Inorganica Chimica Acta, 115 (1986) 107–114

Stereospecific Complexation of Uranyl Ion with Tartaric Acids Studied by NMR Spectroscopy

M. TERESA NUNES

Departamento de Química, Instituto de Energia, LNETI, 2685 Sacavem, Portugal

and VICTOR M. S. GIL

Departamento de Química, Universidade de Coimbra, 3000 Coimbra, Portugal

Received November 11, 1985

Abstract

A full pH range ^{1}H and ^{13}C NMR study was performed on the complexation of UO_2^{2+} with (D,L)- and *meso*-tartaric acids, for variable concentrations and molar ratios, in comparison with (D)-tartaric acid. The main result is that, in spite of the already high number of complexes formed with the active ligand, an additional species occurs with the racemic mixture for which experimental evidence indicates a cyclic trimer structure. A smaller number of complexes is formed with *meso*-tartaric acid. Information on the conformation of bound ligand is also obtained.

Introduction

NMR spectroscopy has proved to be a powerful technique in speciation studies of complexation of oxoions with hydroxycarboxylic acids [1–4] and other ligands [5] in aqueous solution. The formation of complexes undergoing comparatively slow exchange processes, especially at temperatures close to 0 °C, is revealed by the observation of different spectra for different species, namely for the free ligand and for the various situations of bound ligand. This enables the determination of the number of species and their concentrations as a function of pH and concentration conditions and, in some cases, the determination of their stoichiometries and geometries. In favourable instances exchange processes can also be investigated [1].

One of the systems we have previously studied in this manner is uranyl ion + (D)-tartaric acid (*R*,*R*(+)-tartaric acid) in aqueous solution [1]. Proton and Carbon-13 NMR evidence for the existence of at least six complexes was obtained as a function of pH. For some of them, it was also possible to gain insight on the corresponding stoichiometries and conformation of bound ligand.

We now extend this study to (D,L)-tartaric and *meso*-tartaric acids ((*R*,*S*)-tartaric acid), as stereospecific effects are expected on complex formation. We also resume the uranyl + (D)-tartaric acid system in a systematical manner at higher radio frequency and at lower temperature, thus identifying new species. A brief study in DMSO-d_6 is also made.

Experimental

(D)-, (D,L)- and *meso*-tartaric acids, as well as uranyl nitrate, were commercially obtained. D_2O and DMSO-d_6 solutions were used and the concentrations were established by weight. Concentrated NaOD and DCl were used for adjusting the pH: no corrections were performed on the direct meter reading (pH*).

^{1}H NMR spectra were recorded at 300 MHz on a Bruker CXP-300 spectrometer at 275 K; some of the signals were assigned by spin decoupling techniques. ^{13}C NMR spectra were run at 20 MHz and 50 MHz using Bruker WP 80 SY and Varian XL-200 instruments, respectively, at the probes temperature ($\simeq$302 K) with ^{1}H BB decoupling.

Tert-butanol and *p*-dioxane ($\delta_H = 1.23$ and $\delta_C = 67.40$) were used as internal references when running ^{1}H and ^{13}C spectra, respectively.

Results and Discussion

The proton NMR spectrum of tartaric acid, $CO_2H–CH(OH)–CH(OH)–CO_2H$, bonded to uranyl ion, UO_2^{2+}, can be either a single peak or a quartet (AB or AX spectrum), depending on whether or not the two methyne H atoms are equivalent. The first case applies namely to tartaric acid acting as a bridging ligand between two U atoms in a symmetrical

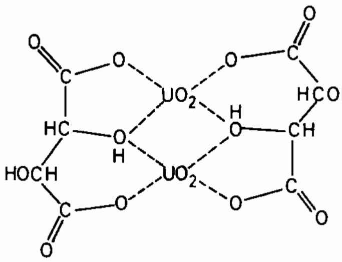
0020-1693/86/$3.50

structure; if the bridged structure is not symmetrical, then an AB type spectrum can be obtained. For a tartaric acid molecule as a terminal ligand involving only one of the hydroxyl groups (as well as one or two carboxyl groups), the expected spectrum will be of the AX type. In the latter two cases, an H–H vicinal coupling constant ($^3J_{HH}$) reflects the approximate conformation of the ligand.

Uranyl Ion + (D)-tartaric Acid

Sixteen distinct spectra (3 of smaller intensity) of bound ligand can be detected at low temperature for the system UO_2^{2+} + (D)-tartaric acid, depending on pH and molar ratio. The type of spectrum and the ^1H and ^{13}C parameters (only the simplest mixtures of complexes were characterized by ^{13}C NMR) are shown in Tables I and II (we note that there are two similar spectra numbered **12**, two similar complexes numbered **4** and four related species numbered **5**). Although there is a range of concentration and pH conditions for which these spectra are detected, those enabling more precise determination of the NMR parameters are given in the Tables.

