Interaction of Dioxouranium(VI) Acetate and Nitrate with Pyridoxal

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The interaction of dioxouranium(VI) acetate and nitrate with the pyridoxal ligand has been studied. Complexes have been prepared and studied by ir, ^1H NMR and conductivity measurements. The data support the formation of $UO_2(C_8H_8NO_3)(CH_3COO)$-$2H_2O$ and $UO_2(C_8H_9NO_3)_2(NO_3)_2 3H_2O$ compounds, respectively. In the former complex the uranyl group is bound to the phenolic and aldehydic oxygen atoms of pyridoxal and to a bidentate acetato group; the coordination sphere is completed with a molecule of water. In the latter complex the uranyl group is bound to two molecules of neutral ligand through the heterocyclic ring nitrogen and to two bidentate nitrato groups.

Introduction

It is well known that pyridoxal phosphate-containing enzymes catalyze many reactions of aminoacids such as transamination, racemization, decarboxylation, elimination of the α-hydrogen and other reactions [1]. Most of these catalytic activities have been duplicated by non-enzymatic model reactions, in which pyridoxal and metal ions are used as catalysts [2], which have greatly helped in understanding the catalytic role.

In order to obtain information which is expected to be of interest to discuss the interaction between metal ions and pyridoxal, we have started studies on the isolation and characterization of dioxouranium(VI) complexes with such a ligand [3]. We report here the data obtained from infrared, pmr and conductivity studies.

Experimental

A solution of 1 mmol of uranyl acetate or uranyl nitrate in methanol was added dropwise to a solution of 2 mmol of pyridoxal in methanol under stirring and heating at 40 °C. Yellow products were obtained within few hours after addition of diethyl ether. The compounds were filtered, washed and dried under vacuum. *Anal.* Found: C, 22.47; H, 2.87; N, 2.70; U, 44.35. Calcd. for $C_{10}H_{15}NO_9U$: C, 22.61; H, 2.85; N, 2.64; U, 44.80. Found: C, 24.86; H, 2.96; N, 7.11; U, 30.60. Calcd. for $C_{16}H_{24}N_4O_{17}U$: C, 24.56; H, 3.09; N, 7.16; U, 30.42. Uranium was weighted as U_3O_8 following ignition of the products decomposed by HNO_3.

Infrared Spectra

Ir spectra (4000–400 cm^{-1} region) of the solid compounds were taken as KBr pellets or as hexachlorobutadiene mulls with a Perkin-Elmer spectrophotometer model 621.

^1H NMR Measurements

^1H nmr spectra were recorded in CD_3OD at 28 °C on a FT-80A Varian Spectrometer. Chemical shifts were measured in δ/ppm downfield from TMS used as an internal standard.

Conductivity Measurements

The measurements were performed in ethanol at 25 °C by means of an Amel model 131 instrument. Λ_M values are expressed in ohm^{-1} cm^2 mol^{-1}.

Results and Discussion

The elemental analysis is in agreement with the formation of $UO_2(C_8H_8NO_3)(CH_3COO)2H_2O$ (I) and $UO_2(C_8H_9NO_3)_2(NO_3)_2 3H_2O$ (II) complexes when pyridoxal is reacted with uranyl acetate and uranyl nitrate, respectively. Table I shows some ir frequencies characteristic of the free ligand and compounds in the solid state. The spectra of the compounds, compared with the spectrum of the free ligand, exhibit changes in the 3200 and 1430–1300 cm^{-1} range where the O–H····O intramolecular bonded O–H and δ(O–H) frequencies occur respectively. Furthermore, the broad absorption peak at

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TABLE I. Some Significant IR Frequencies (cm^{-1}) of the Dioxouranium(VI) Complexes of Pyridoxal.

Vibration modes	$C_8H_9NO_3$	$UO_2(C_8H_8NO_3)(CH_3COO)2H_2O$	$UO_2(C_8H_9NO_3)_2(NO_3)_23H_2O$
$\nu(O-H\cdot\cdot O)_{intramol}$	3150	–	–
$\nu(C-H)_{ar}$	3075	3100	3095
$\nu(C-H)_{al}$	2990	2975	2970
	2930	2920	2930
$\nu(O-H\cdot\cdot N)_{intermol}$	2735	–	–
$\nu(C=C/C=N)_{ring}$	1621	1630	1614
	1605		
	1541		
$\nu_{as}(COO^-)$		1536	
$\nu_s(COO^-)$		1460	
		1440	
$\nu_{as}(NO_2)$			1490
$\nu_s(NO_2)$			1290
$\nu(N-O)$			1030
$\nu_{as}(O-U-O)$		910	900
$\delta(COO^-)$		675	
$\gamma(COO^-)$		610	

TABLE II. Proton Chemical Shifts (δ/ppm) of the Pyridoxal Complexes in CD_3OD at 28 °C.

