

Synthesis and Characterization of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO₂(VI) Complexes of Schiff Base Derived from Isonicotinoyl Hydrazone

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Gawande, *et al.*: Synthesis and Characterization of Transition Metal Complexes with Isonicotinoyl Hydrazone Schiff Base Ligand

2-hydroxy-5-chloro-3-nitroacetophenone isonicotinoyl hydrazone as a Schiff base ligand and its complexes with Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO₂(VI) metal ions have been synthesized. The ligands as well as their metal complexes were well characterized using various physicochemical techniques such as elemental analyses, molar conductance measurements, magnetic measurements, thermal analysis, electronic and IR spectral studies. On the basis of these studies, square pyramidal stereochemistry for Mn(III) and VO(IV) complexes while octahedral stereochemistry for all the other complexes have been suggested. The complexes were found to be stable up to 60-70° and thermal decomposition of the complexes ended with respective metal oxide as a final product. The thermal data have been analyzed for kinetic parameters using Broido and Horowitz-Metzger methods. The synthesized Schiff base ligand and its complexes were also tested for their antimicrobial activity using various microorganisms.

Key words: Isonicotinoyl hydrazone, Schiff base ligand, TGA, electronic spectral data, antimicrobial

Ligands containing the azomethine (>C=N) group found in Schiff base are constituted by hydrazones. There has been growing interest in the study of hydrazones because of their physiological activity and applications in analytical chemistry^[1]. Several coordination compounds derived from aroylhydrazone chelators possess antituberculosis, antimicrobial, corrosion inhibitors^[2-4] and antineoplastic activity due to their ability to bind intracellular ion^[5]. keeping the above facts in mind, we report here the synthesis and characterization of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO₂(VI) complexes of Schiff base derived from the condensation of 2-hydroxy-5-chloro-3-nitroacetophenone and isonicotinoyl hydrazide.

MATERIALS AND METHODS

All the chemicals and solvents used for the syntheses were of reagent grade and were obtained commercially from S. D. Fine Chem Ltd., Mumbai. Solvents were purified by standard methods.

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Chromium chloride hexahydrate, anhydrous ferric chloride, vanadyl sulphate pentahydrate, uranyl acetate dihydrate were of S. D. Fine Chem Ltd., Mumbai. Mn(OAc)₃·2H₂O was prepared by the oxidation of Mn(OAc)₂·4H₂O using Christensen's method^[6] and zirconium(IV) acetate was synthesized using literature methods^[7].

The infrared spectra of the ligand and complexes were recorded on a Perkin Elmer 842 spectrophotometer using KBr pellets. Elemental analysis (C, H, N) was carried out by Coleman's microanalyses from CDRI, Lucknow, India. ¹H NMR spectrum of a ligand was recorded in CDCl₃ and DMSO on a EM-360, 300 MHz NMR spectrometer using TMS as a internal standard.

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Accepted 22 July 2015
Revised 12 November 2014
Received 29 December 2013
Indian J Pharm Sci 2015;77(4):376-381

Molar conductance of the complexes was determined in dimethylsulphoxide using solution of about 10^{-3} mol concentration. Magnetic susceptibility values were measured at room temperature by Guoy's method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant type magnetic balance. Thermogravimetric analyses were done in the range $40\text{-}700^\circ$ on a Perkin-Elmer TGS-2 system in an air atmosphere with a heating rate of $10^\circ/\text{min}$.

Synthesis of ligand (LH_2):

Hot ethanol solution of isonicotinoyl hydrazide (0.05 mol) was treated with ethanol solution of 2-hydroxy-5-chloro-3-nitroacetophenone and the reaction mixture was heated under reflux on a water bath for 4-6 h. After cooling, the coloured solid was filtered off, washed with ethanol and dried. Finally, it was recrystallized from dimethyl formamide (fig. 1). Yield: 75%, m.p. 280° . $^1\text{H NMR}$: δ 12.95 (1H, s, phenolic OH), 11.34 (1H, s, imino), 9.05 and 9.08 (4H, d, isonicotine), 8.15 and 7.35, (2H, m, phenyl), 3.25 (3H, s, methyl)^[8]. The schematic representation of synthesis of LH_2 is shown in Reaction Scheme 1.

