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Schiff Base Metal Complexes of Chromium(III), Manganese(III), Iron(III), Oxovanadium(IV), Zirconium(IV) and Dioxouranium(VI)

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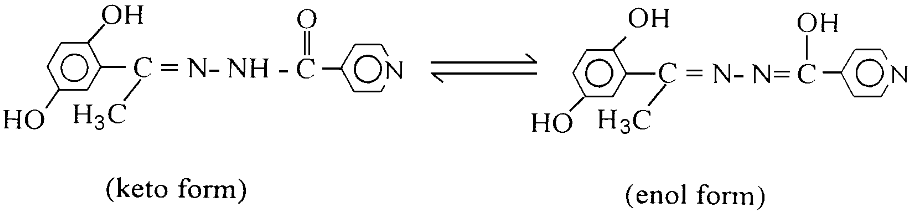
The Schiff base 2,5-dihydroxyacetophenone isonicotinoyl hydrazone (H_2L) has been synthesized by condensation of 2,5-dihydroxyacetophenone with isonicotinoyl hydrazide in ethanol. Metal complexes of the Schiff base were prepared from salts of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI). Characterization of the ligand and its metal complexes were carried out by elemental analysis, molar conductivity, magnetic susceptibility measurements, IR, ^{1}H NMR, electronic and thermogravimetric analysis in air. The Schiff base behaves as flexidentate ligand and commonly coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. The thermal data have been analyzed for the kinetic parameters by Broido and Horowitz-Metzger methods. All the compounds were also screened for their antimicrobial activity by agar cup-plate method against various organisms and the results have been compared.

Key words: Schiff base complexes, spectral, TGA and antimicrobial

The coordination chemistry of acyl, aroyl and heteroaroyl hydrazones and related ligands has been reviewed by Dutta and Hossain [1]. Due to facile keto-enol tautomerism and availability of several donor sites of variable potentialities, these ligands can coordinate with transition and inner-transition metal ions to give stable metal complexes. Variety of metal complexes of symmetrical heteroaroyl hydrazone with aldehydes or ketones have been reported [2–8]. Keeping in view the various possibilities of interactions of these ligands with metals, efforts were undertaken to synthesize and characterize the Schiff base ligand (**I**) derived from isonicotinoyl hydrazide and



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2,5-dihydroxyacetophenone and its metal complexes with Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI). Efforts were also undertaken to study their thermal behaviour and biological activities.

EXPERIMENTAL

2,5-Dihydroxyacetophenone was prepared according to [9]. Manganese(III) acetate dihydrate was prepared by Christensen method [10]. Chromium chloride hexahydrate, ferric chloride, vanadyl sulphate pentahydrate, zirconyloxychloride octahydrate and uranyl acetate dihydrate were obtained from BDH, Germany. Isonicotinoyl hydrazide was purchased from E. Merck (India). Other reagents and solvents were of AR grade.

Carbon, hydrogen and nitrogen analysis of the ligand and complexes were carried out by the micro analytical section of R S I C, C D R I, Lucknow (India). The ^{1}H NMR spectra of ligand was recorded on a EM-360 spectrophotometer. IR spectra of ligand as well as complexes were recorded in KBr pellet on a Perkin-Elmer 842 spectrophotometer in the region 4000–400 cm^{-1} at R S I C, Punjab University, Chandigarh (India). The diffuse reflectance measurements were recorded on a Carry-2390 in 200–1000 nm region at R S I C, I I T, Chennai (India). The magnetic measurements were carried out by Gouy method at room temperature using $Hg[Co(SCN)_4]$ as the calibrant. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant of 1.00 cm^{-1} at room temperature. Thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2 thermobalance in air with 10^0 min^{-1} heating rate.

Synthesis of ligand: To a hot solution of isonicotinoyl hydrazide (1.375 g, 10 mmol) in 25 ml absolute ethanol, 2,5-dihydroxyacetophenone (1.522 g, 10 mmol) dissolved in 25 ml hot ethanol was added dropwise with continuous stirring. The mixture was refluxed for 4 h on a water bath with stirring. On cooling to room temperature, crystalline solid which separated was filtered off, washed several times with ethanol and dried in air. Finally it was recrystallized from DMF. Yield 80%, m.p. 310°C.

