

SYNTHESIS AND CHARACTERISATION OF COMPLEXES DERIVED FROM SUCCINYL DIHYDRAZIDE AND 3-ACETYL-6-METHYL-2H-PYRAN-2, 4(3H)-DIONE

Ashwini Khamamkar and [#]Venkateshwar Rao Pallapothula

Department of chemistry, Nizam College, (Autonomous), Hyderabad, Telangana 500 001, India.

Article Info

Received 29/10/2014

Revised 16/11/2014

Accepted 09/12/2014

Keywords :-

DHA, Succinic acid dihydrazide, Schiff base, metal complexes, antimicrobial studies.

ABSTRACT

Schiff bases of 3-Acetyl-6-methyl-2H-pyran-2, 4(3H)-Dione are widely studied in previous years. We present the Schiff base derived from Succinic acid dihydrazide and 3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione [DHA(Dehydroacetic acid)]. Further the complexes were characterized by FT-IR, UV-Vis, Mass, TG-DTA, NMR, Elemental analyses, magnetic moment and C, H, N analyses. The complexes were further screened for antimicrobial activity. Based on the above characterization, the structures of the complexes were elucidated.

INTRODUCTION

Compounds containing an Azomethine group (-CH=N-) are known as Schiff bases. Schiff bases are generally bi or tridentate ligands capable of forming very stable complexes with transition metals. Due to the great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behavior studied [1]. They have been synthesized from a variety of compounds, such as aminothiazoles, 2-hydroxy-1-naphthalaniline, amino sugars, aromatic aldehydes, Isatin, the triazole ring, thiosemicarbazides, amino acids, pyrazolone etc, [2-6].

Literature survey shows that Schiff bases show bacteriostatic and bactericidal activity [7]. Antibacterial, antifungal, antitumor, anticancer activity has been reported and they are active against a wide range of microbes like *C. albicans*, *E.coli*, *S.aureus*, *B.polymyxa*, *P.Vitticola* etc, [8-10]. Many Schiff bases are known to be medicinally

important and are used to design medicinal compounds [11, 12].

The preparation of Schiff bases containing -C=O & -C=N- groups with potential ligating ability has drawn a lot of attention over a period of decade or so because of their use as chelating agents, analytical reagents, metal indicators in complexometric titrations and colorimetric reagents, in addition to their use in biochemical research[13].

Succinyl dihydrazide & Glyoxal were condensed by template method and their respective Cr(III), Fe(III), & Mn(III) complexes were synthesized by Singh et.al[14]. Considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications [15]. Oxalyl dihydrazide derived complexes with 2-furane carboxaldehyde, 2-thiophene carboxaldehyde were studied by Chohan et al [16].

Schiff base derivatives of Dehydroacetic acid were studied widely by M.C. Ganorkar et al [17,18]. Recently Schiff base derived from Oxalyl dihydrazide & DHA were reported by Rao PV et al [19].

In view of the above application of metal

Corresponding Author

Venkateshwar Rao Pallapothula

Email: - pallapothulav@yahoo.com

Research Article



complexes derived from Schiff bases, we report in this paper, the synthesis, characterization and biological activity of V(IV), Cr(III), Mn(II), Fe(III), Co(II), Cu(II), Ni(II), Zn(II), Cd(II), complexes with DHA (3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione) and SAHH (Succinyl dihydrazide). All the complexes were characterized by elemental analyses, I.R., ¹H-NMR spectra, electronic spectra, magnetic susceptibility measurements and thermo gravimetric analyses (TGA), ESR, etc.

EXPERIMENTAL

Materials

All the chemicals and solvents were of Anal R grade and used without further purification. Metal salts (CuSO₄, CoCl₂, NiCl₂, ZnCl₂ etc) and other chemicals were obtained from Merck (reagent grade). Hydrazine hydrate, Succinyl diester was obtained from Sigma Aldrich chemicals.

