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Synthesis, characterization and Biological studies of Cu(II) and Ni(II) complexes with New Bidentate Shiff's base ligands as 4-hydroxy-3-(1-(arylimino)ethyl)chromen-2-one

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Abstract

New Bidentate Shiff's base ligands, 4-hydroxy-3-(1-(arylimino)ethyl)chromen-2-one were synthesized by condensation of primary aromatic amines with 3-acetyl-4-hydroxychromen-2-one. These were characterized by IR, ^{1}HNMR, ^{13}CNMR and mass spectral analysis. Cu(II) and Ni(II) complexes were synthesized and characterized by their mass, IR, electronic and XRD spectral analysis. Magnetic moments and molar conductance properties were studied using standard methods. Octahedral geometry around these metal ions has been proposed on the basis of magnetic and spectral studies. In vitro biological screening effects of the investigated compounds were tested against the bacterial species Staphylococcus aureus, Escherichia coli, Salmonella typhi and Bacillus subtilis by Agar cup method. Fungal species Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme and Aspergillus flavus by the posion plate method. A comparative study of inhibition values of the Schiff base ligands and their complexes indicates that the complexes exhibit higher antimicrobial activity than the free ligands.

Keywords: Schiff base, spectra, antibacterial, antifungal.

Introduction

There are a number of reports that natural and synthetic coumarin derivatives possessing antimicrobial activity[1]. 4-Hydroxy-3-substituted coumarins, a class of fused ring heterocycles, occur widely among natural products and have importance in medicine[2]. Many natural products with the coumarinic moiety exhibit interesting biological and pharmacological properties. They are antibacterial, anti-HIV active[3] and antihelimenthic[4]. The Schiff base ligands and their metal complexes find paramount applications in the field of biological studies[5], clinical[6], dyes industry[7], and food industry[8].

Literature survey reveals that work has been carried out on lanthanide complexes of Schiff bases derived from 8-formyl-7-hydroxy-4-methyl-2H-chromen-2-one[9]. Studies on metal complexes with Schiff base derived from 3-formyl-4-hydroxychromen-2-one and semicarbazone were reported[10]. Less work seems to have been carried out on the metal complexes of Schiff bases derived from 4-hydroxy-3-(1-(arylimino)ethyl)chromen-2-one and primary aromatic amine. In the views of above facts, we report here the preparation of 3-acetyl-4-hydroxychromen-2-one from 4-hydroxychromen-2-one by earlier reported method[11] with some modification and was condensed with aromatic amines such as aniline, 4-toluidine, 4-chloroaniline and 4-anisidine to synthesize 4-hydroxy-3-(1-(arylimino)ethyl)chromen-2-one (L_1 to L_4). Using these ligands their complexes were synthesized with cu^{II} and Ni^{II} metal ions. The structure of the complexes has been established using analytical, magnetic susceptibility, IR, electronic spectral data and powder XRD technique. The results obtained are in good agreement with the ligand–field splitting energy (10Dq).

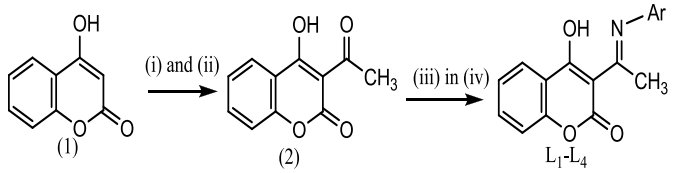
Material and Methods

All the chemicals and solvents used were of A.R. grade. All chemicals used were of E-Merck and S.D. fine Ltd. Melting points were determined in an open capillary tube and are uncorrected. The purity of the compound has been checked by TLC. Elemental analyses (C, H and N) were performed on a Perkin- Elmer 2400 CHN elemental Analyzer. IR spectra were recorded in $CHCl_3$ on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}HNMR (300 MHz) and ^{13}CNMR (70 MHz) were run on a Bruker Avance DPX-250 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. Chemical shift values are given in d scale.

Mass spectra were recorded on Finnigan Mat LCQ Mass Spectrometer using methanol as mobile phase. The electronic spectral measurements were made on Systronics UV-visible spectrophotometer (model 119). The metal contents in complexes were determined by atomic spectra on Perkins Elmer atomic absorption spectrophotometer (model 2380). The conductivity of dilute solutions ($1x10^{-4}$M) in DMSO is measured on conductivity meter. Magnetic measurements at room temperature were carried out using Gouy's balance.

