New NMR Evidence on the Uranyl–Citrate Complexes

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Abstract

A ^{1}H and ^{13}C NMR study of the complexation of citric acid to uranyl ion is reported over a wide pH range (1.3–10.3). At least six complexes are formed. Structures are proposed for four of them; in particular one of the complexes dominant at high pH values seems to be a cyclic trimer (3:2).

Introduction

The complexation between uranyl ion and citric acid has been investigated by several authors using potentiometry [1, 2] and low-field nuclear magnetic resonance spectroscopy [3]. The formation of polynuclear species associated with hydrolysis reactions rendered the potentiometric data very difficult to interpret. On the other hand, the early ^{1}H NMR spectra were only obtained at low pH values ($\simeq 2$); the corresponding data were treated assuming a fast exchange process between free and bound ligand. Thus, the number and the stoichiometry of the complexes, the sites of the ligand involved in coordination, and the geometry of the various species remain open questions.

Carbon-13 and high-field proton NMR spectroscopy have proved to be valuable means of elucidating the complexation of uranyl ion with α-carboxylic acids [4, 5], as well as of oxo ions of W(VI), Mo(VI) [6] and V(V) [7]; particular reference should be made to the study of the complexation of Mo(VI) with citric acid [8], a system which has been the object of a recent potentiometric study [9]. The successful application of NMR is based on the general observation of separate signals for free and bound ligands, since ligand exchange in those systems is slow in the NMR time scale. It was thus possible to find new evidence of the complexation of UO_2^{2+} with citric acid in aqueous solution.

Experimental

Citric acid and uranyl nitrate of analytical grade were used; both reagents were lyophilized from D_2O solutions and D_2O solutions were used throughout. The pH was adjusted with NaOD and DCl; the values reported in the text are not corrected for the isotope effect of deuterium.

^{1}H NMR spectra were run at 300 MHz on a Bruker CXP-300 spectrometer at 275 K; ^{13}C NMR spectra were obtained using a Bruker WP 80 SY instrument ($\simeq$302 K); *tert*-butanol ($\delta(^{1}H) = 1.23$ ppm) and *p*-dioxane ($\delta(^{13}C) = 67.4$ ppm) were used as internal references.

Results and Discussion

A proton NMR spectrum of the AB type is obtained for citric acid, $CO_2H-CH_2-C(OH)CO_2H-CH_2-CO_2H$, in aqueous solution due to the non-equivalence of the hydrogen atoms in each methylenic group (for example, at pH = 1.4, $\delta = 2.9$, $\delta = 3.1$ and $J_{AB} = (-)16.2$ Hz). The carbon-13 spectrum obtained in the ^{1}H broad band decoupling mode shows four signals at δ-values 177.6, 174.3, 74.1 and 44.1, assigned to the α-carboxyl group, the terminal carboxyl groups, the carbon nucleus directly bonded to the alcoholic hydroxyl group and to the methylenic groups, respectively.

Proton and carbon-13 spectra of uranyl nitrate plus citric acid solutions of different molar ratios and various concentrations were obtained in the pH range 1.2–10.3. As an illustration, Figs. 1 and 2 show the relevant ^{13}C and ^{1}H spectra corresponding to the pH-titration of solutions of uranyl nitrate and citric acid. By correlating the whole ^{1}H and ^{13}C data (both chemical shifts and signal intensities), the formation of six complexes is unequivocally established. Tables I and II give, respectively, the proton and carbon chemical shifts of the complexes relative to the free ligand at the same pH

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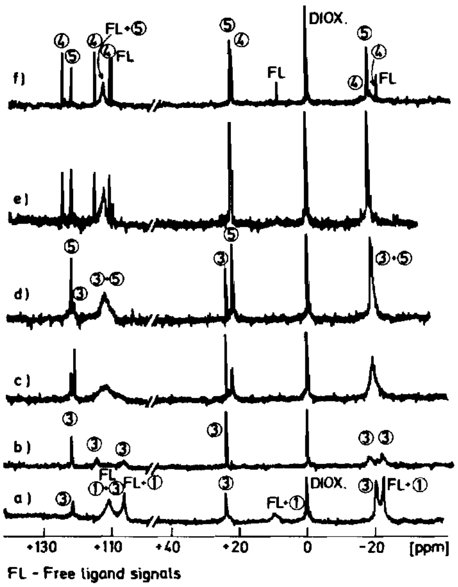


