



SYNTHESIS, CHARACTERIZATION, ELECTRICAL AND BIOLOGICAL STUDIES OF VO(IV), MoO₂(VI), WO₂(VI), Th(IV) AND UO₂(VI) COMPLEXES WITH HYDRAZONE LIGAND

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Oxovanadium(IV), dioxomolybdenum(VI), dioxouranium(VI), thorium(IV) and dioxotungsten(VI) complexes of hydrazone ligand derived from 2-hydroxy-5-methylacetophenone and 2-furoic acid hydrazide have been synthesized and characterized by elemental analyses, magnetic moment, electronic and IR spectra and thermogravimetric analyses. Thermogravimetric studies suggest the presence of water/methanol molecules in the complexes and analyzed for the kinetic parameters using both Coats-Redfern and Horowitz-Metzger methods. Using standard equations, thermodynamic parameters such as ΔS and ΔG are calculated. The solid-state electrical conductivity of the complexes was studied in the temperature range from 313-413 K. All compounds show semiconducting behavior as their conductivity increases with increasing temperature. The ligand and its complexes have also been screened for their antibacterial and antifungal activities.

INTRODUCTION

Acid hydrazides and hydrazones are useful chelating agents and are of biological important. The presence of an additional amino group in the hydrazides causes delocalization of electrons with subsequent changes in energy level associated with the carbonyl oxygen which acts as donor in acid amides. The hydrazones derivatives are used as fungicides and in the treatment of diseases such as tuberculosis, leprosy and mental disorders.¹ The remarkable biological activity of acid hydrazides R-CO-NH-NH₂, their corresponding hydrazones, R-CO-NH-N=CH-R¹ and the dependence of their mode of chelation on the transition metal ions present in the living system have offered significant interest in recent years.²⁻⁵ In the recent past there has been a growing interest in the Chemistry of aroylhydrazones derived from ketones.⁶⁻⁸

In view of the fast growing interest of hydrazones on account of the structural, analytical and biological importance of their metal complexes, the synthesis of 2-hydroxy-5-

methylacetophenone-2-furoylhydrazone [HMAFH] and its metal chelates with VO(IV), MoO₂(VI), WO₂(VI), Th(IV) and UO₂(VI) have been carried out and the results are presented in this paper.

RESULTS AND DISCUSSION

The tridentate *ONO* donor hydrazone ligand used in the present work was derived from the condensation of 2-hydroxy-5-methylacetophenone with 2-furoic acid hydrazide in ethanol. The isolated complexes are bright in color, quite air stable and can be stored for long periods. All the complexes are insoluble in water, soluble to very limited extent in common organic solvents but considerable extent in DMF and DMSO. The elemental analyses (Table 1) indicates that all these complexes except thorium have 1:1 metal: ligand stoichiometry, whereas Th(IV) shows 1:2. The molar conductivity values (11.30-14.50 ohm⁻¹cm²mol⁻¹) of 10⁻³ M DMF solutions indicate that all the complexes are nonelectrolytes in nature.

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Table 1

Analytical and physical data of the compounds

Compound	Color	Analysis % found (Calc.)				Electrical conductivity (σ) $\Omega^{-1}\text{cm}^{-1}$ at 373K	Activation energy (Ea) eV
		C	H	N	M		
HMAFH (H ₂ L)	Pale cream	64.18 (65.11)	5.42 (5.46)	10.01 (10.85)	--	--	--
[VO(L)H ₂ O]	Oracle	48.90 (49.28)	3.99 (4.14)	8.67 (8.21)	14.00 (14.93)	1.01×10^{-9}	0.488
[MoO ₂ (L)H ₂ O]	Smoke gray	42.94 (41.81)	2.86 (3.51)	6.59 (6.96)	23.88 (23.85)	1.06×10^{-9}	0.487
[WO ₂ (L)(NCS) ₂]	Golden brown	31.54 (32.67)	2.11 (2.06)	9.20 (9.52)	30.15 (31.25)	1.03×10^{-6}	0.338
[Th(HL) ₂ (NO ₃) ₂]	Off white	39.32 (40.10)	4.10 (3.13)	10.98 (10.02)	26.88 (27.67)	7.90×10^{-8}	0.458
[UO ₂ (L)CH ₃ OH]	Canary Yellow	33.09 (32.27)	2.65 (2.89)	4.85 (5.02)	41.99 (42.63)	2.23×10^{-10}	0.712

