



Spectroscopic studies on Cr(III), Mn(II) and Zr(IV) complexes with N-donor tetradentate (N₄) macrocyclic ligand

Rajendra H. Satpute, Aashish O. Dhokte, Mahadeo A. Sakhare and Balasaheb R. Arbad*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.), India

ABSTRACT

Cr(III), Mn(II) and Zr(IV) complexes are synthesized with a novel tetradentate (N₄) macrocyclic ligand and characterized by the elemental analysis, conductometry, magnetic susceptibility, UV-visible, FTIR, ¹H NMR spectra, powder X-ray diffraction, and thermal analysis. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal:ligand) ratio. The TGA-DTA data suggest Cr(III) complex is having one nitrate ion, one water molecule and two coordinated nitrate ions, Mn(II) complex is having one lattice water molecule and two coordinated chloride ions and Zr(IV) complex is having one water molecule and two coordinated nitrate ions. The X-ray diffraction data suggest orthorhombic crystal system for Cr(III) and monoclinic crystal system for Mn(II) and Zr(IV) complexes.

Keywords: macrocyclic ligand complexes, Transition metal complexes, Thermal analysis, Powder X-ray diffraction etc.

INTRODUCTION

Synthetic macrocycles are a growing class of compounds with varying chemistry with a wide range of different molecular topologies and sets of donor atoms. The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometry [1-4]. Macrocyclic Schiff base nitrogen donor ligands have received special attention because of their mixed hard-soft donor character and versatile coordination behavior [5,6], and for their biological activities, i.e. toxicity against bacterial growth [7], anticancerous [8] and other biochemical properties [9,10]. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments [11] as well as NMR shift reagents [12]. Transition metals play a central role in the construction of molecular materials, which display magnetic properties and find applications in material and supramolecular chemistry and biochemistry [13-16]. Cr(III) complexes of macrocyclic ligands are well known for their biological importance as well as their anticarcinogenic, antibacterial, and antifungal properties [17].

The complexes of metal ions in combination to macrocyclic ligands are significant, as these resemble with natural system like porphyrin and cobalamine [18, 19]. The new macrocyclic bifunctional chelating agents are used in labeling monoclonal antibodies with radioactive metal [20-22] and for cancer diagnosis [23,24].

In view of the above consideration in this paper, we are reporting the synthesis and spectroscopic characterization of Cr(III) and Mn(II) and Zr(IV) complexes with a novel macrocyclic tetra dentate nitrogen donor ligand.

MATERIALS AND METHODS

Substituted diketone was prepared from 2-hydroxy acetophenone and P-amino benzoic acid by Bekar Vankataraman rearrangement. P-amino benzoic acid, phosphorus oxychloride, pyridine, potassium hydroxide, ethylene diamine of AR grade were used for synthesis of ligand. AR grade metal nitrate was used for the synthesis of complex. The

carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. FTIR spectrum was recorded on Jasco FTIR-4100 spectrometer using KBr pellets. ^1H NMR spectrum of ligand was recorded in CDCl_3 + DMSO using TMS as internal standard. The TGA-DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701, respectively. The UV-visible spectra of complexes were recorded on Jasco UV-530 spectrometer. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

Synthesis of ligand:

A hot ethanolic solution (30 ml) of 1-(4-aminophenyl)-3-(2-hydroxyphenyl)propane-1, 3-dione (5.10g, 0.02 mol) and a hot ethanolic solution (30 ml) of ethylene diamine (1.20 g, 0.02 mol) were mixed slowly with constant stirring. This reaction mixture was then refluxed at 80-90°C for 14-15 h in the presence of few drops of concentrated HCl. On cooling, a solid reddish yellow precipitate was formed, which was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} [25-27]. (Figure 1, Yield: 58 %)

