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Synthesis and Characterization of Transition Metal Complexes with N, O-Chelating Hydrazone Schiff Base Ligand

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Abstract: The mononucleating hydrazone ligand HCMANBH (2-hydroxy-5-chloro-4-methylacetophenone-4-nitrobenzoylhydrazone), a condensation product of 4-nitrobenzoyl hydrazide and 2-hydroxy-5-chloro-4-methylacetophenone, was synthesized and its coordination behavior with Ti(III), VO(IV), Cr(III), Mn(III), Fe(III) and Zr(IV) ions was investigated by isolating and elucidating the structure of the complexes using elemental analyses, magnetic susceptibility measurements, IR, electrical conductivity and diffuse reflectance spectra. The ligand acts as a monobasic tridentate in case of Ti(III), Cr(III) and Fe(III) while dibasic tridentate in case of VO(IV), Mn(III) and Zr(IV) complexes. The complexes were found to be quite stable and decomposition of the complexes ended with respective metal oxide as a final product. The thermal data have been analyzed for kinetic parameters by using Broido's method.

Key words: Aroylhydrazone, Metal complexes, Electronic spectral data, TGA, Electrical study

INTRODUCTION

The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complexes of these ligands have been investigated [1]. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [2-4]. Coordination compounds derived from aroylhydrazones have been reported because of their anti-tuberculosis, antimicrobial and corrosion inhibitors [5-7]. Keeping the above facts in mind and in continuation of our research work [8, 9] on transition metal complexes with Schiff bases, in the present paper we report the synthesis and characterization of Ti(III), VO(IV), Cr(III), Mn(III), Fe(III) and Zr(IV) complexes of Schiff base derived from the condensation of 2-hydroxy-5-chloro-4-methylacetophenone with 4-nitrobenzoyl hydrazide.

EXPERIMENTAL

Materials and Instrumentation: All the chemicals used were of analytical grade. The solvents were dried and distilled before use according to standard procedures [10]. Titanium trichloride, vanadyl sulphate pentahydrate, chromium chloride pentahydrate, ferric chloride were of S.D's fine chemicals. $Mn(OAc)_3.2H_2O$ and zirconium (IV) acetate were synthesized by literature methods [11,12]. IR spectra were recorded in KBr medium on a Perkin Elmer-RX-I spectrophotometer. The ^{1}H-NMR spectrum of a ligand was recorded in $CDCl_3$+*DMSO* on a JEOL GSX-400 spectrophotometer using TMS as internal standard. Reflectance spectra of the complexes were recorded in the range 1200-200 nm (as MgO) on a Beckman DK-2A spectrophotometer. Microanalytical data were performed at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. Magnetic susceptibility measurements of the complexes in the solid state were determine by Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant. Solid state electrical conductivity of compounds was measured in their compressed (3 ton cm^{-1}) pellet form by the two-probe method using the Zentech electrometer. Thermogravimetric analyses of the compounds were studied in the temperature range 40-700°C on Perkin-Elmer TG-2 thermobalance in ambient air with a heating rate of 10°C min^{-1}.

Synthesis of Ligand: A hot solution of 4-nitrobenzoylhydrazide (10 mmol) in 50 ml ethanol was treated with 2-hydroxy-5-chloro-4-methylacetophenone (10 mmol) in 50 ml ethanol and the reaction mixture was gently heated under reflux on a water bath for 4h.

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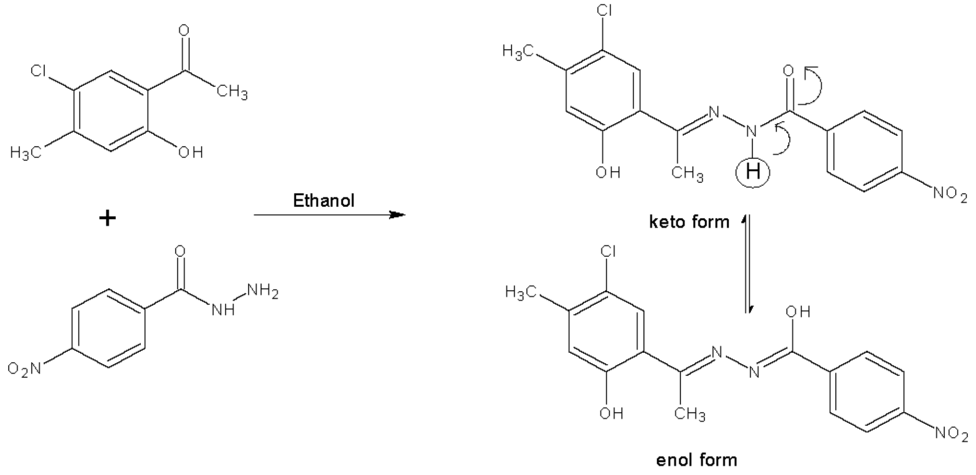

Scheme 1:

After cooling at room temperature the precipitated pale yellow solid was filtered off, washed with ethanol and dried. Finally, it was recrystallised from ethanol. (Scheme I) Yield: 66 %, M.P. 214 °C.

