

Transition metal complexes containing tridentate hydrazone Schiff bases : Synthesis, characterization and biological activity

A. R. Yaul, V. V. Dhande, S. R. Yaul and A. S. Aswar*

Department of Chemistry, Sant Gadge Baba Amravati University, Amravati-444 602, Maharashtra, India

E-mail : aswar2341@rediffmail.com

Manuscript received 23 March 2010, revised 06 September 2010, accepted 05 October 2010

Abstract : The new mononuclear complexes of Ti^{III} , Cr^{III} , Mn^{III} and Fe^{III} with tridentate hydrazone ligands viz. 2-hydroxy-5-chloroacetophenonebenzoylhydrazone (H_2L^1) and 2-hydroxy-3,5-dichloroacetophenone-4-nitrobenzoylhydrazone (H_2L^2) have been synthesized and characterized by elemental analysis, FTIR, reflectance spectra, magnetic susceptibility and thermogravimetric analyses (TG). From the analytical data, the stoichiometry of the complexes has been found to be 1 : 1 (metal : organic ligand). The physicochemical data suggested octahedral geometry for all the complexes. Electrical conductivity measurements of the complexes have been made over a wide range of temperatures and it was found that complexes showed semiconducting behavior. Various kinetic parameters have been evaluated from thermal decomposition data by both Horowitz-Metzger and Coats-Redfern methods and comparable values are obtained. The ligands and their metal complexes were screened for their antibacterial activity against *E. coli*, *S. abony*, *P. aeruginosa*, *S. aureus* and *B. subtilis* and fungicidal activity against *A. niger* and *C. albicans*.

Keywords : Hydrazone complexes, IR, electronic spectra, TGA, biological activity.

Introduction

Schiff bases are most widely used as chelating ligands in coordination chemistry. They are also useful in catalysis, in medicine as antibiotics and to treat industrial wastes¹. Hydrazone Schiff bases are versatile ligands having biological importance as, antitumor agents, plant growth regulators, antibacterial, antineoplastic, antiviral, antileukemic and enzymatic reaction inhibitors²⁻⁹. The complexes with such Schiff bases are very important due to their applications in medicine, particularly in the chemotherapy of cancer¹⁰. In the view of the above importance, we thought of interest to design hydrazone Schiff bases having ONO architecture to bind the metal ions. In this communication, we report the synthesis, spectroscopic characterization, thermal, electrical and biological activity of Ti^{III} , Cr^{III} , Mn^{III} and Fe^{III} complexes with aroylhydrazones Schiff bases; 2-hydroxy-5-chloroacetophenonebenzoylhydrazone (H_2L^1) and 2-hydroxy-3,5-dichloroacetophenone-4-nitrobenzoylhydrazone (H_2L^2).

Results and discussion

The elemental analyses data, colors, electrical con-

ductivity and activation energy of the ligands and their metal complexes are summarized in Table 1. The complexes are air stable and insoluble in common organic solvents but soluble in DMF and DMSO. The elemental analyses show 1 : 1 (metal : ligand) stoichiometry for all the complexes.

Infrared spectra :

The IR spectra of the Schiff base ligands were compared with that of metal complexes to obtain the information about the binding mode of ligands to metal in the complexes. The IR spectra of free ligands show a medium broad band at 2925–2902 cm^{-1} due to hydrogen bonded phenolic hydroxyl group. This band is absent in the complexes, indicating the deprotonation of the phenolic proton to the metal ion. Moreover, the strong band due to $\nu(C-O)$ stretching in the ligands have been shifted to the 1560–1526 cm^{-1} region in the complexes. This shift towards higher absorption also suggested the formation of the M–O bond¹¹. A strong band was observed at 1621–1608 cm^{-1} in the spectra of free ligands, which is the characteristic of the azomethine ($C=N$) group. It is expected that coordination of the nitrogen to the metal ion would reduce the electron density to the azomethine group of the complexes, this band is shifted to 1599–

