

An Energy Dispersive X-ray Diffraction Study of Dioxouranium(VI) in 1 M Lithium Citrate

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An Energy Dispersive X-ray Diffraction (EDXD) study of 0.3 M dioxouranium(VI) in 1 M lithium citrate at pH = 5 is reported. The data are in accordance with the existence of a predominately polynuclear complex containing four U atoms, concluded from potentiometric measurements. The uranium atoms lie at the corners of two triangles sharing one edge.

Five O atoms surround each uranyl group, the uranium coordination polyhedron being a pentagonal bipyramid; four U atoms are linked through double or single O bridges. The U–U distances are 3.95 Å and 4.65 Å.

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Introduction

Speciation of dioxouranium(VI) in the presence of organic ligands containing at least one carboxylate group is a topic that is extremely relevant to the safe disposal of nuclear wastes resulting from the use of fission technologies. Actually, modeling the migration of radionuclides in the environment requires an extensive and accurate knowledge of the equilibria involving the contaminating ion, both in solution and at the solid–solution interface. The solution chemistry of highly radioactive actinides, which may be difficult to investigate directly, is frequently simulated by means of the thermodynamic data existing for uranium in the same oxidation state; so, as an example, UO_2^{2+} is often assumed to closely follow the chemical behavior of the NpO_2^{2+} and PuO_2^{2+} ions. Besides the well-established importance of their mononuclear complexes, with a unique or with different ligands, the formation of polynuclear complexes may substantially influence the speciation involved under specific thermodynamic conditions typical of the environment, for instance by enhancing the solubility of a solid phase. In connection with this, the most instructive example is probably represented by the $[(\text{UO}_2)_3(\text{CO}_3)_6]^{6-}$ complex, which has been since the determination of its formation

constant through potentiometry,^[1] extensively investigated by a large number of different techniques.^[2,3,4] Similar investigations are still performed, first potentiometrically and then by other methods, on the complexes between UO_2^{2+} and acetate, UO_2^{2+} and oxalate, and UO_2^{2+} with ligands containing at least one carboxylic group.

Much interest has also been devoted to the dioxouranium(VI) citrate system,^[5] in which the existence of polynuclear species of general stoichiometry $\text{H}_x(\text{UO}_2)_y\text{L}_z^{(x+2y-3z)+}$ (L indicates the citrate ion, $\text{C}_6\text{H}_5\text{O}_7^{3-}$) with different (x,y,z) coefficients^[5–11] has been demonstrated. Nevertheless, despite large experimental efforts, the actual composition of polynuclear species with $y > 2$ and $z > 2$ is still a controversial topic: amongst the stoichiometries suggested on the basis of data from potentiometry, spectroscopy and other techniques (e.g. Electrospray Mass Spectrometry) there are $(x,2,1)$,^[12] $(x,6,6)$,^[7] $(x,3,2)$, and $(x,3,3)$.^[11] The problem must certainly be tackled by combining a multiplicity of techniques. Electrochemical methods (mainly potentiometry) can be of fundamental importance in determining the stoichiometry and the formation constants of the complexes existing under different analytical conditions. On the other hand, spectroscopic methods may help to determine the actual structure of the species in solution.

The aim of the present work is to explore the possibility of studying the dioxouranium(VI) citrate system by using an approach like the one just described, by combining potentiometry and the Energy Dispersive X-ray Diffraction (EDXD) technique. The main difficulty lies in needing to work at dioxouranium(VI) concentrations (0.1 mol/dm^3 – 0.3 mol/dm^3) which are about one order of magnitude different from those usually used in each technique. A further goal of this work is to determine if the X-ray diffraction

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Table 1. Composition of the solutions analyzed by EDXD; concentrations are given as mol·dm⁻³ (upper values) and as the number of atoms in the stoichiometric unit volume $V/\text{\AA}^3$ (lower values)

Solution	Concentrations		$[\text{ClO}_4^-]$	$[\text{UO}_2^{2+}]$	$[\text{H}_2\text{O}]$	Density (g/cm ³)	$V (\text{\AA}^3)$
	$[\text{Li}^+]$	$[\text{C}_6\text{H}_5\text{O}_7^{3-}]$					
A	3.000	1.000	0.676	—	49.0248	1.161	533.511
	1	0.3333	0.22533	—	16.34163		
B	3.000	1.000	0.6574	0.3004	48.27821	1.228	533.511
	1	0.3333	0.21913	0.10013	16.09276		

pattern of relatively concentrated (about 0.3 molar) uranyl solutions in the presence of a threefold concentration of citrate can be interpreted by assuming the U–U and U–O distances previously reported by a number of authors.^[13–16]

