Inorganica Chimica Acta, *95* (1984) 13–15

^{1}H and ^{13}C Nuclear Magnetic Resonance Study of the Complexation of Uranyl Ion with (D)-Tartaric Acid

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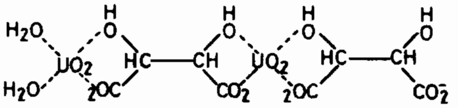
Received October 31, 1983

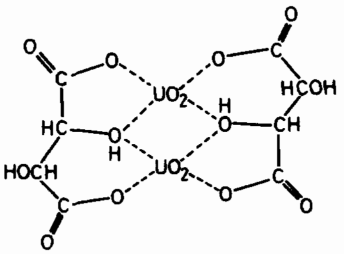
A full pH range ^{1}H and ^{13}C NMR study was performed on the complexation of UO_2^{2+} with (D)-tartaric acid, for variable concentrations and molar ratios. Spectral evidence for the existence of at least six complexes was obtained, and their stoichiometry and dependence on pH were investigated. Preliminary information on the conformation of the bound ligand molecules was also obtained. An attempt to clarify the exchange phenomena involving the various species present is discussed.

Introduction

The interaction of tartaric acid with the uranyl ion is still far from understood [1]. The study of this system is fairly complex: (i) multiple coordinating atoms and several ionization states of the ligand; (ii) hydrolysis of $UO_2(H_2O)_n^{2+}$; (iii) formation of polynuclear species.

On the basis of potentiometric studies, Rajan and Martell [2] concluded that in the pH 2–4 range binuclear complexes are formed, and proposed the alternate structures I and II.





In the pH range 4–8 the dimer hydrolyses (favoring structure I) and further polymerization occurs [2]. A full pH range study using ^{1}H and ^{13}C NMR spectroscopy is in agreement with the existence of complexes with the postulated structures but also reveals the presence of other species.

Experimental

D_2O solutions were prepared from commercially available pure uranyl nitrate and (D)-tartaric acid. The pH was adjusted with concentrated NaOD and DCl; the pH* values quoted are the direct meter readings.

The ^{1}H spectra were recorded on a Bruker CXP-300 and WP 80 SY NMR spectrometer; the ^{13}C spectra were run with proton decoupling in the latter spectrometer.

tert-Butanol (δ = 1.23) and p-dioxan (δ = 67.40) were used as internal references for ^{1}H and ^{13}C resonance respectively.

Results and Discussion

The composition and the structure of the uranyl complexes present in solution are drastically affected by pH. Figure 1 shows the spectra of bound ligand for pH* values ranging from 2.1 to 8.5 in an equimolar solution (0.1 *M*).

The chemical shifts of the protons in the bound ligand range from 3.7 to 6.9 ppm, while those of the free ligand are observed between 3.1 and 3.6 ppm. These ^{1}H data as well as the chemical shifts of the ^{13}C {^{1}H} are summarized in Table I and can be compared with the free ligand spectral parameters given in Table II.

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0020-1693/84/$3.00

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TABLE I. Spectral Parameters of the Complexes Identified.

Complex	^{1}H			^{13}C {^{1}H}	
	CH (OH)			CO$_2$H	CH (OH)
	Nature of the spectrum	δ (PPM)	$^3J_{HH}$ (Hz)	δ (PPM)	δ (PPM)
1	Single peak	+3.70	–	+109.71	+7.08
2	Single peak	+6.90	–	≃+126.5	≃+25.2
3	Single peak	+5.99	–	+118.64	+26.18
4	AX quartet	+5.84* +4.18*	1.88	+120.23 +116.10	+22.82 +10.11
5	AX quartet	+5.57* +4.19*	2.15	+122.11 +117.09	+20.85 +11.01
6	AB quartet	+6.42** +6.22**	8.50	–	–