The infrared spectrum of ligand exhibits bands at 1651 and 3230 cm^{-1} due to $\nu(\text{C}=\text{O})$ and NH stretches, respectively. These bands disappeared in the spectra of VO(IV), MoO₂(VI), WO₂(VI), and UO₂(VI) complexes indicating the transformation of the carbonyl moiety owing to enolization and consequent replacement of proton by the metal ion. A new band appearing in the 1235-1252 cm^{-1} region was assigned to the $\nu(\text{C}-\text{O})$ (enolato) mode. In the case of the thorium complex the $\nu(\text{C}=\text{O})$ mode of the free ligand (1651 cm^{-1}) shifted to lower frequency in the spectrum of complex as a result of coordination of the carbonyl oxygen to the thorium. The $\nu(\text{C}=\text{N})$ (azomethine) mode of the hydrazone appears at 1602 cm^{-1} , and this band is shifted to a lower wave number by 14-20 cm^{-1} in the spectra of complexes, thereby indicating the coordination of the azomethine nitrogen atom. The coordination through the azomethine nitrogen is further substantiated by the observed shift to higher wave numbers by $\sim 30 \text{ cm}^{-1}$ in the $\nu(\text{N}-\text{N})$ mode in the complexes. A medium broad band due to intramolecular hydrogen bonding between the phenolic O-H and the C=N is also absent in the spectra of the complexes. This also supports the breaking of the hydrogen bonding, deprotonation of phenolic oxygen and subsequent coordination of phenolic oxygen atom to the metal. However, the presence of a broad band around 3430 cm^{-1} in VO(IV) and MoO₂(VI) complexes is may be due to coordinated water molecule in this complex. This result is substantiated by TGA data. The presence of a strong band at 967 cm^{-1} in oxovanadium complex is indicative of the V=O group. In dioxomolybdenum and dioxotungsten(VI) complexes bands observed at 895 and 872 cm^{-1} due to cis-MoO₂ and WO₂ structures respectively. On

the other hand dioxouranium complex exhibits band at 914 cm^{-1} indicating the existence of trans structure.⁹ The force constant for the U-O bond of this complex has been calculated by the method of McGlynn *et al.*¹⁰, while bond length for the (U-O) bond was calculated by the method of Jones *et al.* and values are found to be 6.89 m dyne/Å and 1.34Å respectively. These values lie within the range observed for the majority of dioxouranium (VI) complexes. The new bands observed around at 514 and 450 cm^{-1} in the spectra of all complexes are indicative of M-O and M-N modes respectively. The preferred coordination number of thorium is 6 or 8, but higher coordination numbers have also been observed. In the Th(IV) complex two ligand moieties imparting coordination number 6 and the nitrate groups are functioning as bidentate ligand; the coordination number of Th(IV) is ten in this complex. In case of the UO₂(VI) complex the $\nu(\text{C}-\text{O})$ band of CH₃OH occurring at 1034 cm^{-1} undergoes a negative shift indicates the methanol coordination in the complex.¹¹

The room temperature magnetic moment of the VO(IV) complex is found to be 1.76 B.M which is a characteristic value for mononuclear oxovanadium complexes with $S = \frac{1}{2}$ and a d_{xy} or $d_{x^2-y^2}$ ground state. MoO₂(VI), WO₂(VI), Th(IV) and UO₂(VI) complexes are found to be diamagnetic as expected. The electronic spectrum of VO(IV) complex exhibits low intensities d-d bands at 13531, 16977 and 22222 cm^{-1} due to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions, respectively characteristic of a square pyramidal ligand field around V⁴⁺. The electronic spectrum also exhibits a fourth high energy band above 28000 cm^{-1} , which can be assigned as a ligand to metal charge transfer transition which is consistent

with square pyramidal geometry around the VO(IV) ion.¹² The electronic spectra of dioxomolybdenum(VI) and dioxotungsten(VI) complexes exhibit one band at *ca* 24000 cm⁻¹ due to ligand to metal charge transfer transition between the lowest empty d-orbital of the metal and the highest occupied ligand molecular orbital. Similarly dioxouranium(VI) complex exhibits a low intensity band at ~ 22000 cm⁻¹ due to ¹ε_g⁺ → ³π_u transition typical of OVO symmetric stretch frequency for the first excited state.¹³

Thermal analyses of the complexes were studied under dynamic air atmosphere. The TG curves obtained for all the complexes are comparable and weight loss continues till a stable oxide is formed. The Thermogram of the UO₂(VI) complex indicates the loss of one coordinated methanol molecule. In case of the VO(IV) and MoO₂(VI) complexes, loss weight ~5.48 % and ~4.47 % around 140°C corresponds to one coordinated water molecule respectively. The loss of two nitrate groups is observed in the temperature range 205-235°C in the Th(IV) complex. After the total loss of water/methanol molecules the organic moiety decomposes at further increment of temperature

(300-355°C). The second step starts immediately after the first one and partly loses the organic part of the complex. The third stage of degradation covers to the formation of the respective stable metal oxides.

