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Spectral and Biological Studies of Dioxouranium(VI), Dioxomolybdenum(VI), Oxovanadium(II) Complexes of *o*-Hydroxy Acetophenone Oxime

B.H. MEHTA* and F.F. SYED
Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E)
Mumbai-400 029, India

The ketone *o*-hydroxyacetophenone was treated with hydroxylamine hydrochloride for the synthesis of its oxime derivative. The oxime was used to synthesise dioxouranium(VI), dioxomolybdenum(VI) and oxovanadium(II) complexes having metal : ligand stoichiometry 1 : 2. The ligand and the metal complexes were characterised by elemental analyses, molar conductivity measurements, magnetic susceptibility measurements, ESR spectral data, electronic absorption, IR absorption spectral data and ^{1}H NMR spectral data. Dioxouranium and dioxomolybdenum complexes were found to be diamagnetic, whereas oxovanadium complex was found to be paramagnetic in nature. The ligand and the metal complexes were also studied for their antibacterial activity. On the basis of the investigation appropriate geometry was assigned to the metal complexes.

Key Words: Spectral, Biological, UO_2(VI), MoO_2(VI), VO(II) Complexes, *o*-Hydroxy acetophenone oxime.

INTRODUCTION

Organic chelating ligands containing oxime as functional group have found a wide range of applications in analytical chemistry because of their chelating ability with the transition metal ions.[1–3] Literature survey reveals that tremendous work has been done on transition metal complexes of oxime. In the past we have reported vanadyl and uranyl complexes of 5-nitrosalicylaldehyde oxime, resacetophenone oxime and 2-hydroxy-1-napthaldehyde oxime.[4–6] In continuation with our work on higher and inner transition metal complexes of oximes, in the present paper an attempt is made to synthesize dioxouranium, dioxomolybdenum and oxovanadium complexes of *o*-hydroxyacetophenone oxime and study their spectral features and their antibacterial activity.

EXPERIMENTAL

All the chemicals, solvents and reagents used for the synthesis were of L.R. grade. The ligand *o*-hydroxyacetophenone oxime was synthesized by treating *o*-hydroxyacetophenone with hydroxylamine hydrochloride using sodium acetate as buffer. The precipitate obtained was washed with water to remove excess of hydroxylamine hydrochloride. The oxime was recrystallised from methanol. The metal complexes were synthesized by mixing methanolic solution of the ligand (1% w/v) with the metal solution (1 mg/cm^3) at appropriate pH. The solid complexes obtained, were filtered, washed with aqueous methanol and dried in the oven at 60°C. The elemental analyses of ligand and metal complexes were carried out by reported methods.[7] The complexes were examined for solubility using various polar and non-polar solvents, Molar conductivity of ligand and metal complexes was recorded using 5×10^{-3} molar solution in nitrobenzene on a Toshniwal conductivity meter. The electronic absorption spectra of complexes were recorded in the UV-Visible region using DMSO as solvent, while the diffused reflectance spectra were recorded using $BaSO_4$ as a diluent on UV-Vis-2100 spectrophotometer supplied by M/s Shimadzu Corporation. IR spectra were recorded on FTIR-4200 supplied by M/s Shimadzu Corporation using KBr pellets. The ESR spectrum of oxovanadium complex was recorded using Varian E-1700 Endor spectrometer at RSIC I.I.T., Powai (Mumbai). The magnetic susceptibility measurements were made on Gouy's balance using $Hg[Co(CNS)_4]$ as standard. The ^1H NMR spectra for the ligand and the metal complexes were recorded at TIFR (Mumbai) on a Varian-EN360L spectrophotometer using 500 MHz frequency. The experimental findings are summarized in Tables 1–4.

TABLE-1
ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

Compound	Colour	m.w.	Molar cond. $\times 10^{-3}$ Siemens	% Elemental analysis found (calcd.)			
				C	H	N	Metal
$C_8H_9NO_2$	White	151	2..06	62.69 (62.57)	6.20 (5.96)	9.25 (9.25)	— —
$UO_2(C_8H_8NO_2)_2$	Orange	570	0.27	3021 (33.68)	2.81 (3.19)	4.89 (4.61)	40.38 (41.73)
$MoO_2(C_8H_8NO_2)_2$	Cream	427.94	1.56	43.72 (44.78)	3.52 (3.72)	6.64 (6.52)	22.14 (22.41)
$VO(C_8H_8NO_2)_2$	Brown	367	0.30	52.21 (52.31)	4.71 (4.36)	7.46 (7.58)	13.45 (13.87)

