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X-ray Crystallographic Studies of Dioxouranium(VI), Dioxomolybdenum(VI) and Oxovanadium(II) Complexes of *o*-Hydroxy Acetophenone Oxime

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The ketone *o*-hydroxyacetophenone was treated with hydroxylamine hydrochloride for the synthesis of its oxime derivative .The oxime was used to synthesize dioxouranium(VI), dioxomolybdenum(VI) and oxovanadium(II) complexes. Elemental analysis, molar conductivity measurements, magnetic susceptibility measurements, ESR, electronic absorption and IR absorption spectra characterized the ligand and the metal complexes. The elemental analysis reveals the metal : ligand stoichoimetry in the complexes as 1 : 2. Dioxouranium and dioxomolybdenum complexes were found to be diamagnetic, whereas oxovanadium complex was found to be paramagnetic in nature. The XRD data was to index the complexes for monoclinic system with space group $P_{2/m}$, $B_{2/m}$ and $C_{2/c}$.

Key words: X-ray crystallography, UO_2(VI), MoO_2(VI), VO(II) complexes, *o*-Hydroxy acetophenone oximes

INTRODUCTION

Oxime derivatives of aldehydes and ketones are mainly used in analytical chemistry[1]. *o*-Hydroxyacetophenones and their oximes have aroused considerable interest with regard to their chelating ability with the transition metal ions.[2–4] The chemistry of metal-oxime complexes is of interest because these species display a variety of reactivity modes and also because they possess catalytic and biological activity.[5,6] Molybdenum is not only restricted to industrial type catalytic reactions, but nature also has incorporated molybdenum into a number of redox enzymes.[7] Even though, the structural chemistry of molybdenum, uranium and vanadium complexes is not established to the satisfaction of the researcher. It provides a challenge to a researcher investigating various aspects of structural chemistry of these ions.

Literature survey reveals that metal complexes of oximes are generally crystalline; however, the crystallographic investigation is a shortcoming in the structural elucidation, particularly for molybdenum, uranium and vanadium ions. An attempt is made to synthesize dioxouranium, dioxomolybdenum and oxovanadium complexes of *o*-hydroxyacetophenone oxime and study their crystallographic features using powder pattern X-ray diffractograms.

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[8] (Table-1). The complexes were examined for solubility using various polar and nonpolar solvents. Molar conductivity of ligand and metal complexes was recorded using 5×10^{-3} M solution in nitrobenzene on a Toshniwal conductivity meter. The electronic absorption solution spectra of complexes were recorded in the UV-Visible region using DMSO as solvent, while the diffused reflectance spectrum was 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-Powai (Mumbai). The magnetic susceptibility measurement was made on Gouy's balance using $Hg[Co(CNS)_4]$ as standard. The X-ray diffractogram was recorded on XRD diffractogram 6000 using CuKα radiation (CuKα = 1.5418 Å). The X-ray diffractograms were scanned in the 2θ range of 5°–60°.

RESULTS AND DISCUSSION

The oxime of *o*-hydroxyacetophenone is a white crystalline substance having melting point 177°C. The metal complexes derived from this oxime vary in their colour. The elemental analysis suggests metal : ligand stoichoimetry 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 suggests that these complexes are non-electrolytic in nature.

The IR spectra of the ligand and the metal complexes were recorded in Table-1. The prominent features in the spectrum of the ligand *o*-hydroxyacetophenone oxime are sharp and strong absorption bands at 3350–1640 cm^{-1}, characteristic of ν(—O—H) and ν(>C=N) respectively. The IR spectra of metal complexes also exhibit a broad band in the region 3300–3200 cm^{-1}. This indicates that only phenolic oxygen coordinates with the metal ion due to its lower pKa value. The oximic group deprotonates after phenolic OH group because it has higher pKa value. It was expected that both the —OH groups will deprotonate and will give 1 : 1 complex but the presence of a broad band in this region and the elemental analysis data suggest that only the phenolic OH group gets deprotonated. Similarly a strong band appears at 1640 cm^{-1} in the spectrum of ligand, which shows a bathochromic shift of 40–90 cm^{-1} suggesting the involvement of oximic nitrogen in the coordination to the metal ion[9]. Similar observations are reported

