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Chelated transition metal Schiff base complexes derived from 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one with 2-amino-4-phenyl thiazole: A Case Study.

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ABSTRACT

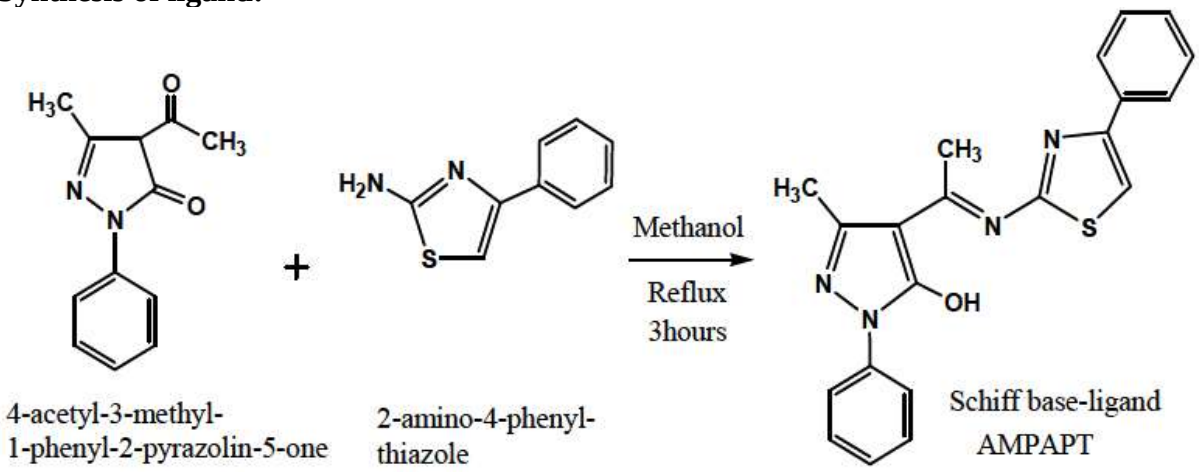
The novel Schiff base has been synthesized from 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one with 2-amino-4-phenyl thiazole. This Schiff base form complexes of type $ML_2.2H_2O$ (Where M= Mn, Fe, Co, Ni and Cu). This Schiff base was characterized by elemental analysis, mass spectra, ^1H NMR spectra ^{13}C NMR spectra and FTIR spectra. Metal complexes were characterized by elemental analysis, Magnetic susceptibility, electrical conductance, electronic spectra, infrared spectra and TGA analysis. All the compounds were tested for their antimicrobial activity. The result indicates that the growth of the tested organism was inhibited by most of the compounds.

Keywords: Pyrazoline, 2-Amino thiazole, Schiff base, Transition metal complexes,Spectroscopy, antibacterial activity.

INTRODUCTION

The 4-substituted-2-pyrazolin-5-one constitutes an interesting class of reagents because of their various medicinal, analytical and commercial applications, *viz.* potential antituberculotic [1], antineoplastic [2], antidiabetic [3], antifertility [4], antibacterial [5], antiviral [6] and antifungal[7] agents. Moreover, it has been demonstrated that they are potential extractants [8-10] and powerful drugs [11]. The chemistry of 4-substituted-2-pyrazolin-5-one is considerable important because of their practical use as potential laser materials [12,13] and also as NMR shift reagents [14-17]. In continuation of our work [18-25] on the metal complexes of Schiff base wereported here the study of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal complexes of Schiff base derived from 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one[AMP] with 2-amino-4-phenyl thiazole [APT]. Synthesis and characterization and antimicrobial activity of above metal complexes with this Schiff base are reported here.

Synthesis of ligand:



