Asian Journal of Chemistry Vol. 12, No. 4 (2000), 1181–1184

Studies on 2N-[3-Nitrobenzalidene] Amino Pyridine Complexes of Thorium(IV) and Dioxouranium(VI)

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Thorium(IV) and dioxouranium(VI) complexes of Schiff base 2N-[3-nitrobenzalidene] amino pyridine (3-NBAPy) derived from 3-nitrobenzaldehyde and 2-amino pyridine having general composition $ThX_4 \cdot nL$ ($X = NO_3^-$ or NCS^-, $n = 2$; $X = I^-$, $n = 4$, L = 3-NBAPy; $X = ClO_4^-$, $n = 6$, L = 3-NBAPy) and $UO_2X_2 \cdot nL$ ($X = I^-$, NCS^-, NO_3^- or CH_3COO^-, $n = 2$; $X = ClO_4^-$, $n = 4$, L = 3-NBAPy) have been synthesized and characterized by molecular weight, conductance, IR and electronic spectral measurements. XRD for two of the representative samples has been done successfully.

INTRODUCTION

Schiff bases may form stable complexes with actinides because of the availability of nitrogen and in some cases oxygen atom also for coordination. Recently we have reported the synthesis and properties of actinides and oxocations complexes of various Schiff bases[1–10].

The literature survey clearly reveals that no report has been published on actinide complexes of 2N-[3-nitrobenzalidene] amino pyridine (3-NBAPy). In the present paper we wish to report the complexes of this ligand with UO_2^{2+}(VI) and Th(IV) in the presence of various anions, *e.g.*, NO_3^-, I^-, CH_3COO^-, NCS^- and ClO_4^-.

EXPERIMENTAL

The ligand 3-NBAPy was prepared as follows: A solution of 3-nitrobenzaldehyde (1 mmol) in absolute ethanol (20 mL) was mixed with 2-amino pyridine (1 mmol) in the same solvent (30 mL) and the mixture was refluxed for 5–6 h. On cooling a yellow crystalline product separated out, which was filtered off and recrystallized in the same solvent.

The metal complexes were prepared by mixing the corresponding metal salts and ligand in the required molar ratio in appropriate solvents, *viz.*, isopropanol or ethanol and refluxing the resulting mixture for 1–1½ h. In each case solid products were obtained on cooling, which were washed with the same solvent and finally with ether and dried *in vacuo* over $CaCl_2$.

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All the physicochemical measurements and analyses were performed as reported earlier[1, 4]

RESULTS AND DISCUSSION

The analytical data (Table-1) indicate that the general composition of the complexes are $ThX_4 \cdot nL$ ($X = NO_3^-$ or NCS^-, $n = 2$; $X = I^-$, $n = 4$, L = 3-NBAPy; $X = ClO_4^-$, $n = 6$, L = 3-NBaPy) and $UO_2X_2 \cdot nL$ ($X = I$, NCS^-, NO_3^- or CH_3COO^-, $n = 2$; $X = ClO_4^-$, $n = 4$, L = 3-NBAPy). The difference in the composition of these complexes is because of the coordinating nature of anions in these complexes. The molar conductance values of Th(IV) complexes in $PhNO_2$ indicate that nitrato and isothiocyanato complexes are non-electrolytes whereas the iodo and perchlorato complexes dissociate in this solvent. The iodo complex appears to be 1 : 2 while the perchlorato complex is a 1 : 4 electrolyte. The uranyl complexes (UO_2X_2(3-NBPAy)$_2$) ($X = I^-$, NO_3^-, NCS^-, CH_3COO^-) are essentially non-electrolytes in $PhNO_2$. The conductance value for perchlorato complex (UO_2(3-NBAPy)$_4$)(ClO_4)$_2$ suggests ionic perchlorate groups. Data on

TABLE-1
ANALYTICAL AND CONDUCTANCE DATA OF THORIUM(IV) AND DIOXOURANIUM(VI) COMPLEXES OF (3-NBAPy) 2N-(3-NITROBENZALIDENE) AMINO PYRIDINE

Complex (Colour)	m.p. (°C)	Analysis %, found (calcd.)			m.w. found (calcd.)	λ_{max} $ohm^{-1}\ cm^2\ mole^{-1}$
		M	N	Anion		
$Th(NO_3)_4 \cdot 2$(3-NBAPy)	198	24.1	–	25.1	930	3.8
(Brown)		(24.8)		(26.5)	(934)	
$Th(NCS)_4 \cdot 2$(3-NBAPy)	197	24.9	16.4	24.3	912	4.3
(Brown)		(25.2)	(15.2)	(25.2)	(918)	
$ThI_4 \cdot 4$(3-NBAPy)	225	13.7	12.2	28.9	558	52.5
(Light brown)		(14.0)	(10.1)	(30.8)	(1648)	
$Th(ClO_4)_4 \cdot 6$(3-NBAPy)	172	10.2	13.3	20.9	548	99.5
(Yellow)		(11.6)	(12.6)	(19.9)	(1992)	
$UO_2I_2 \cdot 2$(3-NBAPy)	195	23.9	9.2	23.2	972	5.7
(Brown)		(24.3)	(8.5)	(25.9)	(978)	
$UO_2(NCS)_2 \cdot 2$(3-NBAPy)	188	27.6	15.2	12.1	832	3.9
(Light brown)		(28.3)	(13.3)	(13.8)	(840)	
$UO_2(NO_3)_2 \cdot 2$(3-NBAPy)	245	27.2	–	13.2	840	3.7
(Dull brown)		(28.0)		(14.6)	(848)	
$UO_2(CH_3COO)_2 \cdot 2$(3-NBAPy)	205	27.3	10.2	12.9	836	3.4
(Yellow)		(28.2)	(9.9)	(14.0)	(842)	
$UO_2(ClO_4)_2 \cdot 4$(3-NBAPy)	170	16.9	13.4	13.2	495	53.8
(Yellow)		(17.3)	(12.2)	(14.4)	(1377)	

the molecular weights of the complexes obtained cryoscopically in freezing $PhNO_2$ are given in Table-1.

