Synthesis and Structural Studies of Thorium(IV) and Dioxouranium(VI) Nitrate Complexes with some Schiff Bases Derived from Pyridine-2-carboxaldehyde and certain Amino Compounds

BABU KUNCHERIA, G. SOBHANA DEVI and P. INDRASENAN*

Department of Chemistry, University of Kerala, Trivandrum 695 034, India

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Abstract

Ten new thorium(IV) and dioxouranium(VI) complexes of some Schiff bases derived from pyridine-2-carboxaldehyde and certain amino compounds have been synthesized and characterized. The Schiff bases employed are *N*-(pyridine-2-carboxaldehyde)isonicotinylhydrazone (PCIH), *N*-(pyridine-2-carboxaldehyde)benzhydrazone (PCBH), *N*-(pyridine-2-carboxaldehyde)salicyloylhydrazone (PCSH), 3*N*-(pyridine-2-carboxalidene)aminophenol (PCAP) and 4*N*-(pyridine-2-carboxalidene)aminoantipyrine (PCAAP). Elemental analysis, molecular weight determination and IR spectral, conductance and magnetic studies of these complexes indicate that they may be formulated as $ThL_2(NO_3)_4$ (where L = PCIH, PCBH, PCSH, PCAP and PCAAP), $UO_2L_2(NO_3)_2$ (where L = PCIH and PCAAP), UO_2L_2 (where L = PCBH and PCSH) and $UO_2(PCAP)(NO_3)_2$. All the ligands are bonded to the Th^{4+} ion in a neutral bidentate fashion and the nitrate ions in a monodentate fashion. In the cases of dioxouranium(VI) complexes, PCIH, PCAP and PCAAP act as neutral bidentate ligands, and PCBH and PCSH act as monobasic terdentate ligands. In all these uranyl nitrate complexes nitrate ions are coordinated to the metal ion bidentately.

Introduction

Several Schiff base complexes of thorium(IV) and dioxouranium(VI) have been reported in recent years [1–8]. It seems from the literature that thorium(IV) and dioxouranium(VI) nitrate complexes of Schiff bases of pyridine-2-carboxaldehyde have not been prepared so far. Therefore, as part of our programme for the synthesis and characterization of actinide nitrate complexes [9, 10], we report herein a series of ten Schiff base complexes of thorium(IV) and dioxouranium(VI) nitrates. The Schiff bases used were *N*-(pyridine-2-carboxaldehyde)isonicotinylhydrazone (PCIH), *N*-(pyridine-2-carboxaldehyde)benzhydrazone (PCBH), *N*-(pyridine-2-carboxaldehyde)salicyloylhydrazone (PCSH), 3*N*-(pyridine-2-carboxalidene)aminophenol (PCAP) and 4*N*-(pyridine-2-carboxalidene)aminoantipyrine (PCAAP).

Experimental

Thorium nitrate and uranyl nitrate (BDH, AnalaR, 99.9% pure) were used as such. The above listed Schiff bases were prepared by refluxing equimolar amounts of pyridine-2-carboxaldehyde and the appropriate amino compounds in ethanol for 2–3 h. The crystals of the Schiff bases separated were filtered after cooling and recrystallized from hot ethanol. The purities of these Schiff bases were checked by taking their TLCs, IR spectra and melting points.

Thorium nitrate complexes were prepared by the following procedure. Solutions of thorium nitrate (2 mmol) and the ligand (4.1 mmol) in hot acetone were mixed and the resulting solution was refluxed on a steam bath for 3 h. Complexes of all the ligands, except PCAP, crystallized out on concentration and cooling, were filtered and washed with hot acetone. For the complex of PCAP, the resulting refluxed solution was concentrated to obtain a viscous mass which was washed several times with hot benzene to remove excess ligand. The solid separated was dissolved in a minimum amount of acetone and the complex was crystallized out by adding diethyl ether and subsequent stirring of the solution.

The uranyl nitrate complexes were prepared by the following method. Solutions of uranyl nitrate (2 mmol) and the Schiff base (4.1 mmol) in minimum quantities of hot acetone (for PCIH, PCBH and PCSH), ethanol (for PCAP) or methanol (for PCAAP) were refluxed on a steam bath for 3 h. On cooling, complexes of PCIH, PCBH, PCSH and PCAP were crystallized out, filtered and washed with diethyl

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*Author to whom correspondence should be addressed.

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ether. For the complex of PCAAP, the reaction mixture was concentrated to get a viscous mass which on repeated washing with hot benzene to remove excess ligand yielded a brown solid mass. This was dissolved in a minimum quantity of methanol and the solution was stirred vigorously while adding diethyl ether whereupon crystals of the complex separated out and were filtered.