Synthesis of 3-acetyl-4-hydroxychromen – 2 - one: To a solution of 4-hydroxy-chromen-2-one (3g, 18.6 mmoles) in acetic acid (16 ml) phosphrous oxychloride (5.6 ml) was added. The mixture was heated at reflux for 30 minutes. After cooling, the precipitate was collected and recrystallized from ethanol. 3-acetyl-4-hydroxy-chromen-2-one is collected as white needles. Yield of 2.7 g (90%), mp 134-36^{0}C.

Synthesis of 4-hydroxy-3-(1-(arylimino)ethyl)chromen-2-one: The ligands L_1-L_4 (scheme 1) were prepared by mixing equimolar solutions of 3-acetyl-4-hydroxy-chromen-2-one and the corresponding aromatic amine in ethanol and refluxing the mixture for 4 hrs. After cooling, the product was crystallized from ethanol. The purity of the ligands was checked by m.p., TLC and elemental analysis. These are also characterized by IR, ^{1}HNMR, ^{13}CNMR and mass spectral studies.



(i) CH_3COOH, (ii) $POCl_3$, (iii) Ar-NH_2 and (iv) C_2H_5OH
Ar = phenyl (L_1), toluyl (L_2), 4-chlorophenyl (L_3) and 4-anisyl(L_4)

Fig. 1 : Synthesis of Schiff's Base Ligands

General procedure for the synthesis complexes: To a hot solution of Ligand **(**0.02 Moles in 40ml of methanol), 0.01 moles of metal salt dissolved in 25ml of methanol was added drop wise. The contents were refluxed for four hours. The precipitated complex was further digested for one hour. The complex formed was filtered and washed with alcohol and followed by petroleum ether (40–60^{0}C). It was dried in vacuum desiccators over calcium chloride.

Results and Discussion

Ligands **(L_1-L_4)** are synthesized as shown in scheme 1. Commercially available (1) is acetylated with acetic acid and phosphorus oxychloride in a hood as safety measure according to literature procedure[11] to afford (2). The ligands 4-hydroxy-3-(1-(arylimino)ethyl)chromen-2-ones **(L_1-L_4)** are obtained by condensation of **(2)** with aromatic amines as aniline, 4-toludine, 4-chloroaniline and 4-anisidine. Investigations are carried out to establish the structures of ligands **(L_1-L_4)**, both in the solid state and in solution using various spectroscopic techniques. Physical, analytical and spectral data of the ligands are listed in table 1.

The synthesized complexes are stable at room temperature, insoluble in water, partially soluble in methanol and ethanol, completely soluble in DMF and DMSO. The elemental analysis, magnetic moments and molar conductance data given in (table 1) are consistent with the general formula $[M(L)_2].2H_2O$. The ligand is a bidentate coordinating through azomethine nitrogen, phenolic oxygen of coumarin moiety via deprotonation. The molar conductance values in DMSO in 10^{-3}M fall in the range 22-30 Ω^{-1} indicating non-electrolytic nature of the complexes[12].

All ligands show a high intensity band observed ca. at 1632-1626 cm^{-1} is assigned to ν(C=N) vibration suggesting the formation of Schiff base. Broad weak band around 3500-2600 cm-1 is assigned to H bonded –OH in the Schiff base. The band at 1567-1483 cm^{-1} is assigned to the combination of ν(C=C) of the aromatic ring. A high intensity band in the region 1338-1335 cm^{-1} is assigned to phenolic ν(C-O) vibration and 1720-1709 cm^{-1} for lactone carbonyl.

The ν(C=N) of ligand (L_1-L_4) appeared at 1632-1626 cm^{-1} has shifted to 1611-1605 cm^{-1} in the metal complexes. This lower shift supports the coordination of metal ion with azomethine nitrogen. The disappearance of the band at 1338-1335 cm^{-1} and appearance of new medium intensity bands in the region 1398-1394 cm-1 for ν(C-O) supports the coordination of phenolic oxygen to the metal ion via deprotonation[9]. The unaltered position of ν(C=O) confirms the non-involvement of lactone in the coordination.

