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Schiff base and their metal complexes: synthesis, characterization And Biological activity

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Abstract

Thermally stable complexes of, Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) metal ions, Schiff bases (L_1) [(4-(1-(4-hydroxy-6-methyl-[(2-oxo-2H-pyran-3-yl) ethylideneamino) phenyl) acetamide.] derived from P – amino acetanilide and the heterocyclic compound Dehydroacetic acid (DHA) and characterized by elemental analysis, IR, NMR,ultra violet visible spectroscopy, conductivity, thermal analysis, magnetic measurements, and a microbial study. The magnetic measurements and ultra violet visible spectral data of the complexes suggest a desorted octahedral geometry around the central metal ion. The molar conductance data revealed that all the complexes were non electrolytes in the ratio 1:2 (metal:ligand). The thermal stability of the complexes were studied by thermogravimetry. The ligands and their metal complexes were screened for biological activity against Aspergillusniger, Fusariumoxysporum, E. coli and Staphylococcus aureus.

Keywords:

Dehyderoacetic acid,Schiff bases, Transition metal complexes, Thermal stability, Antimicrobial activity, Antifungalactivity,

Introduction:

Schiff bases are known to be medicinally important and used to design medicinal compounds[1-4.] Schiff bases are capable of forming coordinate bonds with many of metal ions via its azomethine or phenolic groups[5-8].Schiff bases and their metal complexes possessing novel structural features, interesting spectral and magnetic properties has been the subject of intensive research due to their importance in medical, agricultural, analytical, biological and industrial fields. The role of Schiff bases and their metal complexes in living systems as a catalyst for metabolic process, promoters, storage and transport of metal ion of donor molecules and as an agent for transmission of energy. Here the synthesis and characterization of the Schiff bases derived from biologically active dehydroacetic acid and P – amino acetanilide. The complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) metal ions with this ligands were also prepared. Various studies have shown that, the azomethine group (>C=N-) in Schiff base metal complexes has considerable biological significance[9] and found to be responsible for biological activity such as fungicidal and insecticidal[10] and anti carcinogenic properties catalytic activity and anticancer drug[11] The structure of the complexes has been established using IR, electronic spectral data, thermal analysis, analytical and magnetic properties.

Material and Methods:

The Dehydroacetic acid was used for the making ligands from E-Merck. The other reactants, used for the prepration of Schiff bases and their metal complexes were of AR-grade. The purity of chemicals was checked by melting point, boiling point, and thin layer chromatography. The purification of liquid chemicals and solvents was done by distillation[12]. IR spectra (400–4000 cm^{-1}) were recorded on Shimndzu FTIR spectrophotometer using KBR discs[1], ^1H NMR spectra were taken from IICT Hyderabad, The colour, melting point, molecular weight and percentage of Carbon, Hydrogen and Nitrogen found and calculated theoretically are given in Table1. Magnetic susceptibility measurements of the complexes were carried out by Gouy balance using copper sulphate as the calibrant. The molar conductance of the complexes was measured. TG/DTA scans were recorded on Mettler-Toledo-851 TGA-DTA

Ligand/Complex	Sym.	Mol Wt.	Colour	Elemental Percentage Found (Calculated)				M.P. °C	Mol. CondOhm^1 cm^2mol^{-1}
				C	H	N	% M		
$C_{16}H_{16}N_2O_4$	L_1	300	Light Yellow	63.20 (63.90)	5.30 (5.37)	9.28 (9.33)		214	
$[Cu(L_1)_2](H_2O)_2]$	M1L1	699	Light green	57.80 (54.89)	5.79 (5.14)	8.46 (8.00)	9.55 (9.01)	290	12.88
$[Ni(L_1)_2(H_2O)_2]$	M2L1	694	Pale Green	55.24 (55.27)	5.20 (5.18)	8.10 (8.06)	8.42 (8,44)	280	11.03
$[Co(L_1)_2(H_2O)_2]$	M3L1	694	Light brown	57.24 (57.25)	5.10 (5.18)	8.10 (8.05)	8.45 (8.47)	>300	13.70
$[Mn(L_1)_2(H_2O)_2]$	M4L1	690	Brown	55.47 (55.57)	5.18 (5.21)	8.07 (8,10)	7.90 (7.95)	300	15.20
$[Fe(L_1)_2(Cl)(H_2O)]$	M5L1	709	Brown	56.50 (56.52)	4.70 (4.79)	7.95 (7.89)	7.89 (7.89)	300	10.14