Synthesis of Cr(III), Mn(III), Fe(III), VO(IV) and $\text{UO}_2(\text{VI})$ Complexes:

Equimolar quantities (0.02 mol) of the metal salts and the ligand were dissolved separately in absolute ethanol (25 ml) and in DMF-ethanol (1:4 v/v, 25 ml), respectively. Both the solutions were filtered and mixed in hot condition. The resulting reaction mixture was refluxed for 4-6 h in water bath. The solid product obtained on cooling was filtered, washed several time with hot water followed by ethanol and diethyl ether. Finally, all these complexes were dried at room temperature over CaCl_2 .

Synthesis of Zr(IV) Complex:

Zirconyloxychloride octahydrate (0.002 mol) is dissolved in methanol (15 ml) and to this a methanol

solution of anhydrous sodium acetate (0.004 mol in 15 ml) was added and stirred for 5 min. The separated sodium chloride was filtered off. The ligand (0.002 mol) was dissolved separately in hot DMF-methanol (1:4 v/v). To these solutions, the solution containing oxozirconium(IV) diacetate was added and the mixture was refluxed for 4-6 h. The product obtained was filtered, washed 2-3 times with methanol followed by petroleum ether and dried at room temperature.

RESULTS AND DISCUSSION

All the complexes are coloured solid, non-hygroscopic air stable and insoluble in common organic solvents but soluble in DMF and DMSO. The analytical data (Table 1) of the complexes indicates 1:2, metal:ligand stoichiometry towards 2, 4 and 6 while, 1:1 in all other complexes. The molar conductance data show that all the complexes are non-electrolytes.

In order to study the bonding mode of ligand to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of metal complexes. The structurally significant IR bands for free ligand and its complexes have been reported in Table 2. The band at 2991 cm^{-1} due to intramolecular hydrogen bonded $\nu(\text{OH})$ group in the free ligand spectrum disappeared in spectra of all the complexes and the $\nu(\text{C-O phenolic})$ band at 1531 cm^{-1} , shifted to higher frequency by $4\text{-}11\text{ cm}^{-1}$, suggest the coordination of ligand through phenolic oxygen via deprotonation. The vibrational band at 1617 cm^{-1} assigned to $\nu(\text{C=N})$ in the spectrum of ligand show downward shift by $36\text{-}49\text{ cm}^{-1}$ in the spectra of complexes confirming coordination through azomethine nitrogen^[9]. The coordination through the azomethine nitrogen atom is further supported by the shift of $\nu(\text{N-N})$ vibration observed at 994 cm^{-1} in the ligand and to higher frequency by $9\text{-}26\text{ cm}^{-1}$ in the complexes^[10]. The $\nu(\text{N-H})$ and $\nu(\text{C=O})$ bands of the ligand at 3182 and 1685 cm^{-1} , respectively remain almost unaffected after complexation in the Cr(III), Fe(III) and Zr(IV) complexes, suggesting the keto form of ligand^[11]. It is inferred that the ligand in these metal complexes coordinates in a monobasic bidentate fashion. The spectra of the Mn(III) and VO(IV) do not show the band due to $\nu(\text{N-H})$ and $\nu(\text{C=O})$ frequencies indicating the coordination of ligand to metal in enol form^[12]. It is supported due to presence of $\nu(\text{C-O})$ (enolic) and $\nu(\text{C=N-N=C})$ (azine) group frequencies in their

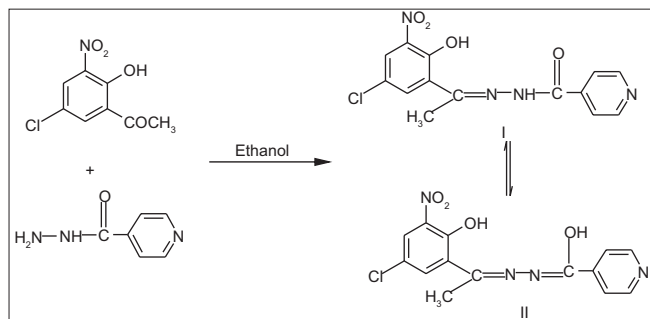


Fig. 1: Reaction scheme.