Figure 1 shows the signals due to the main complexes in 1:2 solutions at variable pH. Figure 2 gives the percentage of bound ligand as a function of pH, for the various complexes present in solutions of 2:1, 1:1 and 1:2 molar ratios. The new species detected in this work relative to our previous low radio frequency study [1] are numbered **9** and **10** (both of small abundance), **11** and **12** (this detected at high pH) and the various complexes **4** and **5** which, being in rapid exchange at room temperature, had been taken as just one conjugated acid–base pair corresponding to structure **I** proposed by Rajan and Martell [6] or its *cis* isomer.



I

By taking the changes of the overall concentration of **4** and **5** as a function of pH (Fig. 2) we get an effective pK_a value of about 5.

The ^1H shifts relative to free ligand in the case of species **4** and **5** fall into two ranges: *ca.* 1 ppm and ca. 2.5 ppm, respectively for a non-bonded CH(OH) group and for a CH(OH) group bonded to a uranium atom, in accordance with structure **I**. A similar situation occurs with species **11** and **12**. The remaining

TABLE I. ^1H NMR Parameters

Complex	Nature of the spectrum	Tartaric acid[a]						Experimental[d] conditions	
		(D)-		(D,L)-		*meso*-			
		Δδ	$^3J_{HH}$	Δδ	$^3J_{HH}$	Δδ	$^3J_{HH}$	pH*	Molar ratio
1	Single peak[c]	0.6	–	0.6	–	0.6	–	2.4	2:1
2	Single peak	3.4	–	3.3	–	3.5	–	3.5	2:1
3	Single peak	2.97	–	2.97	–	–	–	5.0	2:1
6	AB quartet	3.1 3.3	8.5	3.1 3.3	8.5	3.2 3.4	4.7	8.5	1:2
7	Single peak	–	–	2.6	–	–	–	8.5	1:2
8	AB quartet	–	–	2.77 2.73	8.1	–	–	6.0	1:1
	Single peak			3.15					
9	Single peak	4.0	–[b]	4.0	–[b]	–	–	4.5	2:1
10	Single peak	2.9	–[b]	2.8	–[b]	–	–	4.2	2:1
11	AX quartet	A: 0.90 X: 2.51	2.0	A: 0.92 X: 2.57	2.0	A: 0.9 X: 2.5	–[c] –[c]	4.2	2:1
12	AX quartet	A: 1.16 1.14 X: 2.58 2.54	2.0	A: 1.1 X: 2.5	2.0	– –	– –	9.0	1:1

[a] Δδ: Chemical shifts relative to free ligand in ppm. $^3J_{HH}$: Coupling constants in Hz. [b] Less abundant species. [c] Broad signal. [d] Experimental conditions for which the tabulated parameters were obtained.

TABLE II. NMR Parameters of Species **4** and **5** (AX Quartets)

Tartaric Acid	Complex	Solvent D_2O						Solvent DMSO-d_6	
		^1H				^{13}C		^1H	
		$\Delta\delta$	$^3J_{HH}$	Experimental[a] conditions		$\Delta\delta$		$\Delta\delta$	$^3J_{HH}$
				pH*	Molar ratio	CH(OH)	CO_2H		
(D)-	**4**	A: 0.86, 0.89 X: 2.55	1.5	4.0	1:1	3.29 15.71	4.79 9.26	A: 0.98 X: 2.44	–[b]
	5	A: 1.08, 1.12 X: 2.48, 2.52, 2.58, 2.61	1.5	8.5	1:2	3.92 13.76	5.55 10.66	A: 0.84 X: 2.19, 2.24	1.5
(D,L)-	**4**	A: 0.85, 0.88 X: 2.54	1.5	4.0	1:1	3.10, 3.22 16.04, 16.10	4.42 8.55, 8.72	A: 1.0 X: 2.3	1.5
	5	A: 1.05, 1.09 X: 2.46, 2.49, 2.51, 2.54	1.5	8.5	1:2	3.95 14.29	5.37 10.66	A: 0.81, 0.82, 0.84 X: 2.15, 2.19, 2.21	1.5
meso-	**4**	A: 0.70, 0.79 X: 2.30, 2.57	9.6	4.0	1:2	0.0 12.87	6.81 9.92	A: 0.80, 0.84 X: 2.31, 2.39	9.6
	5	A: 1.07, 1.08, 1.09, 1.10 X; 2.35, 2.37, 2.37, 2.38	9.6	8.5	1:2	0.0 9.62	6.28 12.23	A: 0.68, 0.70, 0.71 X: 2.14, 2.19	9.6

[a] Experimental conditions for which the tabulated parameters were obtained. [b] Broad signal.

