NMR comparative study of the complexation of oxoions of V(V), Mo(VI), W(VI) and U(VI) with α-hydroxycarboxylic acids

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Abstract - Multinuclear magnetic resonance spectroscopy has been successfully applied in a systematic structural characterization of the complexes that form between oxoions of vanadium(V), molybdenum(VI), tungsten(VI) and uranium(VI) and α-hydroxycarboxylic acids in aqueous solution, as well as in the determination of their formation constants and in the study of exchange mechanisms in favourable cases. The methodology followed is presented and the main results surveyed involve ten acids of increasing complexity as ligands and the four metals mentioned above.

INTRODUCTION

We have been exploiting the capabilities of nuclear magnetic resonance spectroscopy in a systematic study of the complexes formed, in aqueous solution, between α-hydroxycarboxylic acids (Table 1) and the oxoions of vanadium(V), molybdenum(VI), tungsten(VI) and uranium(VI).

TABLE 1. Hydroxycarboxylic acids used as ligands in this paper

GLYCOLIC ACID	CH_2OH-CO_2H	(L)-MALIC ACID	$CO_2H-CH_2-CHOH-CO_2H$
(L)-LACTIC ACID	$CH_3-CHOH-CO_2H$	(D)-TARTARIC ACID	$CO_2H-CHOH-CHOH-CO_2H$
(L)-3-PHENYLLACTIC ACID	$CH_2(C_6H_5)-CHOH-CO_2H$	(D,L)- " "	
(D,L)-3-CHLOROLATIC ACID	$CH_2Cl-CHOH-CO_2H$	(MESO)- " "	
(L)-MANDELIC ACID	$C_6H_5 - CHOH - CO_2H$	CITRIC ACID	$(CO_2H-CH_2)_2COH-CO_2H$
(D,L)-GLYCERIC ACID	$CH_2OH-CHOH-CO_2H$	(D)-GLUCARIC ACID	$CO_2H-CHOH-CHOH-CHOH-CHOH-CO_2H$

Proton, carbon-13 and vanadium-51 NMR was used in the following way:
a) The number of distinct spectra gives the number of dominant complexes.
b) The intensities of the signals enable the concentrations of the various species to be determined and, consequently: i) pH, concentration and ionic strength effects to be characterized; ii) stoichiometries and formation constants to be established.
c) The proton and carbon chemical shifts of the ligand inform on the coordination sites.
d) The vanadium shifts can indicate the metal coordination number.
e) The analysis of the proton signals to yield coupling constants provides information on the conformation of the bound ligand molecules.
f) The proton line shapes enable, in favourable cases, a study of ligand exchange kinetics.

In this paper we illustrate the application of NMR, as outlined above, in the study of the systems mentioned at the beginning. We shall also present a summary of the main conclusions for all the systems studied so far, with special emphasis on the structures proposed for the main complexes in solution.

RESULTS AND DISCUSSION

NMR spectra, stoichiometries and formation constants

Figure 1 shows a typical vanadium-51 NMR spectrum. The example chosen is that of the system amonium vanadate(V) + (L)-lactic acid (ref. 1). Two signals assigned to two complexes, one largely dominant, are identified. As an illustration, Fig. 2 gives the ^{13}C spectra for an equimolar solution of uranyl nitrate and citric acid at various pH values (ref. 2). Five sets of four signals are detected, corresponding to free ligand and to four complexes.
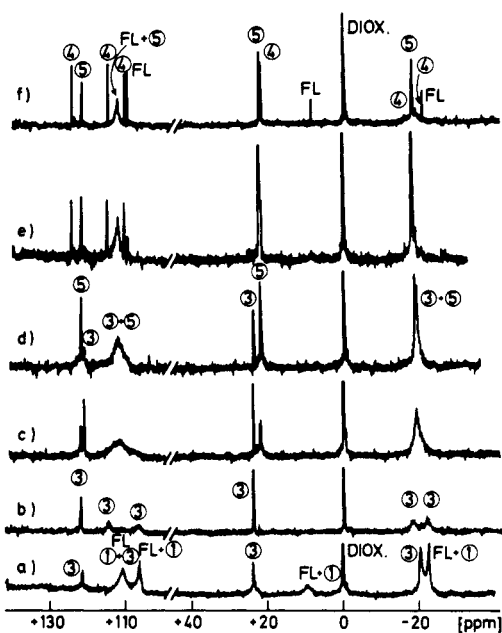
Fig. 1 The 52.6 MHz ^{51}V NMR spectrum of an equimolar solution (0.20M) of ammonium vanadate(V) and (L)-lactic acid in D_2O (pH=5.2) showing the presence of two complexes a, b (ref. 1).