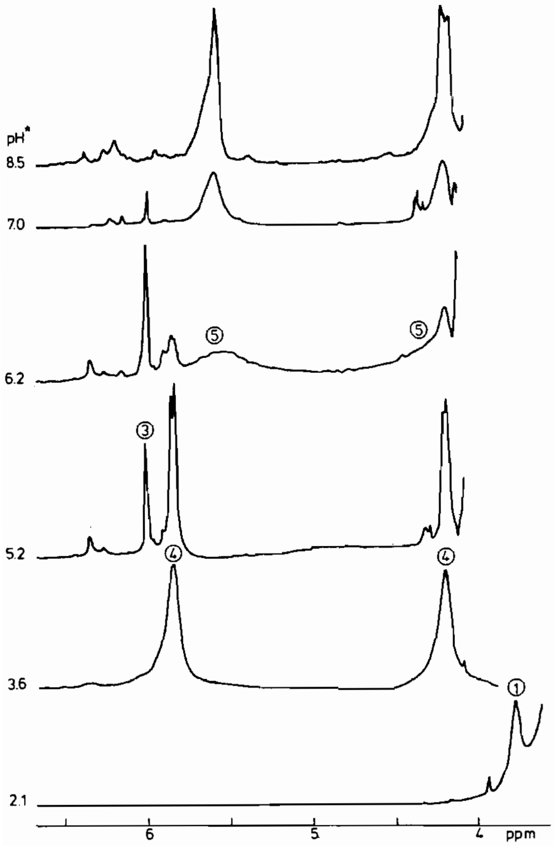

Fig. 1. Spectra of bound ligand in an equimolar solution (0.1 *M*) for the pH* range 2.1–8.5 run at 80 MHz.

TABLE II. Spectral Parameters of the Free Ligand.

pH*	^{1}H		^{13}C {^{1}H}	
	CH (OH)		CO$_2$H	CH (OH)
	δ (PPM)	$^3J_{HH}$[3] (Hz)	δ (PPM)	δ (PPM)
1.15	+3.56	2.30	+108.00	+5.33
4.50	+3.20	1.80	+111.54	+7.09
12.20	+3.08	1.80	+111.98	+7.34

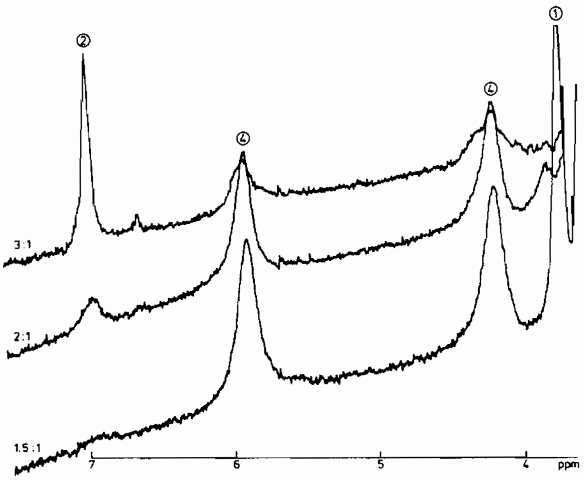

Fig. 2. Spectra of bound ligand for pH* = 2.50 ± 0.12 for metal/ligand ratios 3:1, 2:1 and 1.5:1 run at 300 MHz.

For an equimolar solution at pH* = 2.1 only one broad ^{1}H resonance is observed at 3.7 ppm, correspondingly only one ^{13}C resonance is observed for each of the carbon nuclei groups. The small chemical shifts induced and the equivalence observed suggest that this species, *1*, is a monodentate in which the binding to the uranyl ion is rapidly exchanging from one carboxylic group to the other.

At pH* = 2.50 a different species, *2*, is observed in solutions with higher metal content (Fig. 2). Again only one resonance is identified for this species in the ^{1}H spectrum, and in each CH(OH) and CO$_2$H ^{13}C spectra. This is compatible with a polynuclear species with a stoichiometry N:1 (N > 1) and a structure similar to I, with the second ligand molecule being substituted by two water molecules. Indeed, the large chemical shifts induced are in agreement with the nuclei being influenced simultaneously by the two uranyl ions.

Species *3* appears in a narrow range of pH* (5–7). Similarly to species *2*, this species presents equivalent nuclei and large induced shifts and probably *2* and *3*