Table 1 Analytical data, molecular weight and melting point,MolarConductance

Synthesis of Ligand:

Ligand L1 prepared by the method, in which involves refluxing equimolar mixture of dehydroacetic acid and P – amino acetanilide in dry ethanol. Accordingly 0.1 moles each of dehydroacetic acid with P – amino acetanilide were dissolved in 60 ml ethanol in a round bottomed flask. The reactants were refluxed for about 6 hours on 1 RML Rotamantle, and it cooled to room temperature,after cooling the solid Schiff base has separated by filtration and washed with ethanol. The Schiff base was further purified by recrystallisation from dry ethanol and dried in desiccator. The purity was checked by melting point and TLC technique.

Synthesis of metal complexes:

Take the ratio 2:1 ligand and metal chloride in 30 ml methanol and refluxed for two hours then cooled to observe the occurrence of precipitation which rarely found in the cold reaction mixture, then add ten percent methanolic solution of ammonia was drop wise to increase the pH till the metal complex precipitates out completely. The complexes of different metals were precipitated at different pH range. The precipitate was again digested for one hour, then filtered in hot condition, washed with methanol or petroleum ether.

Result and discussion:

All the metal complexes are coloured solids, stable to air and non hygroscopic. They are insoluble in water but soluble in DMF, DMSO. The physical characteristics, analytical and molar conductance data of the ligands and metal complexes are given inTable 1. The molar conductance values of all the metal complexes in DMSO at the concentration of $1X10^{-4}M$ are very low indicating their non electrolytic nature. The analytical data indicate 1:2 metal:ligand stoichiometry for the Cu(II), Ni(II), Co(II)Mn(II), Fe(III) complexes are given in (Table 1)and.(Fig. 1-3).

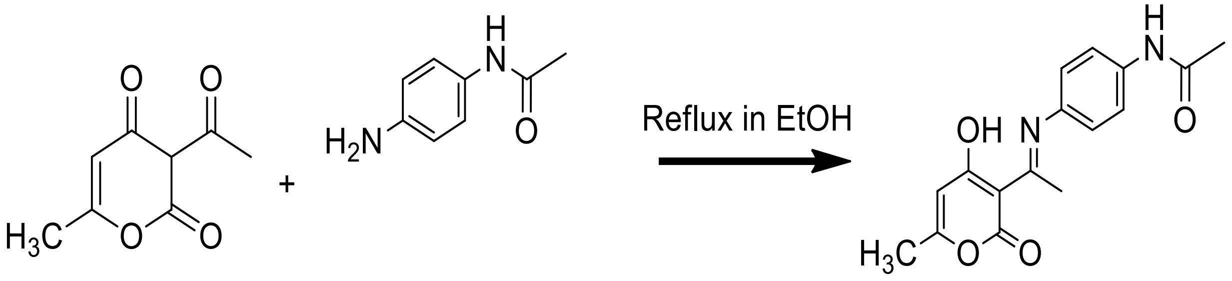

Fig. 1: Synthesis of Ligand

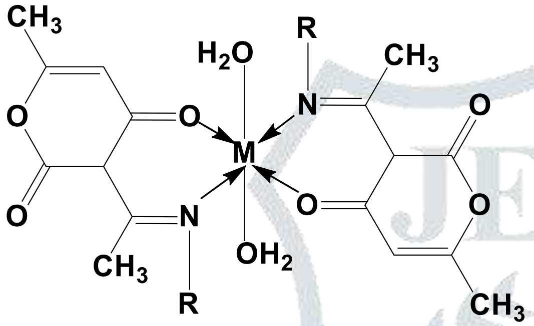

Fig. 2: Proposed structure of Cu(II), Ni(II), Co(II), Mn(II)