Fig. 2 The 20.1 MHz ^{13}C NMR spectra of an equimolar solution (0.50M) of uranyl nitrate and citric acid at various pH values - a) 1.86; b) 4.08; c) 5.11; d) 5.80; e) 6.68; f) 10.25 - showing the formation of four complexes 1,3,4,5 (FL=free ligand) (ref. 2).

Fig. 3 NMR Job's plots for the system V(V) + citric acid at pH values for which each complex is in turn dominant: full line, pH=2.5, 1:1 complex; dashed line, pH=6.7, 2:1 complex. (ref. 4)
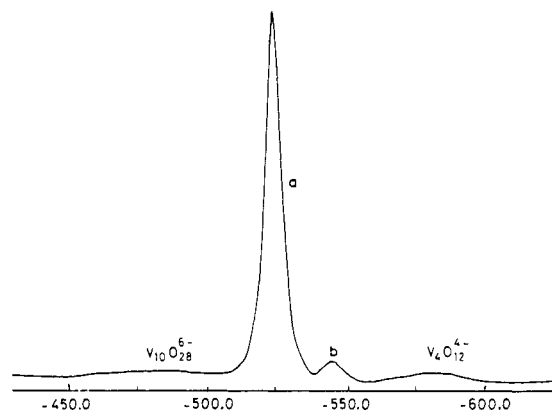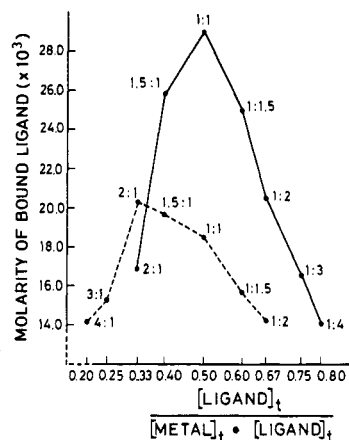
In favourable cases, the stoichiometries of the dominant complexes have been obtained by Job's method of continuous variations using the proton spectral intensities as property proportional to concentration. Figure 3 gives an example. Results are summarized in Tables 2-4.

When the composition of a complex is unambiguously established, intensity measurements of the proton spectra of bound and free ligand lead to an estimate of the formation constant. Some values have been obtained in this manner (Table 3).

Proton and carbon NMR shifts on complexation and the coordination sites

Invariably the signal due to the carbon attached proton of the -CHOH fragment (CH_2OH in the case of glycolic acid) bonded to a carboxyl group shifts to high frequency on complexation, from 0.3-0.8 ppm in the vanadium (V) complexes to 1-4 ppm in the UO_2^{2+} complexes. Smaller or much smaller shifts are in general observed for the other proton signals. This means that OH groups α to CO_2H groups are involved in complexation, together with the carboxyl group.

This conclusion is supported by the carbon high frequency shifts of the carboxyl group and of the neighboring -CHOH- group (or CH_2OH in the case of glycolic acid). For example, for the 1:2 tungsten(VI) + glycolic acid complex, which is largely dominant at pH=5.0, the $^{13}CO_2H$ signal lies at 4.29 ppm to high frequency of the corresponding signal of the free ligand at the same pH, whereas the shift of $^{13}CHOH$ is 11.6 ppm also to high frequency. Similar shifts are recorded for the other complexes.