TABLE-2
UV VISIBLE AND IR SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Ligand/ Complex	Electronic spectral data (cm^{-1})		IR spectral data (cm^{-1})			
	UV-Vis	Reflectance	ν(—OH)	ν(>C=N)	ν(M—N)	ν(M—O)
$C_8H_9NO_2$	32,733 (7.02) 39,215 (8.13)	—	3350 (s)	1640(s)	—	—
$UO_2(C_8H_8NO_2)_2$	23,800 (1.24) 27,020 (1.84) 35,714 (1.96) 39,215 (20.42)	15,432 21,810 28,288	2900 (b)	1640(s)	580	480
$MoO_2(C_8H_8NO_2)_2$	28,571 (4.92) 29,239 (8.45) 30,864 (15.78) 33,557 (18.94)	13,698 18,214 20,790	3300 (b)	1628(s)	550	425
$VO(C_8H_8NO_2)_2$	27,397 (6.89) 30,959 (6.47) 33,222 (7.00)	12,391 17,241 23,584	3200 (b)	1555(s)	618	470

TABLE-3
ESR SPECTRAL DATA OF VANADYL COMPLEX

Complex	$g_{\parallel}$	$g_{\perp}$	g_{avg}	μ_{eff} (from ESR spectra) (B.M.)	μ_{eff} (From Gouy's method) (B.M.)
$VO(C_8H_8NO_2)_2$	1.987	1.999	1.995	1.73	1.67

TABLE-4
^1H NMR SPECTRAL DATA AND ANTIBACTERIAL ACTIVITY OF LIGAND AND MEAL COMPLEXES

Ligand/Complex	^1H NMR spectral data (ppm)				MIC (ppm)	
	δ_{CH_3}	$\delta_{aromatic}$	δ_{OH}	δ_{NOH}	*S. aureus*	*S. typhi*
$C_8H_9NO_2$	2.15	6.3–7.8	11.8	9.6	+ve	+ve
$UO_2(C_8H_8NO_2)_2$	3.3	6.3–7.5	—	11.4	200	200
$MoO_2(C_8H_8NO_2)_2$	3.3	6.8–7.5	—	11.5	200	200
$VO(C_8H_8NO_2)_2$	3.3	6.9–7.7	—	11.5	200	200

RESULTS AND DISCUSSION

The oxime of *o*-hydroxyacetophenone is a white crystalline substance having melting point 117°C. The metal complexes derived from this oxime vary in their colour. The elemental analysis suggests metal : ligand stoichiometry as 1 : 2, indicated by close agreement with the analytical data and theoretical molecular formula. The metal complexes are soluble in nitrobenzene and DMSO. The molar conductance value suggest that these complexes are nonelectrolytic in nature.

The IR spectra of ligand *o*-hydroxyacetophenone oxime exhibit sharp and strong absorption bands at 3350 cm^{-1} and 1640 cm^{-1}, characteristic of ν(—O—H) and ν(>C═N) respectively. The IR spectra of metal complexes also exhibit a broad band pointing in the region 3300–3200 cm^{-1} indicating the involvement of only phenolic oxygen in coordination with the metal ion. Also the oxy-imine stretching vibration is shifted towards lower frequency suggests involvement of oxy-imine nitrogen in coordination.[8] The IR spectra of dioxo complexes show additional bands at 920–900 cm^{-1} and 958–920 cm^{-1} which are assignable to ν(O═U═O) and ν(O═Mo═O) groups respectively[11], whereas the spectra of VO(II) complex show a new band at 990 cm^{-1} corresponding to ν(V═O) vibration. In addition the IR spectra show absorption bands in the region 618–550 cm^{-1} and 480–425 cm^{-1}, which can be assigned to ν(M—N) and ν(M—O) respectively.[9]

Thus, from the IR spectra of the metal complexes it can be concluded that the ligand *o*-hydroxyacetophenone oxime behaves as a monobasic bidentate ligand and coordinates to the metal ion through the oximino nitrogen and phenolic oxygen after deprotonation.[10]

All the complexes were studied with respect to various electronic transitions associated within the UV-visible region. UV-visible spectrum of the metal complexes shows d-d and charge transfer transitions in the region 12,391 cm^{-1} to 23,584 cm^{-1} and around 28,638 cm^{-1} respectively.[11]

The above spectral data suggest the octahedral geometry of UO_2(VI) and MoO_2(VI) complexes of *o*-hydroxyacetophenone oxime and square pyramidal geometry of VO(II) complex.[12]

The magnetic susceptibility measurements of the complexes revealed the diamagnetic nature of UO_2(VI) and MoO_2(VI) complexes, whereas VO(II) complex was found to be paramagnetic in nature with magnetic moment 1.67 B.M. The ESR spectral data show μ_{eff} value as 1.73 B.M. as should be for single unpaired electron. g_{II} value is less than 2.3 which indicates the covalent nature of metal-ligand bond.

The effect of bonding on the oxime was monitored by ^1H NMR spectroscopy. As expected the spectra of the three complexes show the disappearance of OH (phenolic) signal of the ligand in the complexed species indicating the site of coordination with the metal ion. Also the oximic protons shift downfield upon complexation. Similar observations are reported in literature.[13]

The oxime and the metal complexes were tested for their antibacterial activity against bacterial strains S. *aureus* and *S. typhi* and by varying concentration method. Minimum inhibition concentration was found to be 200 ppm for all the metal complexes.

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