Coats-Redfern¹⁴ and Horowitz-Metzger¹⁵ methods have been used to calculate the kinetic parameters of the complexes. The fractional weight loss and the corresponding (1-α)ⁿ values have been calculated from the TG curves at different temperatures, where n depends upon the reaction model and α = (W_o-W_t)/(W_o-W_f). The weighted least square method (LSM) was used for obtaining the best-fit linear plots and kinetics parameters were calculated. The decomposition of all the complexes has been observed to follow first order kinetics; as is evident from the linear plot of -log [-log(1-α)/T²] vs 1/T. The value of frequency factor (Z) and entropy of activation (ΔS*) was calculated from the following equations intercept = log ZR/βE and ΔS* = 2.303R log Zh/kT, where k is Boltzmann constant; h is the Planck's constant, T the peak temperature and β the heating rate. The thermoanalytical data of all the complexes is given in Table 2.

Table 2

Thermal data of the complexes

Compound	Half decomposition Temperature (°C)	Activation energy (kJ mol ⁻¹)			Frequency factor Z (S ⁻¹)		Entropy change -ΔS (J mol ⁻¹ K ⁻¹)	Free energy change ΔG (kJ mol ⁻¹)
		Step	CR*	HM [#]	CR*	HM [#]		
[VO(L)H ₂ O]	470.00	I	40.19	39.36	23.21	23.54	263.29	41.19
		II	45.42	46.21	31.32	32.46	251.28	42.33
[MoO ₂ (L)H ₂ O]	432.50	I	36.22	36.87	27.82	28.21	274.23	37.45
		II	40.33	41.10	33.45	34.51	279.45	34.64
[WO ₂ (L)(NCS) ₂]	446.50	I	39.45	39.86	40.25	40.28	265.81	36.72
		II	55.47	55.79	39.46	39.51	274.56	32.46
[Th(HL) ₂ (NO ₃) ₂]	440.50	I	41.32	40.35	29.33	30.24	231.49	45.66
		II	37.36	36.38	23.19	24.21	239.19	44.73
[UO ₂ (L)CH ₃ OH]	457.50	I	27.28	26.33	20.27	20.84	229.36	46.36
		II	45.43	49.38	24.39	25.17	235.54	47.86

CR* = Coats-Redfern; HM[#] = Horowitz-Metzger

Theoretically, with decreasing the value of E, the value of Z increases and the higher value of activation energy suggest the higher stability. However, there lie some inherent physical and chemical factors, which may cause a change or deviation in this trend. Higher value of activation energy (E) and lower value of frequency factor the reaction to proceed slower than normal. In the present studies, the numerical values of activation energy (E), frequency factor (Z) and apparent entropy altogether indicate about the smooth less

of the feasibility and reaction rate of the initial reactants and intermolecular stage compounds. The negative values for entropy of activation indicates that the activated complexes have a more ordered or more rigid structure than the reactants or intermediates and the reactions are slower than normal.¹⁶ These complexes show similar type of behavior as shown by the E and Z values for each decomposition step.

Solid-state d. c. conductivity of complexes were measured by the two probe method with a Zentech

electrometer from 313-413 K using the standard procedure. The complex powder was pressed to form a pellet by using KBr pellet press. The pellet was placed between two aluminum foils and resistance was measured. The conductivity was determined from the resistivity of the pellet. Resistivity = RA/T ; where R= resistance in ohms, A= area of cross section of the pellet and T= thickness of the pellet

In an attempt to interpret the electrical data of hydrazone complexes, the logarithm of conductivity has been plotted against the reciprocal of absolute temperature. According to band theory, these plot should yield straight lines over the studied temperature range (313-413 K). The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relationship, $\sigma = \sigma_0 \exp(-E_a/kT)$, where E_a is the energy of activation and σ_0 is a constant which provides a measure of carrier mobility. The results of electrical conductivity measurements of the complexes are incorporated in Table 1. From the results of the electrical conductivity, the following conclusions may be drawn. It was observed that the electrical conductivity of the complexes has positive temperature coefficient. That is, with an increase of temperature, conductivity increases exponentially. The increase starts when charge carriers have enough activation energy. Also, during increase of temperature, the mobility of these carriers increases. This is a property of typical semiconductivity.¹⁷ Having larger energy gap shows intrinsic region. At intrinsic region, conductivity is from valence to conduction band and charge carrier concentrations of these materials at room temperature are at low level and also these complexes have low conductivity. All the prepared complexes have low electrical conductivities. This can be explained on the basis that they have semiconducting properties. Hence, the electrons in the available orbital of complexes are not of high mobility. In general, a lower conductivity weakens the conjugation in the chelate ring involved in complex formation. This could be attributed to packing property.¹⁸ The electron or hole migration in these complex semiconductors is attributed to a hopping mechanism. In the model, the electron or hole hops from one localized metal site to the next. When it lands on a new site it causes the surrounding ions to adjust their localizations and electron or hole trapped temporarily in the potential well producing atomic polarization. The electron resides at its new site until thermally activated to migrate another nearby site. Another

