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NMR and Spectroscopic Studies on Interaction of Uranyl Ion with Glutamic Acid and Glutamine

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Introduction

Our recent studies on interactions of UO_2^{2+} ion with aspartic acid (Asp) and asparagine (Asn) [1] as well as with the oligopeptide glutathione [2] have shown that amino acid carboxylates are quite effective in binding uranyl ion (see also 3–5). The mode of the UO_2^{2+}–carboxylate bond, however, is still uncertain *e.g.* it is not clear whether the coordination of two COO^- groups of Asp is a result of chelation of one aminoacid molecule that binds two different UO_2^{2+} ions [1].

To obtain some additional information on the mode of binding of UO_2^{2+} we have chosen another couple of aminoacids such as glutamic acid (Glu) and glutamine (Gln) whose properties can be compared and related to those of the Asp and Asn system (*e.g.* see 6).

Experimental

L-glutamic acid and L-glutamine were used as obtained from Reanal. $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck) was used as the uranyl ion source. The concentration of the ligands in ^2H_2O (99.8%) solutions was 0.2 *M* in the NMR and IR spectra measurements.

^1H NMR spectra of 1:1 and 1:2 metal to aminoacid molar ratio solutions were recorded with a Varian T-60 spectrometer at 25 °C by using methanol as an internal standard, whose methyl signal was 3.34 δ/ppm downfield from TMS. ^{13}C NMR spectra were recorded on a Jeol-PS-100 spectrometer operating at 25 MHz in the FT mode with EC-100 computer at 25 °C with dioxan as an internal standard. IR spectra were measured on a Perkin-Elmer spectrophotometer model 621. The pH values were adjusted with NaOH and HNO_3 and measured with Mera-Elmat and Ratiometer TTT2 pH-meters. No pH corrections for the D_2O solvent were applied.

Results and Discussion

Proton NMR Spectra

In all solutions containing uranyl ion and glutamic acid or glutamine precipitation occurred at pH above

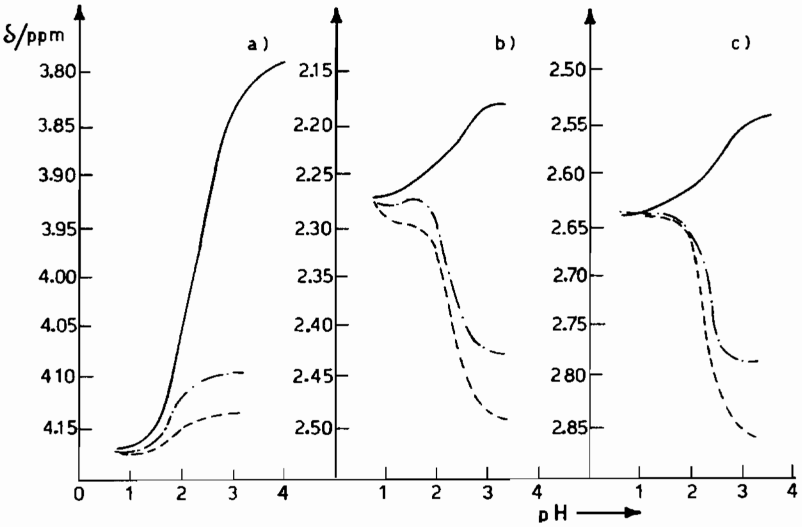

Fig. 1. pH dependence of chemical shifts for α-CH a), β-CH_2 b) and γ-CH_2 c) glutamic acid protons. (———) metal-free ligand; (–·–·–) 2:1 and (– – – –) 1:1 ligand to UO_2^{2+} molar ratio solutions.

TABLE I. ^{13}C Chemical Shifts of Glu in Metal-free and UO_2^{2+} Containing Solutions.

Species	pH	γ-COO$^-$	α-COO$^-$	αCH	γCH_2	βCH_2	$\Delta\gamma$COO$^-$ [a]	$\Delta\alpha$COO$^-$ [a]
Glu	1.07	109.693	104.961	−14.318	−37.009	−41.620		
	2.02	109.395	105.931	−13.590	−36.888	−41.377		
	2.59	110.100	106.500	−13.100	−36.810	−41.301		
	2.76	110.178	106.780	−12.983	−36.645	−41.135		
UO_2^{2+}: Glu 1:1	1.02	109.935	105.810	−13.833	−36.888	−41.499	0.242	0.85
	1.99	111.998	107.994	−12.376	−35.796	−41.013	2.6	2.06
	2.76	116.366	109.329	−11.648	−33.976	−40.528	6.18	2.55
UO_2^{2+}: Glu 1:2	1.03	109.571	104.839	−14.439	−37.130	−41.741	−0.122	−0.122
	2.14	111.634	107.630	−12.610	−36.038	−41.135	2.24	1.7
	2.75	112.969	108.236	−12.255	−35.432	−40.892	2.8	1.56

[a] $\Delta\gamma$ and $\Delta\alpha$ are the chemical shift variations upon UO_2^{2+} coordination of γ- and α-COO$^-$ carbons respectively.

