

SYNTHESIS AND CHARACTERIZATION OF TETRAAZA MACROCYCLIC LIGAND AND IT'S Co (II), Ni (II), Cu (II), Zn (II) COMPLEXES

¹Sopan A.Najan, ²Sanjivani S. Patil, ³Bhagwat B. Nagolkar, ⁴Sunil G.Shankarwar

¹Assit.Professor, ²Assit. Professor, ³Research student ⁴Associate Professor

¹Department of Chemistry,

¹Arts, Commerce and Science College, Sonai, Tal.Newasa, Dist.Ahmednagar, Maharashtra, India

Abstract: 14 membered tetraaza macrocyclic ligand and its metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized biologically active macrocyclic ligand. The ligand was synthesized by condensation of β - diketone 1-(5-bromo -2-hydroxyphenyl) -3- (thiophene -2-yl) propane -1,3-dione with 2,3- diaminopyridine. All the complexes were characterised by conductivity, UV- visible, FTIR, ¹H NMR, Mass spectra, powder X-ray diffraction. From the analytical data, stoichiometry of the complexes has been found to be 1:2(metal:ligand). All the complexes are of high spin type and six coordinated type. On the basis of IR, electronic spectral studies and magnetic behaviour, an octahedral geometry has been assigned to these complexes. The antibacterial and antifungal activities of the ligand and its metal complexes, has been screened in vitro against Gentamycin, Ampicillin, Chloramphenicol, Ciprofloxacin, Norfloxacin, Nystatin and Griseofulvin used as standard drug.

Keywords: Macrocyclic ligand complexes Transition metal complexes Spectral analysis Powder X- ray diffraction Biological activities

I. INTRODUCTION

Coordination chemistry of macrocyclic ligand containing a heteroatom are important complexing agents of cations, anions and molecule. The stability of macrocyclic metal complexes depends upon a number of factors such as number and type of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate ring formed on complexation (*J. Yao et al. 2009*).

The macrocyclic complexes of β - diketone with 2, 3- diaminopyridine in presence of metal ions in ethanol are prepared by the template condensation method have been already reported. Transition metal macrocyclic complexes have received much attention as an active part of metalloenzymes (*H. Yan Li. et al. 2009*) and as biomimetic model compounds (*S. Chandra et al. 2008 and J. Yao et al. 2009*). Schiff base complexes containing phenolic group as chelating moieties in the ligand are considered as models for executing important biological reactions and mimic the catalytic activities metalloenzymes (*Khandar A. A. et al. 2005*). Aza- type ligands appear very promising for potential use as antibacterial and antifungal agents as well as due to their other biological activities. (*Z. H. A. El-Wahab, 2009, A. Chaudhary et al. 2003, D. P. Singh et al. 2007, and R. C. Sharma et al. 2007*). The formation of macrocyclic complexes depends on the size of the macrocyclics, nature of its donor atoms and on the complexing behaviour of the anions involved in coordination (*S. Bhan et al. 2007*). In view of the above applications, in the present paper we report the synthesis, characterisation and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2,3- diaminopyridine containing nitrogen donor [N₄] macrocyclic ligand having 14-membered backbone.

II. MATERIALS AND METHODS

The substituted β - diketone was prepared from 2- hydroxyacetophenone and thiophene-2- carboxylic acid by Beckmann rearrangement. Thiophene-2- carboxylic acid, phosphorus oxychloride, pyridine, potassium hydroxide, 2,3- diaminopyridine of A.R. grade were used for preparation of ligands. A.R. grade metal nitrate was used for synthesis of complexes. The FTIR spectrum was recorded on Shimadzu spectrophotometer using KBr pellets. ¹H NMR spectra were recorded in CDCl₃ using TMS as internal standard. The XRD were recorded on Goniometer, the UV visible spectra of complexes was measured on Shimadzu spectrophotometer and electrolytic conductance was measured on Elico CM- 180 conductivity meter using 1mM solution in DMSO.

