

Synthesis, Spectral and Thermal Studies on Dioxouranium(VI) Complexes of Isatin-3-oxime

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A new series of dioxouranium(VI) complexes derived from indole-2,3-dione (isatin) with hydroxylamine hydrochloride (isatin-3-oxime) were synthesized and characterized by spectral studies, thermal analysis, molar conductance and elemental analysis. A group of six mixed ligand complexes were prepared with various anions such as acetate, lactate, nitrate, perchlorate, sulphate and thiocyanate as secondary ligands and isatin-3-oxime as primary ligand. Isatin-3-oxime acts as a bidentate chelating ligand and coordinates to UO_2^{2+} the metal ion through azomethine nitrogen and carbonyl oxygen atoms of isatin moiety. The complexes were screened for their antimicrobial activities and thermal stabilities.

Key Words: Dioxouranium(VI), Antimicrobial activity, Isatin-3-oxime, Complexes.

INTRODUCTION

A number of complexes with linear dioxouranium(VI) ion in 7,8 or 10 coordination number are known¹⁻⁵. In the present paper, the synthesis and characterization of a series of complexes of dioxouranium(VI) with oxime derived from isatin by condensation with hydroxylamine hydrochloride is reported. In all the complexes the isatin-3-oxime acts as the primary ligand and various anions as secondary ligands.

EXPERIMENTAL

Isatin-3-oxime (IOH) was prepared by the condensation of isatin with hydroxylamine hydrochloride in equimolar ratio. The reaction mixture was refluxed for 8-10 h in presence of sodium acetate. The solution is concentrated and cooled to get yellow crystals of the oxime, which was filtered and recrystallized from alcohol (m.p. 210°C).

The acetate complex was prepared by refluxing alcoholic solutions of uranyl acetate dihydrate and isatin-3-oxime in 1:2 molar ratio for 8 h. The

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solution on concentration gave a bright yellow solid which was filtered, washed with alcohol and finally with pet-ether. All other anionic complexes were prepared by substitution method⁶.

All the complexes were analyzed for their metal, carbon, hydrogen and nitrogen contents. The molar conductance of the complexes in methanol, nitrobenzene and acetonitrile were measured at room temperature ($28 \pm 2^\circ\text{C}$). The IR spectra of the ligand and the complexes were recorded in the range $4000\text{-}400\text{ cm}^{-1}$ using FTIR spectrophotometer using KBr pellets. The electronic spectra were recorded in an UV-visible spectrophotometer in the range $200\text{-}900\text{ nm}$. Thermal studies were carried out in a meter Thermal Analyzer Model TA 3000 at a heating rate of $10^\circ\text{C}/\text{min}$ in air over a temperature ranging from 30 to 900°C .

RESULTS AND DISCUSSION

The complexes are found to be non-hygroscopic and non electrolytes. They are sparingly soluble in methanol and chloroform but completely soluble in acetone and DMSO. The analytical data of the complexes are given in Table-1.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Complex	Molar mass	% Analysis, Calc. (Found)				
		C	H	N	S/Cl	U
[(UO ₂ (IOH) ₂ (NO ₃) ₂)]	718.13	26.74	1.67	11.69	-	33.16
	(718.23)	(26.12)	(1.51)	(11.24)	-	(33.89)
[(UO ₂ (IOH) ₂ (CH ₃ COO) ₂)]	712.13	33.70	2.53	7.86	-	33.42
	(712.01)	(33.21)	(2.24)	(7.53)	-	(33.52)
[(UO ₂ (IOH) ₂ (NCS) ₂)]	710.03	30.42	1.69	11.83	9.01	33.52
	(710.21)	(30.23)	(1.43)	(11.58)	(9.20)	(33.19)
[(UO ₂ (IOH) ₂ SO ₄)]	690.13	27.82	1.74	8.12	4.64	34.49
	(690.18)	(27.30)	(1.61)	(8.10)	(4.58)	(34.14)
[(UO ₂ (IOH) ₂ (ClO ₄) ₂)]	793.00	24.21	1.51	7.06	8.95	30.02
	(792.87)	(24.38)	(1.49)	(7.16)	(8.38)	(30.18)
[(UO ₂ (IOH) ₂ (C ₃ H ₅ O ₃) ₂)]	772.03	34.19	2.85	7.25	-	24.88
	(771.89)	(34.11)	(2.69)	(7.08)	-	(24.32)

The complexes were characterized on the basis of their infrared spectra. It is evident from the spectral data that on complex formation there is a considerable shift in the carbonyl group ($>\text{C}=\text{O}$) and also in the azomethine ($>\text{C}=\text{N}$) group indicating that the ligand binds to the metal ion through carbonyl oxygen and azomethine nitrogen atoms, supporting the bidentate nature of the ligand. The important IR spectral bands are given on Table-2. In the complexes the $>\text{C}=\text{O}$ absorption shows a down shift of $18\text{-}20\text{ cm}^{-1}$ compared to that of the ligand. The $>\text{C}=\text{N}$ group absorbs at 1636 cm^{-1} in

the ligand while it is shifted to a lower frequency in all the complexes. The N-H absorption of isatin moiety is increased by 20-30 cm^{-1} than in the free ligand. This is an evidence for the existence of isatin moiety in the ketonic form during complexation while the free ligand can exist in tautomeric forms. This further supports the coordination of carbonyl oxygen to the metal ion. A broad absorption band at 3420 cm^{-1} in the spectrum of ligand suggests intermolecular hydrogen bonding of -OH group. But in all the complexes a sharp band is observed in this region with an increase in frequency of 25-27 cm^{-1} indicating the disappearance of hydrogen bond.

