The Complexation of Uranyl Ion with Carboxylic Acids Studied by ^{1}H and ^{13}C NMR*

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The interaction between uranyl ion and carboxylic acids has been investigated by several authors, mainly by potentiometric and spectrophotometric methods. The formation of polynuclear species associated with hydrolysis reactions of $UO_2(H_2O)_n{}^{2+}$ render these data very difficult to interpret; thus, the number and the stoichiometry of the complexes, the sites of the ligand involved in coordination, and the geometry of the various species have remained open questions. The successful application of NMR is based on the general observation of separate signals for free and bound ligands, since ligand exchange in some of those systems is slow on the NMR time-scale. It was thus possible to find new evidence about the complexation of $UO_2{}^{2+}$ with the following carboxylic acids in aqueous solution: (–)-lactic, (±)-thiolactic, (+)-malic [1, 2], (±)-thiomalic, ((+)(±),*meso*)-tartaric [3, 4] and citric acids [5].

Experimental

Carboxylic acids and uranyl nitrate of analytical grade were used in the preparation of D_2O solutions with different molar ratios. 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 and ^{13}C NMR spectra were run at 300 MHz and 20 MHz, respectively, on Bruker CXP 300 and WP 80 SY spectrometers; t-butanol ($\delta(^1H) = 1.23$ ppm) and *p*-dioxane ($\delta(^{13}C) = 67.4$ ppm) were used as internal references.

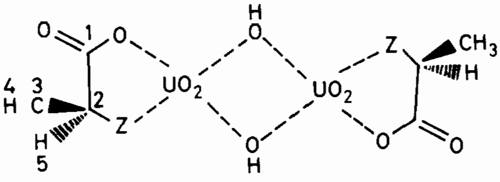
Results and Conclusions

Aqueous solutions of uranyl nitrate plus monocarboxylic acids (lactic and thiolactic acids) were studied by NMR spectroscopy over the pH range 0.5–5.0. A dimeric structure **I** is proposed for one of the complexes identified in the pH range 2–4 in agreement with dilution studies and with the 1:1 stoichiometry obtained from Job's plot (only in the uranyl ion + lactic acid solutions, the NMR signals of the bound thiolactic acid being too broad to be correctly integrated).

TABLE I. Chemical Shifts[a] (ppm) Obtained for the ^{13}C and ^{1}H Nuclei Assigned to the Bound Ligand in the Uranyl Complexes with Structure I

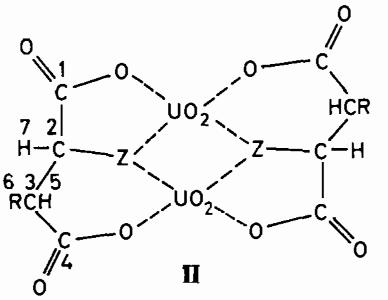
Acid	Z	Nucleus				
		^{13}C		^{1}H		
		(1)	(2)	(3)	(4)	(5)
(+)-Lactic	OH	≃4	≃6	0.5	0.62	3.31
(±)-Thiolactic	SH	b	b	c	c	2.48

[a]The references are the corresponding free ligand signals measured at the same pH values. [b]A single complicated pattern (or [c]a single signal) was obtained for free and bound ligand due to fast exchange processes (on the NMR time-scale).



I

The ^{1}H and ^{13}C chemical shifts (ppm) are shown in Table I; the references are the corresponding free ligand signals obtained at the same pH values. The resonances assigned to other complexes were shifted much less (<1 ppm for the methyne proton); monodentate behaviour for the ligand could be an explanation.



Carboxylic acid	Z	R
Malic acid	OH	H
Thiomalic acid	SH	H
Tartaric acid	OH	OH
Citric acid	OH	CH_2–CO_2H

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TABLE II. ^{13}C and ^{1}H Chemical Shifts[a] and Vicinal Coupling Constants ($^{3}J_{HH}$) Obtained for the Bound Ligand in the Uranyl Complexes with Structure II

Acid	Carbon nucleus				Hydrogen nucleus				
	Chemical shifts				Type of spectrum	Chemical shifts (ppm)			$^{3}J_{HH}$ (Hz)
	(1)	(2)	(3)	(4)		(5)	(6)	(7)	
(+)-Malic	7.9	12.56	1.63	4.6	ABX		0.90	2.62	2.28 10.13
(±)-Thiomalic	≃5	9.8	1.0	≃3	ABX		0.54	2.42	2.9 12.5
meso-Tartaric	9.92	12.87	0.0	6.81	AX	0.70		2.30	9.6
(+),(±)-Tartaric	9.26	15.71	3.29	4.79	AX	0.90		2.55	1.5
Citric	10.66	16.45	4.49	7.54	AB		0.85		

[a] The references are the corresponding free ligand signals measured at the same pH values.

In potentiometric studies of the systems uranyl ion plus malic, tartaric or citric acids, Rajan and Martell [6, 7] postulated a dimeric structure **II** for one of the complexes being formed. The NMR data (Table II) are in agreement with that structure and also show that these complexes are the dominant species in the pH range 2–4.

The stabilities of the dimeric complexes ($(UO_2)_2L_2$) based on the NMR data obtained for the five ring fragments increase in the following order:

(±)-thiolactic acid <(−)-lactic acid <
(±)-thiomalic acid <(+)-malic acid <
meso-tartaric acid <(+)(±)-tartaric acid <citric acid

Although a quantitative study of relative stabilities based on NMR spectral intensities is difficult because of the simultaneous presence of several complexes, the stability order proposed above is supported by a qualitative inspection of the ^{1}H NMR relative spectral intensities due to the bound and free ligand signals obtained, in all the systems studied, under similar conditions.

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