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Synthesis, structural characterization and antimicrobial studies of Cobalt (II), Nickel (II), Copper(II) and Zinc(II) Schiff base complexes derived from hetero cyclic aldehyde and 3-amino 5-ter Butyl Isoxazole.

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Abstract

A Tetradentate Schiff base ligands have been prepared by the reaction of furfural, pyridine 2-carbaldehyde and pyrrole 2- carbaldehyde with a stoichiometry amount of 3-amino 5-ter Butyl Isoxazole in absolute Ethanol The schiff base L$_1$ N-(5-terButyl-3'-Isoxazolyl)-N-[(E)-1-(2-furan)]methylidiline amine [TBIFMA] L$_2$ N-[5-terButyl) -3-Isoxazolyl)]-N-[(E)-1-[2-pyridine)]methylidine amine [TBIP$_1$MA] and L$_3$ N-[5-ter Butyl-3-isoxazolyl]-N-](E)-1-(2-pyrrole)]methylidine amine [IBI P$_2$ MA] have been prepared. the metal chelates of TBIFMA, TBTP$_1$MA and TBIP$_2$MA with Co(II), Ni(II), Cu(II) and Zn (II) complexes are also prepared, those complexes are having the composition M(II) (L)$_2$ 2H$_2$O (where L=ligand M= Co (II), Ni (II), Co(II) and Zn (II)) above complexes are analysis by Elemental analysis, ^{1}H-NMR, Mass IR , Electronic spectral data and magnetic moments. From these studies it is found that the ligands are act as bidentate ligand coordinating through Oxygen and Nitrogen donor atoms. The chelates of Co(II),Ni(II) and Zi (II) appear to be Octahedral and Cu (II) appear to be tetragonal geometry. Antimicrobial activity of those ligands and their metal complexes against bacteria (*bacillus, Pseudomonas)* and fungus (R. *Solani,* A. *niger)* has been carried out . If it found that the metal complexes have higher activities than those free ligands.

Key words: 5-Ter-Butyl Isoxazole Schiff bases, Metal chelate, antimicrobial activity.

1. Introduction

Synthesis of Isoxazole derivaties and their Schiff base complexes has been investigated extensively for last several decades leadings to new synthetic routs of structure and the wide application of such as in pharmaceutical as well agrochemical industry. Numerous compounds contain isoxazole moieties have been shown to exbit anti-inflammatory, anti bacterial, anti viral anti fungal and anti tumor activities [1-9]. The Schiff base ligands have been prepared by hetero cyclic aldehyde, with various hetero cyclic amine having O and N donor atoms have been reported by several scientist [10]. Some synthesis methods have not been entirely satisfactory owing to a number of draw backs such as low yields. Over the past few decades, significant research has been directed towards the development of new Technologies for environmentally research processes (Green chemistry) [11].· Tetra dentate schiff bases with a N$_2$, O$_2$ donor atom set are known to coordinate with metal ions, and this has attracted many researchers [12]. The present Investigate the reaction of tetra dentate shiff base derived from the condensation of heterocyclic aldehyde with 3- Amino 5-ter Butyl Isoxazole with cobalt, nickel, copper and zinc ions. The prepared ligands and complexes were characterized by elemental analysis. ^{1}H-NMR, IR, Mass and electronic spectral data and antimicrobial studies on Schiff base of TBIFMA, TBIP$_1$MA and TBIP$_2$MA and their metal complexes.

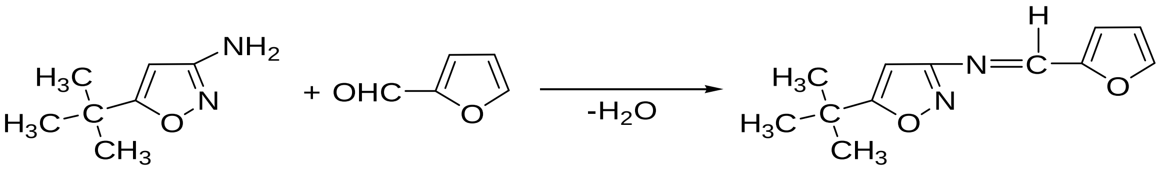
2.1. Material and Methods

All reagent were purchases from commercial sources.^{1}H-NMR (300MHz) and ^{13}C-NMR (100MHz) were recorded on Varian Gemini Unity spectrometer using CDCl$_3$ or DMSO-d$_6$ and TMS is used as internal reference. IR Spectra (KBr) were recorded on a FTIR Spectrophotometer in the range of 400-4000 cm^{-1} Elemental analyses were carried out an element or vireo –EL instrument, purity of the synthesized compounds was checked by means thin –layer chromatography (TLC) glass plates precoated with silica gel (60F, merck), were used .Un corrected melting point were measured in open- capillary Tubes Cl Kofler bench (model WME) Apparatus Electronic spectra of metal complexes in DMSO were recorded on