TABLE 1: ANALYTICAL AND PHYSICAL DATA OF LH₂ AND ITS METAL COMPLEXES

Ligand/complexes	F. Wt	M%	C%	H%	N%	Cl%
		found (calculated)	found (calculated)	found (calculated)	found (calculated)	found (calculated)
(LH ₂)	334.7	-	50.19 (50.24)	03.28 (03.31)	16.64 (16.74)	10.44 (10.59)
[Cr(LH) ₂ (H ₂ O) (Cl)].H ₂ O	790.9	6.43 (6.57)	42.61 (42.52)	3.12 (3.06)	14.33 (14.16)	13.21 (13.44)
[Mn(L) (H ₂ O) (OAc)].H ₂ O	482.7	11.33 (11.38)	39.29 (39.81)	3.15 (3.34)	11.73 (11.60)	7.07 (7.34)
[Fe(LH) ₂ (H ₂ O) (Cl)].H ₂ O	794.4	6.87 (7.02)	41.89 (42.31)	2.97 (3.04)	14.23 (14.09)	13.19 (13.38)
[VO(L)] ₂ .H ₂ O	817.3	12.12 (12.46)	40.97 (41.15)	2.33 (2.47)	13.45 (13.71)	8.49 (8.67)
[Zr(LH) ₂ (OH) ₂].H ₂ O	810.7	11.13 (11.25)	41.03 (41.48)	2.79 (2.98)	13.68 (13.82)	8.57 (8.74)
[UO ₂ (LH) (OAc)]	662.8	35.76 (35.91)	28.73 (28.99)	1.73 (1.98)	8.33 (8.45)	5.23 (5.34)

TABLE 2: INFRARED SPECTRAL DATA OF THE LIGAND AND ITS METAL COMPLEXES

Ligand/complexes	OH...N	C-O	C=N	N-N	N-H	C=O	C-O	M-O	M-N
		phenolic				enolic			
(LH ₂)	2991	1531	1617	994	3182	1685	-	-	-
[Cr(LH) ₂ (H ₂ O) (Cl)].H ₂ O	-	1535	1577	1008	3184	1683	-	476	413
[Mn(L) (H ₂ O) (OAc)].H ₂ O	-	1536	1575	1020	-	-	1252	460	402
[Fe(LH) ₂ (H ₂ O) (Cl)].H ₂ O	-	1535	1568	1000	3184	1682	-	458	408
[VO(L)] ₂ .H ₂ O	-	1536	1581	1003	-	-	1256	470	416
[Zr(LH) ₂ (OH) ₂].H ₂ O	-	1541	1576	1005	3178	1686	-	469	403
[UO ₂ (LH) (OAc)]	-	1542	1575	1014	3180	1647	-	555	519

Values are given in cm⁻¹

spectra, indicating the dibasic tridentate nature of the ligand in these complexes^[13]. The coordination of water in Cr(III), Mn(III) and Fe(III) is indicated by the appearance of bands at 3446-3399, 1636-1602, 852-815 and 755-746 cm⁻¹ assignable to $\nu(\text{OH})$, $\delta(\text{H}_2\text{O})$, $\rho_r(\text{H}_2\text{O})$, and $\rho_w(\text{H}_2\text{O})$ mode, respectively^[14]. The absence of two bands in VO(IV) and Zr(IV) suggest the presence of water of hydration in it. The IR spectra of Mn(III) and UO₂(VI) complexes displays two additional bands at 1620-1600 and 1440-1437 cm⁻¹ are due to $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sy}}(\text{OCO})$ frequency of acetate group, respectively. The spectra of VO(IV), Zr(IV) and UO₂(VI) complexes show new bands at around 958, 1154 and 913 cm⁻¹, respectively due to $\nu(\text{U=O})$, $\nu(\text{Zr-OH})$ and $\nu_{\text{asy}}(\text{O=U=O})$ vibration. The force constant, f U-O was calculated by the method of McGlynn *et al.*^[15]. The force constant in the UO₂(VI) complexes is 6.918 mdyne/A° which is in the usual range (6.58-7.03 mdyne/A°) observed for similar UO₂(VI) complexes. The U-O bond distance (R) was calculated using Jones equation^[16]. $R=1.08 f^{-1/3}+1.17$. The value of R is 1.736 Å which is in agreement with the reported values of 1.60-1.92 Å. Also in addition to above bands all complexes display the bands in the far-infrared region at 555-458 and 519-402 cm⁻¹ assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations^[17].