Table 1. Analytical and physical data of the complexes

Complex	Color	Analysis (%) :				Electrical conductivity $\Omega^{-1} \text{ cm}^{-1}$ at 373 K	Activation energy (eV)
		Found (Calcd.)					
		C	H	N	M		
[Ti(HL ¹)Cl ₂ (H ₂ O)].H ₂ O	Troy	40.72	3.60	6.28	10.81	1.58×10^{-10}	0.247
		(40.69)	(3.64)	(6.32)	(10.82)		
[Cr(HL ¹)Cl ₂ (H ₂ O)]	Daffodil	41.99	3.21	6.48	12.18	6.30×10^{-9}	0.417
		(42.01)	(3.29)	(6.53)	(12.12)		
[Mn(L ¹)(OAc)(H ₂ O)].H ₂ O	Black	46.80	4.11	6.40	12.60	2.51×10^{-10}	0.522
		(46.15)	(4.16)	(6.43)	(12.58)		
[Fe(HL ¹)Cl ₂ (H ₂ O)]	Light olive	41.60	3.23	6.42	12.88	7.01×10^{-9}	0.393
		(41.64)	(3.26)	(6.47)	(12.90)		
[Ti(HL ²)Cl ₂ (H ₂ O)].H ₂ O	Burnt sienna	34.26	2.11	7.37	8.87	2.90×10^{-10}	0.203
		(34.52)	(2.70)	(8.05)	(9.17)		
[Cr(HL ²)Cl ₂ (H ₂ O)]	Safari	34.87	2.23	7.88	9.81	2.01×10^{-8}	0.299
		(35.46)	(2.38)	(8.27)	(10.23)		
[Mn(L ²)(OAc)(H ₂ O)].H ₂ O	Black cherry	39.17	2.96	8.01	10.37	2.17×10^{-9}	0.501
		(39.56)	(3.12)	(8.14)	(10.64)		
[Fe(HL ²)Cl ₂ (H ₂ O)]	Deep umber	34.37	2.01	7.79	10.01	3.09×10^{-8}	0.303
		(35.19)	(2.36)	(8.21)	(10.91)		

1585 cm^{-1} region, indicating the coordination of ligands through azomethine nitrogen atom to the metal ion¹². The IR spectra of free ligands also display absorption at 3329–3186 and 1686–1680 cm^{-1} due to $\nu(\text{N-H})$ and $\nu(\text{C=O})$ stretches, respectively. Both these bands are absent in case of Mn^{III} complexes involving deprotonated ligands indicating ligand enolization followed by hydroxyl proton loss during complexation. In other complexes, the $\nu(\text{N-H})$ is almost unaffected by chelation, whereas the $\nu(\text{C=O})$ absorption band is shifted by 27–12 cm^{-1} to lower wave numbers indicating the bonding of the ligands to the metal ion through the carbonyl oxygen. The IR spectrum of Mn^{III} complexes display two bands around ~ 1617 and ~ 1421 cm^{-1} due to $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ modes respectively. The separation of these bands by ~ 196 cm^{-1} indicate the monodentate coordination of the acetate group to Mn^{III} ion¹³. A band observed in the spectra of all complexes in the range 510–480 cm^{-1} may be attributed to $\nu(\text{M-O})$ stretch. The band at medium intensity observed at 420–405 cm^{-1} is assigned to the $\nu(\text{M-N})$ stretch¹⁴. Thus the IR spectral data reveal that, ligands behave as monobasic tridentate towards Ti^{III} , Cr^{III} and Fe^{III} complexes whereas dibasic tridentate in case of Mn^{III} complexes.