TABLE 2. Vanadium(V) complexes

Ligand	No. of Complexes	DOMINANT SPECIES[a]			
		Metal: ligand ratio	pH-range	Proposed structure (Fig. 4)	Ref.
Glycolic acid	2+	1:1	2.5 - 6.5	I	1
		1:1(?)	5 - 6.5	III or IV	
(L)-Lactic acid	2+	1:1	2 - 7	I	1,11
		1:1(?)	4 - 7	III or IV	
(D,L)-Chlorolactic acid	2	1:1	2.5 - 6.5	I	1
		1:1(?)	4 - 6.5	III or IV	
(L)-Phenyllactic acid	1+	1:1	2 - 7	IV[b]	1
(L)-Mandelic acid	2	1:1	2 - 7	I	1
		1:1(?)	4 - 7	III or IV	
(D,L)-Glyceric acid	2	1:1	2 - 7	II	1,11
(L)-Malic acid	2	1:1	2 - 4.2	II	
		1:1	4.5 - 6.5	III or IV	1
(D)-Tartaric acid	1	2:1	2.5 - 7.5	V	1
Citric acid	2	1:1	2.5 - 5		1
		2:1	5 - 7		

Note a): In aqueous solutions of oxoions + acid with molar ratios from 4:1 to 1:4 and concentrations in the range 0.01M - 1M.

Note b): Only structure IV but not III may require a drastic conformation change of the ligand on complexation, as observed. The occurrence of only octahedral species is in accordance with the prediction of Tracey et al. (ref. 11).

TABLE 3. Molybdenum(VI) and tungsten(VI) complexes

Ligand	No. of Complexes	DOMINANT SPECIES [a]				
		Metal: ligand ratio	pK (b)	pH-range	Proposed structure (Fig. 4)	Ref.
Glycolic acid	1	1:2	-15.7 (W)	2.5 - 7.5	VI	3
(L)-Lactic acid	2(W)	1:2	-	2.5 - 7.5	VI	3,15
	1+(Mo)	1:2	-14.7	2.5 - 7.5	VI	
(D,L)-Chlorolactic acid	2(W)	1:2	-	2.5 - 7.5	VI	3
	1+(Mo)	1:2	-	2.5 - 7.5	VI	
(L)-Phenyllactic acid	2(W)	1:2	-15.8	2.5 - 7.5	VI	3
	1+(Mo)	1:2	-16.0	2.5 - 7.5	VI	
(L)-Mandelic acid	2(W)	1:2	-	2.5 - 7.5	VI	3
	1+(Mo)	1:2	-14.8	2.5 - 7.5	VI	
(D,L)-Glyceric acid	4(W)	1:2	-	2.5 - 7.5	VI	3
		1:2(?)	-	2.5 - 7.5	VI	
	2(Mo)	1:2	-	2.5 - 7.5	VI	
(L)-Malic acid	3(W)	1:2	-	2.5 - 7.5	VI	3,13,16
		1:1	-	2.5 - 7.5	VII	
	4(Mo)	1:2	-	2 - 7.5	VI	
		1:1(?)	-	2 - 7.5	VII	
		2:1	-	2 - 5.5	VIII	
(D)-Tartaric acid	2	1:2	-	2.5 - 7.5	VI	7
		1:1	-	4 - 7	IX	
(Meso)-Tartaric acid	2	?	-	2.5 - 7.5		7
Citric acid	2+	2:1	-		X	17
(D)-Glucaric acid	3	2:1	-	1.5 - 6	XI	9
		1:2(?)	-	3 - 7.5		
		n:1(n>1)		4.5 - 7.5		

Note a): As for Table 2.