Compound	$-CH_{ring}$	$-CHO$	$-CH_2OH$	$-CH_3$ ring	$-CH_3$ acet.
Pyridoxal	7.90	6.52	5.04	2.47	
Complex I	7.88	6.32	5.16	2.70	2.48
Complex II	7.98	6.65	5.20	2.78	

2735 cm^{-1}, assigned to the intermolecular O–H····N frequency of the free ligand [4], is not detectable in the spectra of the complexes. Other changes in the absorption frequencies, arising from C=C/C=N, ν(O–C–C) and C–H bending ring vibrations respectively are observed in the 1630–1530, 1150–1000 and 850–700 cm^{-1} regions. Any carbonyl stretching frequency of pyridoxal is absent, in agreement with its hemiacetalic form [4]. The asymmetric stretching (ν_3) of the O–U–O group occurs in the complexes as an intense band near 910 cm^{-1}. Moreover in the spectrum of $UO_2(C_8H_8NO_3)(CH_3COO)2H_2O$, complex (I), peaks are present at 1536, 1460, 1440, 675 and 610 cm^{-1}, peaks which have been assigned by Jones [5] to the asymmetric and symmetric stretching, deformation and torsion modes respectively of acetato groups coordinated to dioxouranium(VI). The separation value between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ frequencies (Δ = 76 cm^{-1}) should be indicative of a coordinated acetato group acting as a bidentate ligand [6] rather than bridging adjacent uranium atoms [7]. In fact these frequencies are practically coincident with those observed for $NaUO_2(CH_3COO)_3$, where the acetato groups are coordinated as bidentate to uranium(VI) [8]. In the spectrum of $UO_2(C_8H_9NO_3)_2(NO_3)_23H_2O$ complex (II), registered using hexachlorobutadiene mull, the strong band at 1380 cm^{-1} (due to ionic nitrato groups) is absent, whereas the absorptions characteristic of coordinated nitrato groups are present at 1490, 1290 and 1030 cm^{-1} [9]. Thus the coordination sphere of the uranyl group should involve nitrato groups.

Table II reports the proton chemical shifts of the compounds measured in CD_3OD. The spectrum of the free ligand exhibits two singlets at 7.90 ppm and 6.52 ppm, 1 in intensity, which are assigned to the ring proton and aldehydic proton respectively. The signals at 5.04 ppm, 2 in intensity, and 2.47 ppm, 3 in intensity, are assigned to the $-CH_2OH$ and $-CH_3$ protons of pyridoxal. In the spectra of the complexes the signals due to the aldehydic and methyl

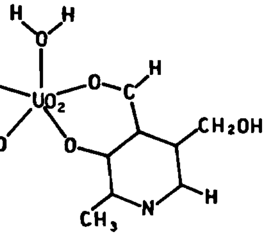
TABLE III. Conductivity Values of the Pyridoxal–Dioxouranium(VI) Complexes in Ethanol ($C = 1 \times 10^{-4}$ *M*, T = 25 °C).

Compound	Λ_M (Ohm^{-1} cm^2 mol^{-1})
Complex I	20
Complex II	55

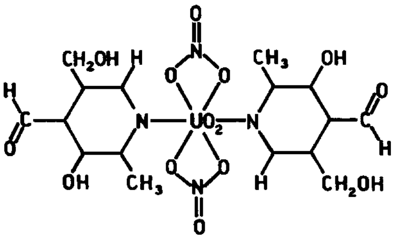
protons show a significant displacement. Furthermore, in the spectrum of the complex I a singlet of intensity 3 is present at 2.48 ppm due to $-CH_3$ acetato protons. The resonance value is indicative of the acetato group coordinated to dioxouranium(VI) since the value of an ionic acetato group occurs at higher field values (*ca.* 2 ppm).

Table III shows the conductivity values, Λ_M, measured for the complexes in ethanol. The low value shown by complex I is consistent with the non-ionic nature of this compound in solution, whereas the relatively high value found for complex II indicates a tendency of such a compound to ionize in ethanol; in fact, a Λ_M value of 50, near to that measured, is also exhibited by an equimolar ethanolic solution of uranyl nitrate in which both the nitrato groups are known to act as bidentate to dioxouranium(VI) [10].

In conclusion the present ir, ^1H nmr and conductivity results are consistent with the coordination of pyridoxal to dioxouranium(VI) according to the formulation of the structure of the complexes shown in Scheme 1 and Scheme 2.



Scheme 1. Proposed structure of the $UO_2(C_8H_8NO_3)(CH_3COO)2H_2O$ complex.



Scheme 2. Proposed structure of the $UO_2(C_8H_9NO_3)_2(NO_3)_2 3H_2O$ complex.

In complex I (Scheme 1) the phenolic oxygen and the aldehydic oxygen are bound to dioxouranium(VI). The acetato group is coordinated as bidentate and a molecule of water completes the pentacoordination of the uranyl group in the equatorial plane.

In complex II (Scheme 2) two pyridoxal molecules are bound as neutral ligands to dioxouranium(VI) through the heterocyclic ring nitrogen, and two nitrato groups are coordinated as bidentate.

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