Electronic spectra and magnetic properties :

The information regarding the geometry of the metal complexes is obtained from their electronic spectral data and magnetic moments. The electronic spectra of the complexes were recorded in the solid state. Ti^{III} complexes exhibit only one broad band around 542 nm corresponds to the ${}^2T_{2g} \rightarrow {}^2E_g$, transition, for an octahedral geometry around Ti^{III} ion. The broad band and double-hump nature of the spectra indicates the presence of Jahn-Teller distortion in the complexes¹⁵. The magnetic moments of Ti^{III} complexes are 1.72 and 1.63 B.M. suggest the presence of the one unpaired electron. The electronic spectra of Cr^{III} complexes show bands at 543–553, 397–401 and 249–252 nm assignable to ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{F})$ and ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$, transitions, respectively, in an octahedral environment around Cr^{III} ion¹⁶. The observed magnetic moment values for the Cr^{III} complexes are 3.92 and 3.89 B.M. corresponds to three unpaired electrons. The interelectronic repulsion parameter B (Table 2) is found to be 723 and 641 cm^{-1} and which is lower than the free ion value (920 cm^{-1}) suggesting delocalization of electron on metal into molecular orbitals which cover both the metal and ligand¹⁷. The electronic spectra of Fe^{III} complexes display three bands at 705–

Table 2. Electronic parameters of the Cr^{III} complexes^a

Complex	Observed bands (nm)			ν_2/ν_1	B (cm ⁻¹)	β	β_0	Dq (cm ⁻¹)
	ν_1	ν_2	ν_3					
[Cr(HL ¹)Cl ₂ (H ₂ O)]	553	401	249	1.37	723	0.787	22	1808
[Cr(HL ²)Cl ₂ (H ₂ O)]	543	397	252	1.36	641	0.69	31	1841

^aThe ligand field splitting energy (Dq), interelectronic repulsion parameter (B) and covalency factor (nephelauxetic ratio) (β) for the Cr^{III} complexes were calculated using the equations given by König²⁰ :

$$10Dq = \nu_1$$

$$15B = (\nu_2 + \nu_3) - 3\nu_1$$

$$\beta = B/B_0 [B_0 (\text{free ion}) = 920]$$

$$\beta_0 = (1 - \beta).100$$

729, 550–559 and 430–432 nm which may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_{2g}$ ${}^4A_{1g}(G)$, transitions, respectively indicating that complexes possesses a high-spin, octahedral configuration. The magnetic moment (5.70 and 5.67 B.M.) is additional evidence for octahedral geometry around Fe^{III} ion¹⁸. The Mn^{III} complexes, shows band at 347–354 nm attributed to the LMCT transition. In second region complexes exhibit several weak $d-d$ bands at 710–715, 593–595 and 492–503 nm which may be due to ${}^5B_1 \rightarrow {}^2B_2$, ${}^5B_1 \rightarrow {}^5A_1$ and ${}^5B_1 \rightarrow {}^5E$, transitions, respectively indicating square pyramidal environment around Mn^{III} ion¹⁹. The observed values of magnetic moments for the complexes are 4.78 and 4.89 B.M. in accordance with the four unpaired electrons.

Thermogravimetric analyses :

The thermogravimetric analysis of the ligands and their metal complexes were carried out within a temperature range 40–650 °C in a dynamic air atmosphere to establish their compositional differences as well as to ascertain the nature of associated water molecules. The thermograms of Cr^{III} and Fe^{III} complexes indicate that complexes decomposed in two steps while Ti^{III} and Mn^{III} complexes decomposes in three steps. The Ti^{III} and Mn^{III} complexes lose their weights up to 120 °C corresponding to one lattice water molecules [% wt. loss obs./calcd. : Ti^{III}L¹ : 4.34/4.06; Ti^{III}L² : 3.12/3.45; Mn^{III}L¹ : 3.98/4.12; Mn^{III}L² : 3.94/3.48]. It has been observed that all the complexes show a loss in weight corresponding to one water molecule in the range 150–230 °C, indicating this water molecule is coordinated to the metal ion [% wt. loss obs./calcd. : Ti^{III}L¹ : 4.68/4.23; Ti^{III}L² : 3.98/3.57; Cr^{III}L¹ : 4.52/4.19; Cr^{III}L² : 3.10/3.54; Mn^{III}L¹ :

4.72/4.29; Mn^{III}L² : 3.12/3.61; Fe^{III}L¹ : 4.78/4.16; Fe^{III}L² : 3.26/3.51]. The presence of such water molecules also appears in infrared spectra and elemental analysis. The final stage of decomposition is fast and proceeds up to 400–650 °C leading to the formation of metal oxide which was stable above this temperature. The compositions of the final products were determined by the observed weights loss in the thermogravimetric analyses.