Preparation of Schiff Base

Schiff base ligand was prepared by reacting 3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione (DHA) and succinyl dihydrazide in 2:1 ratio. DHA was recrystallised from hot alcohol and was treated with succinyl dihydrazide obtained from its diester [20] in alcohol medium on a heating mantle. Immediately a yellow colored product was formed which was recrystallised from alcohol.

Preparation of metal complexes of the Schiff base

The Schiff base ligand was dissolved in methanol (20 ml) (0.432 gms; 2 mmol) and was mixed with transition metals, Mn(II), Co(II), Cu(II), Ni(II), Zn(II), Fe(II), Fe(III), Mo(VI) (1 mmol) in 1:1 ratio, dissolved in methanol with few drops of water. After adjusting the pH to basic medium the reaction mixture was refluxed for 30 min. The complexes that were immediately isolated were further refluxed for 30 min and were filtered and dried in anhydrous CaCl₂.

RESULTS AND DISCUSSION

Measurements

Infrared spectra (4000-400 cm⁻¹) were recorded as KBr pellets on Perkin-Elmer FT-IR system spectrophotometer at CIF, Nizam College. ¹H-NMR spectra were recorded on Avance-300 MHz NMR spectrometer with the samples dissolved in deuterated solvents using TMS as an internal standard at C.F., O. U. Elemental analyses (CHN) were performed using a C, H, N elemental analyzer at ICT, Hyd. UV-Vis spectra were recorded on a Shimadzu make UV-Vis spectrophotometer at CIF, Nizam college. The electronic spectra were measured in DMF and DMSO solvents. The Mass spectra were recorded on Shimadzu, Japan make mass spectrophotometer. Magnetic Susceptibility measurements were carried out at 25°C using Gouy balance with Hg [Co (SCN)₄] as the standard. Magnetic susceptibilities were

calculated as B.M (Bohr magnetons) using the $\mu_{\text{eff}} = 2.83 \sqrt{X_m T}$ equation. Thermo gravimetric analysis (TGA) was performed on Shimadzu DTA 50 model using 10 mg samples at CIF, College of Technology, O.U. The molar conductivity of the ligand and their complexes were determined in DMF and DMSO solvents (10⁻³ M) at RT using Systronics model conductivity meter. Melting points were determined on an open capillary Sisco model melting point apparatus.

IR Spectra

An infra-red spectrum was recorded by KBr pellet method and was determined as solid reflectance method. The phenolic ν_{OH} , $\nu_{\text{C=N}}$ and the aliphatic $\nu_{\text{C=O}}$ frequencies²¹ of the ligand and the metal complexes were observed to confirm the binding of the Schiff base to the metal complex. From the data it was found that the phenolic ν_{OH} of the ligand at 1330 cm⁻¹ increases in the metal complex which confirms the deprotonation and coordination to the metal. The decrease in $\nu_{\text{C=N}}$ frequencies further confirms the coordination of the 'N' of $\nu_{\text{C=N}}$. The $\nu_{\text{C=O}}$ (aliphatic) frequencies which appears at 1700 cm⁻¹ decreases in the metal complexes which shows the coordination of the "O" of C=O to the metal. The non-ligand infra red frequencies which appear around 500 cm⁻¹, 480 cm⁻¹ are due to $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ frequencies respectively. The IR frequencies are given in Table 1.

NMR Spectra

The NMR spectrum of the ligand was recorded in DMSO-d₆. The signal that appeared at δ 0.98 is due to CH₃ (S, 3H, CH₃) attached to azomethine carbon. The signal at δ 1.98 is due to CH₃ (S, 3H, CH₃) which is of pyran moiety. The signal at δ 2.46 is due to methylene protons (S, 4H, CH₂-CH₂). The signal at δ 6.2 is due aromatic proton of pyran moiety. The signal at δ 7.0 is due to NH proton (br, 1H, NH), the signal at δ 15.3 is due to OH proton. The ¹H nmr spectrum very well matches with the structure of the ligand.