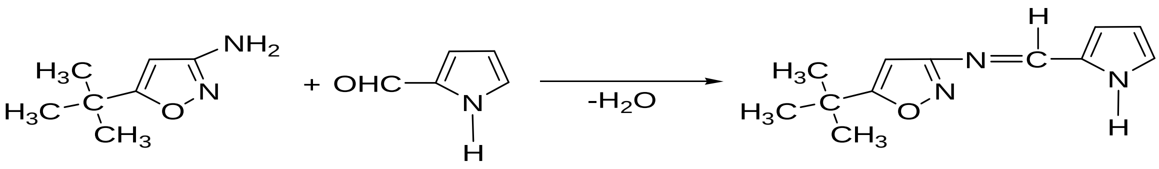
Schimadzu Uv-vis 1601 spectro photometer. Where as the mass spectra of these ligands were obtained using a VG -707 E mass Spectrometer,the Electron impact excitation was 70 eV.

2.2.1. General procedure for preparation of the ligands:

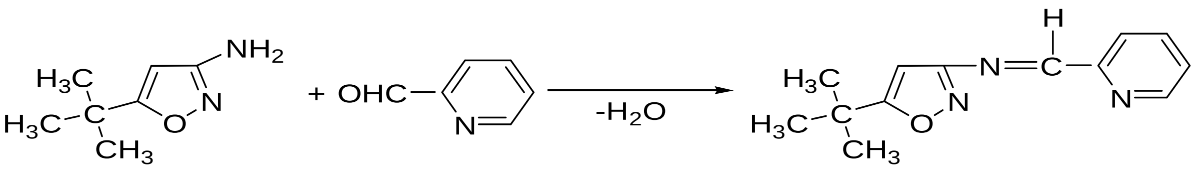
The ligands were prepared by a modification of the reported methods [13]. A solution of 0.1 mol 3-Amino 5- ter Butyl Isoxazole (dissolve in 50ml of Ethanol) was slowly added to a solution of 0.1 mol heterocyclic aldehyde (furfural, phyridine 2-Carbaldehyde and pyrrole 2-carbaldehyde) in 50 ml Ethanol. After the reaction mixture was stirred and refluxed for 3hr at 60-70^{0}C. The precipitate was cooled and collected by filtration. The precipitate washing with distils water several times, and was than washed with Ethanol, followed by recrystalization in Ethanol and drying at 40^{0}C over night.



3-Amino 5- ter butyl Isoxazole , Furfural , L$_1$ N-(5-terButyl-3'-Isoxazolyl)-N-[(E)-1-(2- furan)]methylidiline Amine [TBIFMA], **Fig-1**



3-Amino 5- ter butyl Isoxazole , Pyrrol 2-carbaldehyde , L$_3$ N-(5-terButyl-3'-Isoxazolyl)-N -[(E)-1-(2- pyrrole)]methylidiline Amine [TBIP$_2$MA, **Fig-2**



3-Amino 5-terbutyl Isoxazole,, Pyridine 2-carbaldehyde , L$_2$ N-(5-terButyl-3'-Isoxazolyl)-N-[(E)-1-(2-Pyridine)]methylidiline Amine [TBIP$_1$MA, **Fig-3**

2.2.2. General procedure for preparation of the complexes:

Co(II), Ni(II) Cu(II) and Zn(II) complexes were prepared by the addition of 5m mol of $Co(CH_3COO)_2.4H_20$, $Ni(CH_3COO)_2.4H_2o$, $Cu(CH_3COO)_2.2H_2O$, and Zn $(CH_3COO)_2.2H_2O$. Which were dissolved in about 20-30ml of water, into a hot methanol solution of 10m mol of the ligand(1:2 molar ratio) the color of the complexes changes in a few minutes. The mixture was then refluxed for 2-3 hours. At 50-60^{0}C the precipitated solid were filtered to form the reaction mixture. The solid were washed with methanol and than with diethyl ether, followed by drying at 60^{0}C over night.