aspect of this charge hopping mechanism is that the electron or hole tends to associate with local defects so the activation energy for charge transport may also include the energy of freeing the hole from its position next to defects. The high temperature region of the plot was selected for calculating the activation energy of the complexes. The activation energy increased in the order $WO_2 < Th < MoO_2 < VO < UO_2$. Our observations are in partial agreement with that reported by Patel *et al.*¹⁹ The electrical conductivity at 373 K declines in the order, which is in good agreement with order suggested by Aswar *et al.*²⁰ $WO_2 > Th > VO > MoO_2 > UO_2$.

The antibacterial and antifungal activity of the ligand and their metal complexes were assayed against five different bacteria, *E. coli*, *S. abony*, *S. aureus*, *P. aeruginosa* and *B. subtilis* and two fungi, *A. niger* and *C. albicans*, by cup plate method at the concentration of 1 mg/ml in DMSO. The standard used was gentamycin sulphate 20 µg/ml and solvent control as also put to know the activity of solvent. The activity was measured by measuring the diameter of the inhibited zone in millimeter and given in Table 3. The data show that the antibacterial activity of the ligand was enhanced on complexation, but less than standard used. The activity increases with increase in concentration of the test solution containing new complexes. This is because of the chelation, which reduces the polarity of metal ion due to partial sharing of its positive charge with donor groups and also due to the delocalization of π electrons over while, chelate ring. Thus chelation increases lipophilic character in the complexes and results in enhancement of activity.²¹

EXPERIMENTAL

All the chemicals and reagents used were of AR grade obtained from commercial source and used without further purification. Vanadyl sulphate pentahydrate, uranyl nitrate hexahydrate, sodium tungstate dihydrate and thorium nitrate pentahydrate were analytical reagent grade. $[MoO_2(acac)_2]$ and 2-hydroxy-5-methylacetophenone were synthesized by the methods described in literature.²²⁻²⁴

Synthesis of ligand

A hot solution of 2-furoic acid hydrazide (7.2 g 0.05 mol) in 50 ml ethanol was treated with 2-hydroxy-5-methylacetophenone (0.05 mol) in 50 ml of ethanol, and the reaction mixture was gently heated under reflux on a water bath for 4 h. After reduction of the solvent to *Ca* 15 ml and cooling to room temperature for 2 h, the precipitated pale cream solid was filtered off, washed with ethanol, and dried.

Finally, it was recrystallised from ethanol. Yield: 80%, M.P. 211°C.

¹H-NMR: δ12.92 (1H, s, phenolic OH); 11.08 (1H, s, imino); 7.87-7.22 (3H, m, aromatic); 3.21 (3H, s, methyl) and 2.22 ppm (3H, s, Ar-methyl).

The schematic representation of ligand and its tautomeric forms are shown in Fig. 1.

Table 3

Biological activity of the compounds

Compound	Antibacterial activity					Antifungal activity	
	E. coli	S. abony	S. aureus	P. aeruginosa	B. subtilis	A. niger	C. albicans
HMAFH (H ₂ L)	9	9	8	7	8	10	9
[VO(L)H ₂ O]	12	13	11	11	11	13	12
[MoO ₂ (L)H ₂ O]	11	13	10	10	12	11	12
[WO ₂ (L)(NCS) ₂]	11	10	11	9	11	12	11
[Th(HL) ₂ (NO ₃) ₂]	10	11	10	11	9	13	12
[UO ₂ (L)CH ₃ OH]	10	10	9	9	10	11	10