4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one

2-amino-4-phenyl-thiazole

Schiff base-ligand AMPAPT

EXPERIMENTAL SECTION

All the chemicals used in the present study were of A.R. grade. acetophenone, Iodine, hydrochloric acid, sulfuric acid, thiourea, ethylacetoacetate, sodium acetate, calcium hydroxide, acetyl chloride, phenylhydrazine, 1:4-dioxane and methanol (SD's fine chemical Ltd., and Merck chemicals., Mumbai) were used without further purification. Absolute ethanol from Alembic Chemical Works Co. Ltd., Baroda was used after distillation. The Mn(II), Co(II), Ni(II), Cu(II) metal acetate and Fe(II) sulphate (SD's fine chemical Ltd, Qualigens-Glaxo, Mumbai and Merck chemicals., Mumbai) were used for the preparation of Schiff base metal complexes.
Melting points were taken in one side open capillaries on a Melting point apparatus having model number VMP-D of a make VEEGO. Electronic Spectra were recorded in DMF solution on LAMBDA 19, UV/VIS/NIR ("SICART-CVN" at VallabhVidyanagar, Gujarat, India). The Mass spectra of all ligands were recorded on the instrument named LCMS-2010A of make Shimadzu. Carbon, Hydrogen and Nitrogen were estimated on a Thermo fisher (Thermo electron corporation Limited), Flash Elemental Analyzer-1112. The IR spectra of the ligand and complexes were recorded on a Perkin Elmer IR spectrometer using KBr Pellet method. ^{1}H NMR&and ^{13}C NMR spectra of all the ligands [in Deuterated Chloroform($CDCl_3$)] were recorded on a AVANCE-II 400 of make BRUKER spectro-photometer using TMS [$(CH_3)_4Si$] as internal standard from CDRI Lucknow.

RESULTS AND DISCUSSION

The Schiff base ligand was prepared by condensation of equimolar amount of AMP [26] and APT [27] in minimum quantity of methanol. The reaction mixture was refluxed in rotamental for about three hours. On cooling the yellow solid compound obtained was filtered, washed with methanol and dried in air. For the preparation of complexes, an aqueous solution of metal acetate(0.05 M) and 1:4 Dioxane solution of ligand (0.05M) were mixed in presence of acetate buffer (p^H=6.5) and the mixture was digested on sand bath for 30 minutes, cooled and filtered the precipitate and then washed with water and then methanol to remove excess metal ions and unreacted Schiff bases respectively.

Characterization of Schiff base ligand and their metal complexes:
Schiff base ligand was characterized by elemental analysis, mass spectra, ^{1}H NMR, ^{13}C NMR and FT-IR spectra. The analytical data of ligand and metal complexes, together with physical properties are given in Table 1. The analytical data of the complexes correspond to the general stoichiometry [$ML_2.2H_2O$] where M= Mn(II), Fe(II), Co(II), Ni(II) and Cu(II),

Ligand L=AMPAPT. The value of molar conductance (λ_M) of the complexes in DMSO indicates that the [$ML_2.2H_2O$] are non-electrolytes. Magnetic moments lie in the range 5.72-5.76 B.M., 4.96-5.02 B.M., 4.42-4.48 B.M., 2.89-2.95 B.M., and 1.90-1.94 B.M., for Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes respectively.

Analytical data and physical property of Ligand and their metal complexes:

Table 1

Compound	M W	Color	M P (°C)	λ_M ($\Omega^{-1}cm^{-1}mol^{-1}$)	Yield (%)	Elemental analysis (%) Found (Calculated)					
						C	H	N	S	M	μ_{eff} B.M.
AMPAPT	374.46	Pale Yellow	183	-	75	66.41 (67.36)	4.74 (4.83)	14.40 (14.96)	8.29 (8.56)	-	-
Mn $(AMPAPT)_2.2H_2O$	837.87	Brown	-	12.81	54	60.32 (60.21)	4.75 (4.57)	13.26 (13.37)	7.47 (7.65)	6.41 (6.56)	5.61
Fe $(AMPAPT)_2.2H_2O$	838.78	Brown	-	09.24	67	60.43 (60.14)	4.61 (4.57)	13.23 (13.36)	7.70 (7.65)	6.67 (6.66)	4.98
Co $(AMPAPT)_2.2H_2O$	841.86	Dark Brown	-	12.73	62	60.01 (59.92)	4.56 (4.55)	13.45 (13.31)	7.51 (7.62)	7.08 (7.00)	4.51
Ni $(AMPAPT)_2.2H_2O$	841.62	Green	-	9.87	65	60.05 (59.94)	4.56 (4.55)	13.33 (13.31)	7.25 (7.62)	7.12 (6.97)	2.84
Cu $(AMPAPT)_2.2H_2O$	846.48	Brown	-	11.32	61	61.22 (61.21)	5.05 (5.14)	12.53 (12.41)	7.14 (7.11)	7.19 (7.04)	1.97

Mass Spectral data:
The Positive ion mass spectral analysis of AMPAPT observe at m/z 375.19 (M+), Confirms the theoretical molecular weight i.e. 374.48.