2.3. Antimicrobial Screening

The ligands and their metal complexes screened against bacteria (*Bacillus, Pseudomonas* and fungi (*A.nigger, R.Solani*) were used. The antimicrobial action was studied by paper disc methods. The compounds were dissolved in

DMSO. Filter paper discs of 4mm diameter were prepared. The Filter paper discs were placed on nutrient medium. These Preti dishes were incubated at 35^0c for 48hrs. The inhibition zone was observed after 48hrs.The growth of the microbes was measured by recording the diameter of the inhibition zone .

3. Results and Discussion

Elemental analysis data. Formula weight, colors and melting points are given in **Table -1.** The results of the Elemental analysis of the Schiff bases TBIFMA, $TBTP_1MA$ and $TBIP_2MA$ its complexes are in good agreements with those required by the proposed formula as $[M(L)_2.2(H_2O)]$ where M=Co(II), Ni(II), Cu(II) and Zn(II). The complexes are air stable, non–hygroscopic colored solids, are in soluble in water, partly soluble in Ethanol and methanol and soluble in DMSO. With the chemical yields of those metal complexes in the 80-95% range.

Table-1. Analytical data and some physical properties.

Compound (formula)	Color	Yield%	C% Calc(Found)	H% Calc(Found)	N% Calc(Found)	M% Calc(Found)	Melting Point
L_1 ($C_{11}N_2O_2H_{14}$)	Light yellow	75%	64.076 (64.00)	6.79 (6.47)	13.59 (13.89)	-	150-155^{0}c
Co(II) $(L_1)_2.2H_2O$	Yellow green	89%	53-01 (54.00)	6.425 (6.56)	11.24 (11.67)	10.04 (10.45)	240-242^{0}c
Ni(II) $(L_1)_2.2H_2O$	Green	92%	54.57 (54.87)	6.61 (6.98)	11.57 (11.78)	11.15 (11.46)	256-259^{0}c
Cu(II) $(L_1)_2.2H_2O$	Blue	95%	54.62 (55.34)	6.59 (6.89)	11.61 (11.78)	11.02 (11.56)	261-263^{0}c
Zn(II) $(L_1)_2.2H_2O$	brown	85%	55.02 (55.87)	6.57 (6.78)	11.54 (11.68)	11.09 (11.34)	231-233^{0}c
L_2 ($C_{13}N_3OH_{15}$)	White	78%	63.67 (63.87)	6.12 (6.54)	17.14 (17.67)	-	160-162^{0}c
Co(II) $(L_2)_2.2H_2O$	Light green	83%	57.56 (57.98)	6.27 (6.56)	15.49 (15.67)	9.59 (9.89)	243-245^{0}c
Ni(II) $(L_2)_2.2H_2O$	Green	90%	57.51 (57.87)	6.31 (6.67)	15.41 (15.56)	9.43 (9.65)	257-262^{0}c
Cu(II) $(L_2)_2.2H_2O$	Light Blue	95%	57.49 (57.90)	6.35 (6.56)	15.32 (15.67)	9.73 (9.89)	267-271^{0}c
Zn(II) $(L_2)_2.2H_2O$	Light brown	84%	57.41 (57.78)	6.32 (6.78)	15.37 (15.56)	9.82 (9.89)	233-235^{0}c
L_3 ($C_{12}N_3OH_{15}$)	Light brown	79%	62.60 (62.56)	6.95 (6.99)	18.26 (18.89)	-	146-148^{0}c
Co(II) $(L_3)_2.2H_2O$	Dark Green	86%	56.14 (56.23)	9.62 (9.45)	16.37 (16.45)	10.13 (10.67)	231-233^{0}c
Ni(II) $(L_3)_2.2H_2O$	Green	91%	56.32 (56.78)	6.53 (6.78)	16.39 (16.56)	10.19 (10.78)	269-292^{0}c
Cu(II) $(L_3)_2.2H_2O$	Blue	94%	56.26 (56.45)	6.49 (6.78)	16.26 (16.97)	10.21 (10.45)	249-252^{0}c
Zn(II) $(L_3)_2.2H_2O$	brown	82%	56.30 (56.87)	6.52 (6.67)	16.30 (16.46)	10.17 (10.67)	231-235^{0}c