Note b): For the equilibrium $MO_4^{2-}+2HL^-+2H^+ \rightleftarrows Mo_2L_2^{2-}+2H_2O$

For the 1:2 dominant complexes of W(VI) and Mo(VI) it is found that the $^{13}CO_2H$ shifts on binding to the metal are larger for W(VI); the same occurs with the proton shifts of CHOH; the opposite is found for the $-^{13}CHOH$ shifts. These trends with atomic number of the metal are also verified on going from Mo(VI) to V(V). If should be noted, however, that instead of 1:2 complexes in the case of W(VI) and Mo(VI) we have 1:1 complexes when the metal is V(V).

In the 2:1 complex of Mo(VI) with malic acid (ref. 3) and in the 1:1 complex of V(V) with the same ligand (ref. 1) formed preferably at low pH, the β-carboxyl group also shows a high frequency carbon chemical shift on complexation (4.4 ppm and 4.5 ppm, respectively) which is an indication of being involved in complexation as well as the α-carboxyl and the hydroxyl groups.

Malic acid is also found to act as a terdentate ligand in a 2:2 complex with uranyl, formed at low pH, on the basis of the high frequency carbon shift of both carboxyl groups (7.9 ppm (α), 4.6 ppm (β)) together with -CHOH (12.6 ppm) (ref. 5).

As for tartaric acid (active or meso), it acts as a terminal bidentate ligand in the 1:2 metal: ligand complexes with Mo(VI) and W(VI) (ref. 7). It has a terdentate function in the 2:2 complexes with UO_2^+ (ref. 8) and it is a tetradentate bridge ligand in the 2:2 complexes with Mo(VI) and W(VI) (ref. 7) and in the 2:1 (presumably 4:2) complex with V(V) (ref. 4). Glucaric acid also has a tetradentate function in the 2:1 complex with Mo(VI) (ref. 9).

A particular situation occurs with the high acidity 1:1 complex of vanadium(V) with citric acid. Although only the central carboxyl group and the neighboring OH group bound to the metal, the carbon signal of the terminal CO_2H groups is almost not affected by pH increase up to pH≈5 which suggests that they participate in hydrogen bonding with the VO_n center (ref. 4).

The 2:2 complex of uranyl + citrate, largely dominant at pH≈4, also shows a special feature. At this pH, duplicate signals are observed for the CH_2 proton resonances (two AB quartets) and for the CH_2 carbon and terminal CO_2H carbon resonances; in addition, while one of the CH_2 and one of the CO_2H carbon signals are almost not affected by complexation, (0.33 and 0.02 ppm respectively) the others shift significantly to high frequency (4.49 ppm and 7.54 ppm, respectively for CH_2 and CO_2H). This is in support of the structure
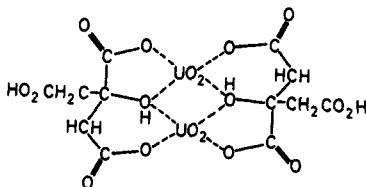
On increasing pH, however, all the above duplicate signals merge into single peaks: one for the protons of the two CH_2 groups (1.10 ppm to high frequency of free ligand at the same pH=6.5), one for the carbon nuclei of both CH_2 (2.88 ppm to high frequency of free ligand) and one for the two terminal CO_2H groups (3.17 ppm to high frequency of free ligand). This is attributed to a relatively fast rearrangement of the terminal CO_2H groups by which they alternate in bonding to UO_2^+, and which is favoured by full ionization of the carboxyl groups and of the hydroxyl group.

