Structural Elucidation Of Transition Metal Complexes of The Schiff base of 5- Nitro Salicylaldehyde And Anthranalic Acid Using ^1H NMR, Thermal Analysis, Diffused Reflectance and ESR data

Paresh S. More^{1*}, Bipin H. Mehta²

¹KETS V.G.Vaze College, Mithagar Road, Mulund(E), Mumbai - 400081, India

²Department of Chemistry, University of Mumbai, Vidyanagari, Kalina Campus, Santacruz(E), Mumbai - 400098, India

*E-mail address: paresh.m34@gmail.com

ABSTRACT

Transition metal complexes of the type $\text{ML.nH}_2\text{O}$ [Where $\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) , $\text{L} =$ Schiff base of 5 nitro salicylaldehyde and anthranalic acid, $n = 0, 1, \dots$] were characterized by using ^1H NMR, TGA, Diffused reflectance and ESR spectroscopy. On the basis of above studies Co(II) , Ni(II) shows tetrahedral structure, Cu(II) shows binuclear structure and Zn(II) shows square planar structure.

Keywords: ^1H NMR, 5-nitrosalicylaldehyde, TGA, Square planar complex

1. INTRODUCTION

Chelating ligand containing O and N donor atoms show broad biological activity and are of special interest because of different ways in which they are bonded to metal ions¹. Schiff base and their metal complexes have been used as a synthetic model for the metal containing sites metallo - protein and enzymes[2-3]. The Schiff base and their transition metal complexes are used as a catalyst for the number of catalytic process such as oxidation, epoxidation and polymerization of alkene [4-6]. Schiff base of 5 nitro salicylaldehyde, anthranalic acid and its metal complexes of $\text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) with their characterization by using elemental analysis, UV-Visible, IR, X-Ray diffraction were already reported by this lab [7]

In this paper we are reporting further investigation of the Schiff base and its metal complexes by using ^1H -NMR, TGA, Diffused reflectance and ESR spectroscopy.

2. EXPERIMENTAL

^1H NMR Spectra were recorded on a Bruker Act 300(300 Mz) spectrophotometer at IIT Bombay, Diffused reflectance spectra were recorded at Department Of Chemistry, University Of Mumbai , ESR spectra was recorded at IIT Bombay and TGA analysis at B.A.R.C., Trombay, Mumbai. Biological studies were carried out at Nicholas Piramal India,Ltd., Goregaon, Mumbai.

3. RESULT AND DISCUSSION

3.1. ^1H NMR Spectra

^1H NMR spectral data of the Schiff base and their metal complexes is as shown in the table1.

^1H NMR spectrum of the Schiff base (L) shows singlet at 10.30 ppm, which can be attributed to the carboxylic group(-COOH) proton, a singlet at 9.10 ppm was observed due to proton of hydroxyl- OH group. A singlet at 8.63 ppm was observed due to azomethine proton [8,9]. Multiple signals in the region of 6.50- 8.40 ppm are assigned to aromatic protons [10-11]. Fig.1 represents ^1H NMR spectrum of the Schiff base (L).

Fig.1. ^1H -NMR spectra of Schiff base (L).

Fig.2. ^1H -NMR Spectra of $[\text{Zn}(\text{L})\cdot\text{H}_2\text{O}]$.

In the ^1H NMR spectrum of the $[\text{CoL.H}_2\text{O}]$ complex the signals due to OH protons(-COOH group) is absent, suggesting the deprotonation of carboxylic group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through carboxylic oxygen atom [12-13]. The singlet due to azomethine proton at 8.63 ppm is deshielded and appears at 8.90 ppm indicates that azomethine group is coordinated to Co(II) ion through nitrogen atom.

In the ^1H NMR spectrum of the $[\text{NiL.H}_2\text{O}]$ complex the signals due to OH protons(-COOH group) is absent, suggesting the deprotonation of carboxylic group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through carboxylic oxygen atom [12-14]. The singlet due to azomethine proton at 8.63ppm is deshielded and appears at 8.90 ppm indicates that azomethine group is coordinated to Ni(II) ion through nitrogen atom.

