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Reactions of Uranyl(VI) Nitrate with Terfunctional 4-Amino Antipyrine Schiff Bases in Neutral and Alkaline pH

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Complexes of uranyl(VI) nitrate with the terfunctional Schiff bases, acetylaceton-4-aminoantipyrine (AcAAP), salicylal-4-aminoantipyrine (SAAP) and 2-hydroxy-1-naphthal-4-aminoantipyrine (HNAAP) of the general formulae $[UO_2L_2](NO_3)_2$ and $[UO_2L_2]$ have been synthesised from neutral or alkaline reaction media and their spectra-structure correlation obtained. These ligands behave differently at different pH of the reaction solution. At pH 8–9 the –OH group in its deprotonated form, bonds to the metal ion along with the other two functional groups >C=O and >C=N̈– in an anionic terdentate manner. In neutral reaction medium (pH *ca.* 7) they form complexes in which the ligand systems coordinate as neutral bidentate and the –OH group involved only in hydrogen bonding with the linear [O=U=O] function.

INTRODUCTION

The reaction between the terfunctional Schiff bases acetylaceton-4-aminoantipyrine (AcAAP salicylal-4-aminoantipyrine (SAAP) and 2-hydroxy-1-naphthal-4-aminoantipyrine (HNAAP) with the transition metals[1] and the lanthanides[2, 3] have been extensively studied. These ligands are reported to form isolable complexes with uranyl(VI) ion also[3], wherein they are coordinated in a neutral bidentate manner without the participation of the –OH group. About the preparation of the uranyl(VI) complexes, earlier workes[3, 4] do not lay stress on the pH of the reaction medium. The present work shows that depending upon whether the reaction solution is maintained neutral (pH *ca.* 7) or alkaline (pH *ca.* 8–9), the ligands could act in a neutral bidentate manner or in a monobasic terdentate manner, to give solid complexes.

EXPERIMENTAL

Uranyl(VI) nitrate was of reagent grade. AcAAP (m.pt. 136), SAAP (m.pt. 196) and HNAAP (m.pt. 209) were prepared as reported earlier[1, 3]. The purity of the ligands was checked by elemental analysis, IR spectral, TLC and melting point data. Physical measurements were carried out as reported earlier[3].

Preparation of Complexes

Method A (Under neutral pH): The Schiff base ligand AcAAP dissolved in hot ethanol was added to an equimolar quantity of aqueous sodium acetate. Enough ethanol was added such that a solution of pH 7 resulted. The solution mixture was kept boiling and an ethanolic solution of uranyl nitrate hexahydrate was added in an 1 : 2 mole ratio. The pH of the reaction solution was maintained at 7 by the addition of a further quantity of NaOAc solution during the course of the reaction. The precipitated crystalline solid product was filtered, washed with ethanol and dried over $CaCl_2$.

Method B (Under alkaline pH): The Schiff base ligand e.g. AcAAP was dissolved in hot ethanol and a 1N NaOH solution was added. To this solution an ethanolic solution of uranyl nitrate hexahydrate was added dropwise in a 1 : 2 mole ratio with stirring. The pH of the solution was maintained at 8–9 by adding appropriate quantity of the base after the addition of the metal salt solution. The precipitated solid product was filtered, washed with ethanol and dried over $CaCl_2$.

RESULTS AND DISCUSSION

The point of interest here is that the chosen terfunctional (ν >C=O, ν > C=N– and –OH) ligands are capable of acting as bidentates or terdentates depending on whether or not the –OH group is involved in coordination. In the present study these ligands are shown to behave as neutral bidentate if prepared from neutral solution or as monobasic terdentate if the complexes are prepared under alkaline (pH *ca.* 8–9) conditions. A comparison of the spectral and analytical data of the free ligands with that of the two sets of the complexes are compiled in Tables 1 and 2 and the relevant spectra-structure correlations are discussed below.

TABLE 1
ANALYTICAL AND CONDUCTIVITY DATA OF THE URANYL(VI) COMPLEXES OF THE TERFUNCTIONAL SCHIFF BASES IN NEUTRAL AND ALKALINE pH

Compound	% Found (Calcd.)				Molar conductance	Type
	U	C	H	N	Λm Ω^{-1} cm^2 mol^{-1}	
Under neutral pH						
$[UO_2(AcAAP)_2](NO_3)_2$	25.1 (24.7)	40.2 (39.8)	4.1 (3.9)	12.1 (11.6)	200	1 : 2
$[UO_2(SAAP)_2](NO_3)_2$	23.4 (23.6)	43.1 (42.9)	3.4 (3.4)	11.1 (11.1)	172	1 : 2
$[UO_2(HNAAP)_2](NO_3)_2$	21.4 (21.5)	48.1 (47.7)	3.5 (3.4)	9.9 (10.1)	181	1 : 2
Under alkaline pH						
$[UO_2(AcAAP)_2]$	29.2 (28.4)	46.1 (45.8)	4.3 (4.3)	10.1 (10.0)	—	—
$[UO_2(SAAP)_2]$	27.2 (27.0)	48.8 (49.0)	3.5 (3.6)	9.6 (9.5)	—	—
$[UO_2(HNAAP)_2]$	24.2 (24.2)	54.1 (53.8)	3.8 (3.7)	8.7 (8.6)	—	—