Chemical Shift (δ value in ppm)	Multiplicity	Assigned Proton
2.47	singlet	3H of methyl (-CH_3) group (11)
2.96	singlet	3H of methyl (-CH_3) group (15)
7.16	singlet	1H of thiazole (1)
7.21	multiplet	1H of aromatic ring (19)
7.33	multiplet	1H of aromatic ring (7)
7.43	multiplet	4H of aromatic ring (6,8,18,20)
7.86	doublet	2H of aromatic ring (17,21)
7.99	doublet	2H of aromatic ring (5,9)
14.07	singlet	1H of alcohol (14)

^{1}H NMR Spectra ($CDCl_3$):
Interpretation: From the recorded^{1}H NMR spectrum, chemical shifts and the multiplicity of thecorresponding protons are shown in table given below.

^{13}C NMR Spectra:

Interpretation: From the recorded^{13}C NMR spectrum, chemical shifts and the multiplicity ofthe corresponding carbons are shown below.

(400MHz, $CDCl_3$) δ=17.95 (C_{15}), 18.47 (C_{11}), 103.58 (C_{12}), 108.56 (C_1), 119.51-128.96 (Tertiary Aromatic Carbon), 133.94 (C_4), 138.65 (C_{16}), 147.92 (C_{13}), 153.11(C_2), 159.49 (C_{14}), 161.13 (C_{10}), 165.39 (C_3)

FT-IR Spectra:

Interpretation: From the recorded IR spectrum, the wave numbers of corresponding groups areshown below.

3134.43cm^{-1} (υ_{C-H} stretching of Aromatic), 2922.25cm $^{-1}$ (υ_{O-H} stretching of saturated hydrocarbon), 1620.26cm^{-1}, ($\upsilon_{C=N}$ stretching of azomethine), 1593.25cm^{-1}, 1483.31,1479.45cm^{-1} ,1122 cm^{-1} (characteristic bands of pyrazolin ring), 1496.81cm^{-1} (Characteristic band of thiazole ring).

The infrared spectra of the ligand show υ_{O-H} (weakly H-bonded) band at 2922.25cm^{-1} [28]. The absence of this band in all the metal complexes indicates the removal of proton of hydroxyl group of pyrazolin ring during the chelation. This is further supported by the shift of C-O frequency from 1310cm^{-1} (in ligand-L) to 1343-1318cm^{-1} (in complexes) [29]. The sharp intense band at 1620.26cm^{-1} in the ligand can be assigned to $\upsilon_{C=N}$ (azomethine). A downward shift (υ =06-35cm^{-1}) in $\upsilon_{C=N}$ (azomethine) is observed upon coordination indicating that the nitrogen of azomethine group is involved in coordination. All the complexes show broad band in the region 3200cm^{-1} to 3450cm^{-1} which may be assigned to υ_{O-H} of coordinated water [30]. To account for the octahedral stereochemistry of the metal complexes, the coordination of two water molecules is expected.

The bands present at ~515cm^{-1} in Mn(II) complex, ~540cm^{-1} in Fe(II) complex, ~585cm^{-1} in Co(II) complex,~490cm^{-1} in Ni(II) complex and ~565cm^{-1} in Cu(II) complex respectively may be due to metal-nitrogen stretching vibration [31,32]. A less intense band at ~1620cm^{-1} in the spectrum of ligands may be assigned to $\upsilon_{C=N}$ (ring) [33]. All the metal complexes do not show shifting in $\upsilon_{C=N}$ compared to its respective ligand. This suggests that the nitrogen atom of the thiazole ring has not participated in the coordination. However, in water containing metal complexes, this band is observed as a broad band with some fine structures this may be due to coupling of the bending mode of coordinated water molecules with $\upsilon_{C=N}$ [34].