1. Results and Discussion

The analysis of the experimental data was performed using the *difference method*. This method has been successfully applied to liquid systems, in neutron diffraction and isotopic substitutions.^[17–22] Here the assumption has been made that the perturbations induced by the presence of the solute has a limited influence on the bulk lithium citrate and perchloric acid solution. The structure of the lithium citrate and perchloric acid solution was mainly preserved because it is three times more concentrated than the solute uranyl perchlorate. The experimental curves from the lithium citrate and perchloric acid solutions were then subtracted from the dioxouranium(vi) experimental curves. In so doing all the interactions occurring in both solutions were cancelled, i.e. water–water, water–lithium citrate and perchlorate, lithium citrate–lithium citrate and perchlorate, and perchlorate–perchlorate. It was then possible to exclusively focus attention onto the interactions of the uranyl–uranyl and uranyl–other constituent in solution. The concentrations of the two solutions that were analyzed are reported in Table 1.

In the following the observed structure functions are reported [in the form $q i(q) M(q)$, in Figure 1, along with the radial distribution functions (*rdf*), in the form $D(r)_{\text{difference}} = D(r) - 4\pi r^2(\rho_0)$ for the water citrate solution and the citrate dioxouranium(vi) solution measured under the same experimental conditions.

The main features emerging from a qualitative analysis of both structure functions and radial distribution functions are significant and the presence in the dioxouranium(vi) solution of evident peaks at high values of r , implies an increase of order in solution for the lithium citrate and perchloric acid solution.

This pattern is particularly evident in the $D(r)_{\text{difference}}$ curves. As shown in Figure 1, the lithium citrate and perchloric acid solution (solution **A**) exhibits a large main peak at 2.5–6.0 Å and a second peak at 6.0–8.0 Å. In the dioxouranium(vi) solution *rdf* (solution **B**), we can discern peaks positioned at the same values of those present in the first solution *rdf*. This is expected because the concentration

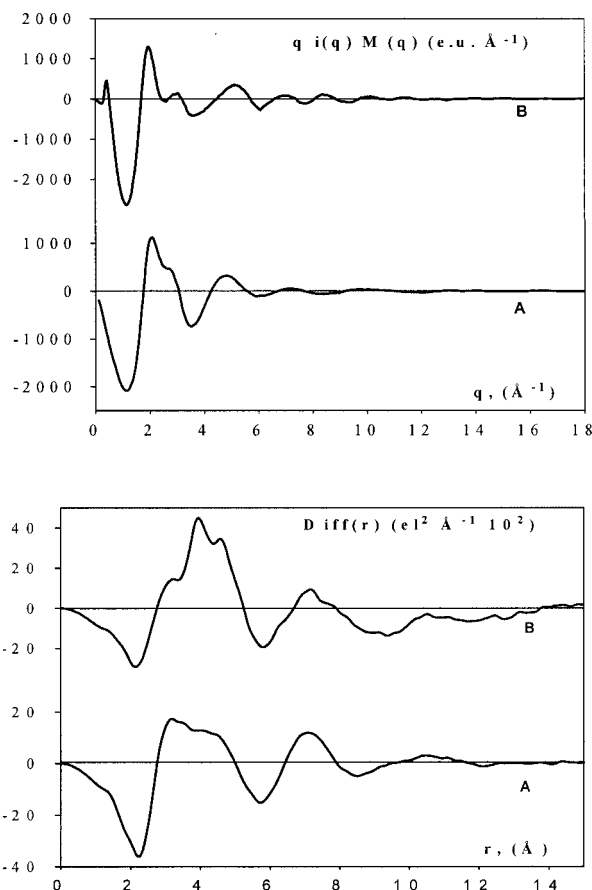


Figure 1. Top: experimental structure function in the form $q i(q) M(q)$: (A) Lithium citrate and perchloric acid solution, (B) dioxouranium(vi) solution; bottom: experimental radial distribution function in the form $D(r)_{\text{difference}} = D(r) - 4\pi r^2\rho_0$: (A) lithium citrate and perchloric acid solution, (B) dioxouranium(vi) solution

of lithium citrate is equal in the two solutions, and the concentration of ClO_4^- ions of the solution containing perchloric acid (solution **A**) is equivalent to the concentration of ClO_4^- ions due to the presence of dioxouranium(vi) perchlorate in the second solution (solution **B**). In the dioxouranium(vi) solution new peaks appear, namely the peak at 3.95 Å due to the interactions of the U atoms between themselves and between the constituent of the solution: water, lithium, citrate and perchlorate ions.

