

Studies of Dioxouranium(VI) Metal Complexes with a Schiff Base of 2-Aminopyridine

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A series of new dioxouranium(VI) complexes with a Schiff base derived from 2-aminopyridine, *i.e.*, 2-N-[benzalidene] aminopyridine (BAPy) has been synthesized. Analytical, conductance, mol. wt. and spectral data reveal that the complexes have the general composition $UO_2X_2(BAPy)_2$ ($X = NO_3, Br, I, NCS^-$ or OAc^-). Uranium atom is either 6 or 8 coordinated depending upon the anions present in these complexes. NMR and antifungal studies of representative compounds have been done successfully.

INTRODUCTION

Actinide metal ions specially thorium(IV) and dioxouranium(VI) are of great interest for most of the workers because of their large size and high positive charge¹. In the recent past studies on these metals with various oxygen and nitrogen donor ligands including Schiff's bases^{2–10} have been reported. In this present paper we wish to report the investigation on high coordination compounds with a Schiff base of 2-amino pyridine namely 2-N-[benzalidene] amino pyridine (BAPy).

The ligand was found to act as neutral monodentate (N) ligand which leads to the formation of high coordination compounds having the general composition $UO_2X_2(BAPy)_2$ ($X = NO_3, Br^-, I^-, NCS^-$ or OAc^-). These complexes are generally soluble in common organic solvents and are quite stable and can be stored at room temperature except iodide complex which decomposes slowly at room temperature with evolution of iodine vapours.

EXPERIMENTAL

All the reagents were used as supplied by B.D.H. and Merck. Uranyl nitrate was obtained commercially and all other salts were prepared by respective reported methods^{11–14}.

IR spectra were recorded on Perkin-Elmer infrared spectrophotometer model 521 KBr/CsI in the range 4000–200 cm^{-1} . Nitrogen was estimated in the laboratory by Kjeldahl's method. All other physico-chemical measurements were done according to the reported method⁵ and metal was estimated as U_3O_8 .¹⁵

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TABLE-1
ANALYTICAL AND CONDUCTANCE DATA OF DIOXOURANIUM(VI) COMPLEXES
OF (BAPy) 2-N-[BENZALIDENE] AMINO PYRIDINE

Complex (Colour)	m.p. (°C)	Analysis, found (calcd.) %			m.w. found (calcd.)	Ω_M ohm ⁻¹ cm ² mole ⁻¹
		M	N	Anion		
UO ₂ (NO ₃) ₂ ·2BAPy (Yellow)	202	31.2 (32.8)	12.2 (11.5)	11.2 (12.6)	720 (726)	3.6
UO ₂ Br ₂ ·2BAPy (Yellow)	208	28.2 (29.9)	8.1 (7.0)	19.2 (20.1)	791 (794)	4.1
UO ₂ I ₂ ·2BAPy (yellow)	210	25.1 (26.8)	7.1 (6.3)	27.3 (28.6)	880 (888)	4.3
UO ₂ (NCS) ₂ ·2BAPy (Yellow)	206	30.2 (31.3)	12.3 (11.2)	14.3 (15.4)	744 (750)	3.5
UO ₂ (OAc) ₂ ·2BAPy (Yellowish brown)	188	30.1 (31.6)	7.9 (7.4)	14.2 (15.7)	745 (752)	3.8

Preparation of ligand

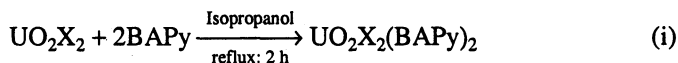
A solution of distilled aromatic aldehyde (benzaldehyde) (1 mmole) in absolute alcohol (50 mL) was mixed with corresponding amine, *i.e.*, 2-amino pyridine (1.1 mmole) in the same solvent and the mixture was refluxed for 3–4 h. On cooling yellow product was separated which was filtered off and recrystallized in the same solvent and dried *in vacuo* over anhydrous CaCl₂.

Preparation of complexes

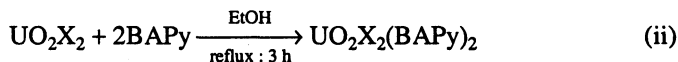
The respective metal salt solutions were treated with ligand solution in required molar concentrations (*ca.* 1:2). In some cases complexes were isolated immediately in cold while in some cases in hot solutions after refluxing the resulting solutions for 2–3 h at 60–80°C. The solvents used were ethanol or isopropanol. The complexes were collected, washed with solvent and finally with anhydrous ether and dried *in vacuo* over CaCl₂.

RESULTS AND DISCUSSION

The reaction of dioxouranium(VI) metal salts with Schiff base ligand results in the formation of UO₂X₂(BAPy)₂ (X = NO₃⁻, Br⁻, I⁻, NCS⁻ or CH₃COO⁻) according to the general equations:



(X = NO₃⁻ or OAc⁻)



(X = Br⁻, I⁻, or NCS⁻)

The elemental analyses of these complexes are given in Table-1. These complexes are quite stable at room temperature (*ca.* 25°C) except the iodide one which decomposes to sticky mass after a few weeks. All are sufficiently soluble in common organic solvents.

Electrical conductance values for these complexes were determined in PhNO₂ medium and it was inferred that all these complexes are essentially non-electrolyte which is in general agreement with stability of U-halogen bond found earlier¹⁰. The ratio of molecular weights to be calculated is *ca.* 0.98 which shows that these complexes are monomeric in solution.

The complexes were found to be either diamagnetic or weakly paramagnetic depending upon the diamagnetism of the other ions and the surrounding fields^{16, 17}. The magnetic susceptibilities are independent of field strength and temperature¹⁸. The ground states of these compounds contain no unpaired electrons. The compounds are, therefore, expected to be diamagnetic as observed^{17, 19, 20}.