¹³C-NMR of the ligand shows a signal at δ 21.0 due to CH₃ (q, CH₃-pyran), δ 11.9 (q, CH₃-C=N); δ 34.3 (t, CH₂-CH₂); δ 168.9 (s, aliphatic -C=O); δ 155.6 (s, azomethine -C=N); δ 162.6 (s), δ 101.0 (d), δ 177.4 (s), δ 103.4 (s), δ 162.8 (s) are signals shown by the pyran carbons.

Electronic spectra

The UV-Visible spectra was recorded from 190-1100 nm in the respective solvents (DMF, DMSO and ethanol). The Vanadium pentagonal bipyramidal complex exhibits three bands i.e. ²A₁ → ²A₂, ²A₁ → ²B₂ and ²A₁ → ²B₁ at 16100, 20900, & at 22500 cm⁻¹. In chromium complexes three bands at 14500, 23000, 31500 cm⁻¹ were observed which were assigned for ⁴A_{2g} → ⁴T_{2g} (v₁); ⁴A_{2g} → ⁴T_{1g} (F) (v₂); ⁴A_{2g} → ⁴T_{1g} (P) (v₃) respectively. The three bands observed at 8200, 16500 and 19400 cm⁻¹ in the



spectrum of cobalt complex were assigned to the three transitions ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1); ${}^4T_{1g}$ (F) \rightarrow ${}^4T_{1g}$ (P) (ν_2); and ${}^4T_{1g}$ (F) \rightarrow ${}^4A_{2g}$ (ν_3) respectively. In Copper(II) complex three transitions were observed ${}^2E \rightarrow {}^2B_2(\nu_1)$; ${}^2E \rightarrow {}^2A_1(\nu_2)$; ${}^2E \rightarrow {}^2B_1$ at 14500, 27000, & 26500 cm^{-1} . In Nickel (II) complex the three bands at 8264, 14814, & 21505 cm^{-1} which are interpreted to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1); ${}^3A_{2g} \rightarrow$ ${}^3T_{1g}$ (F) (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3) transitions in an octahedral stereochemistry. Nephelauxetic ratio and ν_2/ν_1 were further calculated from the UV-Vis spectra and the data is given the following table no.2.

TGA & DTA

Thermal analysis of metal complexes was done in air atmosphere with a gas flow rate of 50ml/min in a platinum pan with 10mg of compound. The temperature rise for the TGA and DTA was 20 $^{\circ}$ C rise/min. The thermal data shows that there is no loss of water molecules from 100 $^{\circ}$ C to 250 $^{\circ}$ C also, which substantiates our predicted octahedral geometry in Cr(III), Mn(II), Fe(III), Co(II), Cu(II), Ni(II), Zn(II), Cd(II), and pentagonal bipyramidal geometry for Vanadium complex. The TG-DTA graphs are given at the end of the main text.

Mass spectra

Mass spectra of the complex shows prominent peaks at m/z 510 (copper complex was analyzed for ESR) which is the metal complex molecular weight and further

peaks at m/z 294 corresponds to the loss of one DHA unit, m/z 265 corresponds to the breakage of bond between the –NH-C=O nearby to the Azomethine linkage, m/z 180, m/z 152 substantiates the ligand and metal complex formation. The fragments are shown in figure 1.

ESR

ESR spectra of copper and Vanadium complex were recorded at liquid N $_2$ temperature at Central facilities, UOH, Hyderabad. Copper complex showed a single peak with a 'g' value of 2.07719, indicating a symmetrical environment around the metal, thus indicating an octahedral geometry. Whereas the Vanadium complex shows a splitting in the ESR spectrum with 'g' values 1.97, 2.03, 2.12 which indicates that g_{xx} , g_{yy} , g_{zz} are different, which supports pentagonal bipyramidal geometry.