^{1}H-NMR: δ13.14(1H, s, phenolic OH); 11.90 (1H, s, imino); 3.50 (3H, s, methyl); 2.30 (3H, s, Ar-methyl); 6.90 and 7.92 (2H, m, phenyl); 7.90 and 8.20 ppm (4H, m, phenyl-NO_2).

Synthesis of Ti(III), VO(IV), Cr(III), Mn(III) and Fe(III) Complexes: The ligand (0.01mol) was dissolved in ethanol (10 ml) by heating at 80°C. To this refluxed ligand solution, an ethanolic solution of appropriate metal salt solution (0.01mol) [in case of VO(IV) DMF was used in place of ethanol] was added drop by drop with continuous stirring and the resulting reaction mixture was further refluxed for 4-6 h. The solid product obtained on cooling was filtered, wash thoroughly with ethanol and finally with petroleum ether to remove unreacted ligand and metal salts. Finally, all these complexes were dried at room temperature over $CaCl_2$.

Synthesis of Zr(IV) Complex: Zirconyloxychloride octahydrate (0.02mol, 0.64 g) was dissolved in methanol (10-15 ml) and to this solution methanolic solution of anhydrous sodium acetate (0.004mol, 0.32 g, in 15 ml) was added and stirred for 5 min. The separated sodium chloride was filtered off. The ligand hydrazone (0.002mol) was dissolved in hot methanol. To this solution, the solution containing oxozirconium(IV) diacetate was added and the mixture was refluxed for 6-8 h. The product obtained was filtered, washed 2-3 times with methanol followed by petroleum ether and dried at room temperature.

RESULTS AND DISCUSSION

The analytical data along with some physical properties of the ligand and its metal complexes are summarized in Table1. The complexes prepared are stable at room temperature and are non-hygroscopic. Elemental analysis indicates 1:1 metal:ligand stiochiometry.

Infrared Spectra: 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 the metal complexes. The structurally significant IR bands for free hydrazone ligand and its complexes have been reported in Table 2. The free ligand exhibits IR bands at ν 3198 (N-H), ν 2947 (OH), ν1637 (C=O), ν 1612 (C=N) and ν 1519 cm^{-1}(C-O phenolic). In the spectra of all complexes the band due to ν(O-H) of the ligand disappeared indicating the coordination of phenolic oxygen to the metal ion via deprotonation. This is further supported by the upward shift of phenolic ν(C-O) mode [13]. The band at 1612 cm^{-1} due to the azomethine group of the ligand underwent a shift to lower frequency (by 16-27 cm^{-1}) after complexation, indicating the coordination of azomethine nitrogen to metal ion and this can be explained by the donation of electrons from nitrogen to empty d-orbital of the metal ions [14]. The spectra of Ti(III), Cr(III) and Fe(III) complexes display ν (N-H) and ν (C=O) vibrations as in the spectrum of the free ligand, suggesting the keto form of the ligand [15]. It is inferred that the ligand HCMANBH and its metal complexes coordinates in a monobasic tridentate fashion. The spectra of the VO(IV), Mn(III) and Zr(IV) do not show the band due to ν (N-H) and ν (C=O) frequencies indicating the coordination of ligand to metal in enol form [16]. It is supported due to

Table 1: Analytical and physical data of HCMANBH ligand and its complexes

				Elemental analysis % found (calcd)			
Compound	Color	Electrical conductivity Ω^{-1} cm^{-1} at 373 K	Activation energy (eV)	M	C	H	N
HCMANBH	Lemon yellow	--	--	--	54.09 (53.26)	3.34 (3.04)	11.98 (11.12)
Ti	Dark crimson	2.51×10^{-9}	0.302	8.96 (9.54)	37.89 (38.32)	3.01 (3.42)	8.17 (8.38)
VO	Chartreuse	2.09×10^{-9}	0.481	10.21 (10.89)	40.99 (41.09)	3.73 (4.09)	8.27 (8.98)
Cr	Olive dark	7.01×10^{-9}	0.276	10.11 (10.66)	39.01 (39.41)	2.71 (3.10)	7.91 (8.62)
Mn	Chestnut	1.08×10^{-9}	0.708	10.27 (11.08)	42.02 (43.61)	3.17 (3.86)	7.91 (8.48)
Fe	Dark chocolate	6.72×10^{-9}	0.321	10.95 (11.36)	38.81 (39.10)	2.83 (3.08)	8.11 (8.55)
Zr	Lemon lime	2.86×10^{-9}	0.309	16.09 (17.05)	40.11 (40.41)	3.85 (4.14)	7.26 (7.85)