Electronic spectra:

The ligand show two absorption bands at 36,364cm^{-1} and 26,316cm^{-1}. No absorption was observed in the visible region for the ligand. In the absence of Quantum mechanical calculation, it is not possible to assign the absorption bands to definite electronic transitions with complete certainty. However, it appears reasonable to assign the bands to $\pi\rightarrow\pi^*$ transitions [35]. The electronic spectra of Mn(II) complex exhibit three very low intense bands, one at 15200cm^{-1}, which may rise due to $^6A_{1g}\rightarrow{}^4T_{1g}$ (G) transition, another band at 18152cm^{-1} assigned to $^6A_{1g}\rightarrow{}^4A_{1g}$(G) transition and the third band at 26121cm^{-1} may be assigned to $^6A_{1g}\rightarrow{}^4A_{1g}$, ^4E_g,(G) transition for Mn(II) ion in octahedral environment. The μ_{eff} (Table-1) value of the complex suggests the spin $3d^5$ configuration [36]. The electronic spectra of Fe(II) complex shows a broad band at 23110 cm^{-1} and 15413 cm^{-1} which may be assigned to the $^5T_{2g}\rightarrow{}^5E_g$ transition. The magnetic moment value 4.98 BM which indicates that the complex is spin-free and it has octahedral geometry [37]. The electronic spectra of Co(II) complex exhibited absorption bands in the region 8350 cm^{-1} to 9650 cm^{-1} corresponding to υ_1 and υ_3 transitions $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)(\upsilon_1)$;$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$. In the present investigation, Co(II) complex shows the absorption bands at 8810 cm^{-1} and 19750 cm^{-1}, corresponding to υ_1 and υ_3 transitions respectively. These bands are the characteristics of high spin octahedral Co(II) complexes. However, υ_2 band is not observed because of its proximity to strong υ_3 transition. The magnetic measurement of Co(II) complex display magnetic moment value of 4.51 B.M. which is in the octahedral range 4.40 to 4.53 B.M. The Ni(II) complex

exhibited three bands at 10540 cm^{-1}, 16214 cm^{-1} and 25980cm^{-1} which are attributed to the $^3A_{2g}\rightarrow{}^3T_{2g}(F)$ (υ_1); $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (υ_2) and $^3A_{2g}\rightarrow{}^3T_{1g}(p)$ (υ_3) transitions respectively indicating octahedral geometry around Ni(II) ion. Ni(II) complex showed the magnetic moment value of 2.84 which is in the range of 2.90 to 3.02 B.M suggesting consistency with their octahedral environment [38]. For the Cu(II) complex with D_4h symmetry, three spin allowed transitions $^2B_{1g}\rightarrow{}^2A_{1g}$ (υ_1), $^2B_{1g}\rightarrow{}^2B_{2g}$ (υ_2) and $^2B_{1g}\rightarrow{}^2E_g$ (υ_3) are possible but the electronic spectra of Cu(II) complex display two bands at 13790 cm^{-1} and 21687 cm^{-1}. There should be third transition but we could not observe the same which may be due to very close energy values of different states. Absence of any spectral band below 10000 cm^{-1} rules out the possibility for tetrahedral structure of the present complexes and also suggests distorted octahedral geometry of the complexes [39]. The low molar conductance values in DMF solution for all metal complexes (Table-1) are indicating that the complexes are nonelectrolytes.

TGA analysis:

Thermo gravimetric analysis of Schiff base ligand and its metal complexes are used to:

(i) Get information about the thermal stability of these new complexes,

(ii) Decide whether the water molecules (if present) are inside or outside the inner coordination sphere of the central metal ion and

(iii)Suggest the general scheme for thermal decomposition of metal complexes.

In the present investigation, heating rates were suitably controlled at 10°C min^{-1} under nitrogen atmosphere and the weight loss was measured from the ambient temperature up to ~1000°C. [40-42] The data are provided in the Table: 2.

Number of coordinated or lattice water molecule/molecules present in the complexes were calculated from the percentage weight loss of the complexes from the thermograms.

Generally, the loss of lattice water will be at a lower temperature than that of coordinated water [43-46]. From the nature of the thermograms and percentage weight-loss, the complexes studied in the present work can be classified in the following three groups [47-49].

TGA Analysis of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal complexes:

The thermograms of this group of metal complexes show three stage decomposition. All the metal complexes do not show weight loss below 120°C, it indicates the absence of lattice water in the metal complexes.

The first stage decomposition is obtained in the temperature range 140-210°C. The % weight loss in this range corresponds to the loss of two coordinated water molecules. [50-53]

The second stage decomposition is obtained in the temperature range 210-400°C. The % weight loss in this range corresponds to % weight loss of two Schiff base ligands.

The third stage decomposition range is obtained in the temperature range 400-900°C. The % weight loss in this range corresponds to % weight loss of metal oxide residue. The decomposition pattern for the metal complexes of this category may be as follow:

On the basis of TGA and analytical data of all Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes studied in the present work correspond to $[ML_2.2.H_2O]$ group.