C, H, N M analysis

C, H, N, M analysis was done on elemental analyzer and the results are as given in table no.3.

Anti-microbial activity

The complexes were found to be active against some of the microbes like E.Coli, Staph. aureus. Their activity was checked by disc diffusion method in which two different concentrations were checked (5 μ gms and 10 μ gms). Before checking the activity, the solvent was also tested. The results are given in the following table no.4.

Table 1. Infra Red spectra: (in cm^{-1})

Complex	ν_{C-OH} (phenolic)	$\nu_{C=N}$	$\nu_{C=O}$ (aliphatic)	ν_{M-O}	ν_{M-N}
Ligand	1330	1600	1700	-	-
VOL	1350	1559	1687	470	527
Cr(III)	1364	1566	1676	488	525
Mn(II)	1354	1567	1678	475	515
Fe(III)	1352	1554	1695	470	531
Co(II)	1356	1573	1681	488	514
Ni(II)	1354	1555	1684	485	514
Cu(II)	1360	1574	1651	476	531
Zn(II)	1356	1559	1684	476	527
Cd(II)	1363	1560	1676	475	527

Table 2. UV-Vis Calculations

Metal ion	Racah parameter [B] [#]	$\beta = B'/B$	ν_2/ν_1
Vanadium(IV)	-	-	20900/16100=1.298
Chromium(III)	918	0.798	23000/14500=1.586
Cobalt(II)	971	0.775	16500/8200=2.012
Copper(II)	-	-	27000/14500=1.862
Nickel(II)	1030	0.745	14814/8264=1.792

B values are given in Inorganic chemistry by James E. Huheey [22]

Table 2. Analytical and Physical data of Schiff base ligand and their Metal complexes

Metal complex	% yield	μ_{eff} BM	Mol.wt	Solubility
Ligand	All the compl.	-	445	Complexes were
[VOL]SO4		1.9	512	



[Cr(III)L]Cl	Were more than 60%	4.95	497	found to be soluble in DMF/DMSO/ gl.CH ₃ COOH
[Mn(II)L]		5.8	500	
[Fe(III)L]Cl		5.9	501	
[Co(II)L]		4.5	504	
[Ni(II)L]		3.8	504	
[Cu(II)L]		2.0	508	
[Zn(II)L]		0	510	
[Cd(II)L]		0	557	