The IR spectra of the complexes, when compared with those of the ligand, show a considerable shift in $\nu(C{=}N)$ azomethine absorption to the lower frequency indicating a decrease in the stretching force constant of C=N as a consequence of the coordination through azomethine nitrogen, the double bond character between carbon and nitrogen is reduced[11–14]. The strong bands observed at *ca.* 1470 and 1070 cm^{-1} are tentatively assigned to antisymmetric and symmetric $\nu(C{=}C)$ and $\nu(C{-}N)$ 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 cm^{-1} in the complexes where the ligand has no absorptions. These bands are tentatively assigned to $\nu(M{-}N)$ stretching modes. The partial IR data are given in Table-2.

TABLE-2

PARTIAL IR DATA (cm^{-1}) FOR THORIUM(IV) AND DIOXOURANIUM(VI) COMPLEXES OF (3-NBAPy) (2N-(3-NITROBENZALIDENE) AMINO PYRIDINE

Complex (Colour)	$\nu(C{=}N)$ str. azomethine	Pyridine ring breathing and deformation bands		$\nu(M{-}N)$
		$\nu(C{=}C)$	$\nu(C{-}N)$	
$Th(NO_3)_4\cdot 2(3\text{-NBAPy})$	1662s	1469s	1085m	418m
$Th(NCS)_4\cdot 2(3\text{-NBAPy})$	1650s	1461m	1082m	410m
$ThI_4\cdot 4(3\text{-NBAPy})$	1658s	1463s	1080m	410m
$Th(ClO_4)_4\cdot 6(3\text{-NBAPy})$	1650s	1465s	1082m	420m
$UO_2I_2\cdot 2(3\text{-NBAPy})$	1651s	1477m	1078m	418m
$UO_2(NCS)_2\cdot 2(3\text{-NBAPy})$	1660s	–	1080sh	435m
$UO_2(NO_3)_2\cdot 2(3\text{-NBAPy})$	1666s	1479s	1071m	418m
$UO_2(CH_3COO)_2\cdot 2(3\text{-NBAPy})$	1641s	1469s	1076m	432m
$UO_2(ClO_4)_2\cdot 4(3\text{-NBAPy})$	1650s	1470m	1070m	430m
3-NBAPy	1675s	1465s	1085s	–

The electronic spectral studies of these complexes are of less interest since metals do not contain unpaired electrons in their outermost shell. All the complexes exhibit three bands at around 240 nm, 280 nm (sh) and 310 nm while ligand spectrum shows bands at about 240 nm and 300 nm (sh). This is in agreement with previous observation[15].

X-ray powder diffraction studies of two complexes, *viz.*, $UO_2(CH_3COO)_2\cdot(3\text{-NBAPy})_2$ and $ThI_4(3\text{-NBAPy})_4$ have been done successfully with wavelength (= 1.54178 Å). $UO_2(CH_3COO)_2\cdot(3\text{-NBAPy})_2$ was found to be orthorhombic with parameters a = 17.3512(3) Å; b = 9.3599(600) Å and c = 6.9643(5) Å and $ThI_4\cdot(3\text{-NBAPy})_4$ was found to be monoclinic with parameters a = 8.1068(9) Å, b = 10.1484(6) Å, c = 11.7015(7) Å and B = 83.111(2) Å. This is in agreement with previous observations[16, 17]

Configuration of complexes

The probable coordination number of Th(IV) is 6 or 10 in present complexes depending upon the anions present. In isothiocyanato complex conductance, mol. wt. data suggest that in this complex Th(IV) has coordination number six. Iodo complex which shows 1 : 2 electrolytic nature shows that two iodo ions are present outside the coordination sphere generating the coordination number six for Th(IV) metal ion; similarly in perchlorato complex coordination number is six as all the perchlorato ions are outside the coordination sphere. Since nitrato groups are bidentate in nature in $[Th(3\text{-}NBAPy)_2(NO_3)_4]$, the Th(IV) ion is surrounded by 8 oxygen (from 4 nitrato ions) and 2 nitrogen (from the ligand) atoms creating the coordination number 10 for Th(IV) atom[18].

In dioxouranium(VI) halo and isothiocyanato complexes, both the anions are covalently bonded. In these cases, it may be considered to have an eight-coordinated uranium atom. The IR data of $(UO_2L_2(NO_3)_2)$ suggest the bidentate nature of nitrato groups in these complexes, thus suggesting coordination number of 8 for U-atom. In perchlorato complex both the perchlorato groups are ionic in nature and are present outside the corrdination sphere, thus generating coordination number equal to six for the uranium atom[18].

ACKNOWLEDGEMENT

One of the authors (RCG) sincerely acknowledges the financial support from UGC Central Regional Office, Bhopal in the form of minor research project for this work.

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(*Received:* 9 May 2000; *Accepted:* 8 July 2000) AJC-2072