THERMO ANALYTICAL RESULTS OF METAL COMPLEXES OF AMPAPT

Compounds	Stage-I [140-210°C]	Stage-II [210-400°C]	Stage-III [400-900°C]
	Mass Lose Obs. (Calc.)	Mass Lose Obs. (Calc.)	Mass Lose Obs. (Calc.)
$[Mn(AMPAPT)_2(H_2O)_2]$	4.31 (4.30)	86.62 (86.52)	9.37 (9.42)
$[Fe(AMPAPT)_2(H_2O)_2]$	4.28 (4.29)	86.33 (86.42)	9.48 (9.51)

$[Co(AMPAPT)_2(H_2O)_2]$	4.11 (4.28)	87.01 (87.06)	8.79 (8.90)
$[Ni(AMPAPT)_2(H_2O)_2]$	4.09 (4.28)	88.73 (88.98)	6.84 (6.97)
$[Cu(AMPAPT)_2(H_2O)_2]$	4.16 (4.25)	86.62 (86.58)	9.33 (9.39)
Assignment	**Loss of two coordinated water molecules**	**Loss of two Schiff base ligand molecules**	**Metal Oxide/Metal**

Antibacterial activity:

The antibacterial activity was estimated against E.coli, B. subtilis and S. aureus and evaluated by using of agar disc diffusion method on the basis of the size of inhibition zone formed around the paper discs. For each concentration, the mean diameter (mm) of inhibition zone developed was calculated. The test compounds in measured quantities were dissolved in DMF to get concentrations of 200 and 100 ppm of compounds. Twenty five milliliter nutrient agar media was poured in each Petri plates. After solidification, 0.1mL of test bacteria spread over the medium using a spreader. The discs of Whatmann no. 1 filter paper having the diameter 5.00 mm, were placed at four equidistant places at a distance of 2 cm from the center in the inoculated Petri plates. Filter paper disc treated with DMF served as control and Amoxyciline used as a standard drug. These Petri plates were kept in refrigerator for 24 hours for pre diffusion. Finally, Petri plates were incubated for 24 hours 30^oC. The zone of inhibition was calculated in millimeters carefully.

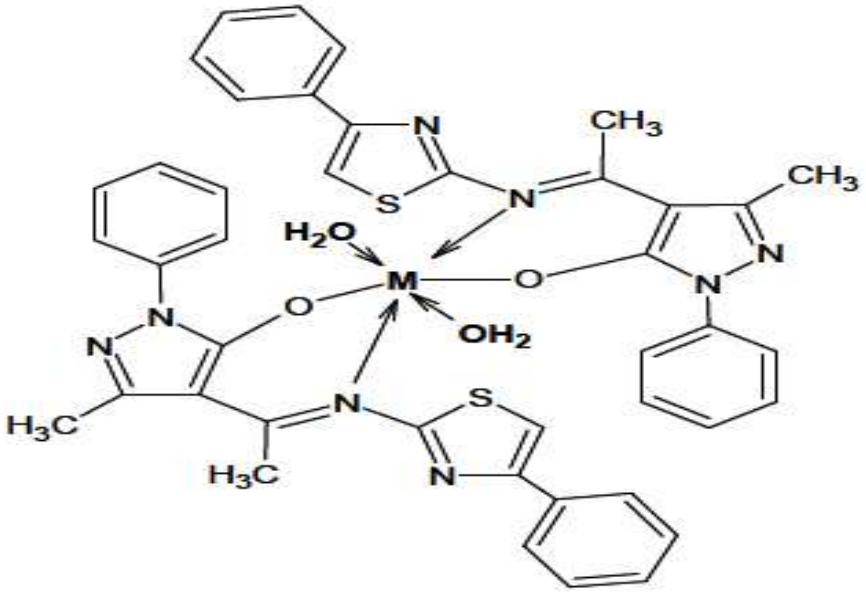
The Schiff base ligand was found to be biologically active (Table:2). It is known that chelation tends to make ligands act as more powerful and potent bactericidal agent [54]. The values indicate that the metal complexes had a higher antibacterial activity than the free ligand. Such increased activity of the metal complexes can be explained on the basis of the overtone concept[55] and chelation theory [56]. According to the overtone concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials, due to which liposolubility is an important factor controlling the antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a great extent due to the overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with donor groups. Furthermore, it increases the delocalization of electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complex into the lipid membrane and blocks the metal binding sites on the enzymes of the microorganism.[55]