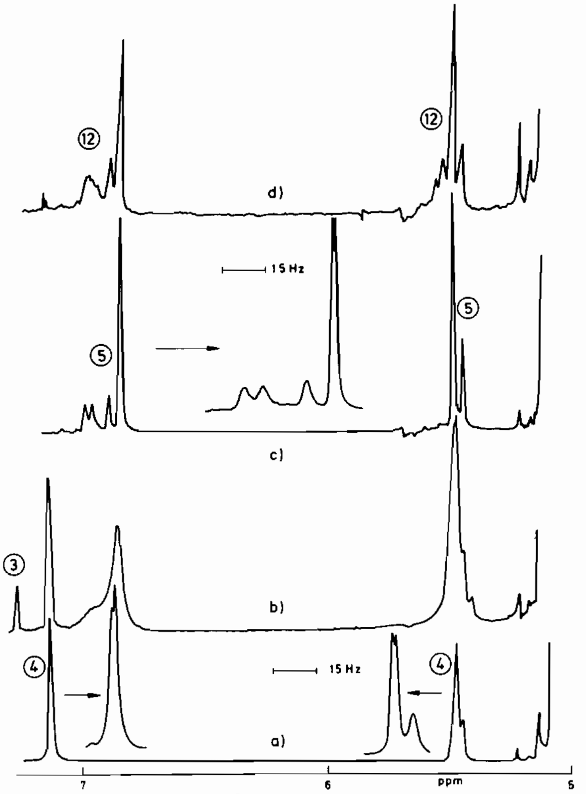


Fig. 1. Spectra of UO_2^{2+}:(D)-tartaric acid solutions; molar ratio = 1:2, obtained for the following pH* values: (a) 4.03, (b) 5.91, (c) 8.54 and (d) 9.37.

complexes, except **1**, give rise to well-shifted single signals ($\Delta\delta \simeq 3$–4 ppm) thus indicating a simultaneous involvement of both OH groups in complexation. The position of the broad signal for **1** is highly affected by pH in the region 1–2.5; this is probably a result of exchange processes too complex for us to pursue at this stage.

The values for $^3J_{HH}$ (1.5–2 Hz) in complexes **4**, **5**, **11** and **12** show that the ligand has the two methyne protons in approximately a *gauche* orientation with respect to each other. In contrast, the mutual arrangement of these protons is basically *trans* in species **6**, as indicated by $^3J_{HH}$ = 8.5 Hz.

The ^{13}C shifts for **4** and **5** (only averaged spectra for all species **4** and all species **5** are obtained) are in agreement with the proposed structure **I**: the ^{13}C shift for the bound CH(OH) group relative to free ligand is large (14–16 ppm) and that for the neighboring carboxylate group (in a five-membered ring) exceeds that for the other carboxylate group (in a six-membered ring). The decrease of $\Delta\delta$ for the bound CH(OH) group upon deprotonation of species **4**, with little change in the signal of the other CH(OH) group, agrees with the ionization of the bound CH(OH) group on going from **4** to **5**. The approximate pK_a value of 5 obtained from the ^1H NMR data is therefore assigned to this OH group.

Dilution of a 1:1 solution of U(VI) + (D)-tartaric acid, at pH* 6.0, from 0.1 M:0.1 M to 0.0125 M: 0.0125 M leads to a transfer of population between