Table 2: Most important IR spectral bands of HCMANBH ligand and its metal complexes

Compound	ν(OH) + ν (NH) OH---N	ν(C-O) Phenolic	ν(C=N)	ν(N-N)	ν(N-H)	ν(C=O)	ν(C-O) Enolic	ν(M-O)	ν(M-N)
HCMANBH	2947	1519	1612	994	3198	1637	--	--	--
Ti(III)	--	1541	1587	1012	3216	1642	--	466	454
VO(IV)	--	1528	1596	1017	--	--	1236	472	514
Cr(III)	--	1547	1591	1020	3215	1647	--	488	418
Mn(III)	--	1538	1585	1009	--	--	1239	510	424
Fe(III)	--	1544	1593	1012	3211	1646	--	412	432
Zr(IV)	--	1536	1587	1011	--	--	1242	482	502

Table 3: Thermal, magnetic moment and electronic spectral data of HCMANBH ligand and its metal complexes

				Electronic spectra	
Compound	Half decomposition temperature (°C)	Activation energy* (KJ mol^{-1})	μ_{eff} B.M.	Absorption band (cm^{-1})	Assignment
HCMANBH	340	27.42	--	--	--
Ti(III)	432	43.56	1.52	18553	$^2T_{2g} \rightarrow {}^2E_g$
VO(IV)	472	51.09	1.62	13532	$^2B_2 \rightarrow {}^2E_1$
				16584	$^2B_2 \rightarrow {}^2B_1$
				22371	$^2B_2 \rightarrow {}^2A_1$
				22523	LMCT
Cr(III)	460	38.55	3.82	18796	$^4T_{2g}(F) \rightarrow {}^4T_{2g}(F)$
				24449	$^4T_{2g}(F) \rightarrow {}^4T_{1g}(F)$
				40650	$^4T_{2g}(F) \rightarrow {}^4T_{1g}(P)$
Mn(III)	470	56.55	4.42	13850	$^5B_1 \rightarrow {}^5B_2$
				17065	$^5B_1 \rightarrow {}^5A_2$
				20325	$^5B_1 \rightarrow {}^5E$
				28490	LMCT
Fe(III)	453	37.45	5.72	13477	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
				17301	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$
				22624	$^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$
Zr(IV)	420	42.13	--	--	--

* Broido method

presence of ν (C-O) (enolic) and ν (C=N-N=C) (azine) group frequencies in their spectra, indicating the dibasic tridentate nature of the ligand in these complexes. In case of Ti(III), VO(IV), Cr(III), Mn(III) and Fe(III) complexes, IR spectra exhibits four bands in the region 3479-3424 ν(OH), 1639-1630 δ(H_2O), 831-815 ρ_r(H_2O) and 784-744 ρ_w(H_2O) cm^{-1} suggesting the presence of coordinated water molecules in each of them [17]. The presence of band at ~ 972 cm^{-1} indicates methanol coordination in Zr(IV) complex. In the spectra of VO(IV) and Zr(IV) complexes, the additional bands observed at 964 and 1127 cm^{-1} due to ν(V=O) and δ(Zr-OH) modes respectively [18].

The Mn(III) complex displays two additional bands due to the presence of the acetate group. The bands at 1617 and 1425 cm^{-1} are due to ν_{asy} (OCO) and ν_{sy} (OCO) frequency, respectively. The difference of 192 cm^{-1} between the two bands and their positions indicates the monodentate nature of the acetate [19].