All the ten complexes were dried *in vacuo* over phosphorus(V) oxide. The complexes were analyzed for their metal contents by the gravimetric methods [11]. The CHN data of the complexes were obtained from the Central Drug Research Institute (Lucknow, India) on a payment basis. Molar conductance values of the complexes in acetonitrile, methanol and nitrobenzene (~10^{-3} M solutions) were measured at room temperature (28 ± 2 °C) using an ELICO conductivity bridge type CM82 with a dip type cell (CC-03) having platinum electrodes (cell constant, 1.26 cm^{-1}). The IR spectra of the ligands and the complexes were recorded in the 4000–400 cm^{-1} range on a Perkin-Elmer 397 IR Spectrophotometer using the KBr disc technique. The molecular weights of the complexes (~10^{-3} M solutions) were determined by the cryoscopic method using nitrobenzene as the solvent [12].

Results and Discussion

All the complexes are nonhygroscopic coloured crystalline solids which are moderately soluble in acetone, acetonitrile, methanol, ethanol, nitrobenzene and dimethyl formamide [except $UO_2(PCSH)_2$], and insoluble in benzene, diethyl ether and petroleum ether. Analytical and molecular weight data of the complexes (Table 1) show that they have the following compositions: $ThL_2(NO_3)_4$ (where L = PCIH, PCBH, PCSH, PCAP and PCAAP), $UO_2L_2(NO_3)_2$ (where L = PCIH and PCAAP), UO_2L_2 (where L = PCBH and PCSH) and $UO_2(PCAP)(NO_3)_2$. The molar conductance values of the complexes in acetonitrile, methanol and nitrobenzene (Table 1) indicate that all the complexes act as nonelectrolytes [13] and hence the nitrate ions present in the complexes are coordinated to the metal ions. The molar conductivities and the molecular weight of $UO_2(PCSH)_2$ could not be determined as it is insoluble in the above three solvents.

The important IR spectral bands of the ligands and the complexes are presented in Table 2. All the ligands have a ν(C=N) band at 1590–1610 cm^{-1} in their spectra. This band appears at 1560–1590 cm^{-1} in the spectra of the complexes with a shift of ~30–

TABLE 1. Analytical[a], Molecular Weight[a] and Conductance Data of Thorium and Uranyl Nitrate Complexes with some Schiff Bases

Complex	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Molecular weight	Molar conductance[b]		
						Acetonitrile	Methanol	Nitrobenzene
$Th(PCIH)_2(NO_3)_4$	24.78 (24.90)	30.98 (30.90)	2.30 (2.15)	18.00 (18.02)	980 (932)	32.58	90.15	3.32
$Th(PCBH)_2(NO_3)_4$	24.68 (24.95)	33.68 (33.55)	2.51 (2.37)	14.87 (15.05)	950 (930)	40.17	80.64	3.51
$Th(PCSH)_2(NO_3)_4$	24.01 (24.12)	32.27 (32.43)	2.43 (2.29)	14.19 (14.55)	1003 (962)	42.68	70.81	3.78
$Th(PCAP)_2(NO_3)_4$	26.41 (26.49)	32.58 (32.87)	2.20 (2.28)	12.53 (12.78)	920 (876)	47.18	90.48	6.71
$Th(PCAAP)_2(NO_3)_4$	21.61 (21.81)	38.87 (38.34)	3.32 (3.01)	15.31 (15.79)	1050 (1064)	45.28	85.23	5.98
$UO_2(PCIH)_2(NO_3)_2$	27.94 (28.13)	33.79 (34.04)	2.27 (2.36)	15.84 (16.55)	808 (846)	11.00	73.45	1.30
$UO_2(PCBH)_2$	33.36 (33.24)	43.53 (43.45)	2.30 (2.79)	11.80 (11.70)	670 (718)	36.66	67.20	7.90
$UO_2(PCSH)_2$	31.68 (31.73)	41.49 (41.60)	2.75 (2.67)	10.87 (11.20)				
$UO_2(PCAP)(NO_3)_2$	39.97 (40.20)	23.98 (24.32)	2.22 (1.69)	9.13 (9.46)	640 (592)	9.67	37.44	0.16
$UO_2(PCAAP)_2(NO_3)_2$	24.60 (24.34)	41.16 (41.72)	3.30 (3.27)	13.97 (14.31)	1008 (978)	20.58	67.47	7.02

[a] Calculated values in parentheses. [b] ~10^{-3} M solutions used; ohm^{-1} cm^2 mol^{-1}.

TABLE 2. Important IR Spectral Bands (cm^{-1})^a of some Schiff Bases and their Thorium and Uranyl Nitrate Complexes

Compound	ν(O–H)	ν(C=O) (ring)	ν(C=O) (side chain)	ν(C=N)	$\nu_4(NO_3)$	$\nu_1(NO_3)$	$\nu_2(NO_3)$	ν_3(O=U=O)
PCIH			1650s	1600m				
$Th(PCIH)_2(NO_3)_4$			1620m	1570m	1390s	1280s	1020w	
$UO_2(PCIH)_2(NO_3)_2$			1630s	1590m	1500m	1290s	1020m	910s
PCBH			1650s	1600m				
$Th(PCBH)_2(NO_3)_4$			1600s	1560s	1390s	1280s	1030w	
$UO_2(PCBH)_2$			Absent	1560m	–	–	–	910s
PCSH	3400br		1630s	1610w				
$Th(PCSH)_2(NO_3)_4$	3400br		1600s	1560s	1390s	1280s	1020w	
$UO_2(PCSH)_2$	3400br		Absent	1560s	–	–	–	910s
PCAP	3400br			1590s				
$Th(PCAP)_2(NO_3)_4$	3350br			1570sh	1390s	1280s	1020m	
$UO_2(PCAP)(NO_3)_2$	3350br			1560m	1480m	1280m	1020w	910s
PCAAP		1640s		1590s				
$Th(PCAAP)_2(NO_3)_4$		1600s		1570s	1390s	1280s	1020m	
$UO_2(PCAAP)_2(NO_3)_2$		1600s		1560s	1500w	1280s	1020w	920s