In the ^1H NMR spectrum of the $[\text{2Cu(L)}_2]$ complex the signals due to OH protons(-COOH group) is absent, suggesting the deprotonation of carboxylic group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through carboxylic oxygen atom [14-16]. The singlet due to due to azomethine proton at 8.63ppm is deshielded and appears at 8.95 ppm indicates that azomethine group is coordinated to Cu(II) ion through nitrogen atom [17-18].

In the ^1H NMR spectrum of the $[\text{ZnL.H}_2\text{O}]$ complex the signals due to OH protons(-COOH group) is absent, suggesting the deprotonation of carboxylic group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through carboxylic oxygen atom [12-13]. The singlet due to due to azomethine protonat 8.63ppm is deshielded and appears at 8.73 ppm indicates that azomethine group is coordinated to Zn(II) ion through nitrogen atom[19]. The representative ^1H NMR spectrum of $[\text{ZnL.H}_2\text{O}]$ is as shown in the Fig.2.

3.2. Diffused reflectance spectra

Diffused reflectance spectrum of Schiff base L

Diffused reflectance spectrum is very important analytical tool for the diagnosis of various d-d transition and charge transfer spectra. The bands observed in the reflectance spectrum appears at 11481 cm^{-1} , 12330 cm^{-1} , 26570 cm^{-1} , 28901 cm^{-1} and 37597 cm^{-1} which may be assigned to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$. The position of these bands can be utilized for calculating shift in the corresponding position in the respective spectra of the metal complexes²⁰⁻²¹. Fig.3 indicates diffused reflectance spectrum of Schiff base (L).

The bands observed in the reflectance spectrum of the $[\text{CoL.H}_2\text{O}]$ complex of ligand shows absorption at 11709 cm^{-1} , 11904 cm^{-1} , 26809 cm^{-1} , 37453 cm^{-1} and 42553 cm^{-1} respectively which can be assigned to the transition $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{F})$, $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ and charge transfer bands. On the basis of paramagnetic nature and position of various d-d transition and charge transfer transition complex $[\text{CoL.H}_2\text{O}]$ may be assigned tetrahedral geometry. [22],[23],[24],[25]

Diffused reflectance spectrum of $[\text{NiL.H}_2\text{O}]$

The bands observed in the reflectance spectrum of the $[\text{NiL.H}_2\text{O}]$ complex of ligand shows absorption at 25380 cm^{-1} , 26525 cm^{-1} , 27777 cm^{-1} , 29154 cm^{-1} and 36363 cm^{-1} respectively which can be assigned to the transition $^3\text{T}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$, $^3\text{T}_{1g}(\text{F}) \rightarrow ^3\text{A}_{2g}(\text{F})$ and

charge transfer band. On the basis of paramagnetic nature and position of various d-d transition and charge transfer transition complex $[\text{NiL} \cdot \text{H}_2\text{O}]$ may be assigned tetrahedral geometry.[22,23,24,25]. The representative diffused reflectance spectra of $[\text{Ni}(\text{L}) \cdot \text{H}_2\text{O}]$ is as shown in Fig.4.

Fig.3. Diffused Reflectance Spectrum of Schiff Base (L).

Fig.4. Diffused Reflectance Spectrum of $[\text{Ni}(\text{L}) \cdot \text{H}_2\text{O}]$.

Diffused reflectance spectrum of $[\text{2Cu}(\text{L})_2]$

The bands observed in the reflectance spectrum of the $[\text{2Cu}(\text{L})_2]$ complex of ligand shows absorption at 11337 cm^{-1} , 28350 cm^{-1} , 27777 cm^{-1} , 33333 cm^{-1} and 36101 cm^{-1} respectively which can be assigned to the transition ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and charge transfer band respectively. On the basis of paramagnetic nature and position of various d-d transition and charge transfer transition complex $[\text{2Cu}(\text{L})_2]$ may be assigned binuclear structure.[26-32]

Diffused reflectance spectrum of [ZnL.H₂O]

The Diffused reflectance spectrum of the [ZnL.H₂O] complex of shows absorption at 11299 cm⁻¹, 24813 cm⁻¹, 27100 cm⁻¹, 30959 cm⁻¹ and 38314 cm⁻¹ respectively.

Table 1. ¹H NMR spectral data of the Schiff base and their metal complexes is as shown in the table 1.