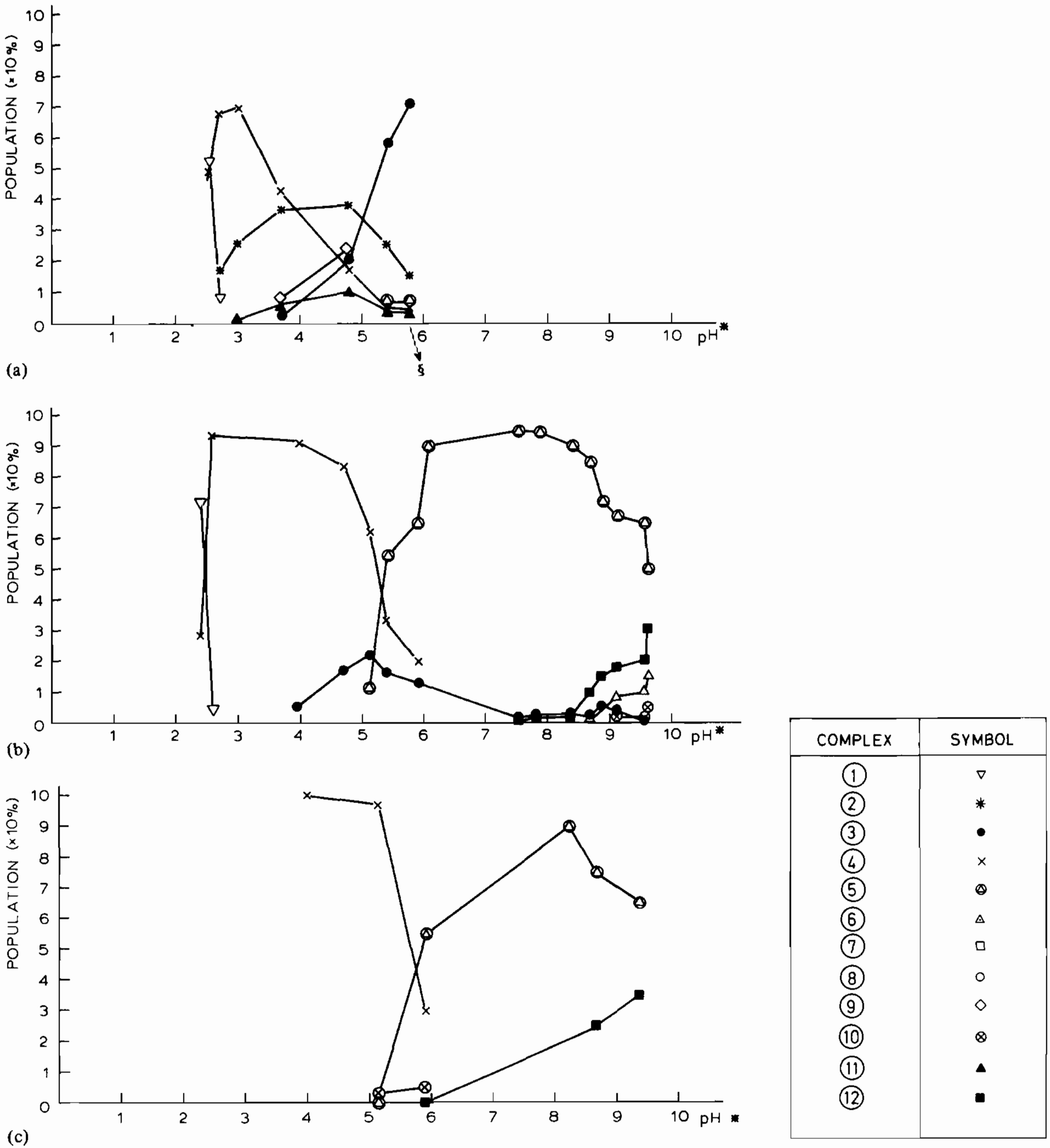


Fig. 2. Populations of bound ligand *vs.* pH* values for the system UO_2^{2+} + (D)-tartaric acid. Molar ratio: (a) 2:1, (b) 1:1 and (c) 1:2. § Precipitation occurs.

species **5** and **3**; a sharpening of the residual free ligand signal is also observed, implying the existence of exchange processes involving bound and free ligand.

The number of proton NMR signals of species **4** or **5** is smaller in DMSO-d_6 solution; but due to changes in chemical shifts this does not enable us to conclude unequivocally for a smaller number of complexes present. The fact that the spectra are similar in DMSO-d_6 and D_2O rules out the existence of olation bridges in these species, an hypothesis advanced by Feldman *et al.* [7].

Uranyl Ion + (D,L)-tartaric Acid

As expected, all species identified in the previous system are also present in aqueous solution of uranyl