2.1 Synthesis of β - diketone step I

Equimolar amount of thiophene-2- carboxylic acid and 5-bromo-2 hydroxyacetophenone were dissolved in 50 ml pyridine. The reaction mixture was then cooled 0°C. To this phosphorus oxychloride (0.06 mol) was added drop wise maintaining temperature below 10°C. The reaction mixture was kept overnight at room temperature. It was then poured on crushed ice with vigorous stirring. The crimson coloured solid (ester) was obtained which was filtered and washed several times with ice-cold water. Ester was then crystallized with distilled ethanol. Purity of the compound was checked by the TLC. Ester was subjected to well-known Baker-Venkatraman transformation. Ester (0.003 mol) was dissolved in 15 ml dry pyridine. To this mixture, powdered KOH (1g) was added and the reaction mixture was stirred on magnetic stirrer at room temperature for 5 h. Then it was poured over crushed ice and acidified with concentrated hydrochloric acid. Finally yellow colour product was obtained which was recrystallized from ethanol (Yield 55-58%). Purity of all synthesized β -diketone was checked by TLC using silica gel and melting points (see Scheme 1).

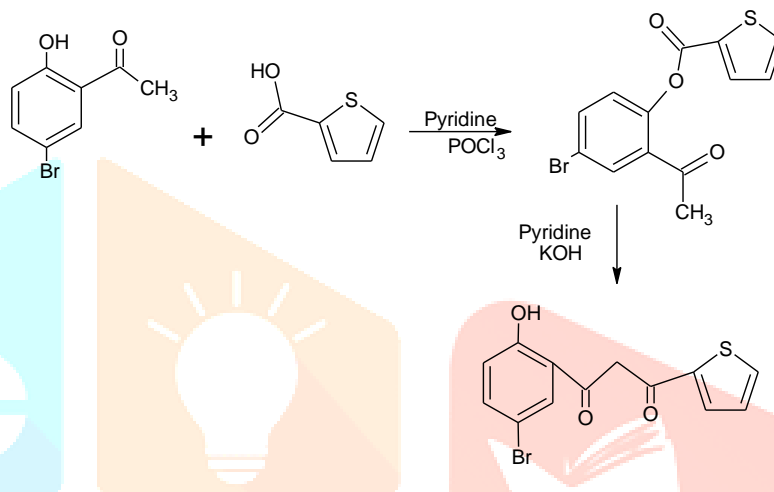


Fig.1 Proposed Structure of β - diketone

2.2 Synthesis of Ligand

A hot ethanolic solution of 30ml of β - diketone (0.02 mol) and a hot ethanolic solution 30ml of 2,3-diaminopyridine (0.02mol) were mixed slowly with constant stirring. This reaction mixture was then refluxed at 80-90°C for 14-15 hrs. in the presence few drops of conc. HCl (pH= 3-4) on cooling a solid yellow precipitate was formed, which was filtered, washed with cold ethanol and dried under vacuum over P₄O₁₀ (yield- 59-60%)

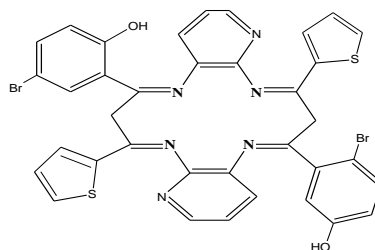
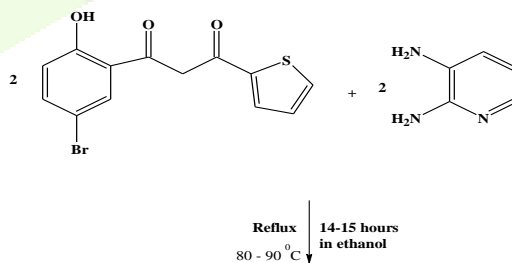


Fig.2 Proposed Structure of Ligand

2.3 Synthesis of Complexes

A hot ethanolic (20 ml) solution of the ligand (0.01mol) and a hot ethanolic (20ml) solution of corresponding metal nitrate (0.01mol) were mixed together with constant stirring. The pH of the mixture was adjusted in the range of 7-8 by adding 10% alcoholic ammonia solution. The reaction mixture was refluxed for 7-8 hrs. at 80-90°C on cooling, a coloured precipitate was formed. It was filtered and wash with cold ethanol and dried under vacuum over P₄O₁₀ (yield 55-57%).