Synthesis of the complexes: All the metal complexes [except Zr(IV)] were prepared in a similar fashion by the following method. Equimolar quantity of metal salts [$CrCl_3·6H_2O$, $Mn(OAc)_3·2H_2O$, $FeCl_3$, $VOSO_4·5H_2O$ and $UO_2(OAc)_2·2H_2O$] and ligand H_2L were dissolved separately in absolute ethanol and in DMF-ethanol (l:4 v/v) respectively. Both the solutions were filtered and mixed in hot conditions. The reaction mixture was refluxed for 4–6 h on water bath. The Zr(IV) complex was prepared by the following method. To a hot solution of 2 mmol of zirconyloxychloride in 15 ml methanol, 4 mmol of sodium acetate dissolved in 30 ml methanol was added with constant stirring. The separated NaCl was filtered off. The hot solution of 2 mmol of H_2L in DMF-methanol (1:4 v/v) was added and refluxed for 5 h. The coloured products obtained with different metals were filtered, washed several times with hot water followed by methanol and diethyl ether and finally dried over fused calcium chloride. The complexes are soluble in DMF and DMSO and insoluble in water and common organic solvents. The complex **6** is also soluble in methanol, ethanol and acetone. Yield, colour and melting points are given in Table 1, while IR data are presented in Table 2.

Table 1. Colour, melting point and yield of the complexes.

No.	Complex[a]	Colour	M.P. (°C)	Yield %
1	$[Cr(LH)_2(H_2O)(Cl)]·H_2O$	Rust	300[b]	64
2	$[Mn(L)(H_2O)(OAc)]·H_2O$	Brown	280	54
3	$[Fe(LH)_2(H_2O)(Cl)]·H_2O$	Black	320[b]	67
4	$[VO(L)]_2$	Olive	300[b]	71
5	$[Zr(LH)_2(OH)_2]·3H_2O$	Yellow	290	65
6	$[UO_2(LH)(OAc)]$	Orange	300[b]	68

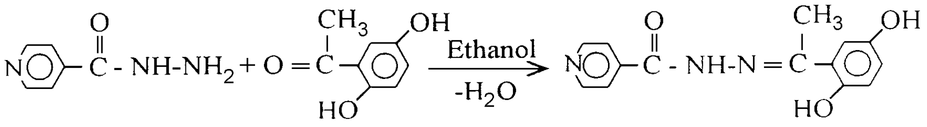
[a]For abbreviation see structure of ligand; [b]Decomposition temperature.

Table 2. Physical data of the compounds.

Compound	Λ_M	IR cm^{-1}					μ_{eff}
	(Ω^{-1} cm^2 mol^{-1})	ν(C=O)	ν(C=N)	ν(C–O)	ν(M–O)	ν(M–N)	B.M.
H_2L	–	1668.5	1603.2	1485.5	–	–	–
1	24.9	1669.8	1584.9	1498.2	475.8	413.6	4.03
2	21.2	–	1578.0	1505.9	472.4	429.1	4.89
3	23.3	1667.1	1585.3	1501.9	474.3	410.9	5.89
4	18.8	–	1577.6	1501.8	470.8	419.6	1.63
5	27.3	1667.9	1580.4	1496.9	488.3	413.1	–
6	23.4	1652.1	1582.3	1500.0	577.1	532.7	–

RESULTS AND DISCUSSION

Scheme 1 represents the synthesis strategy of the ligand. The presence of phenolic proton at 12.85 ppm and imino proton at 11.35 ppm indicates the formation of expected ligand. Analytical and IR data further supplement the proposed structure.



Scheme 1. Scheme for the synthesis of ligand (H_2L).

Reaction of metal salts with H_2L under reaction conditions mentioned in the experimental section give stable metal complexes of stoichiometry presented in Table 1. Analytical data agree well with the formula suggested. The metal complexes are air stable and nonhygroscopic. The molar conductance values in DMF (10^{-3} M) solution (Table 2) show that all complexes are non-electrolytes [11].