Vanadium chemical shifts and the coordination of V(V)

^{51}V chemical shifts in vanadium complexes are sensitive to the coordination number and to the nature of the ligands (ref. 10,11). For vicinal diol ligands and α-hydroxycarboxylic acids, ^{51}V signals at ∿520 ppm to low frequency relative to external $VOCl_3$ have been attributed to trigonal-bipyramidal structures, those at ∿535 ppm to octahedral species and those at higher fields to tetrahedral vanadates (ref. 11). Thus signal a in Fig. 1 will be due to a 1:1 trigonal-bipyramidal complex (ref. 1,11); b has been assigned to a dimeric (2:2) octahedral species (ref. 11). Similar results are obtained with glycolic acid, (D,L)-chlorolactic acid, (L)-mandelic acid and (D,L)-glyceric acid (ref. 1). For (L)-phenyllactic acid ($\delta_V=-534$) the octahedrally bound vanadium is dominant at any pH (a n:n complex). With citric acid, the two main complexes detected (molar ratios 2:1 and 1:1) are probably also octahedral species ($\delta_V\approx543$). For (D)-tartaric acid as ligand, $\delta_V\approx-525$ and a trigonal bipyramidal geometry around V is proposed (in a 2:1 species) (ref. 4,12). As for (L)-malic acid, the 1:1 complex dominant at low pH is taken as octahedral ($\delta_V=534$), whereas the 1:1 species more abundant at higher pH is either octahedral or tetrahedral ($\delta_V=546$).

Vicinal proton–proton constants and the conformation of the bound ligand

As it is well known, vicinal H-C-C-H coupling constants are strongly dependent on the HCCH dihedral angle. The ligands 3-phenyllactic, 3-chlorolactic, glyceric, malic, tartaric and glucaric acids all possess vicinal proton coupling constants capable of leading to conformation information.

Whereas for the free ligand in solution an averaged (pH dependent) conformation must be considered, due to rapid internal rotation, in the quite strong complexes the ligand assumes a more rigid conformation. In some cases it is found that the conformation preferred by the free ligand is essentially maintained when bound. Examples are as follows: i) phenyllactic acid bound to W(VI) (in the dominant 1:2 metal:ligand complex), with the coupling constants (pH=5.3) of 8.2 and 3.9 Hz for the free ligand and 7.7 and 3.5 Hz for the bound ligand (ref. 3) consistent with a preferred conformation close to (a); ii)

(a)   (b)

3-chlorolactic acid bound to V(V) (in both complexes formed) with the couplings (pH=2.7) of 2.9 and 4.3 Hz for the free ligand and 2.2, 2.0 and 3.0, 2.3 Hz for bound ligand (ref. 1) indicating a preferred conformation close to (b). In other examples, the values of the coupling constants remain approximately the same on complexation, but no unambiguous conclusion can be directly drawn. That is the case of the 1:2 complexes of Mo(VI) + malic acid (ref. 3,16) and Mo(VI) + tartaric acid (ref. 7). For the former we have (pH=4.8) the values 8.2, 2.7 Hz and 9.9, 3.0 Hz (or 3.0 and 9.9 Hz) respectively for J_{AX} and J_{BX} of free and bound ligand and the main conformation of the free ligand (c) is either retained

(c)   (d)
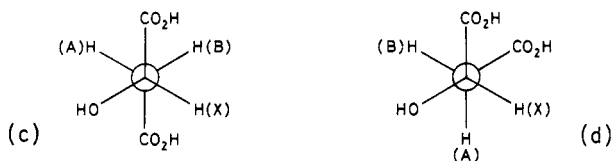
on complexation or is replaced by (d). For the latter, the value is 1.8 Hz both for free and bound ligand (pH=4.5) and the preferred conformation of free ligand (e) is again either retained on complexation or gives (f).

(e)   (f)
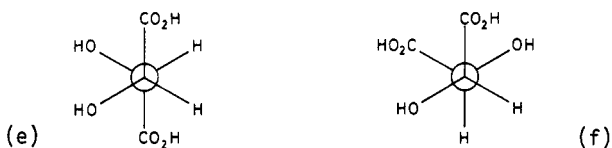
However, when taking both systems simultaneously it is found that only alternatives (c) and (e) are consistent with each other: a <u>trans</u> arrangement of the CO_2H groups coupled with <u>gauche</u> arrangements of CO_2H and OH. We are thus led to choose alternatives (c) and (e). The same reasoning can be applied to the 2:2 complexes of UO_2^+ with active malic and tartaric acids.