III. RESULT AND DISCUSSION

All the complexes were coloured solids, air stable and soluble in polar solvents like DMSO and DMF. Micro analytical data and molar conductance of ligand and metal complexes are given in (Table1). The metal contents in complexes were estimated by gravimetric analysis (*V. Dier et. al. 2007*)(11). All the complexes show low conductance which indicates their non-electrolytic nature. The magnetic measurement studies show that the Co(II) and Cu(II) paramagnetic whereas the Ni(II) and Zn(II) shows diamagnetic behaviour (Table 1).

3.1 ¹H NMR spectra of ligand

The ¹H NMR spectra of the ligand was recorded in DMSO. It shows following signals at 1.6 (s, 4H, -CH₂), 6.7 (s, 2H, Ar-OH), 6.7-8.4 corresponding to phenyl ring protons (m, 18H).

3.2 Magnetic measurements and electronic spectra

Cobalt(II) complexes. The magnetic moments of the cobalt (II) complexes were measured at room temperature and were found in the range 4.95 – 4.98 μB, which is consistent with three unpaired electrons. The solution spectra of Co(II) complexes shows 13547 cm⁻¹ and 17503 cm⁻¹ were assigned ⁴T_{1g} → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) respectively. Suggesting octahedral geometry around the Co(II) ion. (*S.Chandra et al.2007*)

Nickel(II) complexes. The magnetic moments of the nickel(II) complexes were measured at room temperature and were found in the range 2.93 – 2.95 μB, which is consistent with two unpaired electrons. The solution spectra of Ni(II) complexes shows 14388 cm⁻¹ 15503 cm⁻¹ and 22471 cm⁻¹ were assigned ³A_{2g} → ³T_{2g}, ³A_{2g} → ³T_{1g}(F), and ³A_{2g} → ³T_{1g}(P) respectively. Suggesting octahedral geometry around the Ni(II) ion. (*A.S. Stella Shalini, et al. 2014*)

Copper(II) complexes. The magnetic moments of the copper(II) complexes were measured at room temperature and were found in the range 1.74 – 1.82 μB, which is consistent with one unpaired electron. The solution spectra of Cu(II) complexes shows 13123 cm⁻¹ and 15503 cm⁻¹ were assigned ²B_{1g} → ²B_{2g} and ²B_{1g} → ²A_{2g} respectively. Suggesting octahedral geometry around the Cu(II) ion. (*S. Chandra et al., 2010*)

3.3 FTIR spectra

The IR spectrum of the macrocyclic ligand (L) and its complexes shows a ν(C=N) peak at 1665 cm⁻¹, (*S. Ilhan, H. et al. 2007*). and the absence of ν(C=O) peak at around 1700 cm⁻¹ and ν(NH₂) peak at around 3250 cm⁻¹ corresponding is indicative of Schiff's base condensation (*K. Nakamoto(1968)*) The IR spectrum of ligand, appearance of a new strong absorption band at 1643 cm⁻¹, attributable to the characteristic stretching frequencies of the imino linkage ν(C=N), which provides strong evidence for the presence of cyclic product. On complete formation the ν(C=N) shifted towards lower side by 12-11 cm⁻¹. Hence the ligand is tetra dentate, nitrogen donor coordinates through nitrogen of ν(C=N) group. The band in the 419-468 cm⁻¹ regions may be assigned to ν(M-N) vibration (*Tyagi M, et al. 2014, K. Nakamoto. 1970, S. Chandra et al., M 2007*). The ν(OH) vibration of phenolic proton appears as a broad band in the region 3200-3600 cm⁻¹ probably due to the overlapping of the symmetric and antisymmetric OH stretching vibration of lattice water *W. Radecka – Paryzek, (1980)*. The spectrum also shows the band at 1460, 660, 468 due to pyridine ring deformation, in plane ring deformation and out of plane ring deformation, respectively. The absorption bands show the positive shift in complex which indicates that the nitrogen of pyridine ring is involved in coordination (*S.Chandra et al. 2010, M.K. Biyala et al. 2004*). The appearance of strong band in the range 1373-1375 cm⁻¹ indicate the presence of ionic nitrate. (*K.Nakamoto (1978)*)

3.4 Mass spectrum of the ligand – L

The spectrum of the ligand L shows the peaks at [M + 1]⁺ m/z = 796. The peak at m/z = 786, 721, 636, 582 and 291 are due to the stepwise fragmentation of the macrocyclic ligand. The intensity of the peak at 291 is 100% because it corresponds to the macrocyclic moiety. Some other peaks also present in the spectrum at 246 and 185 due to the other fragmented ions. *J. H. Beynn (1960)*. The peaks area provides an idea of abundance of these ions.