Fig. 1. $^{13}C\{^{1}H\}$ spectra of an equimolar solution (0.5 M) of uranyl nitrate and citric acid obtained for the following pH values: (a) 1.86; (b) 4.08; (c) 5.11; (d) 5.80; (e) 6.68; (f) 10.25. Shifts relative to dioxane from different spectra are identified.

values, together with the experimental conditions under which the quoted values were measured; the type of proton spectrum obtained is also indicated. The geminal coupling constant of the various bound ligand molecules in complexes 3, 4 and 6 are similar to the value obtained for free citric acid.

At very low pH values (1.3) only one set of (broad) ^{13}C signals and one AB proton spectrum are obtained, irrespective of concentration conditions; no separate spectrum of the free ligand is observed and the shifts of the recorded signals relative to the free ligand at the same pH increase upon increasing the metal:ligand molar ratio. The observed proton and carbon spectra are thus taken as averaged spectra of rapidly exchanging free and bound ligand in complex 1. A high acidity species has been previously assumed to be the monomer $UO_2H_2Cit^+$ [3].

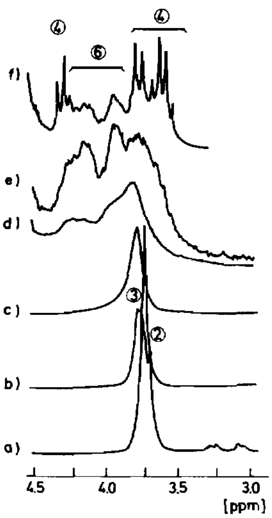


Fig. 2. ^{1}H NMR spectra of a 2:1 solution (0.16:0.08 M) of uranyl nitrate and citric acid obtained at the following pH values: (a) 2.21; (b) 3.00; (c) 3.65; (d) 4.56; (e) 5.27; (f) 5.95.

The other five complexes which form at higher pH give distinct spectra in appropriate concentrations and pH conditions (Figs. 1–3); the conditions for which the concentration of each one is maximum are given in Table III. Some other minor species are present, but their ^{1}H signals are very weak and broad and no attempts to assign them were made at this stage.

At pH 3.5 complexes 2 and 3 coexist, the latter being dominant for the molar ratio range covered (2:1 to 1:2). A maximum at 1:1 occurs for complex 3 in a Job's plot of ^{1}H signal intensities. On the other hand, the concentration of complex 2 increases for n:1 with $n > 1$. This is probably a 2:1

TABLE I. ^{1}H NMR Chemical Shifts

Complex	Type of spectrum	Chemical shifts (ppm)[a]			Experimental conditions[b]	
					pH	Molar ratio
1[c]	AB quartet	0.13		0.11	1.72	1:1
2	single peak ($\Delta\nu_{1/2} = 6$ Hz)		0.82		2.99	2:1
3	AB quartet	0.80		0.89	3.02	1:1
	AB quartet	0.84		0.79		
4	AB quartet	1.03		1.08	7.70	1.5:1
	AM quartet	1.73		1.29		
5	single peak ($\Delta\nu_{1/2} = 16$ Hz)		1.10		8.45	1:1.5
6	AB quartet	1.54		1.38	6.03	1.5:1

[a] Relative to free ligand signals obtained at the same pH value and assuming the same relative positions of signals assigned to protons A and B on going from free to bound ligand; positive values are shifts to high frequency. [b] Experimental conditions under which the reported data were obtained. [c] In fast exchange with free ligand.

TABLE II. $^{13}C\{^1H\}$ NMR Chemical Shifts

Complex	^{13}C Chemical shifts (ppm)^a				Experimental conditions^b	
	$^{13}CO_2H–C(OH)$	$^{13}CO_2H–CH_2$	$^{13}C(OH)$	$^{13}CH_2$	pH	Molar ratio
1^c	2.36	0.91	3.13	0.78	1.86	1:1
2	11.28	5.45	16.67	3.25	3.58	2:1
3	10.66	7.54 0.02	16.45	4.49 0.33	4.08	1:1
4	12.37	5.80 1.38	13.69	5.19 2.09	6.11	1.5:1
5	10.10	3.17	13.97	2.88	6.52	1:2
6^d	10	7	15	2	5.84	1.5:1

[a] Relative to free ligand signals obtained at the same pH value; positive values are shifts to high frequency. [b] Experimental conditions under which the reported data were obtained. [c] In fast exchange with free ligand. [d] The shifts are referred to the center of the corresponding signals.