The features discussed above were used to build a structural model, the theoretical structure function and the theoretical distribution function, which best explained the

experimental data. Theoretical peaks were calculated by the Fourier transformation of a model structure function obtained by the Debye Equation (1) for pairs of interactions using the same sharpening factor, the same $q_{\max}$ value as for experimental data and assuming σ_{mn} to be the root mean square (r.m.s.) variation in the interatomic distance.

$$i_{mn}(q) = \{f_m \cdot f_n \cdot [\sin(r_{mn} \cdot q) / r_{mn} \cdot q] \cdot \exp(-1/2 \cdot \sigma_{mn}^2 q^2)\} \quad (1)$$

Instead of using a σ_{mn} value for each distance r_{mn} , the number of the parameters has been reduced, by assuming the same σ value for distances within predefined ranges; predefined ranges used are reported in Table 2.

Table 2. Final values of the adjusted r.m.s. σ for the model used

σ Values ($\text{\AA}$)	Distance range ($\text{\AA}$)
0.05	$0.0 < r \leq 1.9$
0.13	$1.9 < r \leq 3.0$
0.20	$3.0 < r \leq 5.6$
0.25	$5.6 < r \leq 9.0$
0.30	$r > 9.0$

As previously noted, the “difference method” was used to test the experimental data. The experimental $D(r)$ curves of both solutions, namely (A) lithium citrate and perchloric acid solution and (B) dioxouranium(VI) solution, and the difference curve between the two experimental $D(r)$ curves are reported in Figure 2.

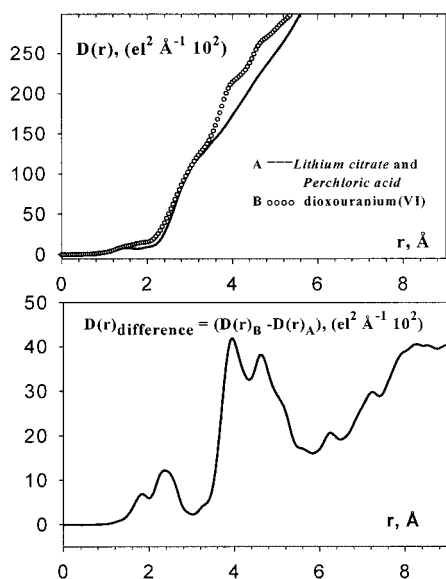


Figure 2. Top: experimental radial distribution function in the form $D(r)$; (A) lithium citrate and perchloric acid solution, (B) dioxouranium(VI) solution; bottom: experimental difference curve between the experimental radial distribution functions of solution (B) [dioxouranium(VI) solution], and solution (A) (lithium citrate and perchloric acid solution)

The experimental $D(r)$ difference curve only contains the interactions involving the UO_2^{2+} ions and the other constituent of solution B. Thus all the interactions which are

also present in solution A have been eliminated from solution B. In fact the first peak in the difference curve occurs at 1.78 $\text{\AA}$ and corresponds to the U–O distances in the UO_2^{2+} ion and there are no peaks at lower distances due to the bond lengths in the citrate and perchlorate ions. Hence the first peak is exactly reproduced, in the theoretical peak shape function; on the basis of the two interactions U–O at 1.78 $\text{\AA}$, with a σ value 0.05, it can be assumed that the second peak at 2.4 $\text{\AA}$ represents only the metal O coordination peak. The coordination number has been determined as five; the U–O distances are not equal for all the interactions, but are in the range 2.35–2.50 $\text{\AA}$, i.e. two O atoms are coordinated at 2.35 $\text{\AA}$, two at 2.40 and one at 2.50, with an average value of 2.40 $\text{\AA}$: all these considered distances are in the range 1.9–3.0 $\text{\AA}$ to which a σ value 0.20 is attributed. The theoretical functions and the experimental one are shown in Figure 3.

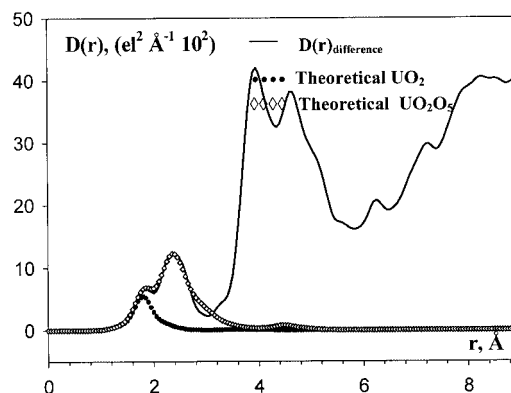


Figure 3. Experimental radial distribution functions difference curve $D(r)_{\text{difference}}$ (—), the theoretical peak shape function of U–O interactions in UO_2^{2+} ion (solid circles), and the theoretical peak shape function of U–O interactions in UO_2^{2+} ion coordinating five O atoms (open diamonds)

The bond lengths, and their spatial disposition are in good agreement with the literature data: dioxouranium(VI), in solution and in the solid state, is coordinated with five neighbors; the uranium atoms are at the centers of neighboring pentagonal bipyramids.^[14]

The large peak at about 3.95 $\text{\AA}$ indicates that the five O atoms, positioned on the equatorial plane of the pentagonal bipyramid, do not belong to the citric anions present in solution. The contributions of the five C atoms, bound to the O atoms, are altogether inadequate to fit the experimental peak.