The electronic spectra and magnetic moments of the metal complexes are listed in Table 3. The reflectance spectrum of Cr(III) complex exhibit three transitions

TABLE 3: ELECTRONIC SPECTRA, MAGNETIC MOMENTS AND MOLAR CONDUCTANCE DATA OF METAL COMPLEXES

Complexes	Electronic spectral bands (nm)	μ_{eff} (B.M.)	Conductance/ohm/cm ² mol
[Cr(LH) ₂ (H ₂ O) (Cl)].H ₂ O	549, 416, 258	3.99	13.9
[Mn(L) (H ₂ O) (OAc)].H ₂ O	731, 598, 512, 394	4.82	11.8
[Fe(LH) ₂ (H ₂ O) (Cl)].H ₂ O	810, 575, 450	6.00	18.9
[VO(L)] ₂ .H ₂ O	740, 599, 457, 344	1.58	8.8
[Zr(LH) ₂ (OH) ₂].H ₂ O	417	Diameter	20.1
[UO ₂ (LH) (OAc)]	541, 430, 271	Diameter	13.9

at 549, 416 and 258 nm due to the ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{F})$ and ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ transitions, respectively, suggesting an octahedral geometry around the Cr(III) ion^[18]. The magnetic moment value was found to be 3.99 BM, which is also agree well with the known values for Cr(III) complex in octahedral geometry. The solid reflectance spectrum of Mn(III) complex show bands at 731, 598, 512 and 394 nm, which may be assigned to ${}^5B_1 \rightarrow {}^5B_2$, ${}^5B_1 \rightarrow {}^5A_1$, ${}^5B_1 \rightarrow {}^5E$ and LMCT transition, respectively, towards square pyramidal structure around Mn(III) ion^[19]. The observed value for the Mn(III) complex is 4.82 BM. in accordance with the four unpaired electrons corresponding to square pyramidal geometry. The electronic spectrum of Fe(III) complex displays three bands at 810, 575 and 450 nm assignable to ${}^6A_{1g}(\text{S}) \rightarrow {}^4T_{1g}(\text{G})$, ${}^6A_{1g}(\text{S}) \rightarrow {}^4T_{2g}(\text{G})$ and ${}^6A_{1g}(\text{S}) \rightarrow {}^4E_g, {}^4A_{1g}(\text{G})$ transition, respectively, indicating that the complex possesses a high spin octahedral configuration^[20].

The oxovanadium complex show all the expected three bands at 740, 599, 457, and 344 nm which are assigned to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$, ${}^2B_2 \rightarrow {}^2A_1$ transition, respectively. The fourth band appears at 2905.5 cm^{-1} may be due to charge transfer transition, indicating square pyramidal geometry to the complex^[21]. The VO(IV) complex shows magnetic moment 1.58 BM. The electronic spectra of Zr(IV) complex show a single broad band at 417 nm, which may be assigned due to LMCT. The band at 541, 430 and 271 nm in the electronic spectrum of $\text{UO}_2(\text{VI})$ complex are consistent with the vibronic structure of triatomic entity of UO_2 group^[22].