TABLE III. pH Values Corresponding to Maximum Concentrations of the Various Complexes for Different Molar Ratios

Molar ratio	Complex					
	1	2	3	4	5	6
2:1	≃1.3	2.2–3.7		5.3–6.0		3.7–6.0
1:1	≃1.3	2.2–3.0	3.0–5.8	6.5–10.3	5.1–6.5	6.5–8.5
1:2	≃1.3		3.0–6.5		5.8–8.5	

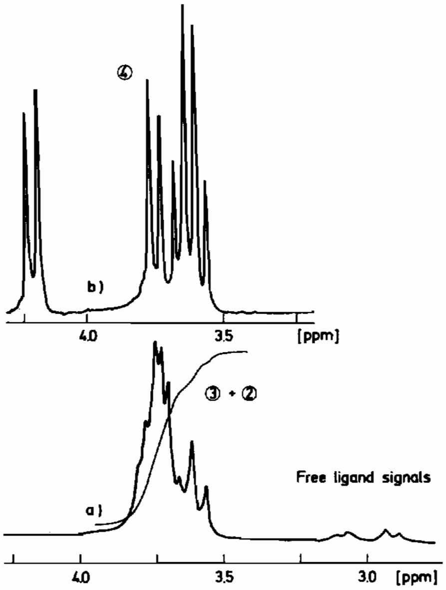
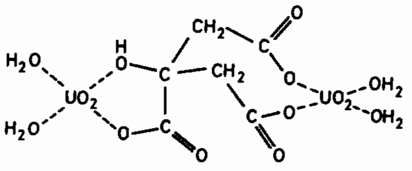


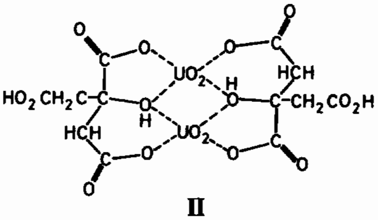
Fig. 3. (a) ^{1}H NMR spectrum of an equimolar solution (0.5 M) of uranyl nitrate and citric acid obtained at pH = 2.99; (b) ^{1}H NMR spectrum of a 1.5:1 solution (0.06:0.04 M) run at pH = 8.30.

species in which the two methylenic groups are magnetically equivalent, the same applying to the terminal carboxyl groups (Tables I, II). The carbon shifts observed on complexation (Table II) point to strong involvement of the alcoholic hydroxyl group and of the α-carboxyl group in coordination, and a weaker participation of the terminal carboxyl groups. Structure I proposed for this complex is compatible with the above observations. A single peak is assigned to the H atoms; some accidental magnetic equivalence of the methylene protons would result.



I

Complex 3, a *n:n* species, gives rise to two AB quartets of equal intensity in the proton spectrum and just one set of carbon peaks showing non-equivalence of the methylene carbon atoms and also non-equivalence of the terminal carboxyl groups; one of these is not coordinated. The two ^{1}H AB quartets must thus be attributed to the two CH_2 groups in a same ligand molecule. We identify this species with the 2:2 complex (structure II) previously proposed by Rajan and Martell [2]:



II

Similar dimeric structures have been proposed for the uranyl ion plus malic acid [4] and uranyl ion plus tartaric acid systems [5].

The coalescence of the resonances assigned to the terminal carboxyl groups (also observed for the methylene groups) shown in the ^{13}C spectrum obtained at pH = 1.86 (Fig. 1a) is explained by an exchange process taking place: while the five ring fragment remains, the other carboxyl groups are rapidly alternating in the binding to the uranyl ion. At pH = 3.48 all the ^{13}C signals of complex 3 are resolved, and a similar result is shown in Fig. 1b for pH = 4.08, the CH_2 and terminal CO_2H signals being broader than the others. This is a result of a lower rate of molecular rearrangement upon increasing pH in this region.