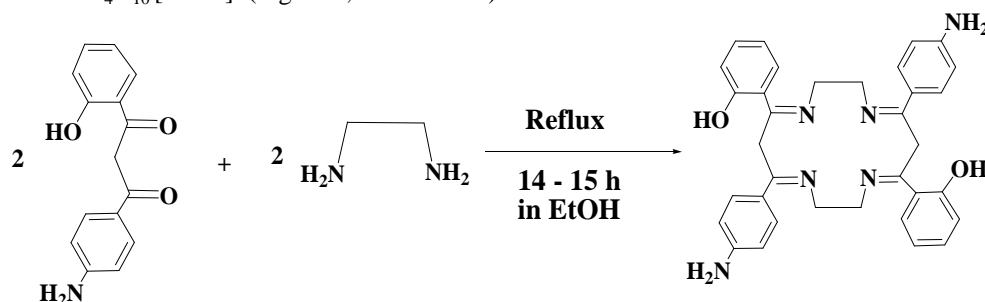


Figure 1: Synthesis of ligand

Synthesis of complexes:

A hot ethanolic (20 ml) solution of the ligand (0.001 mol) and a hot ethanolic (20 ml) solution of the corresponding metal salt (0.001 mol) were mixed together with constant stirring. The p^{H} of the reaction mixture was adjusted in the range 7-8 by adding 10% alcoholic ammonia solution. The reaction mixture was refluxed for 5-6 h at 80-90°C. On cooling; colored precipitate was formed. It was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} [25-27]. (Yield 50-55%).

RESULTS AND DISCUSSION

Physical characteristics, micro analytical, molar conductance data of ligand and metal complexes are given in Table 1. The analytical data of complexes reveals 1:1 molar ratio (metal:ligand). The presence of water molecules, chloride and nitrate ions was confirmed by TGA-DTA analysis as well as by FTIR spectroscopy. The X-ray diffraction data suggest orthorhombic crystal system for Cr(III) and monoclinic crystal system for Mn(II) and Zr(IV) complexes. The metal chelate solutions in DMF shows low conductance which supports non-electrolyte nature of metal chelates.

^1H NMR spectra of ligand:

^1H NMR (CDCl_3 -DMSO): δ = 2.6 (s, 4H, $-\text{CH}_2$), 3.9 (s, 8H, $\text{N}=\text{C}-\text{CH}_2$), 5.9 (s, 2H, Ar-OH), 4.1 (s, 4H, Ar- NH_2) 6.8-8.4 (m, 16H, Ar-H).

FTIR spectra:

The IR spectrum of the ligand (L) shows a $\nu(\text{C}=\text{N})$ peak at 1632 cm^{-1} , and the absence of a $\nu(\text{C}=\text{O})$ peak at around 1700 cm^{-1} is indicative of Schiff's base condensation. The IR spectrum of ligand, appearance of a new strong absorption band at 1632 cm^{-1} , attributable to the characteristic stretching frequencies of the imino linkage $\nu(\text{C}=\text{N})$, which provides strong evidence for the presence of cyclic product. On complex formation, the $\nu(\text{C}=\text{N})$ shifted towards lower side by 25-33 cm^{-1} , hence the ligand is tetradentate, nitrogen donor coordinates through nitrogen of $\text{C}=\text{N}$ group [28]. The $\nu(\text{OH})$ vibration of the phenolic proton appears as a broad band in the region 3200 - 3346 cm^{-1} probably due to the overlapping of the symmetric and antisymmetric OH stretching vibrations of lattice water [29-30]. The presence of lattice water is also established and supported by TGA-DTA analysis of these complexes. Cr(III) complex exhibit absorption bands at 1319 , 1390 and 1425 cm^{-1} due to the coordinated nitrate ion and band in the range 260 - 390 cm^{-1} , assigned to (Cr-N) stretching vibration [31-32]. Mn(II) complexes with a tetradentate macrocyclic N donor ligand and reported that infrared spectra of the complexes exhibited band in the range 440 - 550 cm^{-1} , assigned to (Mn-N) stretching vibration [33] and 335 - 340 cm^{-1} , assigned to (M-Cl) stretching vibration [34] and Zr(IV) complex exhibit absorption bands in the range 600 - 682 cm^{-1} , assigned to (Zr-N) stretching vibration [35]. On the basis of above discussion, a six coordinated structure is proposed for all the complexes in which the ligands coordinate *via* four azomethine nitrogens (Table 2).

