

Studies on Spectral Properties of Uranyl(VI) Complexes with *o*-Hydroxy Oximes

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Three oximes were synthesised by reacting 5-nitrosalicylaldehyde, 2-hydroxy-1-naphthaldehyde and resacetophenone with hydroxylamine hydrochloride. These oximes were used to synthesise uranyl(VI) complexes using aqueous uranyl acetate. Uranyl complexes were characterised by elemental analyses, molar conductivity, electronic absorption spectra and infrared spectra. On the basis of experimental data probable structures were assigned to these uranyl complexes.

Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals.¹⁻⁵ Literature survey reveals the extensive research done on transition metal complexes; hence it was thought worthwhile to study the uranium(VI) complexes for the purpose of our research.

EXPERIMENTAL

All the chemicals and solvents used for synthesis were of LR grade. Oximic ligands were synthesised by treating hydroxylamine hydrochloride with respective aldehyde or ketone in presence of sodium acetate. Aldehyde or ketone (0.1 M) was dissolved in methanol and mixed with excess of hydroxylamine hydrochloride (in minimum quantity of distilled water). The mixture was stirred continuously with addition of sodium acetate solution (1 M) till oximation is complete. The precipitate obtained was filtered and washed with water to remove excess of hydroxylamine hydrochloride. These oximes were recrystallised from aqueous methanol. Uranyl(VI) complexes were synthesised by mixing ligand solution in methanol with aqueous solution of uranyl(VI) acetate in 2 : 1 molar ratio. Solution was stirred for 2 h and pH was adjusted around 7. Complexes were digested on water bath for 0.5 h. These complexes were filtered and washed with water and then recrystallised from suitable solvents. The elemental analyses of ligands and complexes were carried out using reported methods⁶. Uranyl(VI) complexes were tested for solubility in different polar and nonpolar solvents. Conductivity of 10^{-3} molar solutions of ligands and complexes were recorded on Toshniwal conductivity meter using DMSO as solvent. The electronic absorption in the

UV-Vis region as well as diffused reflectance spectra were recorded using BaSO₄ as diluent on spectrophotometer supplied by Shimadzu Corporation. Infrared spectra were recorded on FTIR-4200 supplied by Shimadzu using KBr pellets.

RESULTS AND DISCUSSION

Table-1 summarises analytical and physico-chemical properties of uranyl(VI) complexes. All the ligands and uranyl(VI) complexes were crystalline in nature. The elemental analyses of these compounds agree very well with theoretically calculated values. All the uranyl complexes have metal : ligand stoichiometry 1 : 2. All the complexes are anhydrous in nature and are stable at room temperature. The ligands as well as complexes are insoluble in water. The uranyl(VI) complexes are insoluble in petroleum ether, chloroform, benzene, ethyl acetate and methanol but are soluble in DMSO, DMF and nitrobenzene. The 10⁻³ M solutions of the complexes in DMSO were used to determine molar conductance. The low molar conductance values suggest non-ionic character of ligand as well as complexes. All the uranyl(VI) complexes were having colour yellowish orange to brown.

TABLE-1
ANALYTICAL AND PHYSICO-CHEMICAL PARAMETERS OF LIGANDS AND UO₂(VI)
COMPLEXES.

Compound	Colour	m.p. (°C)	m.w.	Molar conductivity × 10 ⁻³ siemens	% found (calcd.)			
					C	H	N	M
C ₇ H ₆ N ₂ O ₄ 5-NSALO (HL ₁)	Yellow	126	182.1	8.3	46.01 (46.16)	3.26 (3.32)	14.57 (15.37)	-
UO ₂ (C ₇ H ₅ N ₂ O ₄) ₂ [UO ₂ (L ₁) ₂]	Orange yellow	-	632.2	11.8	26.26 (26.60)	1.38 (1.59)	8.02 (8.86)	42.56 (42.71)
C ₁₁ H ₉ NO ₂ 2-HNAO (HL ₂)	Cream white	157	187.2	3.8	70.16 (70.58)	5.11 (4.85)	7.47 (7.48)	-
UO ₂ (C ₁₁ H ₈ NO ₂) ₂ UO ₂ (L ₂) ₂	Brown	-	642.4	13.6	41.07 (41.14)	2.26 (2.51)	4.32 (4.36)	42.11 (42.03)
C ₈ H ₉ NO ₃ RAPO (HL ₃)	White	198	167.2	8.0	57.32 (57.48)	5.28 (5.43)	8.06 (8.38)	-
UO ₂ (C ₈ H ₈ NO ₃) ₂ UO ₂ (L ₃) ₂	Brown yellow	-	602.4	8.8	31.43 (31.90)	2.40 (2.68)	4.52 (4.65)	39.24 (39.52)

TABLE-2
SALIENT FEATURES OF ELECTRONIC ABSORPTION SPECTRA

Compound	Electronic Absorbance (cm ⁻¹)	
	UV-Vis	Reflectance
HL ₁	32840	24390
	38095	48661
UO ₂ (L ₁) ₂	24390	21408
	33445	25000
HL ₂	28328	26178
	45248	45454
UO ₂ (L ₂) ₂	24390	27359
	28328	42462
HL ₃	30303	20661
	32258	27778
UO ₂ (L ₃) ₂	25641	27624
	36231	54248