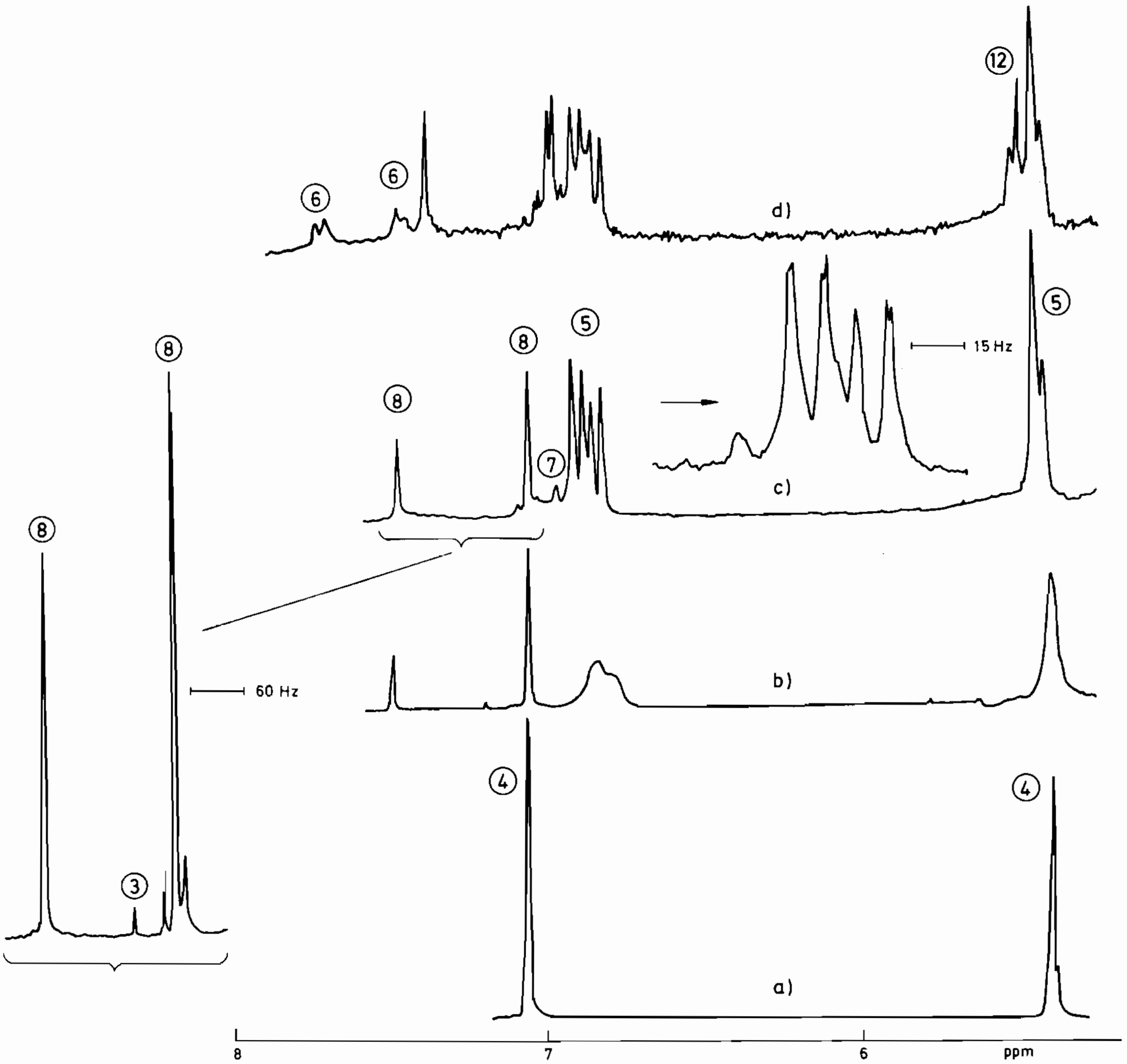
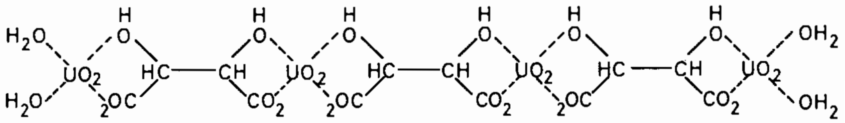


Fig. 3. Spectra of UO_2^{2+}:(D,L)-tartaric acid solutions; molar ratio = 1:2, obtained for the following pH* values: (a) 3.96, (b) 6.06, (c) 8.44 and (d) 9.46.

ion with (D,L)-tartaric acid, but some differences are detected (Tables I and II). Firstly, all the species denoted by **5** are now of similar stability, leading to signals of approximately equal intensity (Fig. 3). The other major difference is the formation of a new species [8] which is dominating from pH* 5 to pH* 8 in a 1:1 solution (Fig. 4). This gives rise to an AB quartet ($^3J_{AB}$ = 8 Hz) at about 2.7 ppm to high frequency of free ligand and a single peak with $\Delta\delta$ = 3.15 ppm. The value of $^3J_{HH}$ = 8 Hz points to a ligand conformation in which the vicinal protons are approximately *trans* to each other.

We have assigned these two signals to different ligand molecules belonging to the same complex on account of a constant intensity ratio of 2:1 irrespective of pH and concentration conditions (molar ratio and dilution effects). A polymer (4:3) of formula **II** could account for the spectrum observed (this formula does not attempt to show the fact that the various UO_2^{2+} axes are not parallel to each other).