TABLE-1
ANALYTICAL AND SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Compound	Molar conductivity $\times 10^{-3}$ siemens	Elemental analysis % Found (calcd.)				Electronic absorbance (cm^{-1}) ($\varepsilon \times 10^3$) dm^3 $mole^{-1}$ cm^{-1}		IR spectral data (cm^{-1})			
		C	H	N	M	UV Visible	Reflectance	ν(O—H)	ν(C=N)	ν(M—N)	ν(M—O)
$C_8H_9NO_2$	2.06	62.69 (62.57)	6.20 (5.96)	9.25 (9.27)	—	32,733 (7.02) 39,215 (8.13)	—	3350	1640 s	—	—
$UO_2(C_8H_8NO_2)_2$	0.27	30.21 (33.68)	2.81 (3.19)	4.89 (4.61)	40.38 (41.73)	23,800 (12.4) 27,020 (18.4) 35,714 (19.6) 39,215 (20.42)	15,432 21,810 28,288	3290 b	1600 s	580 m	480 m
$MoO_2(C_8H_8NO_2)_2$	1.56	43.72 (44.78)	3.52 (3.72)	6.64 (6.52)	22.14 (22.41)	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 m	425 m
$VO(C_8H_8NO_2)_2$	0.30	52.21 (52.31)	4.71 (4.36)	7.46 (7.58)	13.45 (13.87)	27,397 (6.89) 30,959 (6.47) 33,222 (7.00)	12,391 17,241 23,584	3200 b	1555 s	618 m	470 m

in literature suggesting bonding through phenolic oxygen and oximic nitrogen[10]. 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 spectrum of VO(II) complex shows 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.[12]

TABLE-2
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR $UO_2(C_8H_8NO_2)_2$

a (Å) = 8.6674 ± 0.0116	Volume $(Å)^3$ = 2244.1730
b (Å) = 8.3080 ± 0.0121	D_{cal} (gm/cm^3) = 1.68
c (Å) = 31.8263 ± 0.0829	D_{obs} (gm/cm^3) = 1.66
α = 90°	Z = 4
β = 78.3°	Crystal system = Monoclinic
γ = 90°	Space group = $P_{2/m}$

I/I_0	D_{obs}	D_{cal}	h	k	*l*
54	4.404	4.400	0	1	6
89	4.118	4.119	0	2	1
57	3.894	3.876	2	0	5
64	3.835	3.818	2	1	2
66	3.779	3.782	2	1	0
64	3.671	3.678	2	1	4
60	3.526	3.535	2	1	5
73	3.488	3.485	1	2	4
100	3.416	3.409	1	2	–3
29	3.064	3.071	1	1	–8
52	2.799	2.805	3	0	5
55	2.652	2.660	2	2	–4
40	2.482	2.477	1	3	5
33	2.436	2.437	3	1	8
39	2.293	2.299	2	3	4
50	2.195	2.189	3	0	–7
37	1.958	1.958	3	3	–1
39	1.896	1.895	4	2	10
40	1.606	1.608	5	1	10

TABLE-3
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR $MoO_2(C_8H_8NO_2)_2$

a (Å) = 8.7043 ± 0.0090	Volume $(Å)^3$ = 2283.9650
b (Å) = 8.3367 ± 0.0205	D_{cal} (gm/cm^3) = 2.266
c (Å) = 32.0130 ± 0.6557	D_{obs} (gm/cm^3) = 2.482
α = 90°	Z = 8
β = 79.48°	Crystal system = Monoclinic
γ = 90°	Space group = $B_{2/m}$