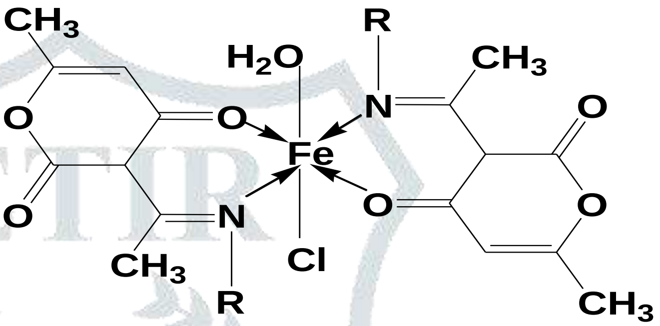

Fig:3 Proposed structure of Fe (III) complex.

^{1}H-NMR spectrum of the ligands:

The ^{1}H-NMR spectra of the free ligands in $CDCl_3$ at room temperature showed the following signals at δ(ppm):2.10 (3H,s)C_6-Methyl hydrogen of DHA moiety, 2.20(3H,s,)Methyl hydrogen bond carbon azomethine,2.50(3H,s,)C-CH_3 hydrogen acetamide moity on phenyl ring, 5.80(1H,s,)CH_5- hyderogen DHA moiety.,7.30(2H,d)two hyderozen (Ha) of penyl moity,7.70 (2H,d) two hyderozen (Hb) of penyl moity,10.40(1H,s) hyderogen acetamide moity, 15.60(1H,s,)Enolic (OH) hydrogen of DHA moiety.

IR Spectra:

The Characteristic IR frequencies (cm^{-1}) of the ligands and their complexes are shown in Table2. The IR spectrum of the free ligands show a broad weak band 3410 cm^{-1} attributed to intramolecular bonding ν(OH). The bands 1710, 1660,1568, 1350, 1238cm^{-1} are assigned to ν(C=O) (Lactone carbonyl), ν(C=N) (azomethine), ν(c=c)Aromatic, ν(C-N) (aryl azomethine) and ν(C-O) (enolic) streaching modes, respectively. The disappearance of IR band at 3410cm^{-1} (intramolecular hydrogen bonding) in the spectra of all the complexes indicates deprotonation of enolic oxygen and azomethine nitrogen in coordination to the metal ion[13]. It is further supported by an upward shift in ν(C-O) in all complexes. A downward shift in ν(C=N) by indicates participation of azomethine nitrogen in complex formation. The IR spectra of the metal complexes showed new bands in the 505-557 cm^{-1} and 420-480 cm^{-1} region, which can be assigned ν(M-O) and ν(M-N) vibrations respectively [14].(Table 2).

Compound	**Bond vibrational modes (stretching- υ). Band Positions (cm^{-1})**							
	Lactone (C=O)	**Azomethine (C=N)**	**Aromatic (C=C)**	**Aryl Azo methine (C-N)**	**Enolic C-O)**	**Enolic (C-OH)**	**New Peaks**	
							M-O	**M-N**
L$_1$	**1710**	**1660**	**1568**	**1350**	**1238**	**3410**		
M1L$_1$	**1680**	**1650**	**1556**	**1382**	**1253**		**538**	**480**
M2L$_1$	**1724**	**1658**	**1583**	**1360**	**1242**		**557**	**434**
M3L$_1$	**1705**	**1650**	**1564**	**1360**	**1265**		**516**	**420**
M4L$_1$	**1700**	**1640**	**1587**	**1352**	**1245**		**505**	**440**
M5L$_1$	**1691**	**1647**	**1599**	**1360**	**1267**		**550**	**440**

Table 2: Ligand field parameters of Cu (II), Ni (II) and Co (II) Complexes

Magnetic and Electronic Absorption Spectral Data:

Magnetic moment values of the Cu(II) complex observed to be in the range 1.84 B.M. at room temperature corresponding to one unpaired electron, The magnetic moment values of Cu(II) complexes are slightly higher than spin only value for one unpaired electron can be attributed to spin – orbital coupling,[15] indicative of distorted or pseudo-octahedral geometry[16].The electronic absorption spectra of Cu(II) complexes showed a broad band at 15520 (637)cm^{-1}(nm) corresponding to the transition $^2E_g \rightarrow {}^2T_{2g}$ and a charge transfer band at 26315 (380)-28985 (345)cm^{-1}(nm) These values fall within the range of many octahedral or distorted-octahedral Cu(II) complexes reported earlier[17-20]. The electronic spectral data[21] coupled with magnetic moment value suggest a distorted octahedral geometry for the Cu(II) complexes.[22] At room temperature the magnetic moment of Ni(II) complexes fall in the range 2.89B.M, which are supported to octahedral geometry[23]In the present investigation the electronic spectra of Ni(II) complexes studied exhibit a regular pattern of absorption band in three regions as expected for octahedral geometry that is , 9727(1028)cm^{-1}(ν_1), 15384(650)cm^{-1}(ν_2) and 24038(416)cm^{-1}(ν_3). This pattern of absorption may be assigned to transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ (F), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F)and$^3A_{2g} \rightarrow T_{1g}$(p) respectively. These observed transitions may be assigned to the characteristic three spin-allowed transitions of octahedral complexes[24]. The magnetic moments of the Co(II) complexes are observed in the range 4.79. In Co(II) complexes the electronic spectra showed that three bands at 9727(1028)cm^{-1},17482 (572) cm^{-1} and 23522 (444)cm^{-1} which are assignable to $^4T_{1g} \rightarrow {}^4T_{2g}$(F), $^4T_{1g}$(F)$\rightarrow$ $^4A_{2g}$(F), $^4T_{1g}$(F) $\rightarrow {}^4T_{1g}$(P). These values are falling in the range of octahedral Co(II) complexes[25].In the present investigation the magnetic moment of Mn(II) complex are 5.80 B.M. this values are good agreement with the magnetic moments reported for mononuclear high spin octahedral Mn(II) complexes[26].The experiential value of magnetic moments and electronic absorption spectra of Mn(II).The electronic spectral bands at 15315 (653), 22935 (436) and 26315 (380) cm^{-1} were assigned to transitions $^6A_{lg} \rightarrow {}^4T_{lg}$ (^{4}G), $^4T_{1g}$ (^{4}G) and $^4A_{1g}$ (^{4}G) respectively. The observed magnetic moments of 5.85 B.M. suggested octahedral environment. In the present study, Fe(III) complex have magnetic moments values in the range 5.97B.M. Which are almost close to that of required for octahedral geometry. The spectrum shows three bands at 17513 (571), 23529 (425) and 25380 (394),$^{-}$cm^{-1} (nm) which may be, assigned to high spin octahedral complexes, for transitions $^6A_{1g} \rightarrow {}^4T_{1g}$ (G), $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4E_g$respectively corresponds to octahedral geometry[27]. The last d-d band assigned to transition $^6A_{1g} \rightarrow {}^4T_{2g}$ in the present case may be associated with the charge transfer band traveling into visible region of spectra.

Thermal analysis:

In the TG curve of Mn(II) complex of ligand L$_1$ (M4L1) fig 6, the first weight loss 4.73% (cal. 5.81 %) occurred at temperature 152.32-209.52^{0}C, indicates the loss of two coordinated water molecules,this is confermed by an endothermic peak at (ΔT_{max}= 171.36^{o}C). The second weight loss from 233.32-704.72^{0}C with weight loss 85.82%(cal.86.83) indicate that weight loss correspond to decomposition of ligand confirmed by broad exotherm at 376.12^{0}C. thermo gram study indicate that the metal complex of Mn(II) are thermally quite stable,leading to the formation of stable residue metal oxide i.e, MnO obs. 9.44 %,(Cal. 10.27%)[28].(Fig.4)