On the basis of the literature data, tests have been performed for the presence of polynuclear complexes in solution. The first hypothesis tested, was the presence of binuclear complexes; two uranyl groups bonded by two bridging O atoms, with the uranium atoms at the center of neighboring pentagonal bipyramids having one common edge, with an usual U–U distance of 3.95 $\text{\AA}$. Calculating the theoretical peak shape function, by a dimeric compound model, with a σ value of 0.20, a peak positioned at

3.95 Å appears, but is still largely inadequate to reproduce the experimental one, as is shown in Figure 4.

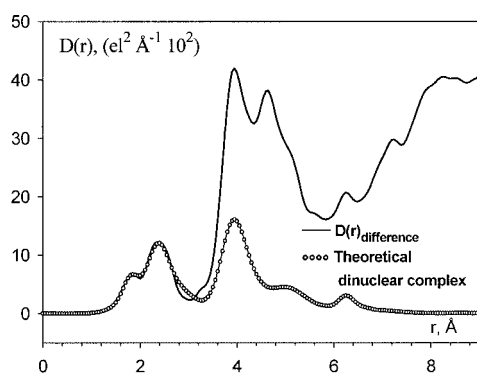


Figure 4. Experimental radial distribution functions difference curve $D(r)_{\text{difference}}$ (—), the theoretical peak shape function of U–O interactions in binuclear complex $[(\text{UO}_2^{2+})\text{O}_5]_2$ (open circles)

The theoretical peak shape function was calculated for a model containing only the U–O interactions. The model of the binuclear complex is shown in Figure 5. Adding the U–C interactions, arising from the citric anions, bound to the O atoms, the experimental peak height is not reached.

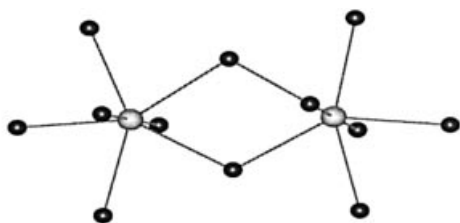


Figure 5. Picture of the model of the binuclear complex

A trinuclear model was successively tested. The position of the three U atoms, in a triangular unit, was supposed to be both symmetric and asymmetric; each U atom was considered to be surrounded by seven O atoms, and the coordination polyhedron was a pentagonal bipyramid, with the two apical O atoms belonging to the uranyl atoms. The model was constructed imposing the distance values previously obtained; 1.78 Å for the uranyl U–O distance and an average value of 2.42 Å, with a variation from 2.35 to 2.50 Å, for the remaining five O atoms. The three U atoms were positioned at the corner of an equilateral triangle with an edge length of 3.95 Å, or at the corner of a scalene triangle with an average edge length of 3.95 Å. The theoretical peak shape function obtained applying the model previously described only reproduces the experimental one with regards to the peak at 3.95. Adding the interactions arising from the citrate anions, belonging to the oxygen atoms that are free in the trinuclear complex, the height of the successive peak in the experimental function is not reached.

On the basis of the former considerations and of the potentiometric results it was supposed that a tetranuclear complex is present in solution of. The complex had to main-

tain the distorted pentagonal bipyramidal configuration around the U atoms, three U–U interactions at 3.95 Å and it had to create U–U interactions at 4.65 Å.

The structure of the tetramer is shown in Figure 6. The four uranium atoms lie at the corners of two isosceles triangles, with two edge length of 3.95 Å and the other edge length of 4.65 Å. The two triangles share one of the edges measuring 3.95 Å. They are not coplanar showing a dihedral angle of 35.30°. Each uranyl group is surrounded by five O atoms, as in dinuclear and trinuclear tested complexes.

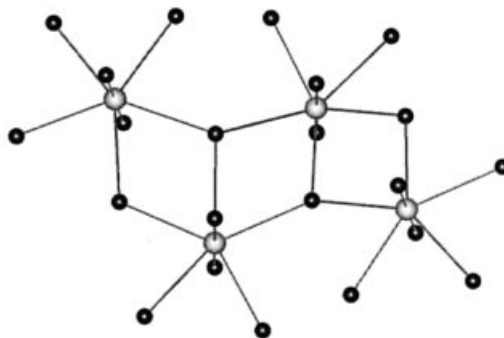


Figure 6. Picture of the model of the tetranuclear complex

In Figure 7 the experimental radial distribution function in the difference form $D(r)_{\text{difference}}$ is compared to the theoretical one, obtained from the model shown in Figure 6.