IR spectra: A partial list of important infrared bands with assignments are given in Table 2. In the IR spectra of the ligand the most characteristic bands appeared at 3424 ν(OH at C_5), 3240 ν(N–H), 2850–2950 ν(O–H intramolecular H-bonded at C_2), 1668 ν(C=O) amide, 1603 ν(C=N azomethine) and 1485 cm^{-1} ν(C–O phenolic). The band due to azomethine group shifts to lower wave number by 18 to 26 cm^{-1} indicating the coordination of azomethine nitrogen. The band due to intramolecular H-bonded O–H disappeared in the complexes. At the same time ν(C–O phenolic) band shifted to higher frequency by 12 to 21 cm^{-1} after complexation, which indicates the coordination of ligand to metal atoms by oxygen of the hydroxyl group [12,13]. In complexes **1**, **3** and **5** the ν(N–H) and ν(C=O) bands remain nearly constant as in the spectrum of ligand indicating non-involvement of amide oxygen in the coordination [14]. However, the ν(N–H) and ν(C=O) disappeared in the spectra of **2** and **4** indicating the destruction of the carbonyl moiety as a result of enolisation and subsequent coordination of the enolic oxygen after proton replacement [13]. The shift of ν(C=O) to lower frequency by 16 cm^{-1} in the spectrum of compound **6** indicates coordination of amide oxygen to metal [15]. The infrared spectra of acetato complexes display two bands near 1605–1615 and 1410–1420 cm^{-1} and these are assigned to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ respectively. The separation of these peaks by 195 cm^{-1} indicates the monodentate coordination of acetate group [11]. A new broad band at 3050–3300 cm^{-1} in the spectra of compounds **1**, **2** and **3** is probably due to ν(O–H) of coordinated water molecules [16]. The bands at 968 and 1155 cm^{-1} in the spectra of compound **4** and **5**, respectively, are assigned to ν(V=O) and δ(Zr–OH) [17,18].

The characteristic δ(O=U=O) stretching mode is found at 905 cm^{-1} in the case of compound **6**, which indicates presence of *trans*-UO_2 structure. The force constant f_{U-O} calculated by the method of McGlynn *et al.* [19] was found to be 6.80 mdyne/Å. This value agrees well with those of similar dioxouranium(VI) complexes [20]. The U–O bond length (R) was also calculated using Jones equation [21], $R_{U-O} = 1.08\ f^{-1/3} + 1.17$. The obtained value of 1.74 Å lies well within the expected range of 1.60–1.92 Å calculated for the majority of dioxouranium(VI) complexes.

Magnetic and electronic spectral studies: The electronic spectrum of Cr(III) complex shows three bands at 18880, 24830 and 40201 cm^{-1} due to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (ν_2) and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively suggesting the octahedral environment around Cr(III) ion [22]. The magnetic moment (4.03 B.M.) also favours the octahedral geometry. The ligand field parameters have been calculated by known relations [23] and Dq = 1888 cm^{-1}, B = 560 cm^{-1} and β = 0.60. The reduction of Racah parameters (B) from the free ion value suggests appreciable covalent character in the metal–ligand bonds. The Mn(III) complex exhibits a magnetic moment of 4.89 B.M. and displays bands near 13970, 16810, 20090 and 25530 cm^{-1} respectively, which are assigned to the transtions $^5B_1 \rightarrow {}^5B_2$, $^5B_1 \rightarrow {}^5A_1$, $^5B_1 \rightarrow {}^5E$ and LMCT [24], suggesting square-pyramidal geometry. The magnetic moment of 5.89 B.M. for Fe(III) complex is in agreement with high spin octahedral geometry. This complex exhibits three bands at 13790, 17890 and 22390 cm^{-1} respectively, which are assigned to the transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$ [25]. The VO(IV) complex possesses μ_{eff} value of 1.63 B.M. The lowering in the magnetic moment from the spin only value for one unpaired electron (*i.e.* 1.73 B.M.) may be due to the quenching of orbital contribution. The electronic spectrum of VO(IV) complex displays bands at 13690, 16755, 22010 and 29199 cm^{-1} respectively. These bands are due to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow {}^2A_1$ and LMCT transitions, respectively, corresponding to square pyramidal geometry [26].

The Zr(IV) and UO_2(VI) complexes are found to be diamagnetic as expected for d^0 ion system and may have octahedral geometry [18,20].