A broad band at 3500-3300 cm^{-1} and a peak at 955-948 cm^{-}1 in the complexes indicates the presence of coordinated water molecules.[13] Further the presence of coordinated and non coordinated water molecules is confirmed by the TGA studies. The appearance of two strong bands at 528-492 cm-1 and at 415-405 cm^{-1} are assignable to ν(M-N) and ν(M-O) vibrations respectively[14-15].In thermal studies, no weight loss was found on constant heating for 1 h at 120^{o}C which is indicative of the presence of coordinated water. The TG analysis shows the percentage loss corresponding to two coordinated water molecules in cu^{II} and Ni^{II} complexes. The loss of water in these complexes was found to be one-step process as only one endothermic peak was observed at 200-220^{o}C[16].

The electronic spectra of the Cu^{II} complexes shows a band in the 16260-16666 (ε = 40.50) cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ characteristic of distorted octahedral stereochemistry with D_{4h} geometry[17]. Beside the above bands, the band observed at ~ 27700 cm^{-1} may be assigned due to charge transfer. The cu^{II} complex exhibit normal magnetic moment which are in the range 1.73-1.82 BM support the octahedral structure.
The ESR spectra of the Cu(II) complexes were recorded at room temperature table 3. The anisotropic G values have been calculated by Kneubuhl's method[18] G= ($g_{\|}$-2.003) / ($g_{\perp}$-2.003) which measures the exchange interaction between copper(II) centers. One unpaired electron in Cu(II) complex with $^2B_{1g}$ as ground state lies in d_{x2-y2} spectrum of Cu(II) complex of ligand orbital and follows the trend $g_{\|} > g_{\perp} > g_e$ (g_e = 2.0036 free ion value). The axial spectrum with $g_{\|} > g_{\perp} >$ 2.03 is consistent with a distorted octahedral geometry

around the Copper(II) ion[19]. The spectra $[Cu(L_1)_2(H_2O)_2]$, $[Cu(L_2)_2\ (H_2O)_2]$, $[Cu(L_3)_2(H_2O)_2]$ and $[Cu(L_4)_2(H_2O)_2]$ exhibited pronounced peak at $g_{\perp}$ =2.07 ± 0.02 and a broad and shallow quadruplet at $g_{\parallel}$ =2.28±0.04. Such spectral features are characteristic of the Cu^{2+} ions present in axially distorted octahedral sites[20]. The calculated G value for the present complexes appeared in the range 3.13 to 3.66 indicate the existence of a negligible exchange interaction between copper, as G < 4[21].

The Ni^{II} complexes exhibit three absorption bonds 12987-13333 (ε = 8) (ν_1), 19417-19802 (ε = 6) (ν_2) and 27777-29411 (ε = 20) (ν_3) which may attributed to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2), $^3A_{2g}F) \rightarrow {}^3T_{1g}$ (P) (ν_3), respectively indicating octahedral geometry[22-23].

The magnetic values are in normal range (3.11–3.37 B.M.) of octahedral structure. This structure is further confirmed by the ratio V_2/V_1 (1.44 – 1.50), the value expected for octahedral structure. The reduction of Racah parameters (B^1 = 527.43-601.83) form the free ion value 1080 and β = 0.488-0.557, less than unity suggest appreciable amount of covalent character in the metal–ligand bonds[24,25].

X-ray diffraction pattern of $Cu[L_1]_2.2H_2O$ and $Ni[L_1]_2.2H_2O$ revealed sharp refluxes suggesting highly crystalline monoclinic nature for the complexes[26]. The position of each reflux was accurately measured and by using Bragg's equation the inter planar distance d was calculated. The d-spacing values of each reflux were used to calculate lattice parameters assuming the probable crystal monoclinic system.