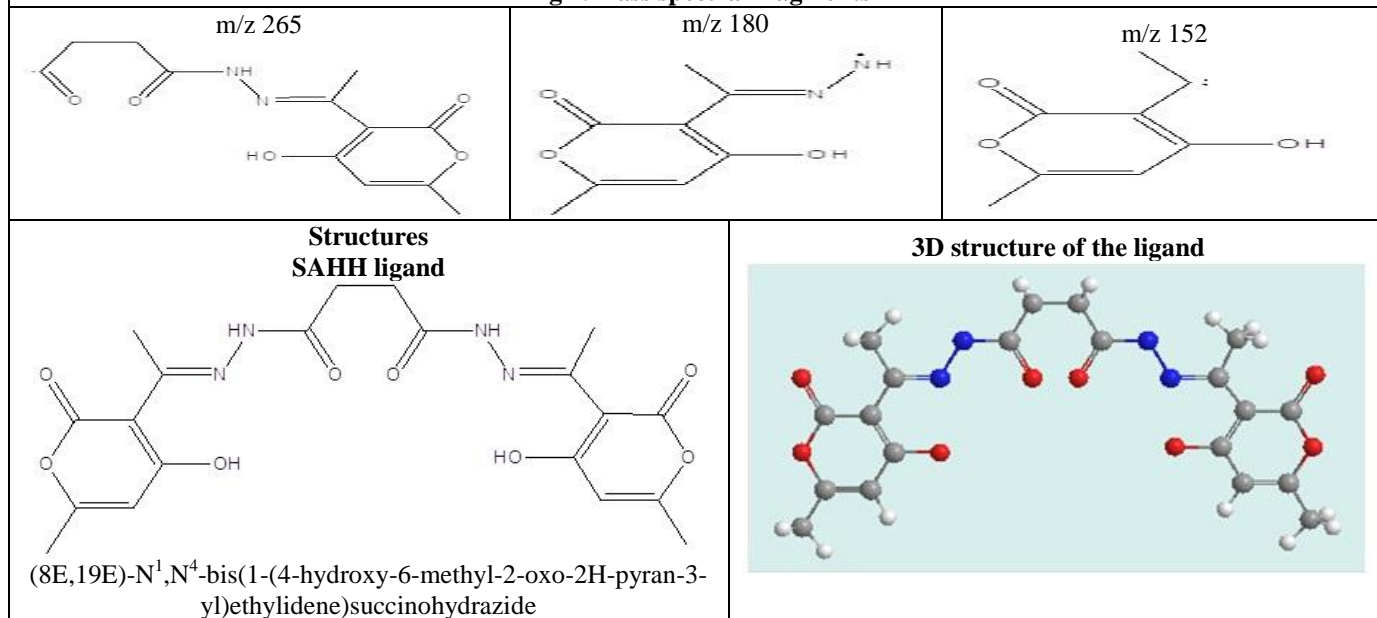
Table 3. C, H, N, M analysis

Complex	%C(calc)	%H(calc)	%N(calc)	%M(calc)
Ligand	53.94(53.93)	4.48(4.49)	12.57(12.58)	-
VOL	46.88(46.87)	3.91(3.90)	10.95(10.93)	9.97(9.96)
Cr(III)	48.27(48.28)	4.03(4.02)	11.27(11.26)	10.45(10.46)
Mn(II)	48.1(48.0)	4.01(4.0)	11.24(11.2)	11.1(11.0)
Fe(III)	47.91(47.90)	3.98(3.99)	11.19(11.17)	11.18(11.17)
Co(II)	47.62(47.61)	3.97(3.96)	11.18(11.11)	11.72(11.70)
Ni(II)	47.61(47.61)	3.97(3.96)	11.13(11.11)	11.71(11.70)
Cu(II)	47.26(47.24)	3.94(3.93)	11.04(11.02)	12.41(12.40)
Zn(II)	47.07(47.05)	3.95(3.92)	10.97(10.98)	12.76(12.74)
Cd(II)	43.09(43.08)	3.60(3.59)	10.06(10.05)	20.11(20.10)

Table 4. Antimicrobial activity of the complexes

complex	E.coli	Staph.aureus
VOL	-	-
Cr(III)	+	+
Mn(II)	-	+
Fe(III)	-	-
Co(II)	+	+
Ni(II)	+	+
Cu(II)	+	+
Zn(II)	-	+
Cd(II)	+	+