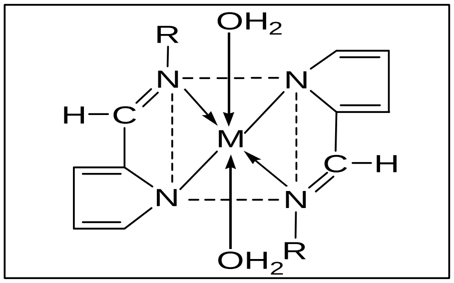
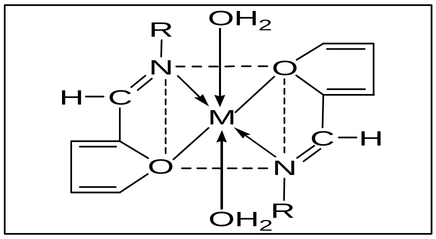
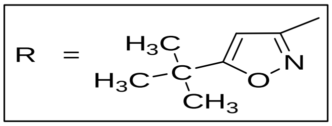


Fig.4,Proposed Structure of Complex M(II) $(L_2)_2.2H_2O$**Fig-5.** Proposed Structure of Complex M(II) $(L_3)_2.2H_2O$,





M= Co(II), Ni(II), Cu(II) and Zn(II)

Fig-6. Proposed Structure of Complex M(II) $(L_1)_2.2H_2O$

3.1. 1.^{1}H-MNR and Mass spectrum of TBIFMA (L_1).

In ^{1}H-NMR ($CDCl_3$) the imino proton appeared at 8.53δ, ter Butyl proton at 1.31δ, (S, 9H),I n the furan aromatic ring at 6.35-6.91δ(3H) and isoxazole ring at 6.21δ (S,1H) appeared. The Mass spectrum of ligand (L_1) showed molecular ion peak m/z =218, other fragments 151, 136, 121, 57 and 42 are assignable to possible fragments respectively, thus conforming the stiochiometry of the ligand (L_1) as proposed **Fig-1**

3.1.2. ^{1}H-MNR and Mass spectrum of TBIP$_1$MA (L_2).

In ^{1}H-NMR ($CDCl_3$) the imino proton appeared at 8.56δ, ter Butyl proton at 1.34δ, (S,9H), in the pyridine aromatic ring at7.41-8.76δ (d,2H, t,2H) and isoxazole ring at 6.74δ(S,1H) appeared. The Mass spectrum of ligand (L_2) showed molecular ion peak (M+1) =230, other fragments 78, 57 and 42 are assignable to possible fragments respectively, thus conforming the stiochiometry of the ligand (L_2) as proposed **Fig-3**

3.1.3. ^{1}H-MNR and Mass spectrum of TBIP$_2$MA (L_3).

In ^{1}H-NMR ($CDCl_3$) the imino proton appeared at 8.42δ, ter Butyl proton at 1.37δ, (S,9H), in the pyrrole at 9.08δ (b, 1H, N-H)and isoxazole ring at 6.29δ (S,1H) appeared. The Mass spectrum of ligand (L_3) showed molecular ion peak m/z =217, other fragments 65, 57 and 42 are assignable to possible fragments respectively, thus conforming the stiochiometry of the ligand (L_3) as proposed **Fig-2**

3.2. Infra Spectrum of ligands and metal complexes:

In general, the ligands exhibited very similar features (**Table-2**) IR spectra of all the ligands displayed a medium intensity band around 1612-1624 cm^{-1} due to $\boldsymbol{\nu}$ $(C = N)$ shifted to lower or higher frequency region to the 10-25 cm^{-1} in complexes. Indicating of azomethine is coordinated to the metal ion [14, 15]. The medium sharp bond at 1557 cm^{-1} in TBIFMA is due to furan moiety of ν $(C - O - C)$ bond is shifted to higher frequency region to extent 10-20 cm^{-1} in complexes, indicating the Oxygen of furan is coordinated to metal ions [16, 17].

The strong band at 1216 cm-1 in TBIP1MA is due to pyridine moiety of ν (C-N-C)band is shifted to higher or lower frequency region to 10-15 cm-1 in complexes, indicating the Nitrogen of Pyridine is coordinated to metal ion[18]. The strong band 1220 cm-1 In TBIP2MA is due to pyrrole moiety of ν (C-N-C) Band is shifted to lower or higher frequency region to 5-10 cm-1 in complexes indicating the nitrogen of pyrrole is coordinated to metal ion[19]. Further more, some new bands have been observed between 452 and 569 cm-1 . The bands in the range 559-569 cm-1 are attributed to ν (M-N=C) all ligands complexes. And those at 452-464 cm-1 are assigned to ν (M-O) in TBIFMA Ligand complexes.The hetero cyclic ring skeleton vibrations ν (C=C) Hetero cylic ring skelton vibration were consistent in all ligands and unaffected by complexes. All the metal complexes showed a

Table-2: IR Absorption frequencies of liands and metal complexes.