Table-1
Physical, analytical and spectral data of the ligands

S.No	Specification	Data of Ligand L_1	Data of Ligand L_2	Data of Ligand L_3	Data of Ligand L_4
1	Yield	90%	85%	82%	83%
2	Colour	Yellowish Green	Yellowish Green	Yellowish Green	Yellowish Green
3	Melting Point	203^0C	210^0C	237^0C	243^0C
4	IR (KBr, cm^{-1})	3600-2600 (broad phenolic ν_{OH}) , 1710 ($\nu_{C=O}$) lactone , 1628 ($\nu_{C=N}$) of imine, 1564, 1483 aromatic ($\nu_{C=c}$) 1335 (ν_{C-O}) phenolic	3600-2600 (broad phenolic ν_{OH}) , 1709 ($\nu_{C=O}$) lactone , 1630 ($\nu_{C=N}$) of imine, 1567, 1483 aromatic ($\nu_{C=c}$) 1336 (ν_{C-O}) phenolic	3600-2600 (broad phenolic ν_{OH}) , 1720 ($\nu_{C=O}$) lactone , 1626 ($\nu_{C=N}$) of imine, 1565, 1484 aromatic ($\nu_{C=c}$) 1336 (ν_{C-O}) phenolic	3600-2600 (broad phenolic ν_{OH}) , 1710 ($\nu_{C=O}$) lactone , 1632 ($\nu_{C=N}$) of imine, 1563, 1483 aromatic ($\nu_{C=c}$) 1338 (ν_{C-O}) phenolic
5	^{1}H-NMR ($CDCl_3$) in δ (300 MHz)	2.66 (S,3H, $-CH_3$), 7.5-7.0 (m, 5H, Ph–H), 8.06 and 7.5-7.2 (Ar-H of coumarin moiety), 15.75 (S,1H, O–H).	2.65 (S, 3H, imne – CH_3), 2.38 (S, 3H, for p-Phenyl-CH_3) 7.5 and 7.08 dd, 4H, (-C_6H_4-*p*) 8.04 and 7.2-7.5 (Ar-H of coumarin moiety), 15.74 (S,1H, O–H).	2.68(S, 3H, imne – CH_3), 7.19 and 7.47dd, 4H, (-C_6H_4-*p*) 8.04 and 7.2-7.5(Ar-H of coumarin moiety), 15.92 (S,1H, O–H).	2.66 (S, 3H, imne –CH_3), 3.84 (S, 3H, for p-Phenyl-0CH_3) 6.97 and 7.14dd, 4H, (C_6H_4-*p*) 8.05 and 7.2-7.5(Ar-H of coumarin moiety), 15.68 (S,1H, O–H).
6	^{13}C-NMR ($CDCl_3$) in δ (300 MHz)	20.39 (imine-CH_3 carbon), 98.12 for ^{3}C, 138-116 for aromatic carbons, 154 for ^{9}C, 162.4 for lactone carbon, 175.9 for ^{4}C, and 181.7 for imine carbon	20.38 (imine-CH_3 carbon), 21.04 (*p*-CH_3) 98.07 for ^{3}C, 138-116 for aromatic carbons, 154 for ^{9}C, 162.38 for lactone carbon, 175.99 for ^{4}C, and 181.78 for imine carbon	20.43 (imine-CH_3 carbon), 98.07 for ^{3}C, 133.9-116.7 for aromatic carbons, 154.1 for ^{9}C, 162.12 for lactone carbon, 176.13 for ^{4}C, and 182.11 for imine carbon	20.34 (imine-CH_3 carbon), 55.60 (*p*-OCH_3 carbon) 98.04 for ^{3}C, 138.8-114.9 for aromatic carbons, 154 for ^{9}C, 159.7 for lactone carbon, 176.07 for ^{4}C, and 181.59 for imine carbon
7	Mass Spectra	$[M^+]$=279.08	$[M^+]$=294.35	$[M^+]$=314.23 and 316.19 (in isotopic ratio of Chlorine)	$[M^+]$=309.98