3.4.1 Mass spectrum of the [CoL (NO₃)₂·2H₂O]

The ESI mass spectrum of the complex shows [M+1]⁺ peak at 1014 .which is equivalent to their molecular weights. The M (CoC₃₆H₂₈Br₂N₈O₁₀S₂) molecular ion peak recorded at m/z 1014 under goes fragmentation by as 855, (CoC₃₆H₂₄Br₂N₆O₂S₂), 787 (CoC₃₄H₂₄Br₂N₆OS), 716 (CoC₃₁H₂₄Br₂N₆O), 700 (CoC₃₀H₂₂Br₂N₆O), 634 (CoC₂₆H₂₀Br₂N₆), 489 (CoC₂₁H₁₉Br N₆), 400 ,(CoC₂₀H₁₉ N₆), 330 (C₁₉H₁₈ N₆), 290 (C₁₆H₁₄N₆), is a base peak.

3.4.2 Mass spectrum of the [NiL (NO₃)₂·2H₂O]

The ESI mass spectrum of the complex shows [M +1]⁺ peak at 1014. Which is equivalent to their molecular weights. The M (CoC₃₆H₂₈Br₂N₈O₁₀S₂) molecular ion peak recorded at m/z 1014 under goes fragmentation by as 855 (CoC₃₆H₂₄Br₂N₆O₂S₂), 787(CoC₃₄H₂₄Br₂N₆OS), 716 (CoC₃₁H₂₄Br₂N₆O), 700 (CoC₃₀H₂₂Br₂N₆O), 634(CoC₂₆H₂₀Br₂N₆), 489 (CoC₂₁H₁₉Br N₆), 400(CoC₂₀H₁₉ N₆), 330 (C₁₉H₁₈ N₆), 290 (C₁₆H₁₄N₆) is a base peak

3.4.3 Mass spectrum of the [CuL (NO₃)₂·2H₂O]

The ESI mass spectrum of the complex shows [M +1]⁺ peak at 1020 which is equivalent to their molecular weights. The M (C₃₆H₂₈Br₂CuN₈O₁₀S₂) molecular ion peak recorded at m/z 1020 under goes fragmentation by as 862(C₃₆H₂₄Br₂CuN₆O₂S₂), 838(C₃₄H₂₄Br₂CuN₆O₂S₂), 803(C₃₄H₂₄Br₂CuN₆O₂S), 787(C₃₄H₂₄Br₂CuN₆OS), 721(C₃₁H₂₄Br₂CuN₆O), 704(C₃₀H₂₂Br₂CuN₆O), 694(C₂₉H₂₂Br₂CuN₆O), 678(C₂₈H₂₀Br₂CuN₆O), 662(C₂₈H₂₀Br₂CuN₆), 652(C₂₇H₂₀Br₂CuN₆), 639(C₂₆H₂₀Br₂CuN₆), 497 (C₂₁H₁₉BrCuN₆), 408 (C₂₀H₁₉ CuN₆), 330 (C₁₉H₁₈ N₆), 290 (C₁₆H₁₄N₆) is a base peak.

Table1. Physical characterisation, analytical and molar conductance data of ligand (L₁₂) and its metal complexes.

Compound	F.W	M.P. in ° C	Colour	Molar conductance cm ² mol ⁻¹ mho.
L [C ₃₆ H ₂₄ Br ₂ N ₆ O ₂ S ₂]	796	146	Brown	-
[CoL] (NO ₃) ₂ ·2H ₂ O	1017	180	pink	10.25
[NiL] (NO ₃) ₂ ·2H ₂ O	1017	162	Green	11.09
[CuL] (NO ₃) ₂ ·2H ₂ O	1022	184	Dark green	12.25
[ZnL] (NO ₃) ₂ ·	985	165	Dark- white	10.12

Table2. FTIR spectra of ligand (L₁₂) and its complexes (cm⁻¹)