The various kinetic parameters for Cr^{III} and Mn^{III} complexes as representative case have been determined by both Horowitz-Metzger²¹ and Coats-Redfern²² methods. The results showed that the values obtained by two methods are comparable (Table 3). The values of kinetic parameters are nearly similar for each complex. This indicates that the basic steps involved in the thermal decomposition of the complexes are same. The ΔS values are negative for both the complexes suggesting that activated complexes have more ordered or rigid structure than reactants and the reactions are slower than normal²³. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer electronic transitions.

Electrical conductivity :

The solid-state electrical conductivity of the complexes in compressed pellet form was measured by two-probe method over a wide range of temperature, i.e. from room temperature to 403 K. The temperature dependence of electrical conductivity and the activation energy values of the complexes are given in Table 1. A plot of $\log \sigma$ vs $1/T$ of complexes obey the equation $\sigma = \sigma_0 \exp(-Ea/kT)$, the symbols having usual significance²⁴. In all the compounds conductivity increased with increasing temperature indicating that these complexes lie in the range of

Table 3. Thermal data of the complexes

Compd.	Half decomposition temperature (°C)	Activation energy (kJ mol ⁻¹)			Frequency factor (s ⁻¹)		Entropy change (-ΔS) (J mol ⁻¹ K ⁻¹)	Frequency change (ΔG) (kJ mol ⁻¹)
		Step	CR ^a	HM ^b	CR ^a	HM ^b		
[Cr(HL ¹)Cl ₂ (H ₂ O)]	480	I	34.24	35.26	28.29	27.89	231.84	45.83
		II	52.33	50.24	32.26	32.34	264.32	40.39
[Mn(L ¹)(OAc)(H ₂ O)].H ₂ O	472	I	24.41	23.36	28.33	28.79	252.02	43.66
		II	39.52	38.48	21.46	22.12	269.94	40.38
		III	50.53	51.08	32.41	33.32	271.03	38.95
[Cr(HL ²)Cl ₂ (H ₂ O)]	438	I	31.37	36.36	29.10	29.96	236.32	43.36
		II	45.88	49.10	29.12	30.23	258.78	41.70
[Mn(L ²)(OAc)(H ₂ O)].H ₂ O	502	I	22.83	24.72	27.81	30.74	243.69	39.98
		II	31.35	35.27	22.38	23.01	261.92	33.17
		III	47.82	51.08	26.23	24.56	283.47	31.14

^aCR = Coats-Redfern; ^bHM = Horowitz-Metzger.

semiconductors²⁵. The electrical conductivity of the complexes gives the positive temperature coefficient. Electrical conductivity of the complexes at 373 K lies in the range of 1.58×10^{-10} – $3.09 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$. The activation energy of electrical conduction of these complexes was found to be in the range 0.203–0.522 eV.

Antimicrobial activity :

The results of the antibacterial and antifungal activities are presented in Table 4. The ligands and the complexes showed varying degrees of inhibitory effect on the growth of the bacterial/or fungal strain tested. From results, it reveals that some complexes are more active as

compared to free ligands. This enhancement of the activity can be rationalized on the basis of their structures possessing an additional C=N bond. Furthermore, chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible π -electron delocalization over the whole ring^{26–28}. Thus, the chelation increases the lipophilic nature of the central metal, which subsequently favors permeation through the lipid layer of the cell membrane. The Cr^{III} complexes exhibits higher activity against *A. niger*, while all other metal complexes showed moderate activity against all the bacterial and fungal culture.