Table - 2
Analytical Data of Complexes

S. No.	Complexes	Colour	Found / (calc), %				μ_{eff}. B.M.	Ligand field parameters				
			C	H	N	M		10 Dq (cm^{-1})	LFSE kcal - mol^{-1}	B (cm^{-1})	β	V_2/V_1
1	$[Cu(L_1)_2(H_2O)_2]$	Green	62.27 (62.24)	4.35 (4.30)	4.23 (4.27)	10.1 (9.68)	1.78	1316	37.60	-	-	-
2	$[Cu(L_2)_2(H_2O)_2]$	Green	59.93 (63.20)	4.60 (4.71)	4.42 (4.09)	9.60 (9.29)	1.73	1316	37.60	-	-	-
3	$[Cu(L_3)_2(H_2O)_2]$	Pale Green	56.50 (56.32)	3.46 (3.61)	3.52 (3.86)	10.15 (9.78)	1.82	1333	38.03	-	-	-
4	$[Cu(L_4)_2(H_2O)_2]$	Green	60.60 (60.37)	4.26 (4.50)	3.63 (3.91)	8.70 (8.87)	1.76	1333	38.03	-	-	-
5	$[Ni(L_1)_2(H_2O)_2]$	Yellowish Green	62.46 (62.70)	4.60 (4.33)	4.50 (4.30)	9.28 (9.01)	3.11	1298	37.11	601.8	0.557	1.50
6	$[Ni(L_2)_2(H_2O)_2]$	Yellowish Green	63.28 (63.65)	4.66 (4.75)	4.20 (4.12)	8.50 (8.64)	3.17	1316	37.60	527.4	0.488	1.49
7	$[Ni(L_3)_2(H_2O)_2]$	Yellowish Green	56.92 (56.70)	3.46 (3.64)	3.62 (3.89)	8.36 (8.15)	3.20	1333	38.10	576.1	0.533	1.44
8	$[Ni(L_4)_2(H_2O)_2]$	Yellowish Green	60.90 (60.78)	4.60 (4.53)	3.68 (3.94)	8.10 (8.25)	3.37	1333	38.10	558.2	0.516	1.49

Table-3
ESR data of the Cu(II) complexes of the ligand L_1 and L_3

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	G	μ_{eff}
$Cu(L_1)_2(2H_2O)$	2.3303	2.0935	2.174	3.666	1.882
$Cu(L_2)_2(2H_2O)$	2.2674	2.0788	2.141	3.486	1.854
$Cu(L_3)_2(2H_2O)$	2.2625	2.0830	2.142	3.242	1.855
$Cu(L_4)_2(2H_2O)$	2.2826	2.0923	2.155	3.130	1.866

Table-4
Anti Bacterial activity

Compound	Zone of Inhibition (diameter in mm)			
	E. coli	***S. typhi***	***S.aureus***	***B. subtilis***
Penicillin	24	18	21	14
(L_1)	16	-	13	7
$Cu(L_1)_2(2H_2O)$	22	11	17	10
$Ni(L_1)_2(2H_2O)$	19	9	13	7
(L_2)	11	-	9	8
$Cu(L_2)_2(2H_2O)$	15	6	10	5
$Ni(L_2)_2(2H_2O)$	11	-	5	-
(L_3)	20	7	14	11
$Cu(L_3)_2(2H_2O)$	24	12	17	13
$Ni(L_3)_2(2H_2O)$	22	10	15	12
(L_4)	18	-	11	8
$Cu(L_4)_2(2H_2O)$	23	5	14	11
$Ni(L_4)_2(2H_2O)$	20	-	12	9

Table-5
Anti fungal activity

Compound	Growth of Fungi			
	A. niger	**P .chrysogenum**	**F. moneliforme**	**A. flavus**
Gresiofulvin	-	-	-	-
(L_1)	+	++	++	+
$Cu(L_1)_2(2H_2O)$	-	-	-	-
$Ni(L_1)_2(2H_2O)$	-	+	+	-
(L_2)	+	++	++	+
$Cu(L_2)_2(2H_2O)$	-	-	-	-
$Ni(L_2)_2(2H_2O)$	-	+	+	-
(L_3)	-	-	+	-
$Cu(L_3)_2(2H_2O)$	-	-	-	-
$Ni(L_3)_2(2H_2O)$	-	-	-	-
(L_4)	+	++	++	+
$Cu(L_4)_2(2H_2O)$	-	-	-	-
$Ni(L_4)_2(2H_2O)$	-	+	+	-