II

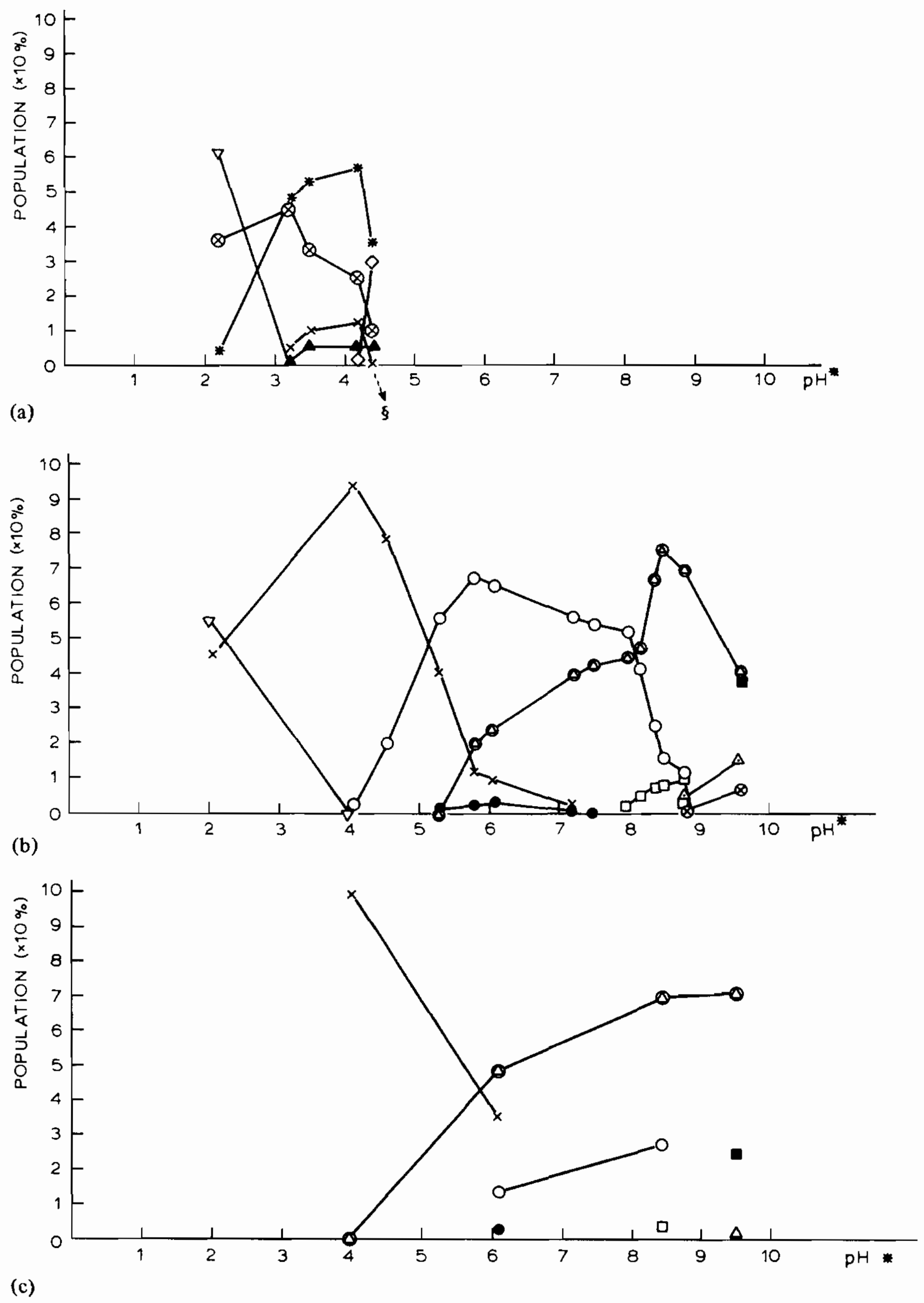
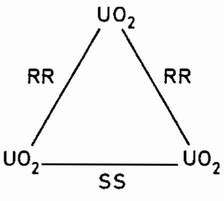


Fig. 4. Populations of bound ligand *vs.* pH* values for the system UO_2^{2+} + (D,L)-tartaric acid. Molar ratio: (a) 2:1, (b) 1:1 and (c) 1:2. Symbols as for Fig. 2. § Precipitation occurs.

The existence of three pairs of CH(OH) and CO_2H signals in the ^{13}C spectrum supports the proposal of the above structure; the respective $\Delta\delta$ values are 18.26, 17.86, 17.46 ppm and 8.14, 7.20, 7.07 ppm.

However, this hypothesis is difficult to sustain as it would mean a stable 4:3 complex only when the central ligand has a different configuration (*RR* or *SS*) from that of the two remaining ligand molecules (*SS* or *RR*). An alternative structure in agreement with the ^1H and ^{13}C data able to form stereospecifically would be a cyclic trimer of C_2 symmetry involving two *RR* (or *SS*) ligand molecules and one *SS* (or *RR*) ligand schematically as follows:



III

The *RR* ligands would give rise to the AB pattern at $\Delta\delta = 2.77$ and 2.73 ppm, whereas the *SS* ligand would give the single line at $\Delta\delta = 3.15$ ppm. We note that the existence of a trimer complex of uranyl and tartaric acid had been suggested by Rajan and Martell [6]. An unstrained molecular model for **III** (or its enantiomer) can be constructed provided that a *cis* disposition of CO_2^- (or OH) groups is assumed around each UO_2^{2+} center (Fig. 5). With this structure the HC–CH fragments have an approximately *trans* conformation which is in accordance with the observed coupling constant of about 8 Hz.