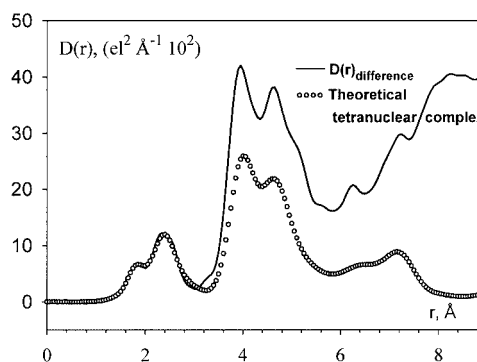


Figure 7. Experimental radial distribution functions difference curve $D(r)_{\text{difference}}$ (—), the theoretical peak shape function of U–O interactions in tetranuclear complex $[(\text{UO}_2^{2+})_4\text{O}_{14}]$ (open circles)

Even if the trend of the theoretical curve, calculated with the tetranuclear model, is analogous to that of the experimental curve, it is not reproduced. The theoretical peaks are remarkably lower than the experimental ones. For this reason models obtained from a larger number of UO_2 units have been tested. Pentanuclear and esanuclear complexes, arranged according to various geometries, have been tried. The models were constructed imposing the distance values previously obtained (1.78 Å uranyl $\text{U}\cdots\text{O}$ distance and an average value of 2.42 Å for the remaining five O atoms). The five or six U atoms were positioned at the corners of various geometrical figures with edge lengths of 3.95 Å, or

4.65 Å opportunely distributed, in order to reproduce the experimental curve. It turns out that these models are not acceptable since the heights of the obtained peaks, in the theoretical peak shape function, were much too high, with respect to the experimental ones, in order to allow for the presence of a second sphere of coordination around the atom of uranium.

Therefore it was decided to return to the study of the tetranuclear complexes, and to reconsider the second coordination sphere. Since the concentration of citrate anions is three times higher than the concentration of the uranyl cations, it was assumed that at least one oxygen atom, between those bound to the uranyl, belong to a citrate carboxylic group. The theoretical peak shape function, calculated by this model, still did not give a good agreement with the experimental data. Models with a greater number of citrate interactions were tested, but these gave way to theoretical functions that exceeded the experimental ones, especially for the peak at 3.95 Å.

Therefore a further hypothesis was considered; that the contributions that were still lacking came from water molecules and due to hydrogen bonds with the oxygen atoms of the uranyl group a first coordination sphere of the complex could still be considered.

The model was constructed with the geometry parameters previously reported when only the U–O interactions were considered. The four O atoms bridging the four uranyl cations belong to OH[−] groups that, with the four citrate anions, neutralize the positive charge of the uranyles. The possible model of the citrate coordination in the tetranuclear complex is shown in Figure 8 (see a). Six water molecules supplying the other O atoms that surround the U atoms and sixteen water molecules are bound to the eight O atoms of the uranyl cations by hydrogen bond with a O–O distance of about 2.86 Å and OOU angle of about 115°.

In order to simplify the model construction, the tetranuclear complex was considered to have a symmetry center and the citrate anions to have the same spatial configuration. This conformational restriction, regarding the citrate anions, leads to the theoretical function not perfectly reproducing the experimental one. Different citrate anion conformations would allow a greater variability of the distances and therefore a better agreement between the experimental data and the theoretical peak shape function.

In Figure 9, the comparison between the experimental function and the theoretical one, calculated for the model previously described, is shown.

On the basis of NMR literature data, the possibility of the hydroxy group and the α -carboxyl group being involved in coordination was tested. The comparison between the experimental function and the theoretical one, calculated for the model proposed by NMR spectroscopic data, maintaining the uranyl first coordination sphere, unaltered with respect to the previously tested model, shows comparable concordance, Figure 9. For this model, the tetranuclear complex was also considered to have a symmetry center, but the conformational restrictions are superior with respect to

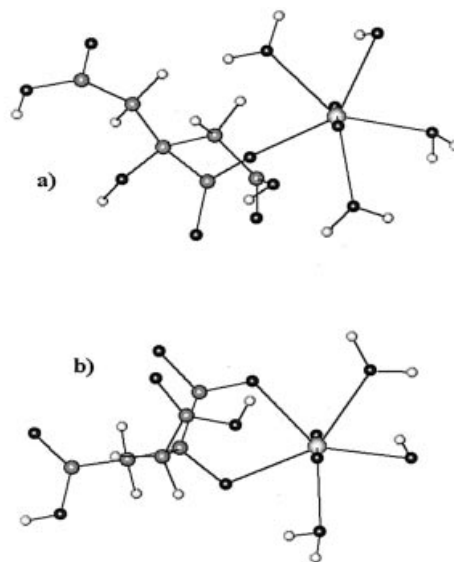


Figure 8. Picture of the models of the citrate coordination in tetranuclear complex: a) $[(\text{UO}_2^{2+})_4\text{Cit}_4\text{O}_6]\cdot 16\text{H}_2\text{O}$ and b) $[(\text{UO}_2^{2+})_4\text{Cit}_4\text{O}_2]\cdot 16\text{H}_2\text{O}$