Moderate growth (++), Reduced growth (+) and No growth (-) of fungi

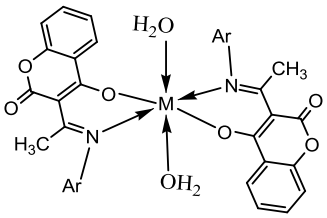
Biological Activity: The antibacterial activity was measured by agar cup method[27]. The bacterial cultures selected were, two gram negative cultures viz. Escherichia coli, Salmonella typhi and two Gram positive cultures viz. Staphylococcus aureu, Bacillus subtilis. Results were recorded by measuring the zone of inhibition in millimeter (mm) using zone reader (table-4). Antifungal activity was performed by Poison plate method.[20] The medium used was Potato Dextrose Agar (Himedia)[27]. Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme, Aspergillus flavus were selected as test fungal cultures. Results were recorded (table-5) as moderate growth of fungi (++), reduced growth of fungi (+) and no growth of inoculated fungi (-) antifungal activity.

The Schiff's bases and their Cu(II) and Ni(II) complexes were evaluated for anti-bacterial and anti-fungal activity with different strains of bacteria and fungi. Results are shown in table-4 and table-5.

All have shown lesser activity against E. coli, S. aureus and B. subtilis compared with penicillin taken as standard. The activity of ligand L_3 and its complexes was higher in comparison and has also shown activity against S. typhi and fungi. Antifungal activity observed against Aspergillus species was encouraging in comparison with Penicillium chrysogenum and Fusarium moneliforme.

Conclusion

Thus from the elemental analysis, molar conductivity measurements, magnetic susceptibilities, electronic absorption and infrared spectral studies and XRD studies, it is concluded that the complexes of Cu^{II}, Ni^{II}, have crystalline monoclinic system with monomeric octahedral geometry scheme 2. It may be concluded from results that antibacterial activity and antifungal activity of Cu(II) complexes was greater than Ni(II) complexes.



Ar = phenyl (L_1), toluyl (L_2), 4-chlorophenyl (L_3) and 4-anisyl(L_4)

Fig. 2: Octahedral structure assigend ti Cu(II) and Ni(II) Complex

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References

1. Zalfiqar A. K., Nasim H. R., Mahammad T. H. and Gul S. K. Design, Synthesis and microbial evaluation of some new 3-alkyl-3-(2'-naphthyl)isocumarine and their (*dl*)-3,4-dihydroderivatives, *Indian J Chem.,* **46B**, 1322 **(2007)**

2. O'Kennedy R. and Thornes R. D., Coumarins, Biology, Applications and Mode of Action, Wiley, Chichester, **(1997)**

3. Hesse S. and Kirsch G., A rapid access to coumarin derivatives using Vilsmeier-Haack and Suzuki cross-coupling reactions, *Tetrahedron Lett,* **43**, 1213-1215, **(2002)**

4. Lee B. H., Clothier M. F., Dutton F. E., Conder G. A. and Johnson S. S., Anthelmintic beta-hydroxyketoamides (BKAs), *Bioorg. Med. Chem. Lett*, **8**, 3317-3320 **(1998)**

5. Lean, Katz, U.S. Pat. **2**, 710, 823, June 14,**(1955)**, Chem. Abstr., **50**, 6519 **(1956)**

6. Hosler J., Tschanz C, Higuite C.E. and Azarnoff D. L., Topical Application of Lindane Cream (Kwell) and Antipyrine Metabolism, *J. Invest. Dermatol*, **74** 51-53, **(1980)**

7. Back Gerhard (Ciba Giegy A-G) Ger. Often DE ; 512, 253 (cl.Cog. 1345104) 17 Oct., 1985, H. Appl. 84/1, 751, 06 Apr. **(1984)**

8. Toa. Gosel Chemical Industry Co. Ltd., Japan. Kokai Tokkya Koho J.P., 60, 35, 260 (85, 35, 26) (cl.G 01 N31122) 23. Feb. **(1985)**

9. Mutalk V. and Phaniband M.A., Synthesis, characterization, fluorescent and antimicrobial properties of new Lanthanide (III) complexes derived from coumarin Schiff base', *J. Chem. Pharm. Res*, **3(2),** 313, **(2011)**

10. Joseph J. and Mehta B.H., Synthesis, characterization, and thermal analysis of transition metal complexes of polydentate ONO donor Schiff base ligand, *Russian Journal of Coordination Chemistry*, **33(2)**, 124, (2007)