Fig 1. mass spectral fragments



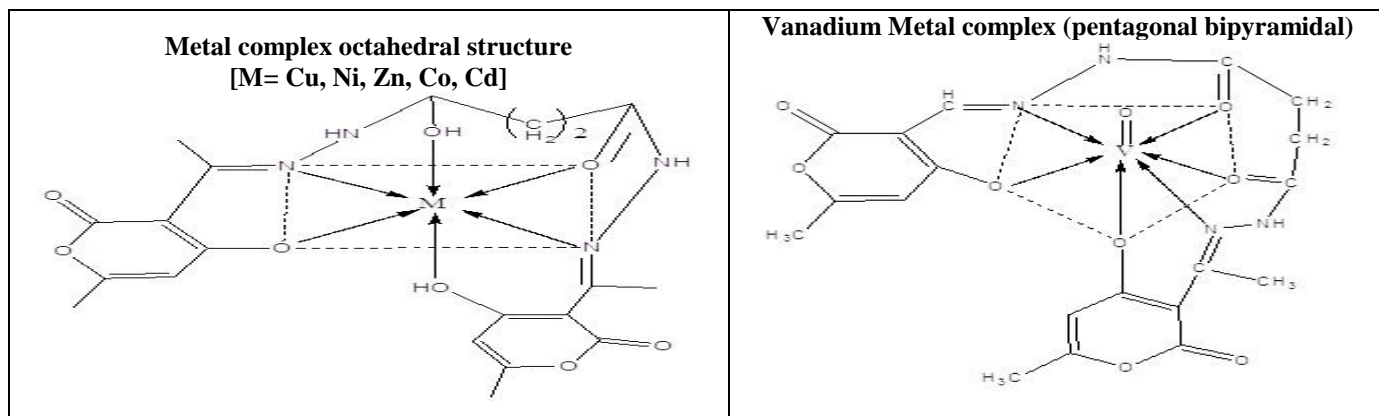
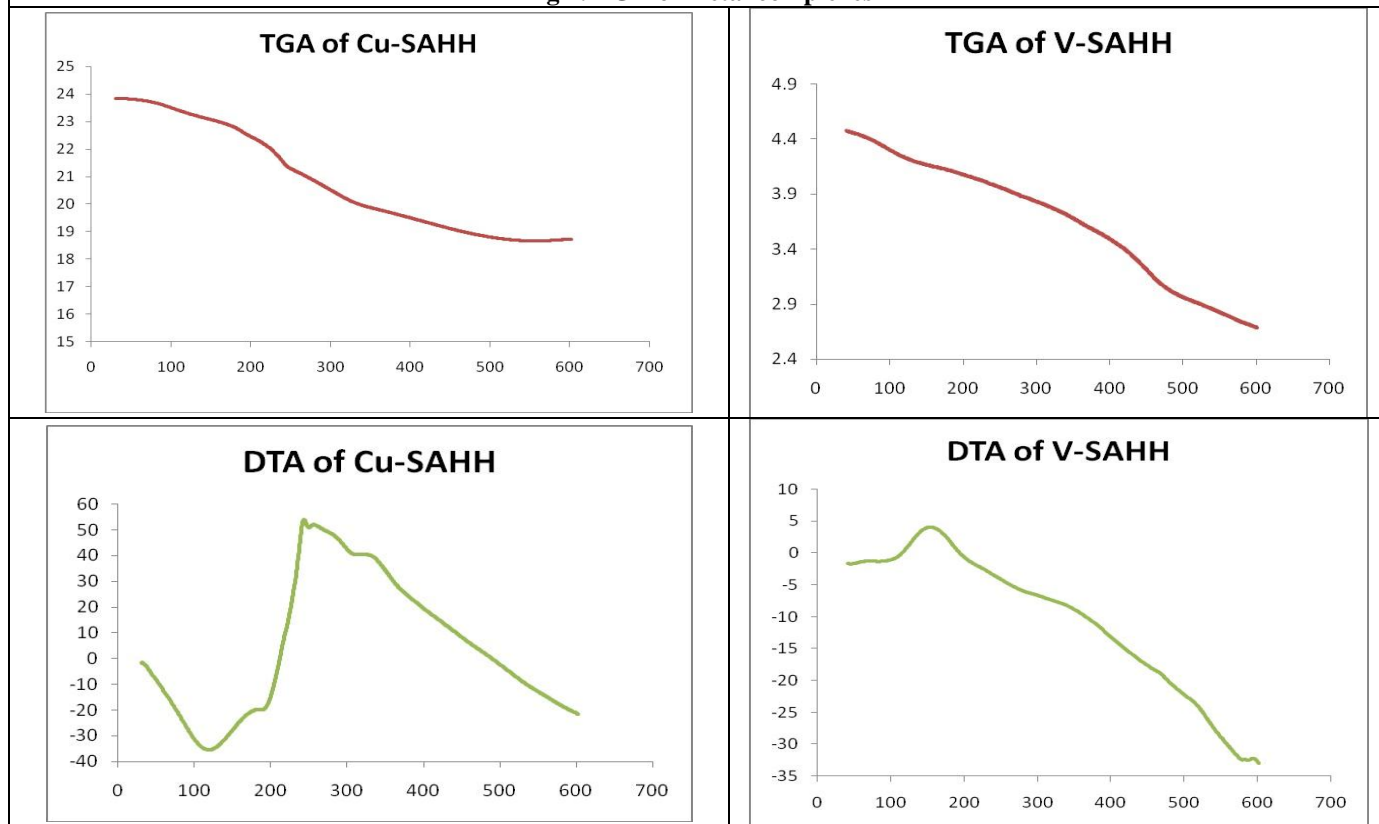