Table: 2

compound	**Antibacterial activity of ligand and its metal complexes Zone of inhibition in mm(concentration in ppm)**					
	E. coli		***B. subtilis***		***S. aureus***	
	100	**200**	**100**	**200**	**100**	**200**
AMPAPT	6	13	7	13	6	12
$[Mn(AMPAPT)_2(H_2O)_2]$	8	15	9	14	8	14
$Fe(AMPAPT)_2(H_2O)_2]$	9	15	10	17	9	15
$Co(AMPAPT)_2(H_2O)_2]$	9	16	11	15	8	13
$Ni(AMPAPT)_2(H_2O)_2]$	14	21	12	18	12	23
$Cu(AMPAPT)_2(H_2O)_2]$	13	19	11	19	13	21
Amoxyciline	17	28	16	22	14	29

CONCLUSION

On the basis of these results obtained for elemental analysis, infrared spectra, electronic spectra, TGA analysis and magnetic susceptibility measurements the following structures are proposed for the Schiff base metal complexes.



Where M= Mn(II), Fe(II), Co(II), Ni(II) and Cu(II).

Structure of Complexes of Schiff base ligand AMPAPT

Antibacterial activity leads to the following conclusions:

1. The metal complexes show more activity than the ligands against tested bacteria.
2. Antibacterial activity of Cu(II) and Ni(II) complexes have higher activity than the other complexes.

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REFERENCES

[1] R Behnischi; H Schmidt; F Mietzch. *A. M, Rev. Tuber*., **1950**, 61, 1.
[2] HG Grag; RA Sharma. *J. Pharm. Sci*., **1970**, 59, 350.
[3] HG Grag; PP Sharma. *J. Med. Chem.*,**1970,** 13, 153.
[4] SS Tiwari; AJ Sharma. *J. Indian Chem. Soc*., **1975,** 52, 153.
[5] S Devi; A Nayak; AS Mittra. *J. Indian Chem. Soc*., **1984,** 61, 640.
[6] SD Bhardwaj; VS Jolly. *Orient. J. Chem*., **1996,** 12, 185.
[7] VS Jolly; MY Dalvi; AK Shrivastava. *J. Indian Chem. Soc*., **1991**, **68**, 513.
[8] EC Okafor. *Polyhedron.*,**1983**, 2, 309.
[9] FR Ruan; F Fu; JJ Mao. *J. Radi. Anal. Nucl. Chem. Lett*., 1987, **119**, 291.
[10] MS Nagar; PB Waikar; MS Subramanium. *Polyhedron.*, 1988, 7, 1964.
[11] CW Noell; CC Chong. *J. Med. Chem*., **1969,** 12, 545.
[12] H Samuelson; A Lempicki. *J. Chem. Phys*., **1963,** 39, 110.