TABLE II. ^{13}C Chemical Shifts of Gln in Metal-free and UO_2^{2+} Containing Solutions.

Species	pH	γ-$CONH_2$	α-COO$^-$	αCH	γCH_2	βCH_2	$\Delta\gamma$CO [a]	$\Delta\alpha$COO$^-$ [a]
Gln	1.03	110.542	104.961	−14.318	−36.038	−41.013		
	2.04	110.542	105.567	−13.833	−36.038	−40.892		
	3.00	110.906	107.023	−12.741	−35.796	−40.528		
	3.78	111.027	107.266	−12.498	−35.694	−40.407		
	3.96	111.027	107.266	−12.498	−35.796	−40.407		
	4.81	111.027	107.387	−12.376	−35.674	−40.407		
UO_2^{2+}: Gln 1:1	1.04	110.664	105.446	−13.954	−36.038	−41.013	0.122	0.485
	1.98	111.149	107.508	−12.498	−35.674	−40.649	0.607	1.941
	2.92	111.149	108.722	−11.770	−35.674	−40.407	0.243	1.699
	3.78	111.149	109.571	−11.648	−35.674	−40.407	0.122	2.305
UO_2^{2+}: Gln 1:2	1.02	110.664	105.203	−14.075	−36.038	−41.013	0.122	0.242
	2.06	110.906	106.902	−12.796	−35.796	−40.771	0.121	1.335
	3.10	111.027	108.115	−12.134	−35.674	−40.407	0.121	1.092
	4.09	111.149	108.722	−11.891	−35.674	−40.285	0.122	1.456

[a] $\Delta\gamma$ and $\Delta\alpha$ are chemical shift differences upon UO_2^{2+} coordination of γCO and αCOO$^-$ carbons, respectively.

3.2 and 4.1, respectively. Hence the NMR and IR studies were performed at pHs below those values.

The uranyl ion coordination to Glu and Gln causes considerable variation of the proton chemical shifts towards lower field (Figs. 1 and 2). The pH dependence of proton shifts observed in the 1:1 and 1:2 UO_2^{2+} to Gln molar ratio solutions suggests that in the case of glutamine complexes the species formed in solution at pH 3–4 are the $(UO_2Gln)^{2+}$ or $[UO_2(Gln)_2]^{2+}$ complex, respectively (see 1). Since the downfield chemical shift of αCH Gln proton is much more distinct than that of γCH_2 upon the UO_2^{2+} coordination it seems that the only coordination site of Gln available for uranyl ion is αCOO$^-$ donor. Glutamic acid (Fig. 1) uses most probably both carboxylates *i.e.* αCOO$^-$ and γCOO$^-$ to coordinate UO_2^{2+} since the downfield shifts of αCH and γCH_2 protons are almost of the same values. The lower downfield shifts of Glu protons upon UO_2^{2+} coordination in 1:2 UO_2^{2+} to Glu solution may suggest that 1:2 UO_2^{2+} to Glu complex is a minor species in solution (see below for ^{13}C NMR results).

^{13}C NMR Spectra

The analysis of ^{13}C NMR spectra of metal-free ligand was carried out according to Rabenstein and Sayer [7]. The chemical shifts of Glu and Gln in the presence of uranyl ion at chosen pH values are given in Tables I and II.

The coordination of uranyl ion to Glu molecule causes considerable downfield chemical shifts of both carboxylate carbons. At pH 2.76 the difference is