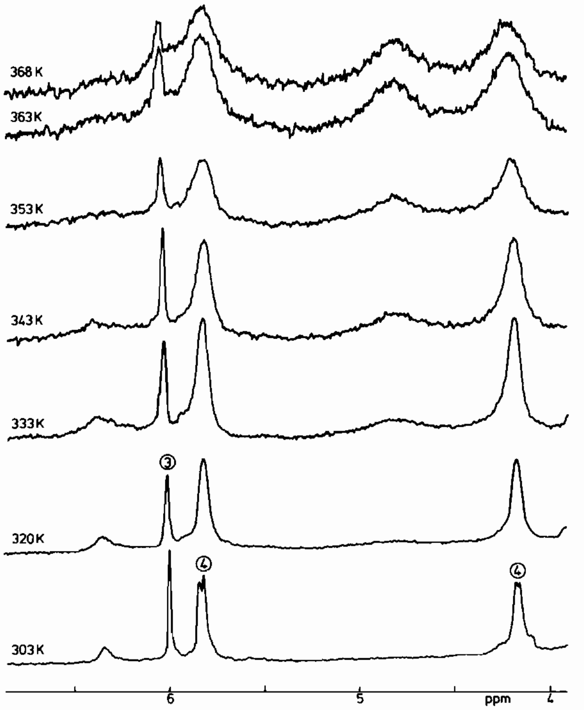

Fig. 3. Spectra of a 1:1 solution, 0.1 *M*, at pH* = 5.15 run at 80 MHz for the temperature range 303–368 K.

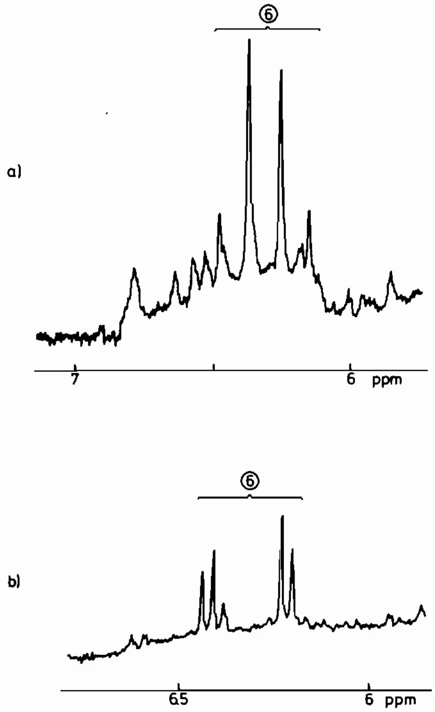

Fig. 4. Spectra of bound ligand, species *6*, in an equimolar solution (0.1 *M*) at pH* = 9.7 run at: a) 80 MHz; b) 300 MHz.

represent the acid and conjugated base forms of the same complex.

Above pH* = 3 species *4* becomes dominating, then broadens and later disappears (Fig. 1). As this species disappears another one, *5*, grows. Again, the pH dependence of the relative populations of *4* and *5* are compatible with these two complexes being an acid and its conjugated base in intermediate to slow exchange ($pK_a \simeq 6.1$). Both these species present an AX pattern with similar coupling constants, 1.88 and 2.15 Hz respectively. These coupling constants indicate that the ligand conformation is such that the carboxylic groups are *trans* [3].

The $^{13}\underline{C}$H(OH) and $^{13}\underline{C}O_2H$ chemical shifts for species *4* and *5* (Table I) are a clear indication for the binding of only one of the OH groups while both carboxylic groups are bound to UO_2^{2+}. These NMR results are in agreement with the structure II, for species *4*, or its isomer of symmetry C_s.

NMR spectra of solutions with different molar ratios, not shown, carried out at pH* = 4.0 ± 0.1 and pH* = 8.7 ± 0.3, are compatible with a 1:1 stoichiometry. However, because of the presence of minor species due to the overlapping of resonances, this value is only a preliminary one.

Temperature studies of species *4* (see Fig. 3) show that at 320 K the AX pattern starts broadening and a new broad single resonance appears at 4.9 ppm. This temperature study indicates that an intramolecular rearrangement, possibly due to exchange of the OH bond, is averaging the environment of the two proton nuclei.

At pH* ≃ 10 the AB pattern of yet another species, *6*, appears at 6.2–6.4 ppm (Fig. 4). The proton vicinal coupling constant is 8.60 Hz, implying a ligand conformation where the two carboxylic groups are gauche [3].

In the present article we attempted to characterize the major species observed by NMR in the solution conditions utilized. A full characterization of this system and a comparison with other similar ones, *e.g.* the uranyl complexes with malic [4] and thiomalic [5] are in progress.

References

1 R. E. Tapscott, *Trans. Metal Chem., 8,* 253 (1982).
2 K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem., 26,* 1927 (1964).
3 J. Ascenso and V. M. S. Gil, *Can. J. Chem., 58,* 1376 (1980).
4 M. T. Nunes, V. M. S. Gil and A. V. Xavier, *Can. J. Chem., 60,* 1007 (1982).
5 M. T. Nunes, V. M. S. Gil and A. V. Xavier, *5th Ann. Meeting of the Port. Chem. Soc.,* Commun. C30-24, Porto (1982).