^{1}H and ^{13}C NMR Evidence for Stereospecific Formation of (D,L)-Malic Uranates

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Abstract

A NMR study of the complexation of uranyl ion with different molar ratios of malic acid enantiomers (in aqueous solution) is reported. An increase of the stability of some species is found, when the two optically active ligand forms are present; the formation of a tetrameric complex is proposed. The concentration of some complexes is quantitatively correlated with the proportion of D and L forms.

Introduction

NMR has proved to be a powerful tool in a systematic study of the complexes formed, in aqueous solution, between α-hydroxycarboxylic or α-mercaptocarboxylic acids and the oxo ions of V(V), Mo(VI), W(VI), and U(VI) [1, 2].

If the acids occur in enantiomeric forms a pure stereoisomer has always been used, whenever commercially available, as this is expected to lead to easier interpretation of the spectra. This is particularly important in view of the complexity of the systems, which involve the formation of various coordination species strongly dependent on concentration and pH conditions. It is then possible to extend the study of speciation to the use of D,L ligands and investigate the stereospecific formation of complexes. In turn, this may lead to further clarification of the systems involving only one of the optically active ligand forms. In addition, it may enable a better understanding of those similar systems which use racemic mixtures of the acids due to the unavailability of the pure enantiomers.

Complexation of uranyl ion with (D,L) and (*meso*)-tartaric acids in comparison with (D)-tartaric acid has already been the object of an NMR study [1d]. In this paper work on the complexation of UO_2^{2+} with (D)- and (L)-malic acids in variable proportions of the ligand enantiomers and for a pH range 2–12, in close relation with a previous detailed investigation of the system UO_2^{2+} + (L)-malic acid [1i], is reported.

Experimental

The uranyl nitrate and (D,L)-malic acid solutions were prepared as described elsewhere [1i]. To obtain ^{1}H and ^{13}C spectra, the total concentration of the species was 0.075 and 0.75 M in 99.8% and 25% D_2O, respectively. The pH values quoted (pH*) are not corrected for the deuterium isotope effect: they are the direct pH-meter readings after standardization with H_2O buffer solutions.

The ^{1}H spectra were run in a Bruker CXP-300 NMR spectrometer at the probe temperature (292 K). The ^{13}C spectra were recorded, using broadband proton decoupling techniques, in a Bruker WP 80 SY and in a General Electric QE 300 spectrometers (at 20 and 75 MHz, respectively). As internal references for ^{1}H and ^{13}C resonances tert-butanol (δ = 1.23) and *p*-dioxan (δ = 67.4) were respectively used.

The ABX spectral analysis was performed by computer simulation using the program PANIC (*mini*-computer version of the LAOCOON type programs currently used on Aspect computers).

Results and Discussion

Proton NMR Spectra

Figure 1 shows the signals due to $HO_2C-CH(OH)-CH_2-CO_2H$ of bound malic acid (X parts of ABX spectra) recorded for an equimolar solution of uranyl nitrate and (D,L)-malic acid (0.075 M) at pH* values ranging from 2.11 to 11.45. Figures 2 and 3 illustrate, for two typical pH values, the effect of metal:ligand molar ratio and the effect of the (D)/(L) ratio of malic acid, respectively. Some differences are observed with respect to the system UO_2^{2+} + (L)-malic acid in similar conditions: (i) the occurrence of a new spectrum (h) at high pH for the (D,L) mixture