Table 4. Antimicrobial activity of the compounds

Compd.	Antibacterial activity (nm)					Antifungal activity (nm)	
	<i>E. coli</i>	<i>S. abony</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>B. subtilis</i>	<i>A. niger</i>	<i>C. albicans</i>
H ₂ L ¹	10	11	11	12	10	11	12
[Ti(HL ¹)Cl ₂ (H ₂ O)].H ₂ O	13	10.50	10	13	12	13	14.50
[Cr(HL ¹)Cl ₂ (H ₂ O)]	12	9	12	13	12	14	13
[Mn(L ¹)(OAc)(H ₂ O)].H ₂ O	12	11	11	12	11	13	13.50
[Fe(HL ¹)Cl ₂ (H ₂ O)]	14	12	10.50	14	12	14	12
H ₂ L ²	9	9	8	10	9	12	10.50
[Ti(HL ²)Cl ₂ (H ₂ O)].H ₂ O	13	12	13	12	13	14	13
[Cr(HL ²)Cl ₂ (H ₂ O)]	13.50	13	11.50	12.50	11	16.50	12.50
[Mn(L ²)(OAc)(H ₂ O)].H ₂ O	13	11	12	14	11.50	13	12
[Fe(HL ²)Cl ₂ (H ₂ O)]	12	12	10	12.50	13	13.50	13

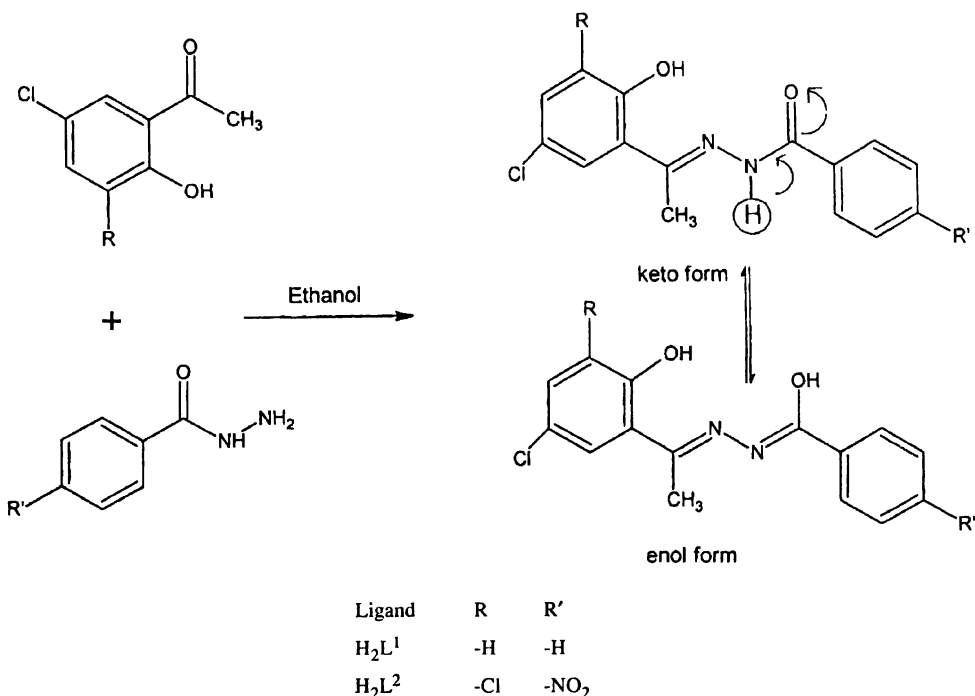


Fig. 1

Experimental

Materials and instrumentation :

All the reagents and solvents were of analytical grade. Titanium trichloride, chromium chloride pentahydrate and ferric chloride were from S. D's fine chemicals. Mn(OAc)₃·2H₂O was synthesized by reported method²⁹. Microanalyses of carbon, hydrogen and nitrogen of the compounds were carried on a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were recorded in KBr pellets on a Perkin-Elmer-RX-I spectrophotometer. The ¹H NMR spectra of the ligands were recorded in CDCl₃ + DMSO on a JEOL GSX-400 spectrophotometer using TMS as an internal standard. Reflectance spectra of the complexes were recorded in the range 1200–200 nm (as MgO) on a Beckman DK-2A spectrophotometer. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using Hg[Co(NCS)₄] as a calibrant and diamagnetic corrections were made by using Pascal's constant. Thermogravimetric analyses of the compounds were studied in the temperature range 40–700 °C on a Perkin-Elmer TG-2 thermobalance in an ambient air with a heating rate of 10 °C min⁻¹. Solid-state electrical conductivity of compounds was measured in their compressed

pellet form by the two-probe method using the Zentech electrometer.