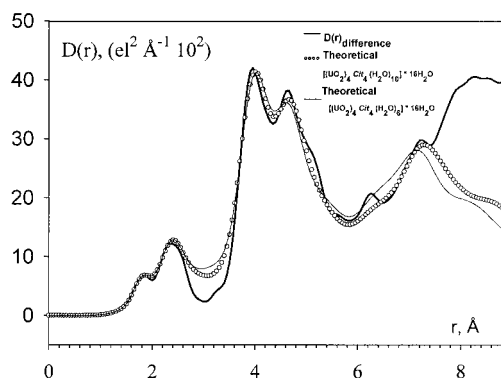


Figure 9. Experimental radial distribution functions difference curve $D(r)_{\text{difference}}$ (bold line), the theoretical peak shape functions of the tetranuclear complex $[(\text{UO}_2^{2+})_4\text{Cit}_4(\text{H}_2\text{O})_{10}]\cdot 16\text{H}_2\text{O}$ (open circles) and $[(\text{UO}_2^{2+})_4\text{Cit}_4(\text{H}_2\text{O})_6]\cdot 16\text{H}_2\text{O}$ (----)

the other model due to the five atom ring formation, Figure 8 (b). The X-ray diffraction in this case, is unable to discriminate between the two citrate coordination manners: for this purpose the information supplied from NMR spectroscopy may be fundamental. A better agreement between the experimental data and the theoretical function was not attempted since a refined structural analysis exceeded the main interest of this study, whose aim was to determine which form had the prevailing polynuclear uranyl citrate complexes.

2. Conclusions

A structural study on a uranyl perchlorate diluted solution in 1 M lithium citrate, with a ratio $[\text{total citrate}]/[\text{U}^{\text{VI}}] > 3$, has been carried out by means of X ray diffraction, on

the basis of a preliminary speciation study of the solution performed potentiometrically. The experimental data, treated and interpreted using the *differences method*, shows the occurrence of tetranuclear dioxouranium(VI) citrate complexes in solution. Further data, both potentiometric and spectroscopic, will be needed in order to unequivocally describe the citrate coordination around the dioxouranium(VI) polynuclear complexes.

3. Experimental Section

3.1 Sample Preparation. Reagents and Materials: All the solutions analyzed, Table 1, were prepared by using doubly distilled water. The uranyl perchlorate stock solution was prepared and standardized, with an accuracy of 0.3%, as suggested in ref.^[1] starting from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka p. a.). Perchloric acid solutions at different concentrations, prepared by diluting the 70% product from Fluka, were standardized using both KHCO_3 or HgO as primary standards (Fluka analytical grade) and methyl red or phenolphthalein, respectively, as indicators; analyses agreed within 0.1%. Concentrated lithium citrate and sodium citrate solutions were prepared from $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 4\text{H}_2\text{O}$ (> 99.5%, Fluka) and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (> 99.5%, Fluka) respectively, which were not further purified. Sodium perchlorate was prepared and standardized as described elsewhere.^[1]

The pH of solution **B** was 5.10 ± 0.02 at 18 °C. It was measured with a Metrohm 691 pH-meter equipped with a 6.0232.100 glass combined electrode (Metrohm); the electrode was calibrated with IUPAC pH standards. The potentiometric data were recorded around the clock using Metrohm 6.0123.100 and 6.0726.100 electrodes, a 34970A Data Acquisition/Switch Unit pursued by Agilent Technologies and automatic burettes 715 Dosimat from Metrohm. Impedance adaptors were used to collect the data with a precision of 0.01 mV. The software TITPOT (by InLab, www.inlab.it) was used to control the experiments through a personal computer.

3.2 Potentiometric Measurements: Potentiometry was used to study the speciation of the uranyl ion in the presence of citrate. While the system is quite well-known at dioxouranium(VI) concentrations lower than 10 mM a preliminary experiments were performed at higher metal concentrations, in order to better define the stoichiometry of the polynuclear complexes other than the dimer. The results of a preliminary experiment are presented here, which is part of a more systematic investigation now in progress.