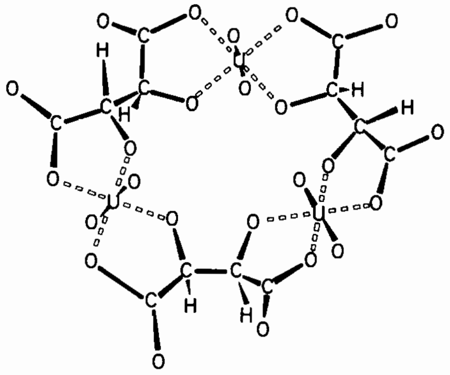


Fig. 5. Molecular model representing the trimer complex numbered 8 in accordance with Scheme 3.

Uranyl Ion + meso-tartaric Acid

It is seen from Table I that *meso*-tartaric acid with uranyl ion gives rise to a smaller number of signals. We have kept the same numbering as for (D) and (D,L)-tartaric acids. Figure 6 shows how the percentage of bound ligand varies with pH for the various

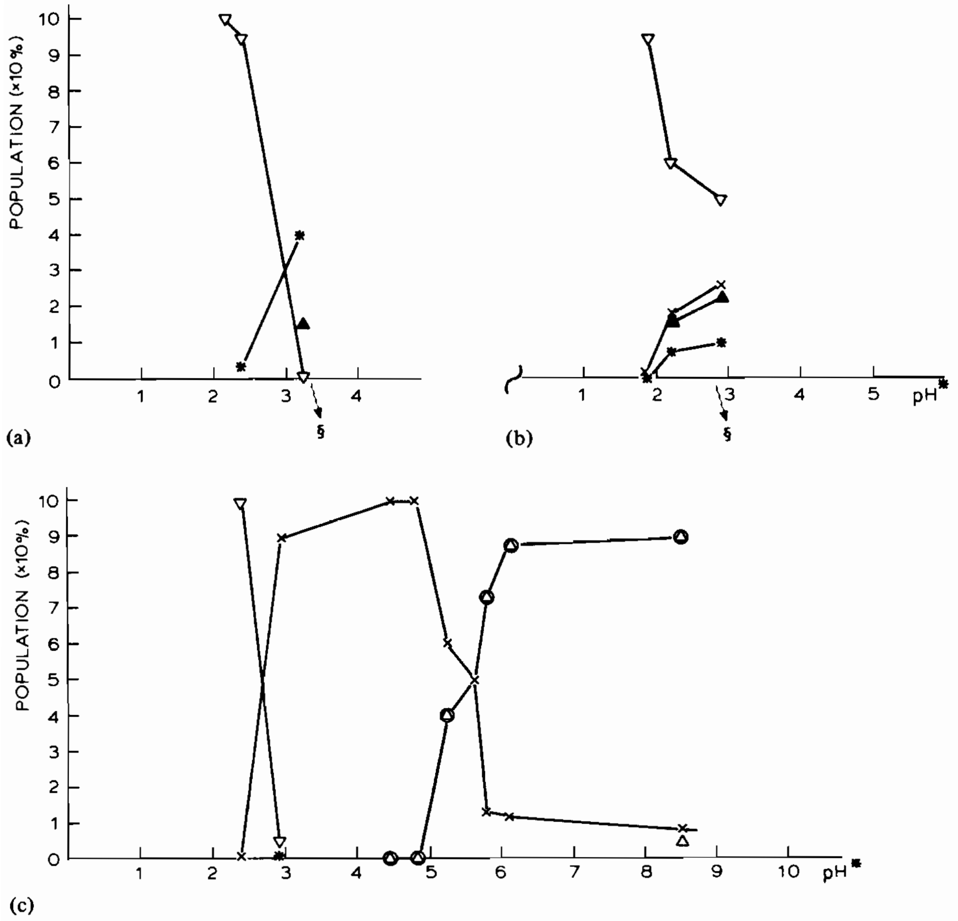


Fig. 6. Populations of bound ligand *vs.* pH* values for the system UO_2^{2+} + *meso*-tartaric acid. Molar ratio: (a) 2:1 (b) 1:1, (c) 1:2. Symbols as for Fig. 2. § Precipitation occurs.