Fig 2. TGA of metal complexes



CONCLUSION

The schiff base metal complexes were synthesized and characterised and the predicted geometries were found to be in sync with the analysis. The metal complexes were further screened for antimicrobial activity and few of them are showing promising results. Further much work can be done on them.

REFERENCES

1. Raman N, Muthuraj V, Ravichandran S, Kulandaisamy A. (2003). *Proc. Ind.Acad.Sci*; 115, 161.
2. Sridhar SK, Ramesh A. (2002). *Ind.J. Chem.Soc*, 41, 668.
3. Wei Z, Qiong C, Chao-gang H, Huazhong SD. (2002). *Xuebao Ziran Kexue ban*, 36, 478.
4. Dong-Dong Y, Yan Lan J, Lu S. (2001). *Chinese J.Chem*, 19, 136.
5. Piotr P, Bogumil B. *Biopolymers*, 67, 61.

ACKNOWLEDGEMENTS

The authors thank the Principal and the Head, Department of chemistry, Nizam College for providing all the facilities to carry out the research work including IR and UV-Visible spectra.



6. Rh.Miao, Li S, Rudong Y, Welbing VLY. (2003). *Ind.J.Chem*, 42, 318.
7. Yuxai Z, Tao Z, Wansham M, Haibin Z, Suifeng C. (2002). *Hauxue Shiji*, 24, 117.
8. Gawad MA, Issa YM, Abd-Alhamid SM. (1993). *Egypt J.Pharm.Sci*, 34, 219.
9. Mulwad VV, Shirodkar JM. (2002). *Ind.J. Heterocyclic Chem*, 11, 199.
10. Sari N, Arshan S, Loguglu E, Sariyan I. (2003). *G.U.J.Sci*, 16, 283.
11. Rao S, Mitra AS. (1978). *J.Ind.Chem.Soc*, 55, 420.
12. Khan SA, Siddiqui AA, Shibeer B. (2002). *Asian J.Chem*, 14, 117.
13. Dey K. (1974). *J.Sci.Ind.Res*, 33, 76.
14. Dharam PS, Vandana M & Ramesh K. (2009). *Research letters in Inorganic chemistry*, article ID 824561.
15. Chohan ZH & Sherazi SKA. (1997). *Metal Base Drugs*, 4(6), 327-332.
16. Zahid HC, Farooq MA & Claudiu TS. (2001). *Metal Base Drugs*, 8(3), 171-177.
17. Rama Rao N, Venkateswara Rao P, Tyagaraju VJ & Ganorkar MC. (1985). *Ind. J. Chem*, 1 24A, 877-879.
18. Shirodkar SG, Arbad BR & Chondhekar TK. (2001). *Ind. J. Chem*, 40A, 648-651.
19. Ashwini K, Rao PV. (2012). *J.Ind.Council Chem.*, 29(1&2).
20. Vogel. *Practical Organic Chemistry*. 5th ed.
21. *Infra red and Raman Spectra* by Nakamoto. 1 & 2.
22. *Inorganic Chemistry-Principles of Structure and Reactivity*, 2nd ed., by James E.Huheey, 418.