Compound	(OH)	v (C=N)	(C-Br)	(M-N)
L[C ₃₆ H ₂₄ Br ₂ N ₆ O ₂ S ₂]	3600	1665	530	----
[CoL] (NO ₃) ₂ ·2H ₂ O	3440	1645	532	419
[NiL] (NO ₃) ₂ ·2H ₂ O	3500	1643	530	468
[CuL] (NO ₃) ₂ ·2H ₂ O	3480	1644	528	468
[ZnL] (NO ₃) ₂ ·	3732	1645	532	418

4. Powder X- ray diffraction

The X-ray diffraction of representative metal complexes was scanned in the range 20 – 80° at wavelength 1.560 Å⁰. The diffractogram of Co(II) complex consists of 104 reflections with maxima at 2θ = 18.580° and its intensity 94.04 a.u. corresponding to d value 4.7716 Å⁰. The unit cell of Co (II) complex yielded values of lattice constant and unit cell volume V= 1648.80. in concurrence with these cell parameters, conditions such as a = 9.741, b = 7.193, c = 23.72 and α = 90°, β = 95.950, γ = 90° required for monoclinic

sample are tested and found to be satisfactory. Hence, it can be concluded that the Co(II) complex belong to monoclinic crystal system.

The diffractogram of Ni(II) complex had 38 reflections with maxima at $2\theta = 18.440^\circ$ and its intensity 84.13 a. u. corresponding to d value 4.8075 \AA . The unit cell of Ni (II) complex yielded values of lattice constant and unit cell volume $V = 1758.94$. in concurrence with these cell parameters, conditions such as $a = 13.55$, $b = 14.89$, $c = 8.718$ and $\alpha = \beta = \gamma = 90^\circ$ required for orthorhombic sample are tested and found to be satisfactory. Hence, it can be concluded that the Ni(II) complex belong to orthorhombic crystal system.

The diffractogram of Cu(II) complex had 41 reflections with maxima at $2\theta = 18.400^\circ$ and its intensity 158.37a.u. corresponding to d value 4.8178 \AA .

The diffractogram of Zn(II) complex had 29 reflections with maxima at $2\theta = 17.500^\circ$ and its intensity 95.79 a.u. corresponding to d value 5.0635 \AA (A.S. Stella Shaliniet.al. 2014)

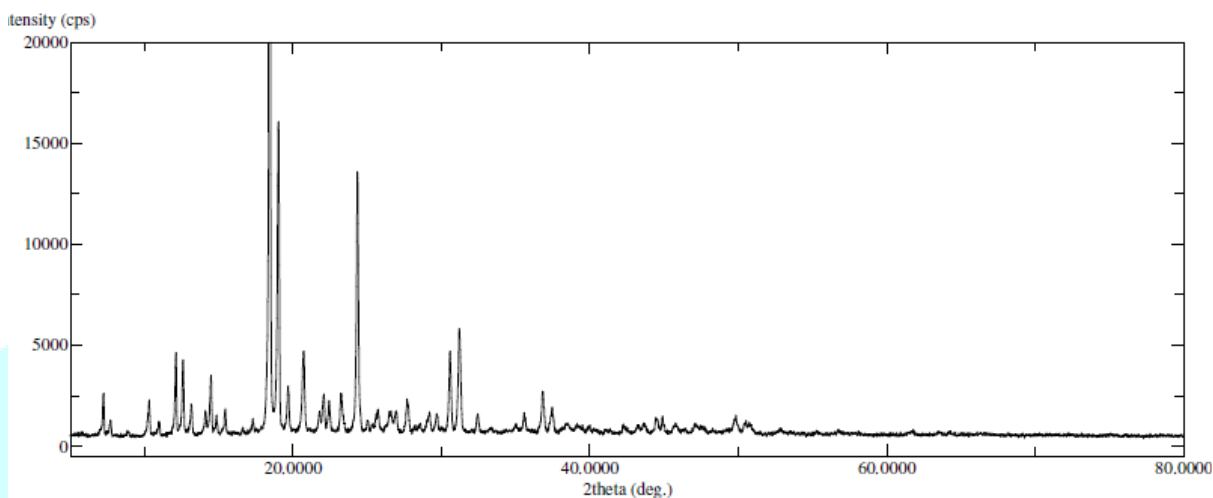


Fig. 3 X- Ray diffraction $\text{CuL}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

5.1 ANTIBACTERIAL ACTIVITY

All the synthesized macrocyclic metal complexes were tested for their *in vitro* antibacterial activities against four test bacterial strain, viz. *E. coli*, *P. aeruginosa*, *S. aureus* and *S. Pyogenus*. These complexes suggested that coordination decreases the polarity of the metal ion mainly because of the partial sharing of its positive charge with donor groups within the whole chelate ring system. Gentamycin, Ampicillin, Chloramphenicol, Ciprofloxacin and Norfloxacin used as standard drug.