Considering the chemical reaction for the formation of complex 3 [$UO_2^{2+} + HCit^{2-} \rightleftharpoons (UO_2)_2(HCit)_2$], and integrating the bound and free ligand signals, an approximate value for the stability constant of this species is determined as $\simeq 10^9$.

On increasing pH, complex 3 gradually gives place to complex 5 and a conjugated acid-base equilibrium is suggested between these forms ($pK_a \simeq 6$). Complex 5 would then possess a structure similar to **II** but with full ionization of the alcoholic group and of all carboxyl groups; the single peaks of CH_2 in both the proton and carbon spectra and the single ^{13}C peak for the terminal carboxyl groups show a relatively fast rearrangement by which these groups alternate in bonding to UO_2^{2+}. Coexistence of complexes 3 and 5 at intermediate pH is shown in Fig. 1c,d. Whereas a common single broad peak is observed for CH_2 and similarly for the terminal CO_2H groups, the quaternary carbon signals differentiate. Since this resonance is mainly affected by deprotonation of the alcoholic OH group, we can conclude that this is a slow process; this is not surprising in view of the geometry of the complex.

On further increasing the pH of an equimolar solution (above pH = 6.5) or on increasing the uranyl content at pH $\simeq$ 5.5, complexes 4 and 6 (less abundant) form. Figure 4 shows the drastic change in the proton spectrum at pH = 5.7 on going from a 1:1 to a 1.5:1 solution. At pH $\simeq$ 8 only complex 4 is present in a dilute 1.5:1 solution (Fig. 3b).

Complex 4 is clearly a very stable species of composition n:1 with $n > 1$ and probably a 3:2 complex. No changes in the spectra were observed in the temperature range 275–320 K, which suggests a rigid structure. The carbon and proton NMR data require that the two ligand molecules are equivalent, the four coordinating sites all being involved in bonding to the metal ions. Whereas the H atoms in one of the CH_2 groups are almost magnetically equivalent, one H atom in the other CH_2 group must occupy a special position with respect to the magnetic anisotropy and electric field effects of the uranyl groups (a shift of 1.73 ppm on complexation as compared to values close to 1 ppm for the remaining H atoms). The structure **III** we propose, having two citrate molecules acting as bridges in a cyclic structure also involving two hydroxo (or oxo) bridges, fits the data.

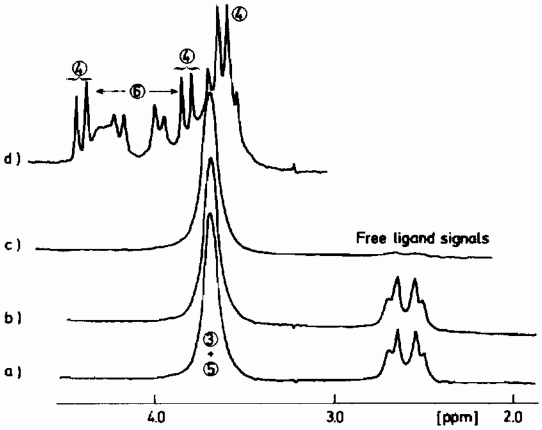
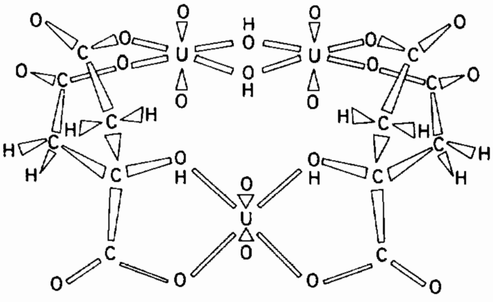


Fig. 4. ^1H NMR spectra of the following molar ratios solutions, having the same total concentration of uranyl nitrate plus citric acid (0.1 M), obtained at pH = 5.7: (a) 1:2; (b) 1:1.5; (c) 1:1; (d) 1.5:1.



III

We note that a cyclic 3:3 complex has been proposed for the UO_2^{2+} plus tartaric acid system [5]. A model suggests that minimization of repulsion is attained by making the equatorial plane of the $-UO_2(OH)_2UO_2-$ moiety perpendicular to the axis of the third uranyl ion.

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