In some other systems the conformation of the ligand is drastically changed by complexation. That is the case of meso-tartaric acid bound to UO_2^+ in a 2:2 complex (ref. 2). The J values (pH=4.5) are 2.7 and 9.6 Hz respectively for free and bound ligand consistent with the preferred conformation (g) for the free ligand and (h) in the complex. Again we have a <u>trans</u> arrangement of the carboxyl groups coupled to a <u>gauche</u> relationship of CO_2H and OH. Another example is provided by the n:n complex of V(V) with phenyllactic acid (pH=5.3): 8.2 and 3.9 Hz for the free ligand and 4.4 and 2.1 Hz for the complex (ref. 1). The conformation of the ligand changes from essentially (a) to approximatly (i). In the 2:1

(g)   (h)   (i)
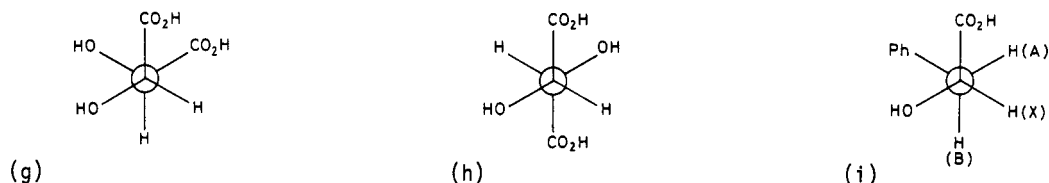
complex of Mo(VI) with (D)-glucaric acid, formed at low pH, there is a considerable decrease of $J_{HC_3C_4H}$ from 4.2 Hz to ~0 Hz which corresponds to the conformational change required for the bonding of each CO_2H group and adjacent OH group to a molybdenum atom.

Conformational changes on complexation can also occur in order to facilitate the establishement of intramolecular hydrogen bonding. We have already referred to intramolecular hydrogen bonding in the 1:1 complex of V(V) with citric acid. Other examples are the 1:1 complexes of Mo(VI) or W(VI) with malic acid (ref. 3).

Line shapes and exchange phenomena

At least three kinds of exchange phenomena in the systems under study can be recognized:
a) ligand exchange between free and bound sites or between bound sites;
b) ligand rearrangement within the same complex;
c) proton exchange in conjugate acid-base pairs.
Frequently ligand exchange is moderately slow at room temperature leading to more or less broad signals specially in high - frequency spectrometers. That is why most spectra have been run at temperatures close to 0°C. Sharpening of the signals are also sometimes obtained by slowing down the intermolecular exchange rate by dilution of the solution. A neat example of this kind of exchange is given by the UO_2^{2+} + malic acid system at low pH in conditions when the 2:2 complex dominates and in presence of excess of ligand. Irradiation of the free ligand -CHOH signal leads to a marked decrease of the intensity of the corresponding signal for bound ligand. This is an indication of a slow exchange process where the lifetimes of the two species are of the same order of magnitude as the proton longitudinal relaxation times. The exchange rates $k_A = 1/\tau_A$ (τ_A is the lifetime of bound ligand) at various temperatures, determined by the method of saturation transfer are as follows (ref. 14):

T/K	273	293	303	313	323
k_A/s^{-1}	0.14	0.19	0.24	0.26	0.29

These values allow rough estimates of 11 kJ mol^{-1} for the Arrhenius activation energy, 12 kJ mol^{-1} for the enthalpy of activation and 270 J K^{-1} mol^{-1} for the entropy of activation.