TABLE-2
IR SPECTRAL (cm^{-1}) DATA OF THE COMPLEXES

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{O}-\text{H})$	$\nu(\text{U}-\text{O})$	$\nu(\text{U}-\text{N})$
IOH	1733	1636	3183	3420	-	-
$[(\text{UO}_2(\text{IOH})_2(\text{NO}_3)_2)]$	1715	1619	3200	3449	524	491
$[(\text{UO}_2(\text{IOH})_2(\text{CH}_3\text{COO})_2)]$	1715	1620	3200	3445	520	491
$[(\text{UO}_2(\text{IOH})_2(\text{NCS})_2)]$	1715	1618	3210	3440	522	492
$[(\text{UO}_2(\text{IOH})_2(\text{C}_3\text{H}_5\text{O}_3)_2)]$	1714	1619	3205	3450	524	491
$[(\text{UO}_2(\text{IOH})_2\text{SO}_4)]$	1715	1619	3210	3445	524	492
$[(\text{UO}_2(\text{IOH})_2(\text{ClO}_4)_2)]$	1714	1620	3209	3448	520	491

In all the complexes, the anions, *viz.*, NO_3^- , CH_3COO^- , NCS^- , $\text{C}_3\text{H}_5\text{O}_3^-$ and ClO_4^- are covalently bonded to the metal ion in a monodentate fashion. The IR spectra of sulphato complexes reveal the bidentate chelating nature of SO_4^{2-} ion, which is covalently bonded through oxygen atom. In the case of nitrate complex, the anions are covalently bonded to the metal ion unidentately. The thiocyanato complex exhibits a sharp band at 2063 cm^{-1} which is assigned to $\nu(\text{C}-\text{N})$ modes of coordinated thiocyanate ion which are absent in the spectra of ligand and other anionic complexes. Since $\nu(\text{C}-\text{N})$ is lower than 2100 cm^{-1} , the thiocyanate ion is coordinated to the metal ion through nitrogen atom in a unidentate fashion. In acetato and lactato complexes, the anions are monodentately bonded to the metal atom through (U-O) bonds. Thus uranium shows a coordination number of eight in all these complexes.

The UV-spectral data along with tentative assignments are detailed in Table-3. The electronic spectra of the ligand and the complexes were analyzed and arrived at the following conclusions. The ligand exhibits absorption bands at 367 nm and 291 nm which are assignable to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of $>\text{C}=\text{N}$ group. Two other absorption bands are observed at λ_{max} of 251 nm and 202 nm, which are attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the $>\text{C}=\text{O}$ group of isatin moiety. In the complexes $\pi \rightarrow \pi^*$ transitions exhibit red shift (lower energy) while the $n \rightarrow \pi^*$ transitions exhibit blue shift (higher energy). An absorption at 423 nm may be due to $\text{L} \rightarrow \text{M}$ charge transfer transitions. The electronic spectrum of $\text{UO}_2(\text{VI})$ complexes

exhibit ligand to metal charge transfer transition arising from the equatorial ligand orbitals to the *5f/6d* orbitals of uranium.

TABLE-3
UV SPECTRAL DATA

Compound	λ_{\max} (nm)	Tentative Assignment
IOH	251	n→ π^* of >C = O
	202	π → π^* of >C = O
	367	n→ π^* C = N
	291	π → π^* of C = N
[UO ₂ (IOH) ₂ X ₂]	243	n→ π^* of C = O (blue shift)
	210	π → π^* of C = O (red shift)
	356	n→ π^* of C = N (blue shift)
	301	π → π^* of C = N (red shift)
	423	L→M charge transfer transition

TG and DTA of [(UO₂(IOH)₂(CH₃COO)₂)] was studied in the temperature range 30 to 900°C in air. The complex do not show any mass loss upto 230°C and the absence of endothermic peak confirms the absence of either lattice held or coordinated water molecule. The first stage of decomposition between 230 and 390°C indicates the loss of ligand moieties (45.27%) leaving uranyl acetate. It is thermally stable upto 740°C, beyond which it decomposes. The final product of decomposition was U₃O₈ (39.45%) at a temperature of 835°C. The DTA peaks are observed at 270 and 344°C corresponding to the above mentioned decomposition product.

On the basis of these experimental evidences a general formula can be suggested for the complexes as [(UO₂(IOH)₂X₂)] where X = NO₃⁻, CH₃COO⁻, NCS⁻, C₃H₅O₃⁻ or ClO₄⁻ and 0.5SO₄²⁻. Thus a coordination number of 8 is assigned to uranium in all these complexes.

Antifungal activity

The ligand and the complexes were screened for their antifungal activities and the results are recorded in Table-4. The tested fungus was *Candida albicans*. The growth of the fungus was inhibited in presence of the ligand and the complex. The complexes show enhanced activity against *C. albicans*.

TABLE-4

Compound	Concentration of antifungal agent (%)	Growth of fungus after	
		24 h	48 h
SDA Control		+	+
IOH	0.5	-	-
[UO ₂ (IOH) ₂ (CH ₃ COO) ₂]	0.3	-	-
[UO ₂ (IOH) ₂ (ClO ₄) ₂]	0.3	-	-

'+' shows growth of fungus, '-' shows inhibition growth

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