11. a) Klosa J., Preparation of 4-hydroxycoumarin ketones with the help of phosphoroxychloride, Arch Pharm Ber Dtsch Pharm Ges, **289(2)**, 104-10 **(1956)**. b) Stephen J. F., and Marcus E.,Concerning the postulated rearrangement of 4-acyloxy-and 4-aroyloxycoumarins to 5-acyl-and 5-aroyl-4-hydroxycoumarins, *J Org.Chem.*, **34(9),** 2764-2766, **(1969)**

12. Gudasi K. B., Shenoy R.V., Vadavi R.S. and Patil S.A., Trinuclear lanthanide complexes of a compartmental ligand N, N' – bis (2-pyridinyl) - 2, 6-pyridinedicarboxamide, a spectroscopic investigation *Spectrochimica Acta.*, Part A, **65**, 598-604, **(2006)**

13. Geary W.J., The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, *Coord. Chem. Rev*., **7**, 81, **(1971)**

14. Ferraro, J.R, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, (**1971**)

15. Singh L.K. and Mitra S., Thermal investigation and stereochemical studies of some cyclic diamine complexes of nickel(II), zinc(II), and cadmium(II) in the solid state *J. Chem. Soc., Dalton Trans*, 2089 (1**987**)

16. Venkatesh M. and Phaniband M. A., Synthesis, characterization, fluorescent and antimicrobial properties of new Lanthanide(III) complexes derived from coumarin Schiff base, *J. Chem. Pharm. Res.*, **3(2)**, 313-330, (**2011**)

17. A.K. Panda, D.C. Dash, P. Mishra and H. Mahanthy, Synthesis and characterization of copper(II), nickel(II) and cobalt(II) complexes with a new Schiff base derivative of isonicotinic acid hydrazide, *Indian J. Chem.Sect A*, **35(4)**, 324–327 (**1996)**

18. Makode J.T. and Aswar A.S., Transition metal complexes of Bis(S-methyldithiocarbazate) resdiacetophenone (BSMZRD), *J. Indian Chem. Soc.*, **80**, 44 **(2003)**

19. Johnson D.K.**,** Stoklosa H.J., Wasson J.R., and Seebach G. L., Copper(II) complexes with antipyrine, diantipyrylmethane and diantipyrylpropylmethane, *J* **.** *Inorg***.** *Nucl***.** *Chem.*, **37**, *1397* **(1975)**

20. Sheikh H.N., Hussain A., Sharma M. and Kalsotra B. L., Synthesis and characterization of indole-3-acetates and indole-3-butyrates of Mo(VI) and W(VI), *Indian J Chem*, **43A** 562, **(2004)**

21. Swartz H.M., Bolton J. R. and Borg D. C., Bio Applications of Electron spin resonance, Wiley Interscience, USA, 411 **(1972)**

22. Patel M.N. and Patel V.J., Studies on Novel Coordination Polymers of a Tetradentate Ligand with Some Transition Metal Ions, *synth React inorg met org Chem*, **19(2)**, 137 (**1989**)

23. Sinn E. and Harris C.M., Schiff base metal complexes as ligands, *Coord. Chem. Rev.,* **4**, 391 **(1969)**

24. Rao T.S.R., Reddy K.L., Swami J. S. and Lingaiah, P., Thermal, Spectral and Magnetic Studies of Complexes of Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) with Substituted Chalcones, *Indian J. Chem.,* **27A**, 942-945 **(1985)**

25. Kumar A., Singh G., Handa R.N., Dubey S.N. and Squattrito P.J., Synthesis and characterization of complexes of cobalt(II), Nickel(II), Copper(II) and Zinc(II) with Schiff Bases Derived from Cinnamaldehyde and 4-Amino-3-ethyl-5-mercapto-s-triazole and 4-Amino-5-mercapto-3-N-propyl-s-triazole, *Indian J Chem* **38 A,** 613 **(1999)**

26. Yun Yang, Li Zhang et al., Syntheses, crystal structures and thermal behaviors of three complexes with 4-acyl pyrazolone derivatives *Inorg. Chimica Acta.*, **360,** 2638–2646 **(2007)**

27. Cruickshank R., Duguid J.P., Marmion B.P., and Swain R.H.A. , Medical Microbiology, Churchill Livingstone, London (**1998)**