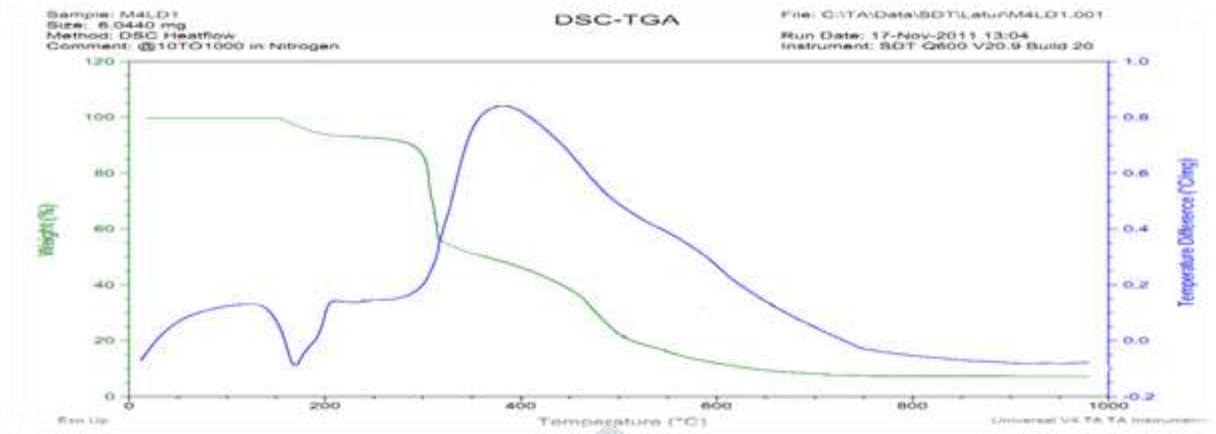

fig 4:TGA-DTA of Mn (II) complex

Antibacterial Activity:

Different concentrations of 500 PPM and1000 PPM, The antibacterial activity of the free ligands, their metal complexes and control (DMSO solvent) was studied *in vitro* against *Escherichia coli* and *Staphylococcus aureus* using *Ciprofloxacin* as standard. by cup plate diffusion method.[29] The compounds were tested at the concentration 0.5mg/ml and 1.00 mg/ml in DMSO and compared with *Ciprofloxacin*. The suspension of each microorganism was added to a sterile Nutrient Agar medium then poured into sterile Petri plates and left to solidification sterile porcelain cups were dipped in respective ligand and their metal complex solutions and kept on the agar surface along with a negative control DMSO and positive control *ciprofloxacin*. The plates were kept in refrigerator for half an hour for diffusion, and then incubated at 37^{0}c for 24 hours Results were recorded by measuring zones of inhibition in mm. The activity was determined by *observing complete inhibition (mm)*.The growth inhibition was compared with the control. The activity of metal complexes increases with increase in concentration.

Test Compound	**Diameter of inhibition zone (mm)**			
	Escherichia coli		***Staphylococcus aureus***	
	500 ppm	**1000 ppm**	**500 ppm**	**1000 ppm**
L_1	**14 (46.66)**	**16 (50.00)**	**12 (40.00)**	**14 (43.75)**
$Cu(L_1)_2$	**18 (60.00)**	**22 (68.75)**	**16 (53.33)**	**20 (62.50)**
$Ni(L_1)_2$	**15 (50.00)**	**17 (53.12)**	**14 (46.36)**	**18 (56.25)**
$Co(L_1)_2$	**17 (56.56)**	**17 (53.12)**	**13 (43.33)**	**16 (50.00)**
$Mn(L_1)_2$	**16 (53.33)**	**17(53.12)**	**16 (53.33)**	**18 (56.25)**
$Fe(L_1)_2$	**15 (50.00)**	**17 (53.12)**	**12 (40.00)**	**16 (50.00)**
Ciprofloxacin	30	32	30	32

Table 3 Antibacterial Activity of Ligands and Their Metal Complexes (% Inhibition).