Compound	¹ H COOH	¹ H- OH	¹ H CH=N	⁷ H Ar H
L(C ₁₄ H ₁₀ N ₂ O ₅)	10.30	9.10	8.63	8.40- 6.50
CoL.H ₂ O	---	9.10	8.90	8.04- 6.64
NiL.H ₂ O	---	---	8.90	7.80- 6.20
[2Cu(L) ₂]	---	---	8.95	8.00- 6.46
ZnL.H ₂ O	---	---	8.73	8.05- 6.40

Table 2. Diffused reflectance spectrum of Schiff base L.

Ligand: -2[[[2-hydroxy-5-Nitrophenyl]methylene]-amino]-Benzoic acid.

Molecular formula: C₁₄H₁₀N₂O₅

Reference: BaSO₄

Range: 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
871	11481	97.66
811	12330	94.83
414	26570	59.50
346	28901	60.39
266	37597	70.72

Table 3. Diffused reflectance spectrum data of Co(II) Complex.

Complex: CoL.H₂O

Molecular formula: C₁₄H₁₀N₂O₆. Co

Reference: BaSO₄

Range: 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
854	11709	93.02
840	11904	91.62
373	26809	37.79
267	37453	32.92
235	42553	38.05

Table 4. Diffused reflectance spectrum data of Ni(II) Complex.**Complex:** NiL.H₂O**Molecular formula:** C₁₄H₁₀N₂O₆.Ni**Reference:** BaSO₄**Range:** 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
394	25380	53.45
377	26525	56.62
360	27777	63.95
343	29154	68.81
275	36363	59.62

Table 5. Diffused reflectance spectrum data of Cu(II) Complex.**Complex:** [2Cu(L)₂]**Molecular formula:** C₂₈H₁₈N₄O₁₀.Cu₂**Reference:** BaSO₄**Range:** 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
882	11337	65.39
388	28350	35.75
360	27777	49.43
300	33333	37.63
277	36101	43.66

Table 6. Diffused reflectance spectrum data of Zn(II) Complex.**Complex:** ZnL.H₂O**Molecular formula:** C₁₄H₁₀N₂O₆.Zn**Reference:** BaSO₄**Range:** 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
885	11299	90.56
403	24813	46.52
369	27100	49.18
323	30959	45.60
261	38314	24.76

Table 7. Thermo gravimetric Analysis Data Of Complexes.

[Compound] Molecular formula (Molecular Weight)	Temp. at which Coordinated water molecule is removed	Thermal	Analysis	Obs(Theor.)%
		Coordinated water content	Organic Content	Metal Oxide Content
[CoL.H ₂ O] C ₁₄ H ₁₀ N ₂ O ₆ .Co (360.93)	310	4.98(5.35)	74.25(73.98)	20.76(20.67)
[NiL.H ₂ O] C ₁₄ H ₁₀ N ₂ O ₆ .Ni (360.69)	180	4.99(5.30)	74.30(73.84)	20.70(20.86)
[2Cu(L) ₂] C ₂₈ H ₁₈ N ₄ O ₁₀ .Cu ₂ (641.08)	---	---	77.68(77.09)	22.31(21.91)
[ZnL.H ₂ O] C ₁₄ H ₁₀ N ₂ O ₆ .Zn (367.39)	440	4.89(4.23)	72.94(73.19)	22.15(22.58)

Table 8. Antifungal and Antibacterial Studies of Schiff Base And Its Metal Complexes.

Compound	Conc. Mg/ ml	ZONE SIZE IN MM			
		<i>Candida albicans</i>	<i>Candida krusei</i>	<i>Aspergillus fumigatus</i>	<i>Staphylococcus aureus</i>
Ligand(L)	5.0	---	---	---	---
	2.5	---	---	---	---
	1.25	---	---	---	---
[CoL.H ₂ O]	5.0	09	12	10	---
	2.5	08	11	09	---
	1.25	08	11	09	---
NiL.H ₂ O	5.0	13	19	13	13
	2.5	12	10	11	---
	1.25	12	09	11	---
[2Cu(L) ₂]	5.0	09	14	15	---
	2.5	08	12	12	---
	1.25	08	12	12	---
[ZnL.H ₂ O]	5.0	09	13	10	---
	2.5	07	12	09	---
	1.25	07	11	09	---

