana, Proc. Indian Acad. Sci,

[4] A.Z. Kaplanciki,. G. Turan – Zitouni, A. Ozdemir and G. Revial, Eur. J. Med. Chem. 2008, 43, 155.

[5] J. Liu, W. Tao, H. Dai, Z. Jin and J. Fang, Heteroatom chem., 2007, 18,376.

[6] P. Panneerselvam, R.R.Nair, G. Vijaya lakshmi, E.H. Subramanium and S.K. Sridhar, Eur. J. Med. Chem. 2005, 738, 253.

[7] M. Yildiz, H. Unver, B. Dulger, D. Erdener, N. Ocak, A. Erdonmez and T.N. Durlu, J. Mol. Struct., 2005, 738, 253.

[8] S.K. Borthakur, Paran Boruah and B.N. Goswami, J. Indian Chemical Soc., 2013, 90, 1005.

[9] A.Rai, S.K. Sengupta and O.P. Pardey, spectrochim. Acta. Part A, 2006, 64, 789.

[10] G.A. Bain, D.X.West, J. Krecji, J. Val des-Martinez, S. Hernan-Dez-Ortega and R. Roscano, Polyhedron, 1997, 16, 855.

[11] K.Singh, D.P. Singh, M.S. Barwa, P. Tyagi and Y. Mirza, Journal of Enzyme Inhibition and Medicinal chemistry, 2006, 5, PP 557-562.

[12] A.D. Kulkarni, S.A. Patil, V. H. Naik and P.S. Badami, Medicinal Chemistry Research , 2011, vol. 20, No. 3, PP. 346-354.

[13] K. Singh, M.S. Barwa and P. Tyagi, European Journal of Medicinal Chemistry, 2006, Vol. 41, No. 1, PP 147-153.

[14] P.G. Avaji, S.a. Patil and P.S. Badami, Journal of coordination Chemistry, 2008 Vol. 61, No. 12, PP. 1884-1896.

[15] A.H. Osman, M.S. Salch and M.M. Sunaa, Synthesis and Reactivity in Inorganic and Metal organic Chemistry, 2004, vol 34, No. 6, PP 1069-1085.