Compounds	**ν (C=N)**	**ν(C-O-C)**	**ν(C-N-C)**	**ν(C=C)**	**ν(M-O)**	**ν(M-N)**	**Water Coordinated**
L_1 [TBIFMA]	1612	1157		1522	-	-	-
Co(II) $(L_1)_2.2H_2O$	1620	1162		1527	464	562	786
Ni(II) $(L_1)_2.2H_2O$	1602	1173		1525	461	559	781
Cu(II) $(L_1)_2.2H_2O$	1626	1176		1529	452	564	779
Zn(II) $(L_1)_2.2H_2O$	1623	1169		1526	459	569	763
L_2 [TBIP$_1$MA]	1620	-	1216	1534	-	-	-
Co(II) $(L_2)_2.2H_2O$	1612	-	1211	1536	-	561	794
Ni(II) $(L_2)_2.2H_2O$	1625	-	1220	1541		567	790
Cu(II) $(L_2)_2.2H_2O$	1631	-	1216	1540		562	786
Zn(II) $(L_2)_2.2H_2O$	1633		1219	1539		568	789
L_3 [TBIP$_2$MA]	1624		1220	1550	-	-	-
Co(II) $(L_3)_2.2H_2O$	1616		1207	1546		563	782
Ni(II) $(L_3)_2.2H_2O$	1633		1211	1537		568	789
Cu(II) $(L_3)_2.2H_2O$	1629		1222	1543		564	794
Zn(II) $(L_3)_2.2H_2O$	1614		1216	1549		561	782

broad diffuse band at 3400-3429 cm-1 and another band at 779-794 cm-1 at lower frequency region indicating that the presence of water molecules in the co-ordination sphere [20]. All of the IR Spectral information supports the idea of the coordination of the imino nitrogen to the metal ions[21].

3.3. Electronic spectrum of metal complexes:

The Electronic spectra of the ligands exhibit three main peaks at about 334, 342 and 394 nm, the first and the second peaks are attributed to pyridine п- п* and imino п- п* transitions, respectively these bands were not significantly affected by chelation the third band in the spectra of the ligands 397 nm is assigned to n- п* transition. This band is shifted to a longer wave length (32nm) along with increasing intensity. This shifted may be attributed to the donation of the lone pair of the nitrogen atoms of the Schiff base to the metal ion (N - M) [22]. All Co(II) complexes should three characteristic bands around 826-872: 530-595 and 421-469 nm are assigned to the Electronic transition $^4T_{1g}$ (F) → $4T2g$ (F) ($\mathbf{v}_1$), $^4T_{1g}$ → $^4A_{2g}$ (F) $\mathbf{v}_2$) and ^{4}T1g → $^4T_{1g}$ (p) ($\mathbf{v}_3$) respectively. These transitions are in fair agreement with the predicted values of Octahedral geometry. The magnctic moment of Co (II) complexes lie in the range 4.67- 514 B.M value suggesting Octahedral geometry [23].

The Electronic spectra of Ni (II) complexes showed there lands around 740-765; 510-548; and 410-462nm assigned to the Electronic transition $^3A_{2g}$(F) → $^3T_{2g}$ (F) , $^3A_{2g}$ → $^3T_{1g}$ (F) and $^3A_{2g}$(F) → $^3T_{1g}$ (F) respectively these transition and magnetic moment of those complexes lie in the range 3.30- 3.70 B.M value suggesting Octahedral geometry [24]. The Cu(II) complexes showed a single broad band 510-761 nm corresponding to the transition ^2E_g → $^2T_{2g}$ the magnetic moment values are in the range 1.72-1.97B.M which is favoring tetragonal geometry[25].

On the basic of the physical and spectral data of the complexes discussed above, one can as some that the metal ions are bonded to the Schiff bases form moiety Oxygen and the imino Nitrogen illustrated in **Fig.4-6**

3.4.1 Antibacterial activity:

Antibacterial active of Co(II), Ni(II),Cu(II) and Zn(II) complexes were screened against *Bacillus* and *Pseudomonas* the results for some representative ligands and their complexes. From the experimental data, its is observed that the ligands are show significant activity. This may be attributed to their ability to chelate with trace metal ion, which is essential for microbial growth and microbial function. The antibacterial activity of metal complexes is higher than that of corresponding force ligands.

