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Synthesis, Spectral, Antimicrobial and Thermogravimetric Studies of Th(IV) and UO_2(VI) Metal Complexes with Schiff Base

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Schiff base was obtained using 2-nitro benzaldehyde and 2-amino pyridine to prepare new complexes of thorium(IV) and dioxouranium(VI) metals by various anions. The synthesized ligands and complexes were analytically studied through spectral studies, elemental analysis and conductance measurements. The complexes showed various co-ordination number and their toxic effects to bacterial and fungal genus was studied by two different methods of measurement.

Key Words: Synthesis, Analytical studies, Thorium(IV) and dioxouranium complexes, Schiff base, Toxicity.

INTRODUCTION

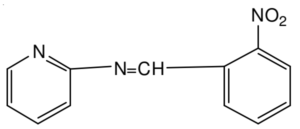
Thorium(IV) and dioxouranium(VI) metal form complexes with variety of Schiff bases and exhibit high coordination numbers. Their enormous complex forming tendency is attributed to the vacant inner 5*f* sub shell which can expand greatly to accommodate a number of ligands. The greater spatial extension of 5*f* orbitals of actinides along with the fact that these orbitals are diffused at the periphery of atom make them suitable to form number of complexes because in such situation the orbitals are disturbed by ligands. Hence actinide complexes are covalent in nature[1].

In this present work the complexes of Th(IV) and UO_2(VI) exhibit coordination number as high as 10 when they are complexed with a Schiff base derived from 2-amino pyridine and 2-nitrobenzaldehyde; *viz*., 2N(2-nitrobenzalidine)aminopyridine.

EXPERIMENTAL

All the chemicals used were of AR grade and were used with further purification wherever necessary. Elemental analysis were carried on Elemental Vario EL III Carlo Erba 1108 CDRI, Lucknow. Conductivity measurements for the complexes have been carried out on Elico 01/01 cell type conductivity bridge. Molecular weights were determined in freezing $PhNO_2$ using Beckmann thermometer method cryoscopically in the laboratory. IR spectra were taken through Shimadzu 8201 PC (4000-400 cm^{-1}) from CDRI, Lucknow. Mass spectra were obtained through Jeol SX-102 (FAB), CDRI, Lucknow. PMR spectra of selected samples were recorded on τ scale through Bruker Avance IT 400 NMR spectrometer SAIF Punjab University, Chandigarh. Electronic spectral studies were done through Perkin Elmer Lambda 15 from CDRI, Lucknow. TGA were carried on Mettler TG balance from Central instrumentation Laboratory from NIPER Mohali. Biocidal studies of representative complexes were conducted on fungal and bacterial species by paper disc method on PDA medium in our laboratory for which the complexes were dissolved in DMF.

Synthesis of ligand: Solution of 2-nitrobenzaldehyde (1 mmol) in *ca.* 30 mL ethanol was mixed with solution of 2-amino pyridine (1 mmol) in *ca.* 30 mL ethanol. The resultant solution was refluxed in round bottom flask fitted with water condenser for 6-8 h. On cooling Schiff base crystallized out which was filtered and recrystallized with proper solvent. The structure of ligand is given in Fig. 1.



2-NBAPy

Fig. 1

Preparation of complexes: Th^{4+} and UO_2^{2+} complexes of Schiff base (2-NBAPy) were prepared by refluxing the nitrate, iodide, isothiocynate, perchlorate salts of Th^{4+} and UO_2^{2+} in proper M:L ratio using ethanol solvent. Uranyl acetate was also complexed with 2-NBAPy in proper M:L ratio. The complexes were left in petri dish to obtain crystalline product and were recrystallised with ethanol.

RESULTS AND DISCUSSION

The analytical data for the ligand and its Th(IV) and UO_2(VI) complexes are listed in Table-1. It is observed that most of the complexes are non-hygroscopic and anhydrous as is evident from molecular weight and hydrogen percentages; which are nearly same for theoretical and experimentally calculated data. It is evident from the results that ratio of m.w. for $ThX_4 \cdot 2L$ ($X = NO_3^-$), $ThX_4 \cdot 4L$ ($X = NCS^-$), for observed and calculated approaches unity (0.98); suggestive of the fact that no change corresponding to ionization occurs in solution for these complexes. This fact is found valid for $UO_2X_2 \cdot 2L$ ($X = NO_3^-$, NCS^-, CH_3COO^-) also[2].

For $ThI_4 \cdot 4L$, this ratio is approximately 0.53; 0.36 for $UO_2(ClO_4)_2$ 4L and approximately one-fifth for $Th(ClO_4)_4 \cdot 6L$. This is suggestive of the fact that anions of the complexes are ionizable, primary valencies of complex and that they ionize furnishing more than one ion in solution[3].

IR spectral studies: For 2-NBAPy the mass spectrum produces (M + 1) peak at m/z 228 of 90 % intensity approx. Other significant peak a m/z 136 of 80 % intensity is obtained after loss of nitrobenzene moiety[4].