Electronic spectra:

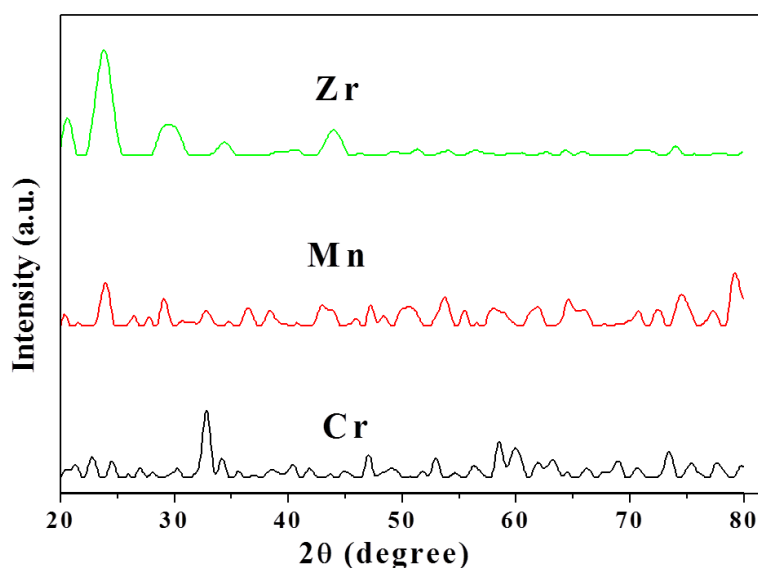
The electronic absorption spectra of Cr(III), Mn(II) and Zr(IV) complexes were recorded in DMF as a solvent. The electronic spectra of the ligand exhibits two transitions in the range 29239 and 30674 cm^{-1} , which may be attributed to the $\eta \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the imine groups. Electronic spectrum of Cr(III) complexes display three electronic spectral bands at 23474, 27933 and 31645 cm^{-1} . The three bands may be assigned to transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ respectively for octahedral geometry [36]. Electronic spectrum of Mn(II) complexes exhibit four absorption bands at 24875, 27624, 29240 and 35714 cm^{-1} . These bands may be assigned to the following transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4A_{1g}({}^4G)$, and ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$, ${}^6A_{1g}({}^4P)$, respectively [36]. Electronic spectrum of Zr(IV) complexes display two electronic spectral bands at 27624 cm^{-1} and 31447 cm^{-1} which may be assigned to $\pi \rightarrow \pi^*$ and LMCT transitions respectively[37,38].

Table 1: Physical characterization, analytical and molar conductance data of ligand and its metal complexes

Ligand/complexes	F.W.	M.P. ($^{\circ}\text{C}$)	Colour	Molar conduc. Mho ($\text{cm}^2 \text{mol}^{-1}$)	% Found (Calcd.)			
					C	H	N	M
(L)	558.67	211	Reddish yellow	3.4	73.09 (73.37)	6.13 (6.31)	15.04 (15.78)	-----
[Cr L (NO ₃) ₂] NO ₃ H ₂ O	814.66	>300	Brown	62	49.78 (50.08)	4.70 (4.41)	15.52 (15.46)	6.30 (6.38)
[Mn L(Cl) ₂] H ₂ O	702.6	>300	blackish	55	58.37 (58.07)	5.23 (5.12)	11.65 (11.95)	7.70 (7.81)
[ZrO L(NO ₃) ₂] H ₂ O	807.89	>300	pink Red	46	50.48 (50.50)	4.54 (4.45)	13.60 (13.8)	11.40 (11.29)

Table 2: FTIR spectra of ligand (L) and its complexes (cm^{-1})

Ligand/complexes	(OH)	(C=N)	(C=O)	(M-N)	Coordinated nitrate	Coordinated Chloride
(L)	3377	1632	1209	---	---	----
[Cr L (NO ₃) ₂] NO ₃ H ₂ O	3339	1602	1184	356	1319,1390,1425	----
[Mn L(Cl) ₂] H ₂ O	3331	1600	1239	522		354
[ZrO L(NO ₃) ₂] H ₂ O	3377	1603	1184	628	1029,848,760	----