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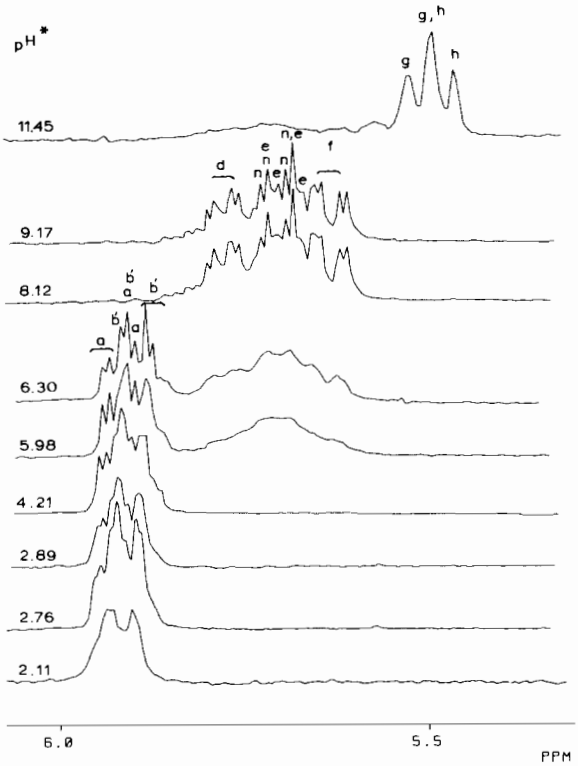


Fig. 1. X sub-spectra of bound ligand, obtained from an equimolar solution of uranyl nitrate and (D,L)-malic acid (0.075 M), at the indicated pH* values.

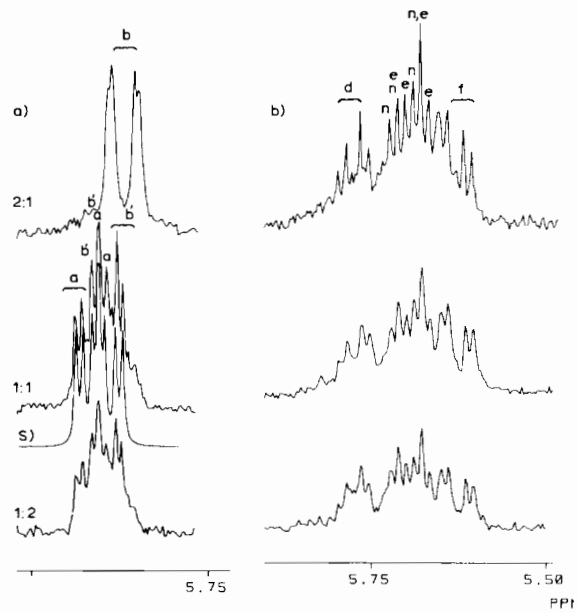


Fig. 2. X sub-spectra of bound ligand, obtained from solutions (uranyl nitrate/(D,L)-malic acid) with 2:1, 1:1 and 1:2 molar ratios (total concentration of the species 0.075 M) at pH* values: (a) 3.98 ± 0.05; (b) 8.96 ± 0.21; (s) simulated spectrum with NMR data from Table 1.

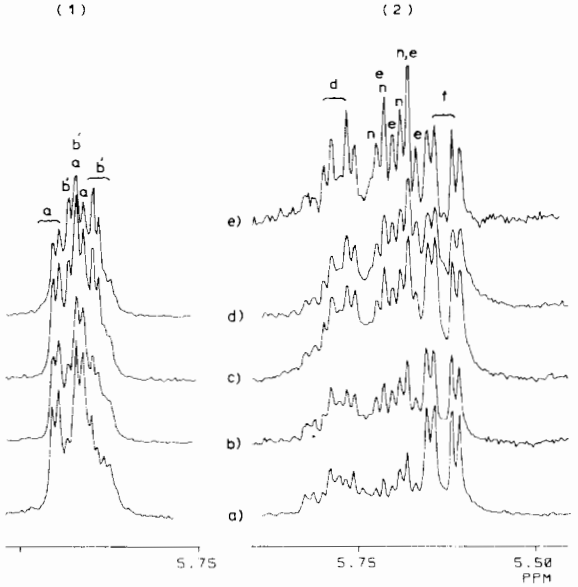
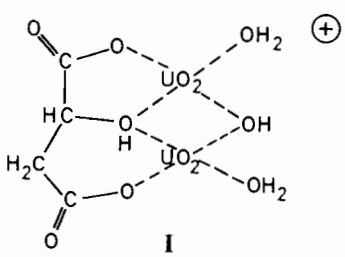