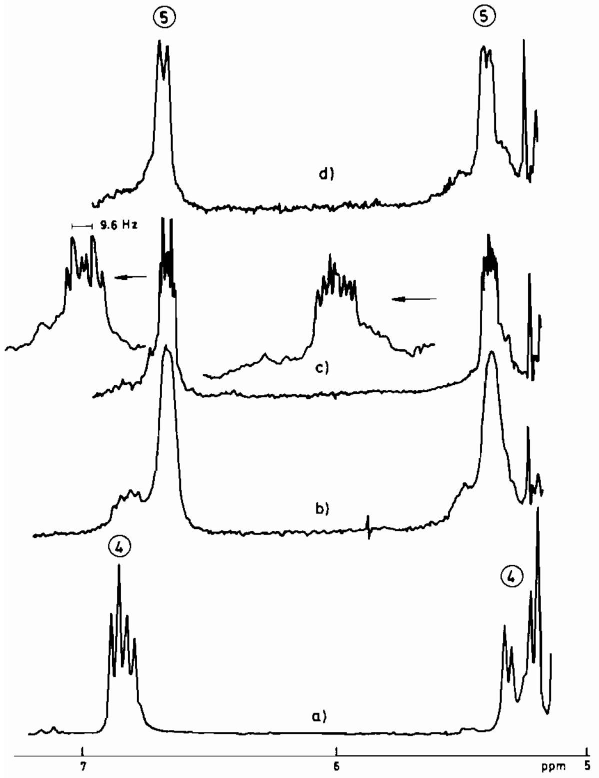
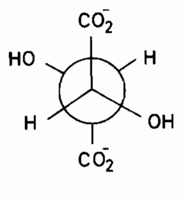


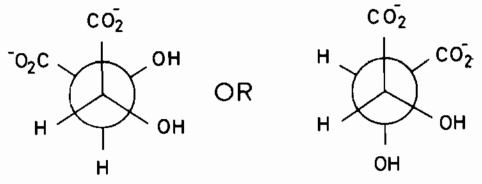
Fig. 7. Spectra of UO_2^{2+}:*meso*-tartaric acid solutions: molar ratio = 1:2, obtained for the following pH* values: (a) 4.11, (b) 6.10, (c) 8.53 and (d) 9.53.

complexes. As with (D,L)-tartaric acid, the signals 5 (and 4) are all of similar intensity (Fig. 7): the corresponding NMR parameters are shown in Table II. An important difference, however, is that the coupling constants in these AX spectra are now about 9.5 Hz. This is a clear indication of an approximately *trans* arrangement of the H atoms which implies the following conformation (C_1) for the bound ligand.



C_1

Although the above rotamer is the least populated in *meso*-tartaric acid solutions at any pH value [8], that conclusion could be expected from the fact that a *gauche* arrangement of the H atoms occurs in the corresponding complexes of (D)-tartaric acid. On the other hand, species **6** shows a $^3J_{HH}$ value of *ca.* 4.5 Hz, more typical of a *gauche* arrangement, whereas the corresponding value with U(VI) + (D) or (D,L)-tartaric acids is *ca.* 8.5 Hz. In the case of the *meso* ligand, the conformation is then approximately C_2 in this complex:



C_2

No evidence is found for a trimer similar to that proposed for (D,L)-tartaric acid as ligand.

Some of the spectra obtained in DMSO-d_6 show very broad signals due to specific exchange processes, probably involving solvent molecules coordinated to the metal ion, which we plan to investigate in the future.

Acknowledgements

The authors are indebted to Dr. P. A. Williams and Prof. A. V. Xavier for very helpful discussions. Thanks are also due to Prof. A. V. Xavier for the facilities concerning the use of the 300 MHz spectrometer.

References

1 M. T. Nunes, V. M. S. Gil and A. V. Xavier, *Inorg. Chim. Acta, 95,* 13 (1984).
2 M. T. Nunes, V. M. S. Gil and A. V. Xavier, *Can. J. Chem., 60,* 1007 (1982).
3 A. M. V. S. V. Cavaleiro, V. M. S. Gil, J. D. P. Jesus, R. D. Gillard and P. A. Williams, *Transition Met. Chem., 9,* 62 (1984).
4 M. M. Caldeira, M. E. Saraiva and V. M. S. Gil, *Inorg. Nucl. Chem. Lett., 17,* 295 (1981).
5 M. M. Caldeira and V. M. S. Gil, *Can. J. Chem., 62,* 2094 (1984).
6 K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem., 26,* 1927 (1964).
7 I. Feldman, C. A. North and H. B. Hunter, *J. Phys. Chem., 64,* 1224 (1960).
8 J. Ascenso and V. M. S. Gil, *Can. J. Chem., 58,* 1376 (1982).