All these complexes of the tested series exhibit antibacterial activities against all the tested bacterial strains (N. Raman *et al.* 2009). It was also observed that some moieties, such as an azomethine linkage or a heteroaromatic nucleus, introduced into such compounds exhibit extensive biological activities that may be responsible for the increase in the hydrophobic character and liposolubility of the molecules in crossing the cell membrane of the microorganism, which increasing the biological utilization ratio and activity of the complexes (D.P. Singh *et al.* 2011). The MIC (minimum inhibitory concentration) shown by the metal complexes against these bacterial strains was compared with the MIC values shown by the standard antibiotics Gentamycin, Ampicillin, Chloramphenicol, Ciprofloxacin and Norfloxacin. The MIC values of complex 1, 3 and 4 found to be better than Ampicillin. The MIC value of complex 2 found moderate activity to Ampicillin.

Table 3 Antibacterial activity of compounds

Sr.No	Code	Minimum Inhibition Concentration ($\mu\text{g/ml}$)			
		E.Coli	P. Aeruginosa	S. Aureus	S.Pyogenus
	No	MTCC 442	MTCC 441	MTCC 96	MTCC 443
1	CoL. $(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	62.5	100	500	250
2	NiL. $(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	500	500	250	500

3	CuL. (NO ₃) ₂ .2H ₂ O	500	250	200	100
4	ZnL. (NO ₃) ₂ .2H ₂ O	100	25	250	250
5	Gentamycin	0.05	1	0.25	0.5
6	Ampicillin	100	100	250	100
7	Chloramphenicol	50	50	50	50
8	Ciprofloxacin	25	25	50	50
9	Norfloxacin	10	10	10	10

5.2 ANTIFUNGAL ACTIVITY

All the synthesized macrocyclic metal complexes were tested for their *in vitro* antifungal activities against three test fungal strain, viz. *C. Albicans*, *A. Niger* and *A. Clavatus*. These complexes suggested that coordination decreases the polarity of the metal ion mainly because of the partial sharing of its positive charge with donor groups within the whole chelate ring system. Nystatin and Griseofulvin used as standard drug.

All these complexes of the tested series exhibit good antifungal activities against all the tested fungal strains. The *MIC* (minimum inhibitory concentration) shown by the metal complexes against these fungal strains was compared with the *MIC* values shown by the standard antibiotics. Nystatin and Griseofulvin. The *MIC* values of complex 2,3 and 4 found to be better than Griseofulvin. The *MIC* value of complex 4 found similar to Nystatin.

Table 4 Antifungal activity of compounds

Sr.No	Code No	Minimum Inhibition Concentration (µg/ml)		
		C. Albicans	A. Niger	A. Clavatus
		MTCC 227	MTCC 282	MTCC 1323
1	CoL. (NO ₃) ₂ .2H ₂ O	1000	1000	1000
2	NiL. (NO ₃) ₂ .2H ₂ O	250	500	500
3	CuL. (NO ₃) ₂ .2H ₂ O	200	500	500
4	Zn L. (NO ₃) ₂ .2H ₂ O	100	1000	1000
5	Nystatin	100	100	100
6	Griseofulvin	500	100	100

IV. CONCLUSION

In this paper, we describe the synthesis and characterisation of hexadentate macrocyclic ligand and its Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ complexes. Based on conductance, infrared electronic visible, mass spectral data, and X-ray powder diffraction pattern these entire complexes exhibit coordination number six. The FTIR spectral data suggest that ligand behaves as a tetradentate ligand with N₄ donor atoms towards central metal ion