I/I_0	D_{obs}	D_{cal}	h	k	l
85	4.440	4.440	0	1	6
74	4.318	4.324	1	0	7
100	3.951	3.947	2	0	–2
83	3.807	3.806	2	1	0
86	3.668	3.671	2	1	4
67	3.659	3.657	2	0	6
77	3.443	3.442	1	2	–3
61	3.351	3.351	2	1	6
40	3.113	3.121	1	2	–5
50	3.057	3.046	0	2	7
44	2.889	2.882	3	0	3
41	2.780	2.781	2	2	–3
44	2.740	2.750	3	1	2
36	2.430	2.426	3	1	8
39	2.341	2.345	3	1	9

The IR spectra of the metal complexes suggest 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.[13]

The electronic absorption spectra of metal complexes display various d–d transitions and charge transfer transitions in the UV-Vis region. UO_2(VI) complex shows strong absorption bands at 15,432, 21,810 and 23,800 cm^{-1} which are assignable to d–d transitions. The band at 28,388 cm^{-1} could be due to charge transfer transition[14]. MoO_2(VI) complex show weak absorption bands at 13,698, 18,214 and 20,790 cm^{-1}, which could be due to d–d transition and a charge transfer transition at 28,449 cm^{-1}. The solution spectrum showing intraligand band at 33,557 cm^{-1} can be assigned to octahedral structure of MoO_2(VI) group. The solution spectrum of VO(II) complex shows bands at 27,397, 30,959 and 33,222 cm^{-1}. The solid spectrum shows d–d transitions at 12,391, 17,241 and 23584 cm^{-1} characteristic of VO(II) complexes. The band at 28,638 cm^{-1} could be assigned as charge transfer transition[15]. 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.[16]

TABLE-4
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR $VO(C_8H_8NO_2)_2$

a (Å) = 8.6845 ± 0.0151	Volume $(Å)^3$ = 2264.3160
b (Å) = 8.3302 ± 0.0177	D_{cal} (gm/cm^3) = 2.158
c (Å) = 31.9204 ± 0.0696	D_{obs} (gm/cm^3) = 2.361
α = 90°	Z = 8
β = 78.68°	Crystal system = Monoclinic
γ = 90°	Space group = $C_{2/c}$

I/I_0	D_{obs}	D_{cal}	h	k	l
38	4.421	4.387	0	1	6
48	4.165	4.160	0	2	0
61	4.113	4.118	2	0	–1
37	3.791	3.798	2	1	0
100	3.673	3.650	2	1	4
24	3.541	3.545	0	1	8
33	3.317	3.314	1	0	–8
40	3.179	3.184	2	1	7
43	3.144	3.161	1	0	10
28	2.919	2.927	2	2	4
18	2.800	2.792	3	0	5
25	2.754	2.758	2	–2	6
28	2.727	2.732	3	1	3
24	2.643	2.640	3	0	7
34	2.549	2.549	1	3	4
28	2.456	2.460	1	3	–4
16	1.728	1.730	3	3	–7

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 observed Hamiltonian parameters were characteristic of vanadyl complexes with square pyramidal geometry.[17]

A good quality of X-ray diffractogram of the complexes indicates the high crystallinity of these complexes. The major refluxes were measured and corresponding 'd' values were obtained using Bragg's equation ($n\lambda = 2d \sin\theta$). The independent indexing of major refluxes was carried out using least square method. The Miller indices h, k, *l* were calculated and refined by using Back-cal program on computer. The complexes were successfully indexed to monoclinic crystal

system with formula factor Z = 4 for MoO_2(VI) and VO(II) complexes and Z = 8 for UO_2(VI) complex.

The lattice parameters along with 'd' values are summarized in Tables 2–4. The correctness of these values was confirmed by comparing the observed density with that calculated from the X-ray diffractogram. It may be concluded that UO_2(VI) and MoO_2(VI) complexes are octahedral in structure and crystallize in monoclinic system with space group $P_{2/m}$ and $B_{2/m}$. VO(II) complex is square pyramidal and crystallizes in monoclinic system with space group $C_{2/c}$.[18]

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