[13] DS Raj; PC Shah; JR Shah. *Synth. React. Inorg. Met.-Org. Chem*., **1992,** 22, 321.
[14] CC Hinckley. *J. Am. Chem. Soc*., **1969,** 91, 5160.
[15] WD Honrocks Jr; JP Sipe. *J. Am. Chem. Soc*., **1971,** 93, 6800.
[16] J Selbin; N Ahmad; N Bhacca. *Inorg. Chem*., **1971,**10, 6800.
[17] SJ Lyle; AD Witts. *Inorg. Chem. Acta*., **1971**, 5, 481.
[18] KT Joshi; AM Pancholi; HR Dabhi; AK Randa. *Orient. J. Chem.*, **1996,** 12 (3) 287.
[19] KT Joshi; HR Dabhi; AM Pancholi; AK Randa. *Acta. Ciencia. Indica.*,**1997,** Vol. XXIII C, No.1, 31.
[20] KT Joshi; HR Dabhi; RK Rai; AM Pancholi; AK Randa. *ActaCiencia. Indica.*,**1999,** Vol. XXV C, No.1, 013.
[21] KT Joshi; AM Pancholi. *Orient. J. Chem.*, **2000,** Vol. 16 (2) 287-290.
[22] ML Chauhan; KT Joshi; AM Pancholi. *ActaCienciaIndica*, **2001,** Vol. XXVII C, No. 2,
043.
[23] AM Pancholi; KT Joshi. *Orient. J. Chem*., **2001,** Vol. 17(1) 135-138.
[24] KT Joshi; AM Pancholi; KS Pandya; KK Singh; AS Thakar. *Asian J. Chem.*, **2010,** Vol. 22, No. 10, 7706-7712.
[25] AS Thakar; KK Singh; KT Joshi; AM Pancholi; KS Pandya. *E. J. Chem*., **2010,** 7(4) 1396-1406.
[26] KA Thaker; NR Manjarmakar. *J. Indian Chem. Soc*., **1971,** 48, 621.
[27] BS Jensen. *Acta. Chem. Scand*., **1968,** 13, 1668.
[28] LJ Bellamy. *The infrared Spectra of Complex Molecules*, Chapman and Hall, London, **1975**,
108.
[29] IA Patel; BT Thaker. *Indian J. Chem*., **1999**, 38A, 431.
[30] AK Randa; JR Shah. *Indian J. Chem***., 1981**, 20A, 615.
[31] K Nakamoto. *Infrared spectra of Inorganic and coordination Compounds*, John Willey, New York **1963**.
[32] DM Adans. Metal-Ligand and related Vibration, Edward Arnold, London, **1967**, 310.
[33] EC Ocafor. *J. Inorg. Nucl. Chem*., **1980,** 42, 1155.
[34] SMF Rahman; J Ahmad; MM Haq. *J. Inorg. Nucl. Chem*., **1973,** 35, 1011.
[35] BA Uzoukwn; K Goie; H Duddeck. *Indian. J. Chem*., 1998, 37B, 1180.
[36] RL Dutta; A Shyamal. *Element of Magneto Chemistry*, Affiliated East-West press, New Delhi, **1982**.
[37] FL Mani. *J. Inorg. Nucl. Chem.*, **1979,** 15, 297.
[38] PP Dholakiya; MN Patel. *Synth. React. Inorg. Met.-Org and Nano-met. Chem*., 2002, **32**, 4.
[39] BN Figgis. *Introduction to ligand fields*, Interscience, New York, **1966.**
[40] N Deb; SD Barudh; N Sen Savma; NN Das, *Thermochim. Acta*., **1998**, 320, 53.
[41] AA Soliman. *J. Therm. Anal. Cal*., **2001,** 221.
[42] AF Petrovic; DM Petrovic; VM Zeovac; M Budimir. *J. Thermal. Anal. Cal*., **1999**, 58, 589.
[43] BS Grag; PK Singh; SK Grag, *Synth. React. Inorg. Met.-Org. Chem*., **1987,** 17 (10), 923.
[44] RC Agarwal; NK Singh; RP Singh. *Synth. React. Inorg. Met.-Org. Chem*., **1948,** 14 (5),
637.
[45] AC Fabretti; CG Franchini; CP Preti; G Toshi. *Can. J. Chem*., **1977**, 55, 344.
[46] J Nakagawa; T Shimanouchi. *Spectrochim. Acta*., **1964,** 20, 429.
[47] DK Rastogi; KC Sharma. *J.Inorg. Nucl. Chem***., 1974,** 36, 2219.

[48] CK Modi; SH Patel; MN Patel. *J. Therm. Anal. Cal.*,**2003,** 73, 347.
[49] PB Pansuriya; P Dhandhukia; V Thakkar; MN Patel. *J. Enz. Inhib. Med. Chem*., **2007**, 22,
477.
[50] NM El-Metwally; IM Gabr; AM Shallaby; AA El-Asmy. *J. Coord. Chem*., **2005,** 58, 1145.
[51] CK Modi; SH Patel; MN Patel. *J. Therm. Anal. Cal.*,**2007**, 87, 441.
[52] GG Mohamed; ZH Abd El-Wahab. *J. Therm. Anal. Cal.*, **2003,** 73**,** 347.
[53] GG Mohamed; FA Nour El-Dien; EA Nadia El-Gamel, *J. Therm. Anal. Cal.*,**2002,** 67, 135.
[54] H Nora Al-Sha'alan, *Molecules.*,**2007,***12*, 1080-1091.
[55] Y Anjaneyulu; RP Rao. *Synth. React. Inorg. Met. Org. Chem.*,**1986,** 16, 257.
[56] L Mishra; VK Singh. *Indian J. Chem.*, **1993,** 32A, 446.