Synthesis of Schiff base ligands (H₂L¹ and H₂L²) :

Both the Schiff base ligands H₂L¹ and H₂L² were prepared by reacting equimolar quantity of benzoyl hydrazide (0.68 g, 50 mmol) and 4-nitrobenzoyl hydrazide (0.90 g, 50 mmol) in 40 mL alcohol with 2-hydroxy-5-chloroacetophenone (0.85 g, 50 mmol) and 2-hydroxy-3,5-dichloroacetophenone (1.02 g, 50 mmol) in 20 mL alcohol respectively and the reaction mixture was then refluxed on a water bath for 5 h. On partial removal (50%) of solvent and cooling the reaction to room temperature, the colored solid was obtained. The resulting solid mass was filtered, washed several time with ethanol, diethyl ether and subsequently dried *in vacuo* over CaCl₂. The purity of ligands was checked by TLC using silica gel as stationary phase (Fig. 1). Yield 67–70%, for H₂L¹, m.p. 201 °C (Found : C, 63.15; H, 4.36; N, 9.73. C₁₅H₁₃N₂O₂Cl Calcd. : C, 62.35; H, 4.54; N, 9.80%); δ 13.00 (1H, s, phenolic OH), 11.30 (1H, s, imino), 7.95–7.00 (3H, m, phenyl), 2.90 ppm (3H, s, methyl). For H₂L², m.p. 192 °C (Found : C, 48.78; H, 2.42; N, 11.22. C₁₅H₁₁N₃O₄Cl Calcd. : C, 48.93; H, 3.01; N,

11.41%); δ 13.85 (1H, s, phenolic OH), 11.85 (1H, s, imino), 7.40 and 6.82 (2H, m, phenyl), 3.01 ppm (3H, s, methyl).

Synthesis of complexes :

An ethanolic solution (20 mL) of the metal salt and alcoholic solution (20 mL) of Schiff base (H_2L^1/H_2L^2) were mixed in 1 : 1 molar ratio. The resulting reaction mixture was refluxed for about 4 h on water bath. The solid product obtained was filtered, washed thoroughly with ethanol and finally with petroleum ether. All these complexes were dried in vacuum over $CaCl_2$.

Antimicrobial activity :

Antibacterial and antifungal activities of the ligands and their metal complexes were screened against the bacteria *E. coli*, *S. abony*, *P. aeruginosa*, *S. aureus* and *B. subtilis* and fungi *A. niger* and *C. albicans* by disc diffusion method³⁰. The DMSO was used as a control and gentamycine was used as standard for bacteriological comparison of the compounds. The test organisms were grown on nutrient agar medium in petri plates. The compounds were prepared in DMSO and soaked in Whatmann No. 1 paper disc of 10 mm diameter. The discs were placed on the previously seeded plates and incubated at 37 °C and the diameter of inhibition zone³¹ around each disc was measured after 24 h.

Acknowledgement

The authors are thankful to SAIF, Lucknow for providing elemental analysis, IR and 1H NMR facilities. The authors are also thanks to Manager (QC), Nicholas Piramal (P) Ltd., Indore, in undertaking the biological studies.