Fig. 3. X sub-spectra of bound ligand obtained from solutions with the following metal/(L)-malic acid/(D)-malic acid molar ratios (total concentration of the species 0.075 M): (a) 1:0.9:0.1; (b) 1:0.85:0.15; (c) 1:0.75:0.25; (d) 1:0.6:0.4; (e) 1:0.5:0.5. The pH* values are: (1) 3.36 ± 0.05 and (2) 9.07 ± 0.12.

and (ii) the increased intensities of the spectra designated by b′, d, e and n in ref. 1i when the ratio (D)-malic acid/(L)-malic acid approaches one.

Table 1 gives the ^{1}H NMR parameters obtained from ABX analysis of the various spectra, including those previously reported for (L)-malic acid as ligand; appropriate molar ratios and pH values were selected for the analysis of each spectrum (see, for example, Fig. 2). It is noted that the number of complexes can be different from the number of ABX spectra observed (10) for bound ligands; in fact, two ligand molecules in the same complex may be non-equivalent and, as it was already found in ref. 1i, conjugate acid–base equilibria involving the OH groups become slow enough on complexation to obtain separate spectra; on the other hand, some stereoisomers may not be distinguished by NMR.

At pH ⩽ 4 three spectra for bound ligand can be detected (affected by exchange phenomena in the more acidic region): a, b, b′ (Fig. 2). Spectrum b has been assigned [1i] to a 2:1 complex having the proposed structure **I**



I

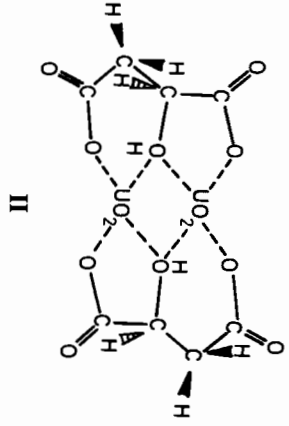
TABLE 1. ^{1}H chemical shifts (in ppm) and coupling constants (in Hz), and ^{13}C chemical shifts of the complexes identified

Spectra	^{1}H NMR parameters[a]						^{13}C chemical shifts[a]			
	δ_A (or δ_B)	δ_B (or δ_A)	δ_X	$^{2}J_{AB}$	$^{3}J_{AX}$ (or $^{3}J_{BX}$)	$^{3}J_{BX}$ (or $^{3}J_{AX}$)	CO_2H	$CH(OH)$	CH_2	CO_2H
a	2.54[b]	2.48[b]	5.93[b]	(–) 17.65[b]	2.38[b]	10.13[b]	122.3	18.0	–22.0	118.0
b	2.55[b]	2.44[b]	5.88[b]	(–) 16.91[b]	0.90[b]	11.61[b]	122.0	17.9	–22.2	118.2
b′	2.55	2.48	5.90	(–) 17.28	2.00	10.86	122.1	17.7	–21.9	118.2
c			5.80[b]		$^{3}J_{AX} + {}^{3}J_{BX}$ =	13.24		17.1		
d			5.76[b]		$^{3}J_{AX} + {}^{3}J_{BX}$ =	13.24	124.4	16.6	–22.2	119.1
e	2.52	2.48	5.69	(–) 17	2	11		16.9	–22.1	
n	2.53	2.48	5.70	(–) 17.0	1.6	11.6	124.2	16.3	–22.3	119.0
f	2.59[b]	2.52[b]	5.63[b]	(–) 16.91[b]	1.64[b]	11.60[b]	123.9	16.1	–22.4	118.9
g	2.41 (2.43)[b]	2.31 (2.33)[b]	5.48 (5.49)[b]	(–) 16.91[b]	1.27[b]	11.97[b]	–[c]	–[c]	–[c]	–[c]
h	2.44	2.34	5.45	(–) 17.0	1.0	11.0	–[c]	–[c]	–[c]	–[c]