^{a}Abbreviations, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

20 cm^{-1} to the lower frequency region indicating that the azomethine group in all the ten complexes is coordinated to the metal ion. In the spectra of the ligands PCIH, PCBH and PCSH a strong band is observed at 1640–1675 cm^{-1} which is assigned to the stretching vibration of the side carbonyl group. In the spectra of the four complexes, $Th(PCIH)_2(NO_3)_4$, $Th(PCBH)_2(NO_3)_4$, $Th(PCSH)_2(NO_3)_4$ and $UO_2(PCIH)_2(NO_3)_2$, the band due to ν(C=O) is shifted to 1630–1600 cm^{-1} indicating that the side carbonyl group is coordinated to the metal ion. In the spectra of $UO_2(PCBH)_2$ and $UO_2(PCSH)_2$ the band due to ν(C=O) is absent indicating that these ligands are coordinated to the uranyl ion in their enol forms. This is supported by the absence of the ν(NH) band in the spectra of these complexes, which occurs around 3200 cm^{-1} in the spectra of free ligands. Thus the enol forms of these two ligands are coordinated to the uranyl ion with deprotonation as indicated by the absence of nitrate ions in the complexes.

In the spectra of the ligand PCSH and its complexes the broad band at 3400 cm^{-1} assignable to ν(OH) indicates that the –OH group does not participate in coordination with both Th^{4+} and UO_2^{2+} ions. However, the ligand PCAP shows a broad band around 3400 cm^{-1} in its spectrum which is assigned to the stretching vibration of the phenolic OH group. In the complexes this band loses sharpness and intensity and is shifted to around 3350 cm^{-1} indicating that the –OH group is coordinated to the metal ions without deprotonation.

A strong band observed at 1640 cm^{-1} in the case of PCAAP is assigned to ν(C=O) of the ring carbonyl group. In the spectra of its thorium(IV) and dioxouranium(VI) complexes this band is shifted to 1620 and 1600 cm^{-1}, respectively indicating the coordination of the ring carbonyl group to the metal ions. In all the ligands the stretching vibrations of the pyridine ring and the out of plane bending vibrations appear at ~1460 and ~780 cm^{-1}, respectively. These bands appear almost in the same regions in the spectra of all the complexes except those of $UO_2(PCBH)_2$ and $UO_2(PCSH)_2$, in which these two bands are shifted to higher regions (~1480 and ~800 cm^{-1} respectively). This shows that the two ligands PCBH and PCSH are coordinated to the uranyl ion through the pyridine nitrogen also and in all other complexes pyridine nitrogen remains uncoordinated.

In the spectra of all the complexes except $UO_2(PCBH)_2$ and $UO_2(PCSH)_2$ three additional bands, which are not present in the spectra of the ligands, are observed. These three bands appear at 1390, 1280 and 1020 cm^{-1} in the complexes of thorium(IV) nitrate, while they appear at 1480–1500, 1280 and 1020 cm^{-1} in the complexes of dioxouranium(VI) nitrate. These three bands are assigned respectively to ν_4, ν_1 and ν_2 modes of the nitrate ion. Since the magnitude of splitting of $\nu_3(NO_3)$ (*i.e.* $\nu_4 - \nu_1$) is ~110 cm^{-1} for the thorium(IV) nitrate complexes, the nitrate ions are coordinated to Th^{4+} ion in a monodentate fashion [14]. The magnitude of splitting, $\nu_4 - \nu_1$ is ~200–220 cm^{-1} in the uranyl nitrate complexes and therefore, nitrate ions are coordinated to UO_2^{2+} ion in a bidentate fashion [14].

The additional band appearing at 910–920 cm^{-1} in all the uranyl nitrate complexes is attributed to the asymmetric stretching vibration, ν_3 of O=U=O group. The absence of the ν_1 mode of O=U=O indicates that the linearity of the UO_2^{2+} species is maintained in the complexes [15].

On the basis of the above discussion the following sets of formulae are suggested for the present complexes: $ThL_2(NO_3)_4$ (where L = PCIH, PCBH, PCSH, PCAP and PCAAP), $UO_2L_2(NO_3)_2$ (where L = PCIH and PCAAP), UO_2L_2 (where L = PCBH and PCSH) and $UO_2(PCAP)(NO_3)_2$. A coordination number of 8 is suggested for all the thorium complexes, and the uranyl complexes of the first set, while a coordination number of 6 is proposed for the other two uranyl complexes without nitrate ions and $UO_2(PCAP)(NO_3)_2$.

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