Magnetic Moment and Electronic Spectral Data: The electronic spectra and magnetic moments of the metal complexes are listed in Table 3. The electronic spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. Only one broad band is observed at 18553 cm^{-1} in the reflectance spectrum of the Ti(III) complex assigned to ${}^2T_{2g} \rightarrow {}^2E_g$ transition which is in conformity with octahedral geometry. The isolated oxovanadium complex show all the expected three bands at 13532, 16584 and 22371 cm^{-1} which are assigned to ${}^2B_2 \rightarrow {}^2E_1$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions, respectively. The fourth band appears at 29239 cm^{-1} may be due to charge transfer transition, indicating square-pyramidal geometry to the complex [20]. Ti(III) and VO(IV) complexes show magnetic moment 1.52 and 1.62 B.M. respectively. The electronic spectrum of Cr(III) complex exhibits three transitions at 18796, 24449 and 40650 cm^{-1} assignable to ${}^4T_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4T_{2g}(F) \rightarrow T_{1g}^4(P)$ transition respectively, suggesting octahedral environment around Cr(III) ion. The magnetic moment value was found to be 3.82 B.M. which is also agree well with the known values for Cr(III) complex in octahedral geometry [21]. The electronic spectrum of the Fe(III) complex displays three bands at 13477, 17301 and 22624 cm^{-1} assignable to ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g}(S) \rightarrow {}^4E_g$, ${}^4A_{1g}(G)$, transitions, respectively, indicating that the complex possesses a high spin octahedral configuration. The magnetic moment of Fe(III) complex was found to be 5.72 B.M. indicating high spin state of complex. The electronic spectrum of the Mn(III) complex shows band 28490 cm^{-1} attributed to the LMCT transition. In second region complex showed a series of weak d-d band at 13850, 17065 and 20325 cm^{-1} which may be due to ${}^5B_1 \rightarrow {}^5B_2$, ${}^5B_1 \rightarrow {}^5A_2$ and ${}^5B_1 \rightarrow {}^5E$ transitions, respectively, indicating square pyramidal configuration around Mn(III) ion. The observed value for the Mn(III) complex is 4.42B.M.in accordance with the four unpaired electrons corresponding to square pyramidal geometry.

Electrical conductivity: The temperature dependence of the solid state electrical conductivity (σ) of the complexes in their compressed pellet form have been measured in the temperature range 313-430 K using two probe method. The electrical conductivity and activation energy values are given in Table 1. It was found that the electrical conductivity values increase with increasing the temperature according to relation [22] $\sigma = \sigma_0 \exp(-Ea/RT)$, where Ea represents ordering activation energy of the conduction process and σ_0 is constant. The plot of logσ vs 1/T are found to be linear in studies temperature range 313-398 K indicating the semiconducting nature [23]. The electrical conductivity of the complexes at 373 K lies in the range of 2.9×10^{-9}-1.08×10^{-9} $\Omega^{-1}cm^{-1}$. The electrical conductivity of the complexes at 373 decreases in the order Cr > Fe > Zr > Ti > VO > Mn.

Thermogravimetric Analyses: The perusal of thermograms of HCMANBH and its metal complexes indicates that the complexes of Ti(III), Mn(III) and VO(IV) decompose in three steps while complexes Cr(III), Fe(III) and Zr(IV) in two steps. The Ti(III), Mn(III) and VO(IV) complexes are stable up to 80°C. The presence of water molecule (lattice or coordinated) in Ti(III), Cr(III), Fe(III), Mn(III) and VO(IV) complexes suggested from IR spectra is confirmed by the weight loss observed in the first decomposition step of the complexes. The Ti(III), Mn(III) and VO(IV) complexes loss their weights up to 120°C corresponding to lattice water molecule [% wt. loss obs/calcd: Ti(III): 3.58/3.26; Mn(III): 3.63/3.48; VO(IV): 7.69/7.40]. Loss of one lattice water molecule in case of Ti(III) and Mn(III) while two for VO(IV) complex. Weight loss up to 220°C corresponding to one coordinated water molecule for Ti(III), Cr(III), Fe(III) and Mn(III) complexes while two for VO(IV) complex [% wt. loss obs/calcd: Ti(III): 3.72/3.42; Cr(III): 3.69/3.12; Fe(III): 3.66/3.38; Mn(III): 3.76/3.26 and VO(IV): 4.16/3.98]. The Zr(IV) complex is coordinated with two methanol group supported by the spectral data [% wt. loss obs/calcd: Zr(IV): 11.96/11.43].The organic moiety decomposes further with increasing temperature. The complete decomposition of ligand occurs at 550-660°C and leaving behind their respective metal oxides. It is observed that the curve of ligand is broader while the curves of its metal complexes steeper suggesting that the decomposition rate of the metal complexes is faster than that of the compounds. The half decomposition temperature and activation energy of ligand and their metal complexes are listed in Table 3. From the half decomposition temperature, the relative thermal stability of the compounds is to be

VO(IV) > Mn(III) > Cr(III) > Fe(III) > Ti(III) > Zr(IV) > HCMANBH.

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