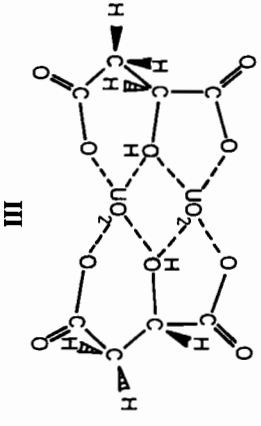
[a] ^{1}H and ^{13}C chemical shifts are reported with respect to tert-butanol and p-dioxan, respectively. [b] Ref. 1i. [c] Not determined due to the formation of insoluble uranates.

Such a complex would be formed equally well either with (D)- or (L)-malic acid, no differences being expected in the NMR spectrum. The fact that no changes in the b spectrum are observed when going from optically active malic acid to the racemic mixture is in accordance with the above structure.

Spectrum a has been shown [1i, 3] to be due to the dimeric complex postulated by Rajan and Martell [4] **II**, or its *cis* isomer **III**, for optical active malate.



II



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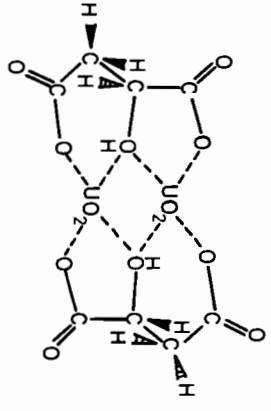
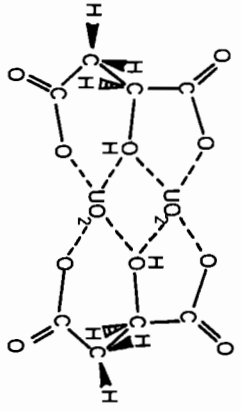


IV



V

In the presence of racemic ligand, however, two additional geometrical isomers could be formed [3]: **IV** and **V**.

For each of these 2:2 complexes there is magnetic equivalence of the ligand molecules. In addition, **II** and **IV** are likely to give rise to almost identical spectra, because the relative orientation of the distant methylene (and methyne) groups of both ligand molecules is not expected to affect proton chemical shifts significantly; the same can be said of **III** and **V**. This is consistent with the observation of two spectra (a, b′), one common to the *trans* isomers **II**, **IV** and one for the *cis* isomers **III**, **V**. That b′ can be due to a 2:2 species is supported by the NMR data of Table 1 for a and b′ and by the fact that the intensities of a and b′ signals remain approximately equal for the racemic mixture upon dilution (at $pH^* = 6.30$). We thus come to a first conclusion that, with active malic acid, the *trans–cis* isomers **II** and **III** have significantly different stabilities which are reflected in the observation of a spectrum a always more intense than b′. Secondly, the weakest structure (b′) becomes stabilized by having (D) and (L) ligands instead of only one of the active forms. Therefore, if the most stable 2:2 complex of UO_2^{2+} with (L)-malic acid has the *cis* structure **III**, then it is the *trans* structure **IV** which is the most stable one for the (D,L)-malic acid complex; conversely, if **II** is preferred to **III**, then **V** is more stable than **IV**. In favour of the former hypothesis is the fact that in both **III** and **IV** the methyne (and the methylene) protons of both ligands are in a *trans* orientation allowing an all-*trans* arrangement of CH, OH, OH, CH groups with minimum repulsive interaction.

At low pH values, the a and b′ signals become broad; in the most acidic solution ($pH^* = 2.11$) only two doublets are recorded in the χ sub-spectra region. This is probably due to an intramolecular rearrangement favoured by the protonation of the carboxylate groups: breaking of UO bonds of the carboxyl groups to the metal centres, followed by the rotation around the axis C–O in the fragment $C–O(H)\cdots(UO_2)_2$ would lead to a moderately rapid *cis–trans* isomerization.