**Figure 2: X-ray diffractogram of Cr(III), Mn(II) and Zr(IV) complexes****Powder X-ray diffraction:**

The X-ray diffraction of representative metal complexes was scanned in the range 20-80 $^{\circ}$ at wave length 1.540 \AA . The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d -values). The diffractogram of Cr(III) complex have 11 reflections with maxima at $2\theta = 32.805^{\circ}$ and its intensity 43.76 a.u. corresponding to d value 2.7278 \AA . The diffractogram of Mn(II) complex shows 20 reflection with maxima at $2\theta = 79.203^{\circ}$ and its intensity 34.52 a.u. corresponding to d value 1.2084 \AA . The diffractogram of Zr(IV) complex shows 17 reflection with maxima at $2\theta = 23.899^{\circ}$ and its intensity 67.81 a.u. corresponding to d value 3.720 \AA . The X-ray diffraction pattern of these complexes with respect to major peaks having relative intensity greater than 10% has been indexed by using computer programme. The above indexing method also yields Miller indices

(hkl), unit cell parameters and unit cell volume. The unit cell of Cr(III) complex yielded values of lattice constants, $a=15.18 \text{ \AA}$, $b = 7.10 \text{ \AA}$, $c = 6.27 \text{ \AA}$ and unit cell volume $V= 675.76 \text{ \AA}^3$. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90$ required for sample to be orthorhombic were tested and found to be satisfactory [39]. Hence, it can be concluded that Cr(III) complex have orthorhombic crystal system. The unit cell of Mn(II) complex yielded values of lattice constants, $a= 13.072 \text{ \AA}$, $b = 6.796 \text{ \AA}$, $c=6.896 \text{ \AA}$ and unit cell volume $V = 530.54 \text{ \AA}^3$. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = \beta = 90$ and $\gamma = 120$ required for sample to be monoclinic were tested and found to be satisfactory [40]. Hence, it can be concluded that Mn(III) complexes have monoclinic crystal system. The unit cell of Zr(IV) complex yielded values of lattice constants, $a= 33.91 \text{ \AA}$, $b = 4.210 \text{ \AA}$, $c=5.91 \text{ \AA}$ and unit cell volume $V = 560.41 \text{ \AA}^3$. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = 90$, $\beta= 123.795$ and $\gamma = 120$ required for sample to be monoclinic were tested and found to be satisfactory [41]. Hence, it can be concluded that Zr(IV) complexes have monoclinic crystal system (figure 2).

Thermal analysis:

The simultaneous TGA-DTA analysis of metal complexes was studied from ambient temperature 50 to 1000 °C in nitrogen atmosphere using $\alpha\text{-Al}_2\text{O}_3$ as reference. Thermogravimetric analysis shows that the Cr(III), Mn(II) and Zr(IV) complexes of ligand exhibit high thermal stability. The lattice water is removed in the temperature range of 55–110 °C and the ionic nitrates are removed in the 178–360 °C range. The macrocycle is lost in the temperature range of 361– 825 °C along with the coordinated nitrate [42].

Cr(III) complexes in which one lattice water and one ionic nitrate ions are removed with mass loss of 10.46 % (calcd.10.27%) between 50-190 °C and two coordinated nitrate ions are removed with loss of 15.70% (calcd.15.21%) between 190-290 °C. An endothermic peak in the range 140-150 °C ($\delta_{\text{max}} 150 \text{ }^\circ\text{C}$) in the DTA curve corresponds to the dehydration and denitration. Second endothermic peak in the range 260-270°C ($\delta_{\text{max}} 270 \text{ }^\circ\text{C}$) corresponds to the denitration step. The macrocycle is lost in the temperature range of 300–820 °C. An endothermic peak in the range 400-500 °C ($\delta_{\text{max}} 450 \text{ }^\circ\text{C}$) in the DTA curve corresponds to the loss of macrocycle step. The mass of final residue corresponds to stable Cr_2O_3 .

Mn(II) complexes in which one lattice water is removed with mass loss of 2.78 % (calcd.2.44 %) between 50-90 °C and two coordinated chloride ions are removed with loss of 9.81% (calcd.10.11 %) between 100-320 °C. An endothermic peak in the range 90-100 °C ($\delta_{\text{max}} 95 \text{ }^\circ\text{C}$) in the DTA curve corresponds to the dehydration and second endothermic peak in the range 315-325°C ($\delta_{\text{max}} 320 \text{ }^\circ\text{C}$) corresponds to the dechlorination step. The macrocycle is lost in the temperature range of 320–820 °C. An endothermic peak in the range 530-540 °C ($\delta_{\text{max}} 540 \text{ }^\circ\text{C}$) in the DTA curve corresponds to the loss of macrocycle step. The mass of final residue corresponds to stable MnO.