It was also found that k_A is a linear function of the concentration of free ligand. This is consistent with a dissociative mechanism of which the first step is the rapid outer-sphere association of a ligand molecule (L):

$$(UO_2)_2 L_2 + L^* \;\xrightarrow{\text{rapid}}\; (UO_2)_2 L_2...L^* \qquad (UO_2)_2 L_2...L^* \;\xrightarrow{\text{slow}}\; (UO_2)_2 LL^*...L$$

The carbon - 13 spectra of Fig. 2 for UO_2^{2+} + citric acid show the simultaneous presence of an intramolecular rearrangement of the ligand and of a conjugate acid - base equilibrium. The former is observed in complex numbered 3; the latter involves this complex and species numbered 5. The occurrence of distinct close ^{13}C signals due to bound $-CO_2H$ groups, to the quaternary COH carbon atoms and to the $-CH_2$ groups of species 3 and 5 (at pH≈5.8) proves that the overall proton exchange between them is comparatively slow. Indeed, slower than the alternating binding of the dangling $-CH_2CO_2H$ branch to the metal at the same pH≈5.8 which we have already mentioned: the two well separate signals observed at pH≈4 for the bound and unbound $-CH_2-CO_2H$ fragments coalesce into averaged broad signals at higher pH. A similar observation is made on lowering pH to about 2. From the carbon chemical shifts for the individual signals - 150 Hz for the carboxyl groups at pH=4.08 and 50 Hz for the COH carbon atoms of species 3 and 5 - we estimate lower and upper limits for the rates of the two processes (at pH=5.8): k (intramolecular rearrangement) $\geq 333s^{-1}$; k (intermolecular proton exchange) $\leq 111s^{-1}$. At pH=4.08, the intramolecular rearrangement is slower than $333s^{-1}$; indeed slower than $185s^{-1}$ so that two $^{13}CH_2$ signals are observed 84 Hz apart from each other.