At $pH^* \simeq 3.4$, a linear fit was obtained (by least-squares method) for the correlation of the ratio (R) (= [(L)-malic acid]/([(L)-malic acid] + [(D)-malic acid])) with the ratio obtained from the concentrations of the 2:2 a and b′ uranyl malate complexes

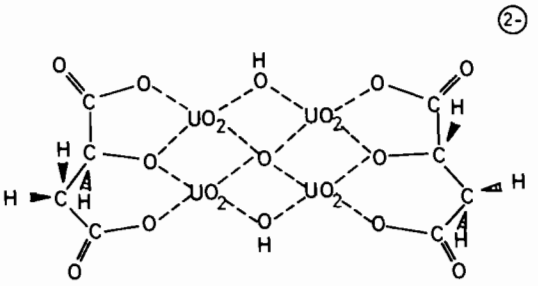
$$R = -0.4\,\frac{[b']}{[a]} + 1.2$$

(correlation coefficient = 0.987)

This method provides an indication of the optical purity of the ligand.

The high stability of dimeric uranyl malate complexes at $pH < 4.5$ is in agreement with $[(UO_2)_2(OH)_2]^+$ being the most abundant species for uranyl salts in aqueous solution at low pH values [5, 6].

At $8 \leqslant pH^* \leqslant 10$, four major patterns assigned to four χ sub-spectra are identified (d, e, n and f in Figs. 1 and 2b)). With (L)-malic acid it was shown [1i] that complex f was the single major species in this pH region and it was proposed as the conjugate base of species a. Just as the intensity of signal b′ increases on going from pure active to racemic ligand so do signals d, e and n. By analogy with the assignment of a and f to a conjugate acid–base pair, one of those signals should be assigned to the conjugate bases of complexes giving rise to b′. We choose d as corresponding to the conjugate base of b′, as spectra n and e become dominant at metal:ligand molar ratios higher than 2 and are, therefore, better assigned to 2:1 species. We propose that they correspond to the *cis* and *trans* isomers of a tetranuclear 4:2 complex (see **VI**)



VI

formed by hydrolysis of complex b (**III**) and dimerization via the establishement of OH (or O) olation bridges. This hypothesis is supported by the fact that the major species in uranyl aqueous solutions at $pH \geqslant 5$ is also tetranuclear: $[(UO_2)_4(OH)_7]^-$ [6].

At $pH^* \simeq 11.5$, two major χ-spectra (g and h in Fig. 1) are identified instead of the single species g detected when using (L)-malic acid [1i]. These are tentatively attributed to the *cis* and *trans* 2:2 complexes with ionization of both OH groups: g and h for species **III** (or **II**) and **IV** (or **V**), respectively. The smaller δ_H values are consistent with this hypothesis. However, due to the formation of insoluble uranates the stoichiometry of these complexes could not be confirmed by variable metal:ligand molar ratio studies.

Carbon NMR Spectra

The ^{13}C chemical shifts obtained for the various complexes are shown in Table 1. The chemical shifts for free malate ion, $^-O_2C–CH(OH)–CH_2–CO_2^-$, are, in this order, 114.1, 3.9, –23.9 and 113.1 ppm from *p*-dioxan. Assuming that the relative position of the carboxylic peaks is similar for free and bound ligand, the ^{13}C chemical shifts shown in Table 1 are in agreement with a terdentate chelation for all uranyl complexes: while the shifts obtained for the