The perusal of thermogram of LH_2 and its metal complexes indicates that the complexes of Cr(III), Mn(III), Fe(III) and Zr(IV) decompose in three steps while complexes $\text{UO}_2(\text{VI})$ and VO(IV) in two steps. All the complexes except $\text{UO}_2(\text{VI})$ are stable up to $60\text{--}70^\circ$. The presence of water molecule (lattice or coordinated) in Cr(III), Mn(III), Fe(III), VO(IV) and Zr(IV) complexes suggested from IR spectra is confirmed by the weight loss observed in the first decomposition step of the complexes. The Cr(III), Mn(III) and Fe(III) complexes is observed in the first step in the range $70\text{--}125$ and $160\text{--}220^\circ$ respectively [%wt. loss, obs./calc: For lattice water: Cr(III): 2.40/2.28; Mn(III): 3.96/3.73; Fe(III): 2.45/2.26; for coordinated water: Cr(III): 2.45/2.28; Mn(III): 3.98/3.73; Fe(III): 2.65/2.26]. The weight loss up to 110° indicates the presence of only one lattice molecule in each of the VO(IV) and Zr(IV) complex [% wt. loss, obs./calc: VO(IV): 2.40/2.20; Zr(IV): 2.34/2.22]. The thermogram of $\text{UO}_2(\text{VI})$, are almost stable up to 220° , indicating the absence of lattice or coordinated water molecule. In case of Cr(III), Mn(III), Fe(III), VO(IV) and Zr(IV) complexes, a sudden weight loss is observed in the temperature range $\sim 300\text{--}450^\circ$, which is due to the part decomposition of the coordinated ligand (fig. 2).

Beyond this temperature, a gradual weight loss is observed corresponding to the decomposition of remaining part of coordinated ligand. The VO(IV) complex show a gradual but continuous weight loss at about $300\text{--}620^\circ$ due to thermal degradation of coordinated ligand. The final stage ends with the aerial oxidation of the complexes and formation of stable metal oxides. The half decomposition temperature, activation energy, frequency factor, apparent entropy of activation and free energy change of ligand and its complexes were calculated by

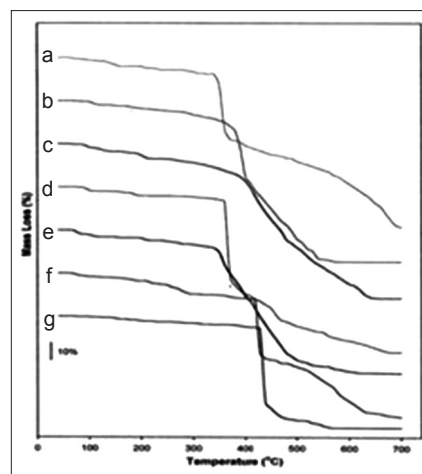


Fig. 2: Thermograms of ligand (LH_2) and its complexes. HCNAIH (a), Cr(III) HCNAIH (b), Mn(III) HCNAIH (c), Fe(III) HCNAIH (d), VO(IV) HCNAIH (e), Zr(IV) HCNAIH (f), $\text{UO}_2(\text{VI})$ HCNAIH (g).

employing Broido and Horowitz-Metzger method are listed in Table 4. From the half decomposition temperature, the relative thermal stability of the compounds is found to be $\text{Mn(III)} > \text{UO}_2(\text{VI}) > \text{Zr(IV)} > \text{VO(IV)} > \text{Cr(III)} > \text{LH}_2 > \text{Fe(III)}$.

The Schiff base and its corresponding Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and $\text{UO}_2(\text{VI})$ complexes were screened for their biological activity by using seven bacteria, *E. coli*, *S. typhi*, *A. aerogenes*, *S. aureus*, *B. subtilis*, *B. megatherium* and *P. vulgaris* strains by the cup plate method. The microbial results are summarized in Table 5. The ligand exhibit bacteriostatic behaviour towards all the bacterial strain used except, *S. aureus*, *P. vulgaris*.