References

1. G. Wilkinson, "Comprehensive Coordination Chemistry", Pergamon Press, Oxford, 1987, p. 166.
2. D. R. Williams, *Chem. Rev.*, 1972, **72**, 203.
3. A. Panico, P. Vicini, M. Incert, V. Cardile, B. Gentile and G. Ronsisvalle, *Il Farmaco*, 2002, **57**, 671.
4. A. El-Dissouky, O. Al-Fulaij, M. K. Awad and S. Rizk, *J. Coord. Chem.*, 2010, **63**, 330.
5. T. M. Sielecki, J. Liu, S. A. Mousa, A. L. Racanelli, E. A. Hausner, R. R. Wexler and R. E. Olson, *Bioorg. Med. Chem. Lett.*, 2001, **11**, 2201.
6. P. Sienkiewicz, K. Bielawski, A. Bielawska and J. Palka, *Environ. Toxicol. Pharmacol.*, 2005, **10**, 118.
7. M. Verma, S. N. Pandeya, K. N. Singh and J. P. Stables, *Acta Pharm.*, 2004, **54**, 49.
8. M. R. Maurya, S. Agarwal, M. Abid, A. Azam, C. Bader, M. Ebel and D. Rehder, *Dalton Trans.*, 2006, **7**, 937.
9. S. Sharma, F. Athar, M. R. Maurya, F. Naqvi and A. Azam, *Eur. J. Med. Chem.*, 2005, **40**, 557.
10. F. A. French and E. J. Blanz, *Cancer Res.*, 1968, **28**, 2419.
11. K. Natarajan, R. Karvembu, S. Hemalatha and R. Prabhakaran, *Inorg. Chem. Commun.*, 2003, **6**, 486.
12. V. V. Dhande, V. B. Badwaik and A. S. Aswar, *Russ. J. Inorg. Chem.*, 2007, **52**, 1206.
13. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, 1970.
14. A. P. Mishra and M. Khare, *J. Indian Chem. Soc.*, 2000, **77**, 367.
15. A. R. Yaul, V. V. Dhande, N. J. Suryawanshi and A. S. Aswar, *Polish J. Chem.*, 2009, **83**, 565.
16. B. T. Thaker, A. Patel, J. Lekhadia and P. Thaker, *Indian J. Chem., Sect. A*, 2000, **39**, 1070.
17. A. Kriza, L. Pricop, A. Meghea and N. Stanica, *J. Indian Chem. Soc.*, 2001, **78**, 448.
18. A. M. Ramadan and I. M. El-Mehasseb, *Trans. Met. Chem.*, 1998, **23**, 183.
19. R. Mukhopadhyaya, S. Bhattacharjee and R. Bhattacharyya, *Dalton Trans.*, 1994, **19**, 2799.
20. E. König, "The Nephelauxetic Effect", in 'Structure and Bonding', Springer Verlag, New York, 1975.
21. H. H. Horowitz and G. Metzger, *J. Anal. Chem.*, 1963, **35**, 1464.
22. A. W. Coats and J. P. Redfern, *Nature*, 1964, **201**, 68.
23. M. Thankamony, K. B. Sindhu, G. Rijulal and K. Mohanan, *J. Therm. Anal. Cal.*, 2009, **1**, 259.
24. A. P. Mishra and L. R. Pandey, *Indian J. Chem., Sect. A*, 2005, **44**, 94.
25. M. Koca, F. Dagdelen and Y. Aydogdu, *Mater. Lett.*, 2004, **58**, 2901.
26. R. Maruvada, S. C. Pal and G. Balakrish Nair, *J. Micro. Bio. Methods*, 1994, **20**, 115.
27. N. Raman, *J. Indian Chem. Soc.*, 2009, **86**, 1143.
28. A. P. Mishra and M. Soni, *Metal Based Drugs*, 2008, **7**.
29. O. T. Christensen, *Z. Anorg. Allg. Chem.*, 1901, **27**, 321.
30. P. K. Mukherjee, K. Shah, S. N. Giri, M. Pal and B. P. Shah, *Indian J. Microbiology*, 1995, **35**, 327.
31. Z. H. A. Wahab, M. M. Mashaly, A. A. Salman, B. A. El-Shetary and A. A. Faheim, *Spectrochim. Acta*, 2004, **A60**, 2861.