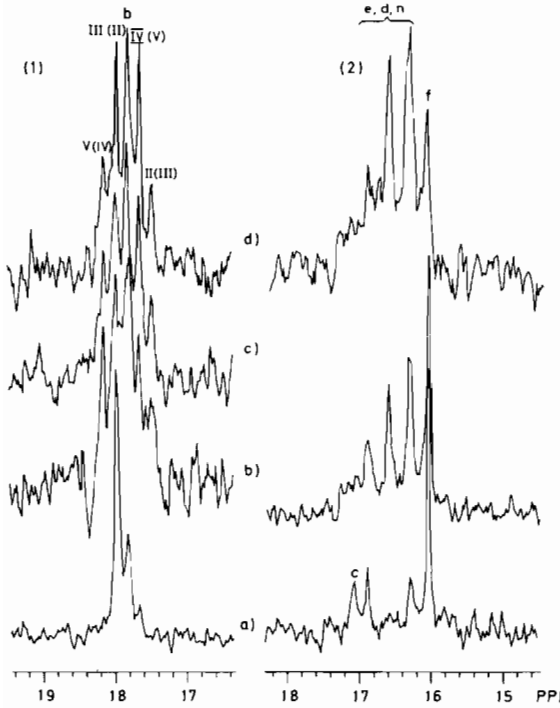


Fig. 4. $^{13}CH(OH)$ spectra of bound ligand obtained from solutions with the following metal/(L)-malic acid/(D)-malic acid molar ratios (total concentration of the species 0.75 M): (a) 1:1:0; (b) 1:0.85:0.15; (c) 1:0.6:0.4; (d) 1:0.5:0.5. The pH* values are: (1) 3.28 ± 0.06 and (2) 9.15 ± 0.05.

methylenic carbons upon complexation are *c.* 2 ppm, bigger low-field shifts are found for carboxylic and methyne groups (⩾6 ppm).

The parameters reported in Table 1 for ^{13}C were measured at 20 MHz. At this low frequency, the complexes formed at low pH (**I**–**V**) give rise to only three spectra as was the case of ^{1}H spectra: one for **I** (b), one for **II** and **IV** and one for **III** and **V** (a,b′). At higher frequency (75 MHz), however, distinct –*C*H(OH)– and α-CO_2^- signals can be observed for the four 2:2 complexes. Figure 4(1) shows the *C*H(OH)– signals obtained from solutions at pH* = 3.28 ± 0.06 with different values of [(L)-malic acid]/[(D)-malic acid]. Five signals are observed; the resonance at 17.9 ppm is assigned to complex b by analogy with the value obtained in experimental conditions where this species becomes dominant (2:1 metal/ligand molar ratio, pH* = 3.98). As similar n0e effects and relaxation times are expected in stereoisomers **II**–**V**, the relative intensities of the signals at 17.51, 17.68, 18.00 and 18.19 ppm can be correlated with proton relative spectral intensities (Fig. 3).

The $^{13}CH(OH)$ spectra obtained from solutions at pH* = 9.15 ± 0.05 with different values of [(L)-malic acid]/[(D)-malic acid] are also shown in Fig. 4. In the spectrum of the solution of uranyl/pure optically active ligand the signal at low-field is assigned to a weak complex c which is not detected when the ligand is the racemic mixture; its existence is not revealed by ^{1}H NMR. Another difference is observed when comparing the carbon spectra in Fig. 4: the increase in the intensities of two central peaks. These signals must be assigned to species involving (D) and (L) ligand molecules.

Conclusions

The main features of the ^{1}H and ^{13}C NMR spectra of the system UO_2^{2+} + (D,L)-malic acid in aqueous solution can be interpreted in terms of the following complexes:

(i) At pH < *c.* 4, a 2:1 metal to ligand complex with structure **I**, and four 2:2 isomeric complexes with structures **II**–**V** of different stability.

(ii) At pH between *c.* 8 and *c.* 10, the base conjugates of **II**–**V**, by ionization of one OH group in each dimer, and a tetranuclear 4:2 complex with its four geometric isomers.

(iii) At pH *c.* 11.5, the 2:2 complexes with both OH groups ionized.

For intermediate values of pH, mixtures of these complexes occur. No evidence was found for the formation of a ternuclear species previously postulated from potentiometric measurements [7].

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