3.3. Thermal studies

Thermal decomposition studies of Cobalt(II) Complexes

The thermogram of $[\text{CoL.H}_2\text{O}]$ shows that the complex starts decomposing gradually till it attains the temperature corresponding to 310°C . Till this point weight corresponding to 1 mole of coordinated water per mole of Co(II) complex is removed. The loss of coordinated water molecule in Co(II) complex is a single step process. The percentage weight loss corresponding to loss of coordinated water molecule from thermogram was found to be 4.98% which is in close agreement with theoretical value (5.35%).

Organic content of the metal complex is removed during this loss and decomposition continue up to the temperature 800°C

The percentage weight loss of organic content from the Co(II) complex was found to be 74.25% which matches with theoretical value (73.98%). After this weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide³³⁻³⁴ (CoO). The percentage weight of the residual metal oxide was found to be 20.76% which matches with theoretical value (20.67%). Thermal analysis further confirms our finding that one mole coordinated water per mole of metal complex is present in case of $[\text{CoL.H}_2\text{O}]$ complex and Schiff base L is tridentate ligand with O:N:O donor sequence and complex is having tetrahedral geometry.

Thermal decomposition studies of Nickel (II) Complexes

The thermogram of $[\text{NiL.H}_2\text{O}]$ shows that the complex starts decomposing gradually till it attains the temperature corresponding to 180°C . Till this point weight corresponding to 1 mole of coordinated water per mole of Ni(II) complex is removed. The loss of coordinated water molecule in Ni(II) complex is a single step process. The percentage weight loss corresponding to loss of coordinated water molecule from thermogram was found to be 4.99% which is in close agreement with theoretical value (5.30%)³⁵⁻³⁶.

Organic content of the metal complex is removed during this loss and decomposition continue up to the temperature 600°C

The percentage weight loss of organic content from the Ni(II) complex was found to be 74.30% which matches with theoretical value (73.84%). After this weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide³⁵⁻³⁶ (NiO). The percentage weight of the residual metal oxide was found to be 20.70% which matches with theoretical value (20.86%). Thermal analysis further confirms our finding that one mole coordinated water per mole of metal complex is present in case of $[\text{NiL.H}_2\text{O}]$ complex and Schiff base L is tridentate ligand with O:N:O donor sequence and complex is having tetrahedral geometry.

Thermal decomposition studies of Copper (II) Complexes

The thermogram of $[\text{2Cu(L)}_2]$ shows that the complex shows decomposition at 383°C . After this Organic content of the metal complex is removed during this loss and decomposition continue up to the temperature 410°C

The percentage weight loss of organic content from the Cu(II) complex was found to be 77.68% which matches with theoretical value (78.09%). After this weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally

stable residual metal oxide [35-36] (2CuO). The percentage weight of the residual metal oxide was found to be 22.31% which matches with theoretical value(21.91%). Thermal analysis further confirms our finding that coordinated water molecule is absent in the $[\text{2Cu(L)}_2]$ metal complex and Schiff base L is tridentate ligand with O:N:O donar sequence and complex is having square planar geometry. Fig 5. represents the TGA of the compound $[\text{2Cu(L)}_2]$.

Fig.5. TGA of the compound $[\text{2Cu(L)}_2]$.

Thermal decomposition studies of Zinc (II) Complexes

The thermogram of $[\text{ZnL.H}_2\text{O}]$ shows that the complex starts decomposing gradually till it attains the temperature corresponding to 440°C . Till this point weight corresponding to 1 mole of coordinated water per mole of Zn(II) complex is removed. The loss of coordinated water molecule in Zn(II) complex is a single step process. The percentage weight loss corresponding to loss of coordinated water molecule from thermogram was found to be 4.89% which is in close agreement with theoretical value(4.23%)³⁵⁻³⁶. Organic content of the metal complex is removed during this loss and decomposition continue up to the temperature 610°C .