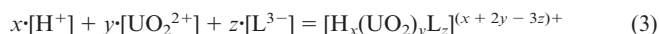
The experiment has been performed as a potentiometric titration. An accurately known volume of the test solution TS [TS: 0.100 M $\text{UO}_2(\text{ClO}_4)_2$, 0.100 M HClO_4 , 2.700 M NaClO_4] placed into a vessel thermostatted at (25.00 ± 0.02) °C, has been titrated in the dark, under a nitrogen stream, with known volumes, V_T , of the solution T (T: 0.100 M $\text{UO}_2(\text{ClO}_4)_2$, 0.700 M Na_3L , 0.150 M NaOH , 2.800 M NaClO_4). After each addition the $[\text{H}_3\text{O}^+]$ was determined from the EMF, E_1 (in mV), of the cell (I). Cell I: Glass Electrode/Test Solution/Reference Electrode by using the Nernst Equation (2).

$$E_1 = E^0 + 59.16 \cdot \log[\text{H}_3\text{O}^+] + E_j \quad (2)$$

In Equation (2) the cell constant E^0 was determined in two separate experiments performed before and after the titration, while the liquid junction potential E_j was evaluated as described elsewhere.^[23] A second type Ag_2AgCl electrode was used as the refer-

ence electrode; it was external to the cell but in electrical contact with TS through a salt bridge: 3.000 M NaClO_4 /0.010 M AgClO_4 , 2.990 M NaClO_4 /AgCl,Ag.

The primary (V_T , E_1) data collected allowed us to span the $1.14 < -\log[\text{H}_3\text{O}^+] < 4.34$ range, and was processed using the least-squares program Hyperquad^[24] in order to determine the equilibrium constant, β_{xyz} , of the general reaction (3)



Several models have been tested. On the basis of the literature data,^[5] under the experimental conditions chosen it is expected that the concentration of mononuclear complexes is very small, and hence negligible. In Table 3 the results that gave the least standard deviation are reported, while in Table 4 the proposed model with the formation constant of each species is presented.^[25–27]

Table 3. Survey of the standard deviation of different speciation models

Model	σ (mV)
(0,1,1), (0,2,2), (1,3,3), (−2,4,4)	0.2299
(0,2,2), (2,3,2), (1,3,3), (−2,4,4)	0.2254
(1,1,1), (0,2,2), (1,3,3), (−2,4,4)	0.1593
(0,2,2), (0,3,2), (1,3,3), (−2,4,4)	0.1456
(0,2,2), (1,3,2), (1,3,3), (−2,4,4)	0.1158

Table 4. Formation constants of the $\text{H}_x(\text{UO}_2)_y\text{L}_z^{(x+2y-3z)+}$ species at 25 °C in 3 M NaClO_4

(x,y,z)	$\log \beta_{xyz} \pm 3\sigma$
(0,2,2)	17.96 ± 0.01
(1,3,2)	20.95 ± 0.06
(1,3,3)	30.19 ± 0.01
(−2,4,4)	28.50 ± 0.02

Owing to the high citrate concentration of the titrant solution, the ionic strength of the titrated solution increased from 3.1 M to about 4.2 M; nevertheless, the actual ionic strength variations are probably smaller, owing to the fact that part of the citrate is not present as the trivalent anion but is in the form of the polynuclear uranyl complexes, variously protonated. Thus the overall accuracy of the reported data is estimated to be of about 2–3%.

Table 5. Auxiliary data used for the calculation of the distribution diagram of Figure 1

Reaction	$\log K$	Ref.
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	−14.22	[25]
$\text{H}^+ + \text{L}^{3-} = \text{HL}^{2-}$	5.16 ± 0.03	[26]
$2\text{H}^+ + \text{L}^{3-} = \text{H}_2\text{L}^-$	9.46 ± 0.03	[26]
$3\text{H}^+ + \text{L}^{3-} = \text{H}_3\text{L}$	12.70 ± 0.04	[26]
$\text{UO}_2^{2+} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	$−5.03 \pm 0.06$	[27]
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})^{2+} + 2\text{H}^+$	$−6.01 \pm 0.02$	[27]
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	$−16.13 \pm 0.03$	[27]

By using the set of constants of Table 4 and the auxiliary data of Table 5 the distribution diagram presented in Figure 10 was constructed. The diagram has been calculated by assuming $[U^{VI}] = 0.3$ M and $[\text{total citrate}] = 1$ M.