Zr(IV) complexes in which one lattice water is removed with mass loss of 1.94 % (calcd.2.21%) between 50-110 °C and two coordinated nitrate ions are removed with loss of 16.71% (calcd.17.79%) between 110-360 °C. An endothermic peak in the range 90-110 °C ($\delta_{\text{max}} 110 \text{ }^\circ\text{C}$) in the DTA curve corresponds to the dehydration and second endothermic peak in the range 340-360°C ($\delta_{\text{max}} 350 \text{ }^\circ\text{C}$) corresponds to the denitration step. The macrocycle are lost in the temperature range of 360–820 °C. An endothermic peak in the range 520-570 °C ($\delta_{\text{max}} 560 \text{ }^\circ\text{C}$) in the DTA curve corresponds to the loss of macrocycle. The mass of final residue corresponds to stable ZrO_2 .

CONCLUSION

Based on analytical, conductance, magnetic, infrared, electronic spectral data, TGA and X-ray powder pattern, all these complexes exhibit six coordination number. A tentative, general structure of Cr(III), Mn(II) and Zr(IV) macrocyclic ligand complexes is given in Figure 3. The FTIR spectral data suggest that the ligand behaves as a tetradentate ligand with N donor atoms towards central metal ion. The X-ray diffraction data suggest orthorhombic crystal system for Cr(III) and monoclinic crystal system for Mn(II) and Zr(IV) complexes. Analytical data obtained from thermal studies reveals that these complexes are thermally stable.

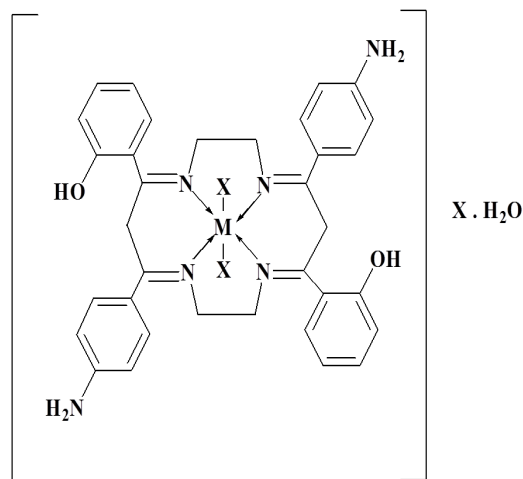


Figure 3: Proposed structure of metal complexes
Where $M = \text{Cr(III)}, \text{Mn(II)}$ and Zr(IV) .
 $X = \text{Cl} / \text{NO}_3$