Thermal studies: Thermal decomposition revealed that the complexes mainly decompose in two stages. The elimination of lattice or coordinate water molecules takes place in the first stage and organic ligand degradates in the second stage [27]. Analysis of thermograms of Cr(III), Mn(III) and Fe(III) complexes indicates that the complexes are stable up to 60°, elimination of one lattice and one coordinated water molecule takes place near 60–120° and 150–220° respectively in these complexes. The observed and calculated weight loss for one lattice and one coordinate water molecule are in good agreement [for lattice water % wt. loss obs. (calcd.): Cr(III) 2.90 (2.71), Mn(III): 4.43 (4.31), Fe(III): 2.86 (2.70), for coordinated water: Cr(III): 2.88 (2.71), Mn(III): 4.47 (4.31), Fe(III): 2.81 (2.70)]. The weight loss up to 140° in Zr(IV) complex corresponding to presence of three lattice water molecules [% wt. loss obs. (calcd.): 8.03 (7.51)].

The VO(IV) and UO_2(VI) complexes are stable up to 250° indicating absence of lattice or coordinated water molecules [28]. Above 250° a gradual but continuous mass loss up to 600–680° occurs in all complexes and finally horizontal curves were observed corresponding to the final pyrolysis products Cr_2O_3, Mn_3O_4, Fe_2O_3, V_2O_5, ZrO_2 and U_3O_8 respectively. The thermal activation energy was calculated by both Broido [29] and Horowitz-Metzger [30] methods and comparable values obtained are given in Table 3. It was found that the decomposition follows first order kinetics in each case. The higher value of activation energy suggests the higher stability, but some other physical and chemical factors cause a change or deviation in this trend. Such kinetic parameters can be treated as indicators of reaction course, under particular conditions, but their particular physical significance and intrinsic behaviour become generalized with the change in experimental conditions. On the basis of thermal activation energy, the order of thermal stability of the compounds is found to be, VO(IV) > Fe(III) > Mn(III) > UO_2(VI) > Zr(IV) > Cr(III) > H_2L.

Table 3. Thermal decomposition data of the complexes.

Complex	Half decomposition temperature (°C)	Activation energy kJ mol^{-1}		Z S^{-1}	ΔS JK^{-1} mol^{-1}	ΔF kJ mol^{-1}
		Broido	Horowitz-Metzger			
1	442.5	34.3	33.6	36.07	–222.2	52.53
2	470	47.5	43.5	60.04	–218.3	62.97
3	475.5	42.2	43.7	48.31	–219.9	62.82
4	527.5	51.6	45.4	70.33	–217.5	65.78
5	475	41.0	39.2	50.34	–219.7	58.56
6	495	43.9	42.3	49.06	–219.5	60.65
H_2L	420	23.0	21.4	18.93	–227.4	37.53

The activation entropy (ΔS), free energy change (ΔF) and frequency factor (Z) have also been calculated with an accuracy of 0.05%. The negative value for entropy of activation indicates that the activated complexes have a more ordered or more rigid structure than the reactants or intermediate and the reactions are slower than normal.

Biological activities: The ligand and its complexes were screened for their antimicrobial activities against *E. coli, A. aerogenes, S aureus, B. subtilis, B. megatherium* and *S. typhi* by agar cup-plate method [26]. The concentrations used were 1 mg/ml in DMF. The growths were compared with DMF as control after 24 h of incubation at 37°C and growths inhibition zone diameter were measured in mm. The results indicate that the ligand is more active towards *E. coli* (17 mm), moderately active against *A. aerogenes* (12 mm), *S. aureus* (11 mm) and *S. typhi* (12 mm) and shows poor inhibitory effect towards *B. megatherium* (9 mm). All the complexes are moderately active against *E. coli, S. aureus* and *A. aerogenes* (12–16 mm). The Fe(III) complex exhibits better activity against *B. subtilis* (22 mm) and *B. megatherium* (21 mm), whereas the Zr(IV) complex shows inhibitory effect to a greater extent against *B. subtilis* (20 mm). The Mn(III), Fe(III) and Zr(IV) complexes are moderately active against *B. subtilis* and *S. typhi* (12–16 mm). The other complexes are found to show either bacteriostatic or weak to moderate bacteriocidal behaviour against *B. subtilis*, *S. typhi* and *B. megatherium* (9–15 mm).

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