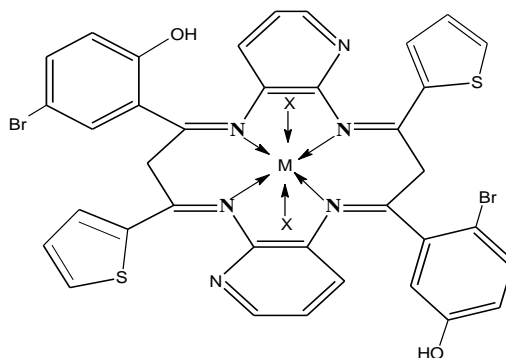


Fig.4 Proposed Structure of Complex, Where M= Co(II), Ni(II), Cu(II) and Zn(II) X= NO₃, H₂O

V. ACKNOWLEDGEMENT

The authors are thanks to the Head, Post Graduate Teaching Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Aurangabad. The authors also thankful to the Principal New Arts, Commerce and Science college Ahmednagar and Principal Arts, Commerce and Science college Sonai for providing necessary research facilities.

REFERENCES

1. J. Yao, W. Dou, W. Liu, J. Zheng, (2009). *Inorg. Chem. Commun.* 12 (430).
2. H. Yan Li, J. Wu, W. Huang, Y. H. Zhou, H. R. Li, Y. X. Zheng, J. L. Zuo, 2009. *J. Photochem. Photobiol.* 208A (110).
3. S. Chandra, D. Shukla, L. K. Gupta, 2008. *J. Indian Chem. Soc.* 85 (800).
4. J. Yao, W. Dou, W. Liu, J. Zheng, 2009. *Inorg. Chem. Commun.* 12 (430).
5. Khandar A. A. Hosseini – Yazdi, S. A. Zarei, S. A. Rabie, U. M. ,2005. *Inorg. Chim. Acta.*, (358). 3211- 3217.
6. Z. H. A. El- Wahab, 2009. *J. Coord. Chem.* 43 (231).
7. A. Chaudhary, N. Bansal, A. Garjraj, R. V. Singh, 2003. *J. Inorg. Biochem.* 96 (393).
8. D. P. Singh, R. Kumar, V. Malic, P. Tyagi, 2007. *J. Enzyme Inhib. Med. Chem.* 22 (119).
9. R. C. Sharma, R. Vats, S. Singh, S. Agarwal, 2007. *J. Inst. Chem.* 74 (119).
10. S. Bhan H. Temel L. Yinhez, M. Sekerci. 2007. *Polyhedron*, 26(12) 2795.
11. V. Dier J.V. Cuevs. G.C. Herbosa. G. Aullon. J.P.H. Charwant, et. al. 2007. *Inorg. Chem.* (46) 568-577.
12. S. Chandra, A. Gautam, M. Tyagi, 2007. *J. Transition Met. Chem.* (32) 1079-1084
13. A.S. Stella Shalini, M. Amaladasan, et. al. 2014. *Arabian J. of Chem.*
14. S. Chandra, M. Tyagi, S. Agrawal, 2010. *J. Serb. Chem. Soc.* 75(7) 935-941.
15. S. Ilhan, H. Temel, I. Yilmaz, A. Kilic, 2007. *Trans. Met. Chem.* 32 (344).
16. K. Nakamoto. 1968. *Infrared Spectra of Inorganic and Coordination Spectroscopy*, first ed., Elsevier, Amsterdam.
17. Tyagi M, Chandra S, Akhtar J and Chand D, 2014. *Spectrochim. Acta A.* (118). 1056 – 1061
18. K. Nakamoto. 1970. *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York.
19. S. Chandra, M. Pundir, 2007. *Spectrochim. Acta, A*(68) 883.
20. W. Radecka – Paryzek, 1980. *Inorg. Chim. Acta.* (45) L- (447).
21. S. Chandra, M. Tyagi, Soni Rani, Sumit Kumar 2010. *Spectrochim. Acta part A* (75).
22. M.K. Biyala, N. Fahmi, R. V. Singh, 2004. *Indian J. Chem.* 43 (A) 1662.
23. K. Nakamoto. 1978. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, third ed. Wiley Interscience, New York.
24. J. H. Beynon. 1960. *Mass Spectroscopy and its Application to Organic Chemistry*. Elsevier. Amsterdam.
25. A.S. Stella Shalini, M. Amaladasan, et. al. 2014. *Arabian J. of Chem.*
26. N. Raman, S.R. Johnson, A. Sakithivel, 2009. *J. Coord. Chem.* 62 (691).
27. D.P. Singh, Vidhi Grover et. al. 2011. *J. Serb. Chem. Soc.* 3 (76).