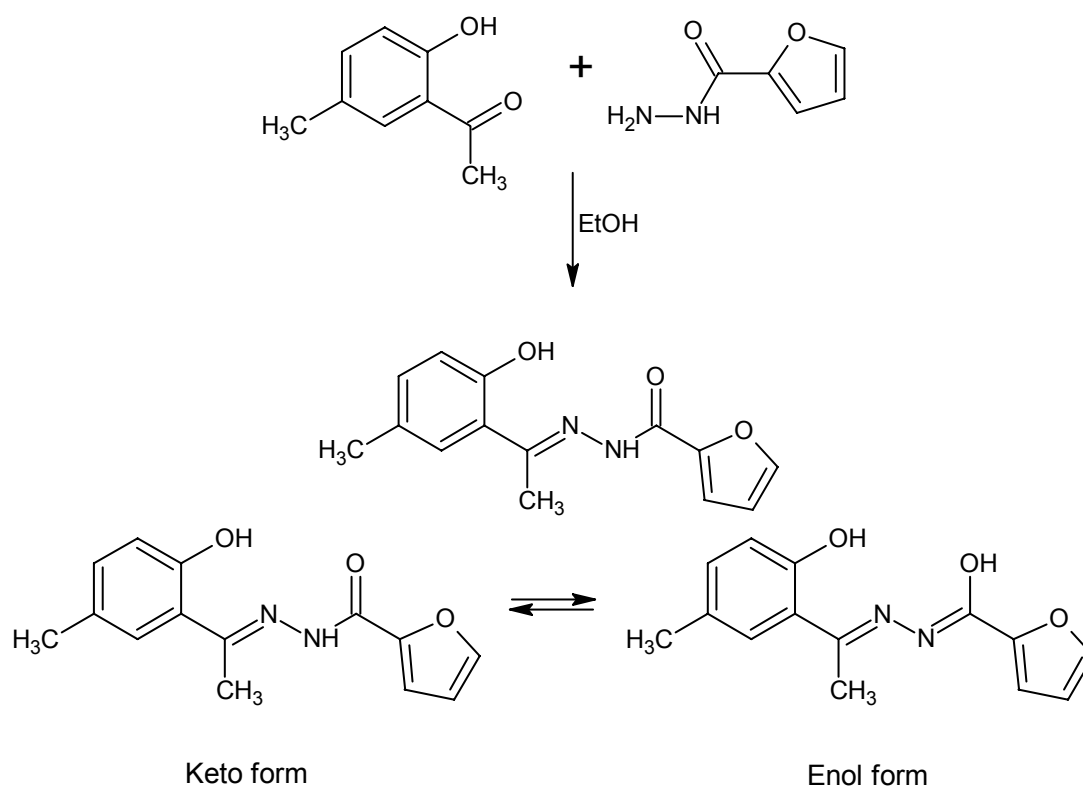


Fig. 1

Synthesis of VO(IV), MoO₂(VI), Th(IV) and UO₂(VI) complexes

Acid hydrazide (0.004 mol) and appropriate metal salt (0.004 mol) were dissolved separately in hot ethanol in a water bath. The resulting solution was refluxed with stirring on a water bath for 4-5 h. It was allowed to cool at room temperature and colored product obtained with different metal ions were suction filtered, washed with ethanol and petroleum ether and dried in vacuo over silica gel at room temperature. Yield: 65-70%.

Synthesis of WO₂(VI) complex

Sodium tungstate dihydrate and ammonium thiocyanate were dissolved in water (30 ml) at room temperature and 7.5 ml of 11M HCl was added to it. The resulting solution was cooled in an ice bath and ethanolic solution (10 ml) of ligand was added to it. The precipitate so formed was filtered under suction, wash 3 to 4 times with water containing few drops of HCl and dried in vacuo. Yield: 68 %.

Physical measurements

Elemental analyses of ligand and complexes were carried out at RSIC, C.D.R.I., Lucknow, India. Metal contents of the complexes were estimated by oxides method.²⁵ IR spectra were recorded as KBr pellets on a Perkin-Elmer-1600 FT-IR spectrophotometer. The reflectance spectra of the complexes were recorded on a Beckman DK-2A spectrophotometer. ¹H-NMR spectrum of the ligand was recorded on JEOL-AMX-400 NMR spectrophotometer in DMSO-*d*₆ and TMS as an internal standard. Magnetic measurements were carried out at room temperature using Gouy's method, employing Hg[Co(SCN)₄] for calibration purposes, and were corrected for diamagnetism by using Pascal's constant. Thermogravimetric analyses of the complexes were carried out using a TGS-2 Perkin Elmer thermal analyzer in the temperature range 50-700°C at a heating rate of 10°C min⁻¹. Solid-state (d. c.) conductivity of the complexes was measured in their compressed pellet form over a range of 313-413 K temperature using Zentech electrometer.

Antibacterial and antifungal activities of the ligand and their complexes were carried out against the bacteria, *E. coli*, *S. abony*, *S. aureus*, *P. aeruginosa* and *B. subtilis* and the fungi *A. niger* and *C. albicans*, by cup plate method.

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