The Cr(III), Fe(III) and Zr(IV) complexes were found to show almost low to moderate bacteriocidal (sensitive) nature against all the bacterial strains. The Cr(III) complex is found to show good activity against *S. aureus* and the Mn(III) complex possess fairly good antibacterial activity against *E. coli* and *S. aureus*. Moderate activities of the VO(IV) and Zr(IV) complexes were found against *S. typhi* and *S. aureus*, respectively, whereas these complexes showed either bacteriostatic or weak bacteriocidal nature against all the organisms. In general, the results reveal that, the activity of the ligand was found to be enhanced on complexation with the metal ions.

From the present investigation it has been observed that there is a possibility of formation of ligand 2-hydroxy-5-chloro-3-nitroacetophenone isonicotinoyl

TABLE 4: THERMAL DECOMPOSITION DATA OF LIGAND (LH₂) AND ITS COMPLEXES

Compound	Half decomposition temperature (°)	Activation energy (kJ/mole)		Frequency factor Z (s ⁻¹)	Entropy change -ΔS (J/mol/K)	Free energy change ΔF (kJ/mol)
		B*	H-M**			
(LH ₂)	395.0	25.54	24.63	20.16	226.72	43.25
[Cr(LH) ₂ (H ₂ O) (Cl)].H ₂ O	407.0	42.80	42.71	42.80	220.49	60.19
[Mn(L) (H ₂ O) (OAc)].H ₂ O	455.0	36.64	41.39	45.39	220.65	61.11
[Fe(LH) ₂ (H ₂ O) (Cl)].H ₂ O	368.0	34.09	30.14	23.68	224.90	47.50
[VO(L) ₂ .H ₂ O	412.0	38.64	45.58	52.50	218.90	63.87
[Zr(LH) ₂ (OH) ₂].H ₂ O	428.0	28.93	26.25	24.60	225.31	45.25
[UO ₂ (LH) (OAc)]	448.0	64.83	67.13	74.90	216.24	85.88

*B: Broido method, **H-M: Horowitz-Metzger method

TABLE 5: ANTIMICROBIAL ACTIVITY OF THE LIGAND AND ITS COMPLEXES

Ligand and its complexes	<i>Escherichia coli</i> (mm)	<i>Salmonella typhi</i> (mm)	<i>Aerobacter aerogenes</i> (mm)	<i>Bacillus subtilis</i> (mm)	<i>Bacillus megatherium</i> (mm)	<i>Proteus vulgaris</i> (mm)	<i>Staphylococcus aureus</i> (mm)
(LH ₂)	R	R	R	R	R	S 9	S 15
[Cr(LH) ₂ (H ₂ O) (Cl)].H ₂ O	S 9	R	S 16	S 9	R	S 11	S 17
[Mn(L) (H ₂ O) (OAc)].H ₂ O	S 11	R	S 18	R	S 12	S 12	S 20
[Fe(LH) ₂ (H ₂ O) (Cl)].H ₂ O	R	S 16	S 13	S 11	R	S 13	S 12
[VO(L) ₂ .H ₂ O	R	R	S 11	R	S 19	R	S 9
[Zr(LH) ₂ (OH) ₂].H ₂ O	S 9	S 9	S 10	R	S 10	S 18	S 9
[UO ₂ (LH) (OAc)]	R	S 9	R	R	S 10	S 9	S 18

S: Sensitive (bactericidal), R: resistant (bacteriostatic)

hydrazone and its complexation with metal ions like Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO₂(VI). The data explain that Schiff base is a monobasic bidentate (ON) donor towards the Cr(III), Fe(III) and Zr(IV), monobasic tridentate (ONO) donor towards UO₂(VI) and dibasic tridentate (ONO) donor towards Mn(III) and VO(IV) complexes. The bonding of the ligand to metal was confirmed by the analytical, IR, electronic, magnetic and thermal studies.

Acknowledgements:

The authors thank the University Grants Commission, India (UGC) for providing financial support, directors of RSIC, Chandigarh for recording of IR and ¹HNMR spectra; SAIF, IIT, Chennai, India for recording of electronic spectra; CDRI, Lucknow, India for elemental analysis.

Financial support and sponsorship:

The University Grants Commission, India (UGC).

Conflicts of interest:

There are no conflicts of interest.

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