The salient features of absorption frequencies of ligands and complexes are summarised in Table-3. The data indicate that oximes exhibit characteristic $>C=N$ stretching frequencies around 1640–1600 cm⁻¹ and hydroxyl stretching frequencies around 3300 cm⁻¹. Comparison of IR spectra of ligand and uranyl(VI) complexes show absence of sharp O—H stretching bands in the region greater than 3400 cm⁻¹ suggesting participation of phenolic oxygen in coordination with metal after deprotonation. The $>C=N$ stretching frequency is shifted to lower wavenumber suggesting involvement of oximic nitrogen in coordination with UO₂(VI) ion. The IR spectra show additional bands in the region 500–480 cm⁻¹ and 610–580 cm⁻¹ are assignable to stretching vibration (U—O) and (U—N) respectively. These assignments are supported by Nakamoto.⁷ The bands in the region of 900 ± 40 cm⁻¹ correspond to (O—U—O) moiety.^{8,9} Thus all these oximes coordinate to the uranyl ion through oxy-imino nitrogen and phenolic oxygen after deprotonation, hence acting as bidentate ligands.

TABLE-3
SALIENT FEATURES OF INFRARED ABSORPTION SPECTRA (cm⁻¹)

Compound	$\nu(O=U=O)$	$\nu(O-H)$	$\nu(C=N)$	$\nu(M-N)$	$\nu(M-O)$
HL ₁	—	3300 (s)	1620 (m)	—	—
UO ₂ (L ₁) ₂	860 (m)	3200 (b)	1600 (m)	580 (w)	500 (w)
HL ₂	—	3300 (s)	1640 (m)	—	—
UO ₂ (L ₂) ₂	900 (m)	3200 (b)	1620 (m)	570 (w)	480 (w)
HL ₃	—	3372 (s)	1645 (m)	—	—
UO ₂ (L ₃) ₂	880 (m)	3400 (s)	1620 (m)	610 (w)	480 (w)

Uranyl(VI) complexes were characterised with respect to various electronic transitions associated with it in the UV-Vis spectral region. Because of poor solubility of the complexes in common organic solvents diffused reflectance studies were performed. Experimental observations are summarised in Table-2. The UV-Vis absorption spectra as well as reflectance spectra exhibit transitions around 25000 cm^{-1} which are charge transfer transitions. Shoulders observed around 21000 cm^{-1} in uranyl complexes are due to vibration of the (O—U—O) group. Also the spectra exhibit no bands below 20000 cm^{-1} proving that the complexes may have more than four equatorial groups.^{10,11} Moreover, the observation of bands in the region $25000\text{--}24000\text{ cm}^{-1}$ may be assigned to the characteristic states of excited electronic states of the uranyl(VI) ion.¹² Based on the following observations uranyl(VI) complexes may have *cis* or *trans* octahedral geometry.

All the oximic ligands and uranyl complexes were tested for their anti-microbial activity *in vitro* against gram negative bacteria (*Escherichia coli*) by paper disc method. Table-4 provides the experimental data for anti-microbial activity. Bacteria cultures were incubated at 37°C for 24 h using nutrient broth as medium. 5-nitrosalicylaldehyde oxime has shown +ve whereas 2-hydroxy-1-naphthaldehyde oxime and resacetophenone oxime have shown -ve activity. Uranyl complexes with 2-hydroxy-1 naphthaldehyde oxime and resacetophenone oxime possess antimicrobial activity. Minimum inhibition concentration was found to be 150 and 270 ppm respectively. The antimicrobial activity of uranyl complex derived from 5-nitrosalicylaldehyde oxime is under investigation. This data confirms antimicrobial activity of uranyl complexes. Hence, we recommend uranyl complexes for antimicrobial application.

TABLE-4
ANTIBACTERIAL ACTIVITY OF OXIMES
AND URANYL(VI) COMPLEXES

Compound	MIC (ppm)
HL ₁	+ve
UO ₂ (L ₁) ₂	Activity to be determined
HL ₂	-ve
UO ₂ (L ₂) ₂	150 ppm
HL ₃	-ve
UO ₂ (L ₃) ₂	270 ppm

+ve represents antimicrobial activity and -ve indicates no activity.

Conclusively, from all the various analytical and spectral investigations it is suggested that uranyl complexes of these oximes have characteristic structural configuration having octahedral geometry. Complexes may be assigned structures as shown in Fig. a and Fig. b.

Representative structure is as shown in Fig. a and Fig. b.

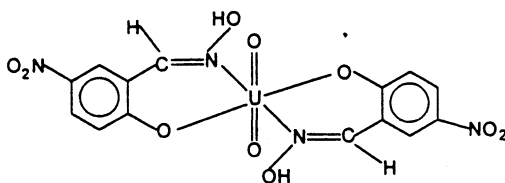


Fig. a. *Trans*-Octahedral $[UO_2(5NSAO)_2]$

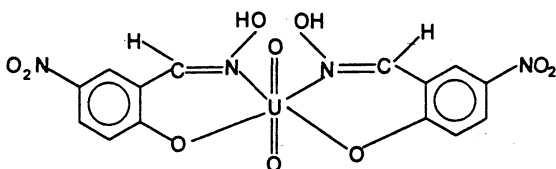


Fig. b. *Cis*-Octahedral $[UO_2(5NSAO)_2]$

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