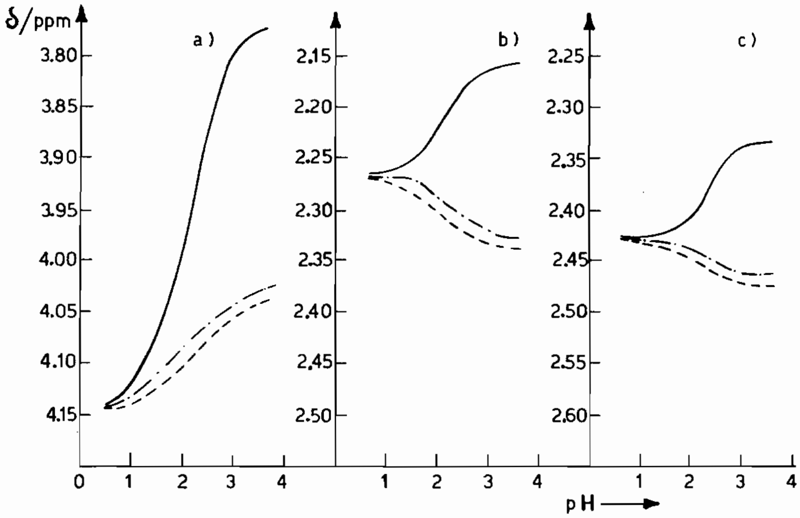

Fig. 2. pH dependence of chemical shifts for α-CH a), β-CH$_2$ b) and γ-CH$_2$ c) glutamine protons. (———) metal-free ligand; (–·–·–) 2:1 and (– – – –) 1:1 ligand to UO_2^{2+} molar ratio solutions.

6.18 and 2.55 ppm for 1:1 solution and 2.8 and 1.56 ppm for 1:2 solution for γCOO$^-$ and αCOO$^-$, respectively. These chemical shift variations strongly suggest that both carboxylates are involved in UO_2^{2+} ion coordination and that the dominant species at pH ~ 3 is a 1:1 molar ratio complex. The chemical shift pattern of the solutions with UO_2^{2+} excess *e.g.* 2:1 UO_2^{2+} to Glu molar ratio solution is almost the same as for the 1:1 solutions. Although the involvement of Glu carboxylates in coordination of UO_2^{2+} ion might suggest the formation of a chelate it seems more likely that α- and γ-carboxyl donors bind two different metal ions since an eight-membered chelate ring would be thermodynamically unfavoured. Thus, the interaction of UO_2^{2+} ion with glutamic acid will lead to formation of polynuclear species with Glu molecule as a bridge between uranyl ion coordinated via two carboxylates in a way resembling that observed for uranyl complexes of glutathione [2]. The ^{13}C NMR results obtained for UO_2^{2+}–Gln system clearly show that the Gln molecule is bound to uranyl ion only via αCOO$^-$ donor since the metal ion coordination causes the chemical shift variation only on the αCOO$^-$ carbon (see Table II). Since downfield chemical shift of α-carboxyl carbon upon UO_2^{2+} coordination for 1:2 molar ratio solution is about 60% of that observed for 1:1 solution (Table II), the ^{13}C NMR results do not support clearly ^{1}H NMR results that in UO_2^{2+}–Gln systems 1:2 molar ratio complex is formed at available pH region as it was found for the UO_2^{2+}–Asn system [1].

IR Spectra

The asymmetric stretching band of O–U–O group ν_3 observed at 952 cm^{-1} in the ligand free solutions shifts to lower frequencies when Glu or Gln is added. In the case of both ligands, at pH $\leqslant$ 3 the ν_3 band was observed at 930 cm^{-1}. The energy decrease of this vibration indicates the equatorial coordination of the ligands to UO_2^{2+} ion. The asymmetric carboxylate stretching vibrations observed at 1720 cm^{-1} (COOH) or 1610–1620 cm^{-1} (COO$^-$) are also influenced by the coordination. Addition UO_2^{2+} to Glu or Gln containing solutions at pH < 3 promotes deprotonation of COOH donor (accelerated vanishing of 1720 cm^{-1} band) and shifts the COO$^-$ band to higher energies of about 10–15 cm^{-1}. The latter value is probably much higher [2] but it is difficult to establish accurately the positions of these broad bands. In any case, IR spectra support the coordination of carboxylates to UO_2^{2+} in the studied systems though no stoichiometry could be drawn from these results.

References

1 H. Wieczorek and H. Kozłowski, *Inorg. Nucl. Chem. Letters, 16,* 401 (1980).
2 A. Marzotto, *J. Inorg. Nucl. Chem., 39,* 2193 (1977).
3 A. Marzotto, *J. Cryst. Mol. Struct., 6,* 259 (1976).
4 A. Marzotto, *Chem. Biol. Interact., 14,* 383 (1976).
5 A. Marzotto, L. Garbin and F. Braga, *J. Inorg. Biochem., 10,* 257 (1979).
6 J. Legendziewicz, H. Kozłowski, B. Jeżowska-Trzebiatowska and E. Huskowska, *Inorg. Nucl. Chem. Letters,* in press.
7 D. L. Rabenstein and T. L. Sayer, *J. Magn. Resonance, 24,* 27 (1976).