Antifungal Activity:

Ligand and newly synthesized metal complexes and *Bavistin* were screened for antifungal activity against fungi, *Aspergillusniger*, *Fusariumoxysporus* at 250 PPM and 500 PPM concentrations separately. The cultures of the fungi were purified by single spore isolation technique. The concentrations of each compound in DMSO were prepared. The toxicity of Schiff base and metal complexes against fungi was studied by cup plate method on solid agar medium**.** The Potato Dextrose Agar (PDA) medium was used for the growth of fungi. Preparation of Potato Dextrose Agar (PDA) plates arethe Potato Dextrose Agar (PDA) medium required for the growth of fungi was prepared by dissolving 200 gm of potato, 6 gm dextrose, 15 gm agar and 0.5 gm of $MgSO_4$ H_2O in one liter of sterile distilled water. The Potato dextrose Agar medium is the sources of carbohydrate and nitrogen, which are activators for growth. PDA was prepared and autoclaved and poured serial in Petri plates. The plates were allowed to solidify.It is observed that The synthesized ligands and their metal complexes were screened for their antifungal activity against fungi (1*) Aspergillusniger* (2) *Fusariumoxysporum*and antibacterial activity against bacteria *Staphylococcus aureus* (gram positive) and *Escherichia Coli* (gram negative) organisms.The ligands and their metal complexes arrested the growth of all the three fungi at 250 and 500 ppm concentrations. The percentage inhibition of all the fungal growth increases with increase in concentration of the test compounds. The ligands L_1 show higher antifungal activity and For each class of fungi higher activity is shown by Cu(II) complexes, it may be because of higher stability of Cu (II) chelates than other complexes. The inhibitory activity decreases as Cu(II) > Ni (II) > Co (II) >Mn(II) > Fe(III). The metal complexes show enhanced activity as compared to their corresponding ligands. The activity of metal complexes increases with increase in concentration.

Test Compound	Diameter of inhibition zone (mm)			
	Aspergillusniger		*Fusariumoxysporum*	
	250 ppm	500 ppm	250 ppm	500 ppm
Bavistin	36	45	36	45
Ligand L_1	13(36.11)	20 (44.11)	10(27.77)	14 (31.11)
Cu(L_1)$_2$	17(47.22)	24 (53.53)	15 (41.66)	20(44.44)
Ni(L_1)$_2$	14(38.88)	22 (48.48)	13 (36.11)	18 (40.00)
Co(L_1)$_2$	16(35.35)	21(46.46)	12 (33.33)	16 (35.55)
Mn(L_1)$_2$	15(41.66)	21 (46.46)	11 (30.55)	15(33.33)
Fe(L_1)$_2$	12(33.33)	20(44.44)	11(30.55)	18 (40.00)

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Table 4: Antifungal Activity of Ligand L_8 and Their Metal Complexes (% Inhibition).

Conclusion:

The work presented in this paper with respect to, the complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) synthesized from Schiff bases of Dehydroacetic acid and 4-.amino acetanalide, melting point of the ligand are in the range of 214^0C it indicating their thermal stability at room temperature. Metals complexes precipitated in basic media. All the metal complexes are stable at room temperature. The conductivity measurements indicate non-electrolytic nature of the metal complexes. By Magnetic moment, colour and EAS spectra of all the complexes, On the basis of various d-d transition observed distorted octahedral structure are assigned to all complexes of metal.The characteristic bands observed in various regions in the IR spectra are useful in assigning the mode of bonding in the complexes. The –OH stretching band disappear in spectra of their respective metal chelates which confirm deprotonation and coordination of oxygen with metal ion. Shifting of the bands (C=N) towards lower frequency confirm the coordination through azomethine nitrogen. The new bands found (M-N) and (M-O) confirm the complexation. The simultaneous use of TGA and DTA is made in the present study of metal complexes with a view to understand stoichiometry, thermal stability, the presence and nature of water molecules. The complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe (III) contain coordinated water according to the TGA-DTA curve.

References

[1]Iqbal M S, Khan A H, Loothar B A, Bukhari I H, *Med Chem, Res,* 18, **(2009)** 31.

[2]Dao VT,Dowd M K, Martin M.T,Gaspard C,Mayer M, Michelot R, *J Euro J Med Chem,* 39, **(**2004) 619.