The percentage weight loss of organic content from the Zn(II) complex was found to be 72.94% which matches with theoretical value(73.19%). After this weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide [35-36] (ZnO). The percentage weight of the residual metal oxide was found to be 22.15% which matches with theoretical value(22.58%). Thermal analysis further confirms our finding that one mole coordinated water per mole of metal complex is present in case of $[\text{ZnL.H}_2\text{O}]$ complex and Schiff base L is tridentate ligand with O:N:O donar sequence and complex is having Square planar geometry[37].

3.4. ESR Spectral studies of copper(II) complex

This technique is used to detect the presence of unpaired electron in a metal cluster. The x-band ESR Spectrum of $[\text{2Cu(L)}_2]$ complex exhibit a single line resulting the interaction of unpaired electron present in the Cu(II) complex. The table reveals that $g_\perp$ factor is found to be 1.9535, while $g_\parallel$ factor is found to be 1.8271. The $g_\parallel$ value is less than 2.3 which suggest existence sufficient covalency in the $[\text{2Cu(L)}_2]$. The solid state ESR spectrum of

[2Cu(L)₂] complex at room temperature yielded a broad signal with $g_{avg} = 1.9114$, indicating unpaired electron lie in $d^{x^2-y^2}$ orbital of Cu(II) complex.[38,39,40] Fig.6. represents the ESR Spectra of the compound [2Cu(L)₂].

Fig.6. ESR Spectra of [2Cu(L)₂].

3.5. Biological studies of schiff base L and Co(II),Ni(II),Cu(II) and Zn(II) Metal complexes

The concentration used for testing 5.0mg/ml, 2.5mg/ml and 1.25mg/ml in DMF. The results from the table reveals that the ligand is inactive towards all the fungi as well as bacterial strains. All the metal complexes were found to have excellent fungi toxic properties even after decreasing concentration of metal complex in the test sample, activity almost remains same with slight decrease. Thus we can conclude that at low concentration metal complexes are most active against fungal and bacterial strains as desirable. In general metal complexes are more active than their parent ligand and hence may serve as vehicle for activation of the ligand as principle cytotoxic species.[12,41,42].

4. CONCLUSION

On the basis of ¹H NMR, Diffused reflectance data and Thermo gravimetric studies, Co(II),Ni(II) shows tetrahedral structure where as Zn(II) exhibits Square planar complex and Cu(II) shows binuclear structure.

Fig.7. [Co(II), Ni(II), Zn(II)].

Fig.8. [Cu(II)].

References

- [1] Syamal A and Maurya M.R., 1989, *Coord. Chem.Rev.*, 95, 183-238.
- [2] N. Kitajima, Moro-Oka, *Chem.Rev.* 94(1994)289.
- [3] K.Geeta, S.K.Tiwari, A.R.Chakravarthy, G.Ananthakrishnan, *J.Chem.Soc.Dalton Trans.*(1999)4463.
- [4] R.M.Wang., C.J.Hao., Y.F.He., Y.P.Wang., S.B.Li. *J.Mol.Catal.* 147(1999) 173
- [5] V.G.Gbson., S.K.Spitzmesse., *Chem.Rev.* 103(2003)283
- [6] R.I.Kureshy., N.H.Khan., S.H.R.Abdi., S.T.Patel., R.V.Jasra, *Tetrahedron: Asymmetr.* 12(2000)433.
- [7] B.H.Mehta and P.S.More, *Asian Journal Of Chemistry*, Vol19, No.5(2007), 3581-3587.
- [8] Mayadevi S., Prasad P.G. and Mohammad Yusuff K.K., *Synth.React. Inorg. Met.- Org. Chem.*, 33(3), 481(2003).
- [9] Reddy PP., Reddy C.K. and Reddy P.S.N., *Bull.Chem.Soc.Jpn.*, 59, 1575(1986).
- [10] Paresh S. More and Santosh G. Singh *International Letters of Chemistry, Physics and Astronomy*, 4(2015)71-80