Main complexes

Tables 2-4 summarize the main findings regarding the number of complexes detected, composition ratios, formation constants (where available) and approximate pH regions for the dominant ones, proposed structures. When minor species exist but have not been minimally studied, a + sign follows the number of main species in the tables. It is noted that some of the complexes are conjugate acid-base pairs. The structures drawn schematically in Fig. 4 allow for the occurrence of isomers. In a few cases, the use of molecular models enable the elimination of some alternatives (ref. 7).
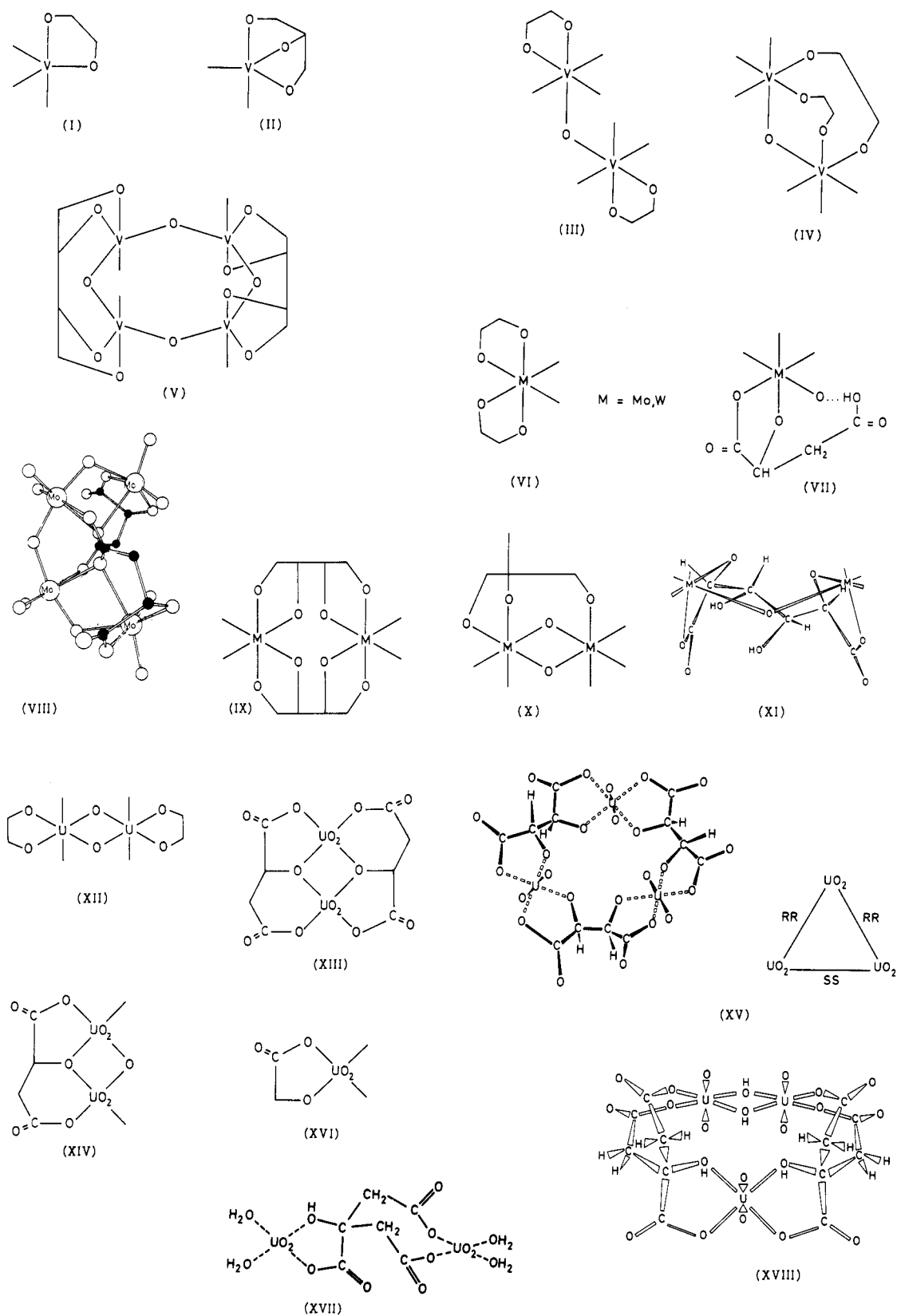
Fig. 4 Proposed structures or structure types for the complexes of V(V), Mo(VI), W(VI) and U(VI) with α-hydroxycarboxylic acids.

TABLE 4. Uranium(VI) complexes

| Ligand | No. of Complexes | DOMINANT SPECIES[a] | | | |
		Metal: ligand ratio	pH-range	Proposed structure (Fig. 4)	Ref.
(L)-Lactic acid	3	1:1	1 - 3.5	XII	18
		?	3 - 5		
		?	4 -		
(L)-Malic acid	4+	1:1	2 - 4	XIII (b)	5
		2:1	2 - 4	XIV	
		1:1	5 - 10	XIII (b)	
		?	∿11		
(D)-Tartaric acid	12+	1:1	2.5 - 5.5	XIII (c)	8
		1:1	5 - 10	XIII (c)	
		?	2.5 - 6		
		?	6.5 - 10		
(D,L)-Tartaric acid	13+	1:1	2.5 - 5.5	XIII (d)	8
		1:1	5 - 10	XIII (d)	
		?	2.5 - 6		
		?	6.5 - 10		
		1:1	5 - 8	XV	
(Meso)-Tartaric acid	6+	1:1	2.5 - 5.5	XIII (e)	8
		1:1	5 - 10	XIII (e)	
		?	2 - 3		
Citric acid	6+	1:1	1 - 2	XVI	2
		2:1	2.5 - 3.5	XVII	
		1:1	2.5 - 6.5	XIII (f)	
		1:1	6 - 10.5	XIII (f)	
		3:2	6.5 - 8.5	XVIII	

Note a): As for Table 2
Notes b), c), d), e), f): Conjugate acid-base pair.

Acknowledgements

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