[3]PatoleJ,Shingnapurkar D,Padhye S,Ratledge C,*Bioorgani &Med. Chemistry Letters*,16, **(2006)** 1514.

[4]Khan A,Sarkar S,SarkarD, *Int J Antimicrobial* R.W.Bashioum,R L.Dieck,T. Moeller, Inorg. Nucl. Chem. Lett. 9 (1973) 773.

[5]Refat M S, El-Korashy S A, Kumar D N, Ahmed A , *SpectrochimActa Part A* 70, 898.**(2007)**.

[6]ChitrapriyaN.,MahalingamV.,ChannelsLC.,ZellerM.,FronczekFR.,Natarajan*Inorg Chim Acta,* 361, 2841.,**(2008)** .

[7]Ren S, Wang R, Komatsu K, Bonaz-Krause P, Zyrianov Y, Mckenna C E, CsipkeC,Tokes Z A, E J Lien, *J Med Chem*,45, 410.**(2002)**.
[8]Syamal A, *Bull ChemSoc Japan*, 15A, **(1971)** 431
[9]Dey K, *J Sci and Res*, 33, **(1974)** 76.
[10]Lean Katz, Pat U S, *ChemAbstr*, 50, (1956) 6519.
[11]Burrow A D,*Sciprog*, 85 (3), **(2002)** 199.
[12]Lewis G N, *J Am Chem Soc*, 38 **(1916)** 762.
[13]K.Nakamoto,Infra spet of inorg and coord comp,3rded.interscience,Newyork,1970,p.159,167 and 214
[14]A. K.Panda,D.C.Dash,P.Mishra,*Indian J. Chem.*,2007,**35A,**751.

[15]AEarnshaw, *Introduction to Magnetic Chemistry*, Academic Press, New York, **(1969),** 35.

[16]M U Malik, R D Sharma, J S Upadhyay,*Indian J Chemistry*, 15(A) ,**(1977)** 152-153.

[17]R N Malik, N K Parihari and B K Mahapatra, *J Ind.Chem.Soc*, 64, **(1987)** 690.

[18]K C.Satpathy, A K Panda, R Mishra and I Panda, *Trans Met Chem*,16**(1991)** 410.

[19]B Sing and A K Shrivastava, *ProcAcadSci (ChemSci)*,106 (1994) 23.

[20]D C Dash,A K Panda,S B Patjoshiand,A.Mahapatra, *J Indian ChemSoc*, 79 **(2002)** 48-50.

[21]G L.Eichhorn and J C.Bailar, *J Am ChemSoc*,75**(1953)** 2905.

[22]B N Figgis, *Introduction to Ligand Fields*, London, **(1966)** 218.

[23]Matu L, Iqbal S A, Raman N, Sharma S K, *E –J Chem* , 7, 1, **(2010)**227.

[24]Charyula K J, Etowah P, Omprakash K L, Reddy M, *Indian J Chem*, 23 A **(1984)** 668.

[25]Modi C K, Patel S H, Patel M N, *J therm anal and Calori*, 87, 2**,(2007)** 441.

[26]Bhargawa P P, Bembi R, Tygai M, *Indian Chem. Soc*. Vol. LX 214-217 **(1983)**.

[27]Mane P S, Shirodkar S G, and Chondhekar T K, *J Indian ChemSoc*, 79(A), **(2002)**154.

[28] Munde A S, Jagdale A N , Jadhav S M, Chondhekar T K, *J Serb ChemSoc*, 75, **(2010)** 349.

[29]P PJumade, U V.Kharabe, D Mude and P G Yeole *Int J chemsci*, 7,3,**(2009)**1518-1530.

[30]Anthony C. Ekennia· AderojuA. Osowole.Lukman O. Olasunkanmi.Damian C. Onwudiwe. Res Chem Intermed.DOI 10.10007/s11164-0116-2841-z.Dec 2017.

[31]Neha Mishra, surendra Singh Gound, Rajesh Mondal, Ritu Yadav, Rampal Pandey.Resuits in Chemistry,doi.org/10.1016/j.rechem.2019.10000G.15 aug 2019.