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REFERENCES

- [1] Tarafder MTH, Saravanan N, Crouse KA, *Trans. Met. Chem.*, **2001**, 26, 613.
- [2] Ali M A, Tarafder MTH, *J. Inorg. Nucl. Chem.*, **1977**, 39,173.
- [3] Chandra S, Gupta K, Sharma S, *Synth. React. Inorg. Met. Org. Chem.*, **2001**, 31,1205.
- [4] Chandra S, Gupta K, *Trans. Met. Chem.*, **2002**, 27, 329.
- [5] Maji M, Chatterjee M, Ghosh S, Chattopadhyay SK, Wu BM, Mak TCW, *J. Chem. Soc., Dalton Trans.*, **1999**, 135.
- [6] Sengupta P, Dinda R, Ghosh S, Sheldrick WS, *Polyhedron.*, **2003**, 22, 447.
- [7] Pujar MA, Hadimani BS, Meenakumari S, Gaddad SM, Neelgund YF, *Curr. Sci.*, **1986**, 55, 353.
- [8] Mishra L, Jha A, Yadav AK, *Trans. Met. Chem.*, **1977**, 22, 406.
- [9] Mishra L, *J. Ind. Chem. Soc.*, **1999**, 76, 175.
- [10] David AB, Andrew LR, *Inorg. Chem.*, **1983**,22, 2199.
- [11] Seto J, Tamura S, Asai N, Kishii N Kijima Yand Matsuzawa N, *Pure and Appl. Chem.*, **1996**, 68,1429.
- [12] Dong W, Yang R, Yan L, *Indian J. Chem.*, **2001**, 40A, 202.
- [13] Chandra S, Kumar R, *Trans. Met. Chem.*, **2004**, 29, 269.
- [14] Chandra S, Kumar R, *Synth. and React. In Inorg. Met.-Org. and Nano-Metal Chem.*, **2005**, 35, 103.
- [15] Chandra S, Kumar R, *Synth. and React. in Inorg. Met.-Org. and Nano-Metal Chem.*, **2005**, 35, 161.
- [16] Madej E, Nsted OM and Kita P, *J. Chem. Soc. Dalton Trans.*, **2002**, 2361.
- [17] Levana A, Codd R, Dillon CT, Lay PA, *Prog. Inorg. Chem.*, **2002**, 51, 145.
- [18] Rosignoli M, Bernhardt PV, Lawrence GA, Maaeder M, *J. Chem. Soc.,Dalton Trans.*, **1997**, 323.
- [19] Fry E, Graham B, Spiccia L, Hockles DCR, Tiekink ERT., *J. Chem. Soc., Dalton Trans.*, **1997**, 827.
- [20] Broge L, Pretzmann U, Jesen N, Sotofte I, Olsen CE, Springborg J, *J. Inorg. Chem.*, **2001**,40, 2323.
- [21] Niu W, Wong EH, Weismann GR, Lam KC, Rheingold AL, *Inorg. Chem. Commun.*, **1999**,26, 361.
- [22] Brandes S, Denat F, Lacour S, Rabiet F, Barbette F, Pulumbi P, Guillard R, *Eur. J. Org. Chem.*,**1998**, 2349.
- [23] Chandra S, Gupta LK, *J. Saudi Chem. Soc.*, **2004**,8, 85; Wessels BW, Rogus RD, *Med. Phys.*, **1984**,11 638.
- [24] Liu Y, Wu C, *Pure Appl. Chem.*, **1991**,63, 427.
- [25] Chandra S, Gautam A, *spectrochemica Acta part A.*, **2008**, 70,1001-1002.
- [26] Chandra S, Gupta LK, *spectrochemica Acta part A.*, **2005**, 61, 1181-1182.
- [27] Chandra S, Gupta LK, *spectrochemica Acta part A.*, **2004**,60, 3079-3080.
- [28] S Chandra, L K Gupta, *Spectrochimica Acta Part A.*, **2004**,60, 3079–3085.
- [29] Sakhare M A, Khillare S L, Lande M K, Arbad B R, *Advances in Applied Science Research.*, **2013**, 4(1):94-100
- [30] Adams H, Bastida R, Blas AD, Carnota M, Fenton DE, Macias A, Rodriguez A, Rodriguez-blas T, *Polyhedron.*, **1997**,16, 567.
- [31] Aranha P E, Santos M P D, Romera S, Dockal E R, *Polyhedron* **2006**, doi:10.1016/j.poly.(2006).11.005.

- [32] Arul V, Aruna J, Alexander V, *Inorganica chemical acta A.*, **1996**,249, 96.
- [33] Chandra S, Gupta L K, *Spectrochimica Acta Part A.*, **2006**,65, 792.
- [34] Singh J, Jain P, Tayagi M, *J.Pharmacy and pharmaceutical Sci.*3, **2014**, 953-964.
- [35] Sobana raj C I, Gnana raj G A, *Int. j. Res. Chem. Environ.*, **2014**,4,36
- [36] Chandra S, Pundir M, *Spectrochimica Acta Part A.*, **2008**,69, 1-7.
- [37] Mandlik P R, Aswar A S, *Polish J. Chem.*, **2003**,77,129-135.
- [38] Nasrin J, Islam S, *J. App. Sci.*, **2007**, 7, 3, 434-441.
- [39] Raj kumar, Masih I, Fami N, *Spectrachimica Acta part A: molecular and biomolecular.*, 101,**2013**,100-106.
- [40] Aguiari A, Bullita E, Casellato U, Guerriero P, Tamburini S, *Inorganic Chim. Acta.*, **1994**,219,135-146.
- [41] Dubey R K, Dwivedi N, Singh A P, *Bulletin of Pure and Applied Sciences.*, **2013**, 32C, 97-109
- [42] Suresh kumar D, Alexander V, *Polyhedron.*, **1999**, 18,1561-1568.