When the IR spectra of ligands are compared with those of complexes then shift in the azomethine (-C=N-) peaks are observed through which the metal atom is believed to be bonded thus the azomethine bond is considered to be a part of coordination[5,6]. Usually the bond in Schiff base ligands are observed around 1599

TABLE-1
ANALYTICAL RESULTS OF 2NBAPy AND ITS COMPLEXES

Base/complex	Elemental analysis (%): Obs. (calcd.)				m.p. (ºC)	Cond. Ω cm^{-1} eq^{-1}
	C	H	N	m.w.		
2NBAPy	61.68 (63.40)	4.28 (4.00)	17.30 (16.50)	228 (227)	172-177	–
$[\mathrm{Th(2NBAPy)_2(NO_3)_4}]$	35.76 (30.83)	2.48 (1.92)	8.53 (14.98)	915 (934)	226	2.30
$[\mathrm{Th(2NBAPy)_4I_2}]\mathrm{I_2}$	38.93 (42.60	2.78 (2.60)	13.67 (12.42)	450 (1352)	183	106.40
$[\mathrm{Th(2NBAPy)_4(NCS)_4}]$	56.21 (58.50)	3.21 (3.50)	18.72 (19.14)	1003 (1024)	209	1.50
$[\mathrm{Th(2NBAPy)_6}](\mathrm{ClO_4})_4$	36.80 (37.45)	2.50 (2.30)	8.80 (9.92)	307 (1538)	211	203.80
$[\mathrm{UO_2(2NBAPy)_2(NO_3)_2}]$	33.80 (34.12)	2.00 (2.13)	12.81 (13.20)	827 (844)	244	2.10
$[\mathrm{UO_2(2NBAPy)_2(NCS)_2}]$	35.80 (37.30)	2.00 (2.10)	13.11 (13.37)	819 (836)	169	1.70
$[\mathrm{UO_2(2NBAPy)_4}](\mathrm{ClO_4})_2$	40.82 (41.95)	2.10 (2.62)	10.68 (12.23)	494 (1373)	210	201.40
$[\mathrm{UO_2(2NBAPy)_2(CH_3COO)_2}]$	31.52 (40.30)	2.28 (2.80)	7.630 (7.08)	816 (833)	155	3.40
$[\mathrm{UO_2(2NBAPy)_2I_2}]$	32.89 (34.80)	2.11 (2.17)	7.08 (7.16)	809 (826)	179	1.94

cm^{-1} which shows a shift towards lower wave number in the complexes as 1527 cm^{-1} for thorium iodide complex, 1507 cm^{-1} for thorium isothiocynate complex and 1586 cm^{-1} for thorium perchlorate complex.

Similarly for uranyl complexes these values shift to lower wave numbers such as 1597 cm^{-1} for uranyl iodide complex and isothiocyanate complex and as low as 1527 cm^{-1} for uranyl nitrate complex.

Another significant feature in IR spectra of these complexes is appearance of M-N peaks which are found absent in the ligand. These peaks appears at 535 cm^{-1} for $\mathrm{Th(NO_3)_4\cdot(2\text{-}NBAPy)_2}$, 514 cm^{-1} for $\mathrm{ThI_4\cdot(2\text{-}NBAPy)_4}$, 509 cm^{-1} for $\mathrm{Th(NCS)_4}$ $\mathrm{(2\text{-}NBAPy)_4}$ and 513 cm^{-1} for $\mathrm{Th(ClO_4)_4}$. $\mathrm{(2NBAPy)_6}$ and at 543 cm^{-1} for $\mathrm{UO_2(CH_3COO)_2\cdot(2\text{-}NBAPy)_2}$, at 544 cm^{-1} $\mathrm{UO_2(NO_3)_2\cdot(2\text{-}NBAPy)_2}$, at 546 cm^{-1} $\mathrm{UO_2I_2\cdot(2\text{-}NBAPy)_2}$ and 514 cm^{-1} $\mathrm{UO_2(NCS)_2\cdot(2\text{-}NBAPy)_2}$.

Infra red absorption frequency for thiocyanato groups for $\mathrm{Th^{4+}}$ appears around 2065 (ν_1) and at 761 (ν_3) and for $\mathrm{UO_2^{2+}}$ complexes around 2070 (ν_1) and at 768 (ν_3)^7.

Electronic spectral studies: The electronic spectra of ligand show important n-π*at 330 nm and π-π* transition at 360 nm. In the complexes the M-N absorption band appears around 319.5 nm for thorium nitrate complexes as high as 368 nm for uranyl perchlorate complexes.