-
- [11] Paresh S. More and Santosh G. Singh *International Letters of Chemistry, Physics and Astronomy*, 8(1)(2015)49-55.
- [12] Henri L.K.W., Tagenine, and Gupta B.M., *Indian J. Chem.*, 40A,999(2001).
- [13] Sena.K., Singh G., Singh K., Noreen R.K., Handa R.N. and Dubey S.N., *Indian J. Chem.*, 36A,891(1997).
- [14] Maurya C.R., Patel P., and Rajput S., *Synth. React. Inorg. Met.- Org. Chem.*, 33(5),836(2003).
- [15] Celik.C., Tumer M. and Serin S., *Synth. React. Inorg. Met.- Org. Chem.*, 32(10),1839(2002).
- [16] Deepa K and Arvindakshan K.K., *Synth. React. Inorg. Met.- Org. Nano-Met. Chem.*, 32,409(2005).
- [17] B.H. Mehta and D.S. Joisher, *Asian J. of Chemistry*, 16,910(2004).
- [18] C.R. Jejurkar and K. Parikh *Asian J. of Chemistry*, 9,624(2004).
- [19] Yilmaz I. and Cukurovali A., *Synth. React. Inorg. Met.- Org. Chem.*, 33(4),657(2003).
- [20] Thomas R. and Parmeswaran G., *J. Indian Chem. Soc.*, 77,256(2000).
- [21] Hankare P. P., Naravane S.R., Bhuse V.M., Delekar S.D. and Jagtap A.H., *Indian J. Chem.*, 43A,1464(2004).
- [22] Prabhu P.M and Mehta B.H., *Orient. J. Chem.*, 13(3),297 (1997).
- [23] Biradar N.S., Pujar M.A. and Marathe V.R., *Indian J. Chem.*, 9A,712(1971).
- [24] Arvindakshan K.K., *Indian J. Chem.*, 26A,241(1987).
- [25] Sharda L.N and Ganorkar M.C. *Indian J. Chem.*, 24A,617(1985).
- [26] Isakdar M.F., Khalil T.E., Hasse W., Werner R., Svoboda I. and Fuess H., *Polyhedron*, 20,2787(2001).
- [27] Castellio I., Fernandez- Gonzalez J.M and Garate- Morales J.L., *Molecular Structure*, 657,25(2003).
- [28] Yang C.T., Moubaraki B., Murray K.S. and Vittal J.J., *Dalton Trans.*, 880(2003).
- [29] Rao R.N., Rao V.P., Reddy V.G., Ganorkar M.C., *Indian J. Chem.*, 26A,887(1987).
- [30] Mukherjee Gurucharan., Pai Shefali and Poddar Shailendranath, *Indian J. Chem.*, 30A,952(1991).
- [31] Rao R.N., Rao V.P., Tyanga Raju V.J., Ganorkar M.C., *Indian J. Chem.*, 24A,877(1985).
- [32] M. Kishita., Y. Muto and M. Kubo., *Naturwissen- Schfaten, Australian J. Chem.* 44,372(1957)
- [33] Duval C., "Inorganic Thermogravimetric Analysis." 2nd Edn., Elsevier Amsterdam(1963).
- [34] Wendlandt W.W., "Thermal Methods Of Analysis," 2nd Edn., Wiley- Interscience(1974).
- [35] Panchal P.K., Patel D.H and Patel M.N., *Synth. React. Inorg. Met.- Org. Chem.*, 34(7),1223(2004).

-
- [36] Patel M.N., Patel N.H and Patel K.N., Dholkia P.P and Patel D.H., *Synth.React. Inorg. Met.- Org. Chem.*, 33(1),51(2003).
- [37] Hankare P.P., Patil R.K., Chavan S.S., Jagtap A.H. and Battase P.S., *Indian J.Chem.*, 40A,1326(2001).
- [38] Shiroadkar S.G., Mane P.S and Chondekar T.K. *Indian J.Chem.*, 40A,1114(2001).
- [39] Singh N.K and Singh S.B., *Indian J.Chem.*, 40A,1070(2001).
- [40] Sharma A.L., Singh I.O., Singh M.A., Singh H.R., Kadam R.M., Bhide M.K., Sastry M.D., *Transition Met. Chem.* 26,532(2001)
- [41] Makode J.T and Aswar A.S., *Indian J.Chem.*, 43A,2120(2004).
- [42] Petering D.H., "Meal ions in biological system," edited by H.Sigel, Vol II Marcel Dekker.

(Received 14 February 2015; accepted 22 February 2015)