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NMR Studies on UO_2^{2+} Complexes with Pyridoxal

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The interaction of pyridoxal with dioxouranium(VI) ions has been studied by ^1H and ^{13}C NMR measurements in D_2O and CD_3OD.

The results indicate that the preferred bonding site is the C-3-O^- donor and the major species under the used experimental conditions is the equimolar complex.

The function of pyridoxal enzyme derivatives together with metal ions in catalyzing several amino-acids reactions is welll known [1–5]

In our laboratory we have undertaken studies on the interaction of dioxouranium(VI) with pyridoxal which yields solid complexes purified and characterized [6]. We report here some results obtained by ^1H and ^{13}C NMR studies on the dioxouranium-

TABLE I. ^1H NMR[a] chemical shifts (δ/ppm) of free Pyridoxal hydrochloride and UO_2 acetate containing solutions in D_2O at pH 3.25.

Compound	C-6-H	C-4'-H	5'-CH_2	2'-CH_3	–CH_3 acet.
Pyridoxal	8.10, 1H	6.76, 1H	5.26, 2H	2.61, 3H	
Pyridoxal + UO_2 acetate 1:0.5	8.04, 1H	6.78, 1H	5.25, 2H	2.68, 3H	2.20
Pyridoxal + UO_2 acetate 1:1	8.02, 1H	6.81, 1H	5.27, 2H	2.77, 3H	2.23
Pyridoxal + UO_2 acetate 1:1.5	8.00, 1H	6.81, 1H	5.27, 2H	2.79, 3H	2.27
Pyridoxal + UO_2 acetate 1:2	7.99, 1H	6.83, 1H	5.27, 2H	2.82, 3H	2.34
Δ ppm =	–0.11	+0.07	+0.01	+0.21	

[a] ^1H nmr chemical shifts are measured downfield from TMS, using dioxane as an internal standard.

TABLE II. ^{13}C NMR[a] chemical shifts (δ/ppm) of free Pyridoxal hydrochloride and UO_2 acetate containing solutions in D_2O at pH 3.25.

Compound	C-3	C-2	C-4	C-5	C-6	C-4'	C-5'	C-2'
Pyridoxal	150.4	144.4	140.0	138.3	125.1	99.0	70.3	14.8
Pyridoxal + UO_2 acetate 1:1	147.2	142.1	138.1		122.9	99.4	70.9	14.8
Pyridoxal + UO_2 acetate 1:2	146.5	141.3	138.1		123.3	99.3	70.9	14.8
Δ ppm =	–3.9	–3.1	–1.9	–0.2	–1.8	+0.3	+0.6	–

[a] ^{13}C nmr chemical shifts are measured downfield from TMS, using dioxane as an internal standard.

TABLE III. ^1H NMR[a] chemical shifts (δ/ppm) of free Pyridoxal hydrochloride and UO_2acetate containing solutions in CD_3OD.

Compound	C-6-H	C-4'-H	5'-CH_2	2'-CH_3	–CH_3 acet.
Pyridoxal	8.35, 1H	6.45, 1H	5.30, 2H	2.72, 3H	
Pyridoxal + UO_2 acetate 1:1	8.00, 1H	6.52, 1H	5.21, 2H	2.92, 3H	2.33
Pyridoxal + UO_2 acetate 1:2	8.00, 1H	6.55, 1H	5.23, 2H	2.96, 3H	2.45
Δ ppm =	–0.35	+0.10	–0.07	+0.24	

[a] ^1H nmr chemical shifts are measured downfield from TMS used as an internal standard.

TABLE IV. ^{13}C NMR[a] chemical shifts (δ/ppm) of free Pyridoxal hydrochloride and UO_2 acetate containing solutions in CD_3OD.

Compound	C-3	C-2	C-4	C-5	C-6	C-4′	C-5′	C-2′
Pyridoxal	151.13	145.13	141.01	140.28	126.20	105.92	71.14	14.74
Pyridoxal + UO_2 acetate 1:1	148.50	142.70	140.15		122.49	107.00	71.07	15.49
Pyridoxal + UO_2 acetate 1:2	148.53	142.83	140.18		122.41	107.10	71.13	15.53
Δ ppm =	−2.60	−2.30	−0.83	−0.10	−3.79	+1.18	−0.01	+0.79

[a] ^{13}C nmr chemical shifts are measured downfield from TMS used as an internal standard.

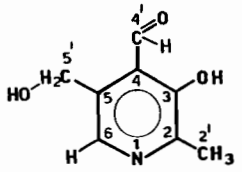

Fig. 1. Pyridoxal.

(VI)/pyridoxal system in aqueous and methanol solutions.

NMR spectra in aqueous solutions. Tables I and II show the ^1H and ^{13}C NMR chemical shifts of free pyridoxal and uranyl acetate/pyridoxal solutions at varying molar ratios. The presence of uranyl acetate in the aqueous solutions containing pyridoxal (PL) at pH 3.25 causes changes of the proton and carbon chemical shifts which may indicate the direct involvement of uranyl ion in the binding to the ligand. The major chemical shifts variations are observed for 2′-CH_3, C-4′-H and C-6-H protons (Table I) and C-2, C-3, C-6 and C-4 carbons (Table II). Since such carbons were found to be sensitive on the deprotonation process of the phenolic group C-3-OH [7] it is conceivable that uranyl ion binds the pyridoxal molecule *via* the C-3-O^- donor.

The ^1H as well as ^{13}C NMR spectra of the solutions at different UO_2^{2+}/PL molar ratios indicate that the major species formed at this pH is the equimolar complex.

The hemiacetal form, under which pyridoxal exists both in aqueous and methanol solutions, appears to be preserved in the complexed ligand molecule since no variation of the chemical shifts is observed for C-4′ and C-5 carbons upon metal binding.

NMR spectra in methanol solutions. Tables III and IV report the ^1H and ^{13}C chemical shifts for the free pyridoxal and its methanol solutions with uranyl acetate.

The chemical shifts variation of the C-6-H and 2′-CH_3 protons and C-2 and C-3 carbons upon metal ion binding to pyridoxal are quite similar to those found in aqueous solutions. This could indicate the same C-3-O^- binding of pyridoxal to UO_2^{2+} in methanol solution as well.

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Spectroscopic Behaviour of U(VI) Containing Glasses

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The aim of our research is to study materials that can have applications as lasers. For this reason, as preliminar work, we prepared in our laboratory some glasses whose composition is $xPbO/yNa_2O/zSiO_2$, doped with U(VI) salts (Table I), to understand the PbO influence on the formation of the UO_2^{2+} moiety, especially because the U(VI) coordination in silicate and in particular lead silicate glasses is not yet completely clarified [1]. Then we measured the absorption and emission spectra at dif-