3.4.2. Antifungal activity:

Antifungal activity of Co(II),Ni(II), Cu(II) and Zn(II) complexes were screened against *A. niger* and *R. Solani.* The results for some representative ligands and their complex. From the Experimental data, it is observed that the ligands are show significant activity. The antifungal activity of metal complexes is higher than that of corresponding free ligands the Order of the metal complexes follow Cu(II) Ni(II) Co(II). The higher activity of metal complexes compare to free legends can be explained on the basic of Overton's concept and chelation theory [26, 27].

4. Conclusion

The result of this investigation supports the suggested structure of the metal complexes. Octahedral and tetragonal structures were suggested for all complexes, the Schiff base ligands were found to be biologically active and their metal complexes display enhanced antimicrobial activity against one or more strains, chelation tends to the ligands act as more powerful and potent bactericidal agent.

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REFERENCES

1. Mauro F.A. A, Vivekananda R. K, Donato D , Piero S. F, Tomas.T ; Tetrahedron, 63, 2007, page 9741.
2. R. Shakru, N.J.P. Subhashini, Satish Kumar k. Shivaraj, J.Chem.pharm. Res, 2(1), 2010, page 38-46.
3. Goda, F.E , Maroul A. R, El-BendoryE. R, Saudi Pharma. J. 3, 2003, page 11 .
4. Elguero J In comprehensive Heterocyclic Chemistry(II).; Katritzky A. Rees, CW. Screven EFV. Eds. Pergamum press oxford, 3 PL. (1996).
5. Maczynski.M Zimeck. M, Ryngs. Acta Pol-pharm, 65, 2008, page 241.
6. EL Sevier Science publishers, B.V, Amster dam. Coordination Chemistry Reviews, 109 , 1991, page 251-281.
7. Kang.L, Shin KJ YOOKH, SeoK, J. et al, Biorg. Med Chem. Letter, 10, 2000, page 95.
8. Y. prasanthi, K. Kiranmai, N J.P Subhashini and Shivaraj Else river, Spectra chi mica Acta Part –A
9. Musad EA, Mohamed R. Saeed BA, Vishwanth Bs Rai KML Bio & Med Chem. Lettersvol. 21, 2011, page 3536-3540.
10. Nuria AI, Francisco Hu. Miguel NMC, JRE, J. Inorg. Bio Chem, 102 (4), 2008, page 647. Bhattachrya A. Purohit V.C Org proc Res Dev , 7, 2003, page 254.
11. R.A.Siddiqui, P Raj and A.K Saxena, Synth. Inorg. Met-org. Chem, 26, 1996, page 1189-1203.
12. Jha N.K; Joshi, D.M Synth. React. Inog. Met-org Chem, 14, 1984, page 455.
13. G.G. Mohamed and Z.H. Abd EI-wahWb J. Thermal Anal, 73, 347, (2003).
14. A.A . Solioman and G.G Mohamed, Thermo Chim, Acta, 421, 2004, page 151.
15. M. Khare and A.P. mishra, J. Indian Chem. Soc, 77, 2000, page 256.
16. E.Menzed, D.R Lorenze, J.K. Wassen, K.R. Redigam and B.J. Mc Cormic, J. Inorg Nucl Chem, 38, 1976, page 993.
17. W.R. Mc Whinnieandj J.D. Miller
18. Adv Inorg. Chem RadioChem, 12, 1969, page 159.
19. G.G Mohamed, Spectro Chimica Acta part-A 64, 2006, page 188.
20. G.wang and J. C chang, Synth, Inorg Met-Org Chem, 24, 1994, page 1091-1097.
21. Ghose B.N: Lasisi K. M Synth react Inorg Met-Org, Chem, 16, 1986, page 1121.
22. N. Mondal D.K Dey, s mitra and K.M Abdul malik, Polyhedron, 19, 2000, p[age 2707.
23. D.R Zhu Y. song Y. xu,s.s.s. Raj, Polyhecdran, 19, 2000, page 2019.
24. E.M Govge and J.E Gdard, Inorganic Chem, 17, 1978, page 270.
25. Smartin, M.R Bermejo, A.M. G deibe, M. Manetlro. C lange and A.J.C Filho, Polyhedron, 19, 2000, page 185.
26. Mishra. L and Singh V.K. Indian. J. Chem, 32 A ,1993, page