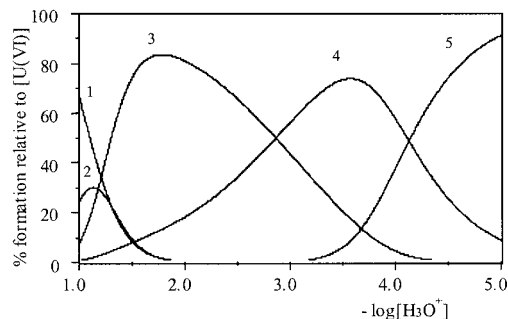


Figure 10. Distribution diagram of the uranyl citrate system; the curves have been calculated by using the data set reported in Tables 3 and 4, and assuming $[U^{VI}] = 0.3$ M and $[\text{total citrate}] = 1$ M; L represents the citrate anion, $C_6H_5O_7^{3-}$; the numbers on the curves indicate the following species: UO_2^{2+} (curve 1); $H(UO_2)_3L_2^+$ (curve 2); $H(UO_2)_3L_3^{2-}$ (curve 3); $(UO_2)_2L_2^{2-}$ (curve 4); $(UO_2)_4(OH)_2L_4^{6-}$ (curve 5)

The results of the potentiometric titration suggested the best experimental conditions for the X-ray measurements: a solution containing 0.3 mol dioxouranium(VI) and 1 mol citrate per dm^3 , in which sodium should rather be substituted by lithium, because the Li–O distances interfere less with the other ones expected in the system.

3.3 EDXD Measurements: Several examples of the application of Angle Dispersive, or Energy Dispersive X-ray Diffraction to pure liquids and solutions of metal ions in various solvents can be found in the literature.^[28–32]

In the present work, the Energy Dispersive X-ray Diffraction (EDXD) technique has been used. Compared with traditional ADXD (angular dispersion), it has several advantages:^[33–38] Diffraction patterns are collected in a much shorter period of time, using only a few reflection angles, but still covering q ranges equal to or larger than those obtained by AD; samples are stored in sealed cells, which avoid evaporation and contamination by moisture in the air.

Experiments were performed by using the noncommercial energy-scanning diffractometer built at the Department of Chemistry, Rome University. Detailed descriptions of the instrument and the technique can be found elsewhere.^[35–37]

Transmission geometry has been employed. The White Bremsstrahlung component of the radiation emitted by a tungsten tube working at 50 kV and 40 mA was used. Scattered intensities for the samples and the empty cell were measured at seven different angles. This choice allowed us to cover a wide range of the scattering variable q , namely between 0.23 – $18 \text{ \AA}^{-1}$. The measuring time at each angle was set so as to obtain a minimum of 1000000 counts per experimental point for $q > 5 \text{ \AA}^{-1}$ and 300000 for $q < 5 \text{ \AA}^{-1}$, where q is given by Equation (4)

$$q = 4\pi \cdot \sin\theta/\lambda = 1.014 \cdot E \cdot \sin\theta \quad (4)$$

When E is expressed in keV and q in $\text{\AA}^{-1}$, measurement angles, the energy range used and scattering parameters are reported in Table 6.

Table 6. Scattering parameters associated with the energy range used (13.0–43.7 keV) for each measurement angle

Scattering angles (degree)	q range ($\text{\AA}^{-1}$)
24.0	5.36–18.00
15.5	3.52–11.84
8.0	1.83–6.17
5.0	1.15–3.86
3.0	0.69–2.32
2.0	0.46–1.55
1.5	0.34–1.16
1.0	0.23–0.77

The primary beam intensity $I(E)$ was measured directly using the same voltage, by reducing the tube current to 10 mA at a zero scattering angle without the sample. Transmission of the sample was measured under the same conditions. Both quantities are needed to carry out necessary conditions to observed scattered intensities.^[35–38] After correction of experimental data for escape peak suppression,^[35–38] the various angular sets were combined and the re-scaled intensity, in electron units (e. u.), was normalized to a stoichiometric unit volume containing one Li atom. Such correction is performed using our program DIF1, written ad hoc. Detailed description of procedures and formulae used can be found in refs.^[25–28]. The atomic and water concentrations, together with stoichiometric volume and density, are reported in Table 1 (in $\text{mol}^{-1} \cdot \text{\AA}^3$ and g/cm^3 , respectively). The “static” structure function $I(q)$ was constructed according to Equation (5), where f_i are the atomic scattering factors, x_i are the number of concentrations of i -type atoms in the stoichiometric unit, $I_{e.u.}$ is the observed intensity in electron units.

$$i(q) = I_{e.u.} - \sum x_i f_i^2 \quad (5)$$

Fourier transformation of $i(q)$ led to radial distributions (rdf)

$$D(r) = 4\pi r^2 \cdot \rho_0 + (2r/\pi) \int_0^{\max} qi(q)M(q)\sin(rq)dq \quad (6)$$

In Equation (6) ρ_0 is the bulk number density of stoichiometric units and

$$M(q) = [f_U^2(0)/f_U^2(q)] \exp(-0.01q^2) \quad (7)$$

is the sharpening factor; the value of $18 \text{ \AA}^{-1}$ was used as the upper limit of integration.

Supporting Information: Primary potentiometric data are available (see footnote on the first page of this article).

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