NMR spectral studies: PMR spectra of 2-NBAPy and one of its complex UO_2(2-NBAPy) $(NCS)_2$ was recorded. Peaks were obtained at δ values; 10.34 ppm 6-7 ppm suggesting shift for protons involved in pyridine ring. Values of coupling constant *J* for protons of pyridine ring appears at 0-1, 1-2, 5-6 and 7-9 MHz. Multiplets are observed in 6-8 ppm range for nitro benzaldehyde and amino pyridine ring which are not observed in the complex. This suggest formation of (-C=N-) linkage in base[8].

Thermogravimetric analysis: In this present work thermal studies and thermal decomposition kinetics of $[UO_2(2NBAPy)_2(NO_3)_4]$ is done. The complexes were heated at 10 °C/min rate and graphs were plotted as rate of loss of mass *versus* temperature. The details are plotted in Table-2. The data discussed in tables are based on equations given by Freemann-Caroll, Coats-Redfern and Horowitz-Metzer[9-11]. Thus a general scheme can be proposed for the thermal decomposition of complexes as:

$$ML_2X_{2-4} \longrightarrow MLaXb$$

$$MLaXb \xrightarrow{\text{in steps}} MO_2 \text{ or } M_2O_3 \text{ or } M_3O_8$$

where M = UO_2 or Th; L = 2NBAPy; X = I^-, CH_3COO^-, NO_3^-; a = 0.9-2.0, b = 1.0-3.5.

TABLE-2
VARIOUS PARAMETERS FROM DIFFERENT TGA METHODS FOR COMPLEX UNDER STUDY

Complex	Decomposition step	Method	E* (KJ)	A (S^{-1})	ΔS
$[UO_2(2NBAPy)_2(NO_3)_2]$	I	FC	0.0248	0.00290	-0.09
		CR	0.0223	0.00190	-0.06
		HM	0.9306	0.27790	-9.20
	II	FC	0.0381	0.09240	-3.09
		CR	0.0205	0.00860	-0.58
		HM	0.4040	0.38100	-12.7
	III	FC	0.0412	0.04370	-1.46
		CR	0.0006	0.00110	-0.03
		HM	0.2320	-1.28000	-4.20
	IV	FC	0.0394	0.01360	-0.45
		CR	0.0040	0.00138	-0.33
		HM	0.0960	0.20980	-0.70

On the basis of these studies the structure of the representative complex is given in Fig. 2.

Antimicrobial studies: Four complexes $[Th(2NBAPy)_4I_2]I_2$, $[Th(2NBAPy)_2(NO_3)_2]$, $[UO_2(2NBAPy)_2 I_2]$ and $[UO_2(2NBAPy)_4(NCS)_2]$ were chosen for antibacterial and antifungal studies. The complex $[Th(_2NBAPy)_4I_2]I_2$ is found to be an effective antifungal agent as it is toxic to both fungal species in increasing concen-

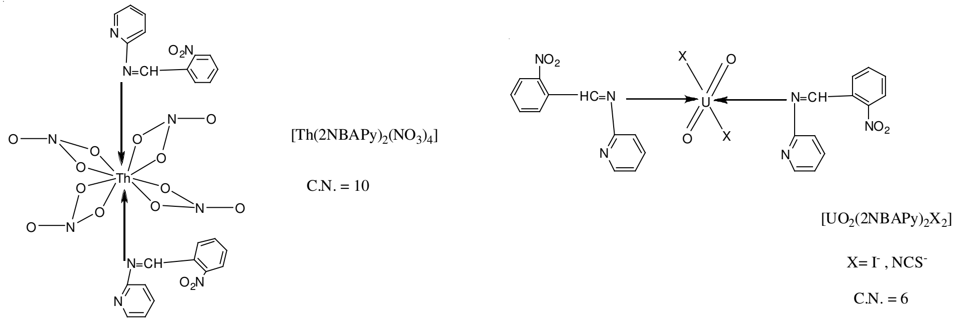


Fig. 2. Structure of represantative complexes

tration. But $[UO_2(2NBAPy)_4(NCS)_2]$ was found to be most effective antifungal agent at high concentration (*Aspergillus* sp.) or at moderate concentration (*Mucor* sp). For antibacterial characerstic $[Th(2NBAPy)_2(NO_3)_2]$ was found to be most effective at minimum and maximum concentration specifically[12-14] (Table-3).

TABLE-3
COLONY DIAMETER/RADIAL DISTANCE
OF COLONY AROUND SAMPLE DISC (cm)

Study	Complex (↓)	Pure DMF	20 % complex	40 % conc. in	60 % (DMF)
Antibacterial *E. coli*	$[Th(2\text{-}NBAPy)_2(NO_3)_2]$	1.1/1.0	0.8/1.6	0.7/1.7	0.5/2.0
Antifungal Aspergillus	$[UO_2(2\text{-}NBAPy)_4(NCS)_2]$	0.2/–	0.05/–	0.02/–	0.00/–
Antifungal Mucor	$[Th(2\text{-}NBAPy)_4I_2]I_2$	1.8/–	1.2/–	1.0/–	0.0/–

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