Infrared spectra

The IR spectra of the complexes, when compared with those of the ligand show a considerable shift in $\nu(\text{C}=\text{N})$ azomethine absorption to the lower frequency indicating a decrease in the stretching force constant of $\text{C}=\text{N}$ as a consequence of the coordination through azomethine nitrogen, the double bond character between carbon and nitrogen is reduced²¹⁻²⁴. The strong bands observed at *ca.* 1570–1575 and 1050–1055 cm⁻¹ are tentatively assigned to antisymmetric and symmetric $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{N})$ of pyridine ring which remain practically unchanged in frequency and band intensities, revealing non-involvement of pyridine nitrogen and metal bonds. Some new medium and weak bands are observed in the range of 450–420 cm⁻¹ in the complexes where the ligand has no absorptions. These bands are tentatively assigned to $\nu(\text{M}-\text{N})$ stretching modes^{25, 26}. The partial IR data is given in Table-2.

TABLE-2
PARTIAL IR DATA FOR DIOXOURANIUM(VI) COMPLEXES OF (BAP_y)
2-N-[BENZALIDENE] AMINOPYRIDINE

Complex	$\nu(\text{C}=\text{N})$ str. (azomethine)	Pyridine ring breathing and deformation bands		$\nu(\text{M}-\text{N})$
		$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{N})$	
BAP _y	1600 s	1570 m	1050 m	—
UO ₂ (NO ₃) ₂ (BAP _y) ₂	1540 s	1575 m	1055 m	450 m
UO ₂ Br ₂ (BAP _y) ₂	1550 s	1570 sh	1050 sh	430 m
UO ₂ I ₂ (BAP _y) ₂	1545 s	1572 sh	1050 m	420 m
UO ₂ (NCS) ₂ (BAP _y) ₂	1540 s	1575 m	1055 m	430 m
UO ₂ (CH ₃ COO) ₂ (BAP _y) ₂	1550 s	1570 m	1050 m	430 m

NMR spectral studies

The NMR spectral study of one of the representative compounds was recorded and was compared with that of the ligand. The NMR spectra of a compound, *i.e.*, $\text{UO}_2(\text{NO}_3)_2(\text{BAPy})_2$ has been recorded either in CDCl_3 or in DMSO-d_6 . The important NMR signals of the ligand are 8.45549 (d); 7.52431 (d); 7.65445 (qt); 6.71831 (d), 4.56626 (qt), 4.24862 (s) and those of the complex $\text{UO}_2(\text{NO}_3)_2(\text{BAPy})_2$ are 8.45559, 8.43182, 8.00776 (d), 7.52441 (t), 7.66445 (qt), 6.71831–6.58978 (d), 6.62662–6.58187 (t), 5.35823 (s), 4.56622–4.39627 (qt) and 4.24628 (s).

TABLE-3
EFFECT OF VARIED CONCENTRATIONS OF DIFFERENT COMPLEXES ON THE
MEAN RADIAL GROWTH (IN cms.) OF FUNGAL COLONIES

Compound	<i>Peronospora sp.</i>			<i>Elbugo sp.</i>		
	30 mg/ 10 mL	20 mg/ 10 mL	10 mg/ 10 mL	30 mg/ 10 mL	20 mg/ 10 mL	10 mg/ 10 mL
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{BAPy}$	0.4*	0.6*	2.2	0.4*	0.5*	2.5
$\text{UO}_2\text{I}_2 \cdot 2\text{BAPy}$	2.0	3.2	3.5	1.9	3.0	3.6

Configuration of complexes

In halo and thiocyanato complexes both the anions are covalently bonded. In these cases, a six coordinated uranium atom may be considered. The IR data of $\text{UO}_2(\text{NO}_3)_2(\text{BAPy})_2$ suggests that nitrate groups are bidentate in nature²⁷. In nitrate complex bands at 1510 (ν_1), 1300–1280 (ν_4), 1030 (ν_2), 810 (ν_6), 750 (ν_3) and 720 (ν_5) appear in IR spectra similar to nitrate the acetate ions are also a potential bidentate ligands; towards uranyl group²⁸. In the present case IR spectra of acetate complex show two bands at 1540 and 1470 cm^{-1} attributed to antisymmetric and symmetric vibrations of COO^- respectively. Thus 8 coordinated U-atom is present in $\text{UO}_2(\text{NO}_3)_2(\text{BAPy})_2$ and $\text{UO}_2(\text{CH}_3\text{COO})_2(\text{BAPy})_2$.

Antifungal studies

Antifungal activities of two of the representative complexes were done successfully. The radial growth and paper disc methods were used to evaluate antifungal activities²⁹. These activities were checked on *Peronospora sp.* and *Elbugo sp.* (Two fungi which were grown on PDA culture on living host tissue, *i.e.*, *Brassica campestris*. Inoculation was made from infected inflorescence of *Brassica sp.* in petriplates containing PDA medium. 10 mm paper disc dipped in solutions of complexes in DMF in varied concentrations^{30,31} were put on petriplates before inoculating them with the fungus. The plates containing unamended PDA were maintained as control. The inoculated plates were incubated at $25 \pm 1^\circ\text{C}$ for 5 days. The radial growths of the fungal colonies were measured on 6th day and the data was statistically analysed. Table-3 shows the effect of concentrations of the complexes on the mean radial growth (in cm) of fungus. The minimum value is shown by asterisk (*). The control petriplate which

does not contain any disc of complex solution shows the radial growth of 4.0–4.5 cm for fungal colonies

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