TABLE 2

IR SPECTRAL DATA OF THE URANYL(VI) COMPLEXES OF THE TERFUNCTIONAL SCHIFF BASE LIGANDS IN NEUTRAL AND ALKALINE pH

Compound	IR Frequencies (cm^{-1})			
	Pyrazolone $\nu_{C=O}$	Azomethine $\nu_{C=N}$	Enolic –OH	ν_{NO_3}
Schiff base ligands				
AcAAP	1680	1520	3180	—
SAAP	1658	1525	3400	—
HNAAP	1638	1540	3240	—
Under neutral pH				
$[UO_2(AcAAP)_2](NO_3)_2$	1610	1560	3040	1380, 1040, 835
$[UO_2(SAAP)_2](NO_3)_2$	1605	1550	3360	1360, 1040, 840
$[UO_2(HNAAP)_2](NO_3)_2$	1595	1555	3240	1390, 1005, 840
Under alkaline pH				
$[UO_2(AcAAP)_2]$	1605	1550	–	–
$[UO_2(SAAP)_2]$	1600	1560	–	–
$[UO_2(HNAAP)_2]$	1585	1540	–	–

PMR spectra

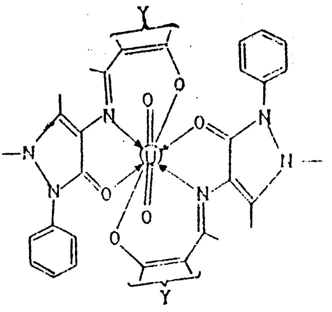
The PMR spectra of the ligands exhibit a signal at 13.5δ (ppm) corresponding to the -OH proton[3] (H-bonded with the $>C=\ddot{N}-$ group). This signal completely vanishes upon coordination under alkaline pH (8–9). In contrast the complexes obtained from neutral pH show a proton resonance (1H) at 13.45δ.

IR spectra

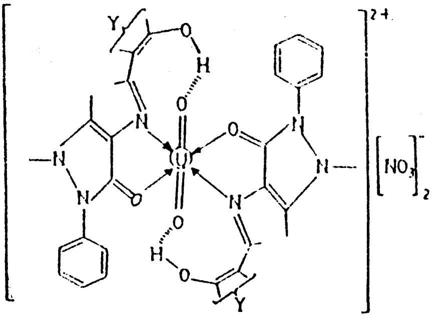
The IR spectral data of a representative ligand (AcAAP) show bands around 3180 (v –O–H....N=)[5,6] at 1680 (v $>C=O$)[7] and at 1520 cm^{-2} (v $>C=N$)[8]. The spectra of the complexes obtained under alkaline pH, on the other hand, exhibit IR bands around 1600 and 1550 cm^{-1} only attributable to $>C=O$ (pyrazolone) and $>C=\ddot{N}-$ vibrations[8] respectively. The distinctive feature of the spectrum is that the band at 3180 cm^{-1} corresponding to (O–H....N=)[5,6] in the ligand completely disappears in the nujol-mull spectra of the complexes. This suggests the involvement of -OH group in its anionic form in metal coordination (Structure I). For the complexes obtained from neutral pH the $>C=O$ and $>C=\ddot{N}-$ occur at 1610 and 1560 cm^{-1}respectively as in the previous case. The occurrence of the –OH group frequency at 3000 cm^{-1} instead of at 3180 cm^{-1} (v O–H....N= of the ligand) shows that –OH group is not participating in coordination to the electropositive metal ion but suggests a possibility of hydrogen bonding with another electronegative hetero atom (Structure II). The IR bands due to the O=U=O group appearing at 960 cm^{-1} ν_{asym} U=O), 800 cm^{-1} (ν_{sym} U=O) and 250

cm^{-1} (O=U=O) indicate that the UO_2 moiety is virtually linear[9] and also suggests the possibility of the H-bonding between the –OH group and the O=U=O group.

These complexes obtained both under neutral and alkaline pH are stable, non-hygroscopic and orange or yellow coloured solids. They are insoluble in acetone, ethanol, chloroform, benzene, etc., but soluble in nitrobenzene, DMF and DMSO. The analytical data are in good agreement with 1 : 2 metal ligand stoichiometry. The complexes obtained from an alkaline pH-reaction solution, of course give a non-conducting solution, whereas the complexes obtained at neutral pH give a 1 : 2 conductance values in DMSO solution[10]. The proposed structures are:



Structure I



Structure II

The essential structural difference between the above two types of complexes prepared from neutral and alkaline reaction conditions relates to the involvement of –OH group in the anionic form or to the non-involvement of –OH group in metal-ligand coordination. This means that in alkaline pH (8–9) the ligands undergo deprotonation to form complexes of the type $[UO_2L_2]$ in which the ligands act as monovalent terdentates giving an overall coordination number 8 to the metal. In neutral pH $[UO_2L_2](NO_3)_3$ type complex is formed with probable coordination number 6.

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