

# Modeling of radionuclides in natural fluids: synthesis and characterization of the $\text{Na}_4(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2$ complex

R. Curini<sup>a</sup>, U. Tentolini<sup>a</sup>, S. Materazzi<sup>a,\*</sup>, E. Vasca<sup>b</sup>, T. Caruso<sup>b</sup>,  
C. Fontanella<sup>b</sup>, G. Palladino<sup>b</sup>

<sup>a</sup>Department of Chemistry, University of Roma "La Sapienza", p. le A Moro 5, 00185, Rome, Italy

<sup>b</sup>Department of Chemistry, University of Salerno, Via S. Allende, 84081 Baronissi, Salerno, Italy

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## Abstract

The coordination chemistry of dioxouranium(VI) with organic ligands may represent an useful model to describe the migration of radionuclides in natural fluids. A new dioxouranium(VI) ternary complex of formula  $\text{Na}_4(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2$  was precipitated at  $\text{pH} \cong 8$ . It was characterized by elemental analysis, ICP and IR spectroscopy, thermogravimetry (TG) and coupled TG–IR evolved gas analysis. Potentiometric measurements in the solution suggest that the equilibrium shifts from the prevalence of the  $(\text{UO}_2)_2(\text{OH})_2(\text{C}_2\text{O}_4)_4^{6-}$  complex to the  $[(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2]^{4-}$  complex before the formation of a solid phase. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

During the last decades, the coordination chemistry of actinides has been extensively investigated [1] mainly owing to their environmental relevance, related to nuclear fuel technology and waste management.

Among the actinides, uranium is certainly the most studied one [2] because of the relatively low radioactivity of the  $^{238}\text{U}$  isotope which allows to safely manipulate the solutions and the solids containing it.

In particular, dioxouranium(VI) complexes with both organic and inorganic ligands are still extensively studied in aqueous solutions by potentiometry [3], NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{19}\text{F}$ ) [4] and Raman spectroscopy

[5] and by combining EXAFS with either potentiometric [6] or other (NMR, Raman, X-ray diffraction) spectroscopic techniques [6].

The formation constants (that is, the free energy of formation) of a large number of uranyl complexes have been determined. Theoretical models describing their dependence from variables, such as the temperature and the ionic strength of the solutions are continuously being refined.

On the other hand there are relatively few systematic investigations aimed to establish correlations between thermodynamic parameters and physicochemical properties of the ligands. Evidently the existence of such correlations should be very useful in order to model uranium migration in the environment.

Since the complexing properties of natural humics isolated from different waters appear to be similar, and because the complexation with carboxylic functional groups has been identified as the most likely

\* Corresponding author. Tel.: +39-6-499-13616;

fax: +39-6-445-3953.

E-mail address: stefano.materazzi@uniroma1.it (S. Materazzi).

mechanism for the interactions with most radionuclides, different articles can be found in the literature regarding the complexation of the  $\text{UO}_2^{2+}$  ion with the oxalate ion [3–5,7,8]. But few of them, however, describe the precipitated complexes, and no thermo-analytical data are available for them.

The aim of this work is the characterization of the solid state compound obtained at  $\text{pH} = 8$  from the reaction of uranyl ion with oxalate ion by means of thermogravimetry (TG), ICP and FTIR spectroscopy. The precipitated complex shows the formula  $\text{Na}_4(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2$ , in agreement with preliminary potentiometric measurements performed in solutions with a ratio  $[\text{C(III)}]/[\text{U(VI)}] \geq 5$ . The analysis of the gases evolved from the thermobalance, on line coupled with the FTIR spectrometer, allows to confirm the stoichiometry of the precipitated compound.

## 2. Experimental

### 2.1. Reagents and analysis

Water was deionized and bidistilled in our laboratory.

The uranyl perchlorate and sodium perchlorate stock solutions were prepared and analyzed as described in [9] and [10] respectively. Standard methods were used to titrate highly pure perchloric acid and sodium hydroxide solutions; the analysis agreed within  $\pm 0.1\%$ . Sodium oxalate (99.92%, by Sigma–Aldrich) was used without further purification.

### 2.2. Synthesis of the complex

The complex was obtained by adding dropwise under stirring to a solution  $S = 5 \text{ mM UO}_2(\text{ClO}_4)_2$ ,  $10 \text{ mM HClO}_4$ ,  $50 \text{ mM Na}_2\text{C}_2\text{O}_4$  equal volumes of the solutions  $T_1 = 200 \text{ mM NaOH}$  and  $T_2 = 10 \text{ mM UO}_2(\text{ClO}_4)_2$ ,  $20 \text{ mM HClO}_4$ ,  $100 \text{ mM Na}_2\text{C}_2\text{O}_4$  until an orange solid precipitated. The solid was washed with bidistilled and deionized water and dried under vacuum.

### 2.3. Instrumental

#### 2.3.1. Potentiometry

Potentiometric measurements were performed at  $(25.00 \pm 0.02)^\circ\text{C}$  into an air thermostatted box,

through the cell (I)

(I)GE/Test Solution/RE

where GE indicates a glass electrode (Metrohm) and RE an Ag, AgCl reference electrode, external to the cell, electrically in contact with the Test Solution through a salt bridge.

The experiments were accurately planned in order to collect data at constant  $[\text{Na}^+] = 1 \text{ M}$  and  $[\text{C(III)}]/[\text{U(VI)}] = 5$ . Thus in a preliminary step of each experiment a known volume of the ionic medium solution  $S_1 = 1 \text{ M NaClO}_4$  was titrated stepwise with increasing volumes of the solution  $T_3 = 20 \text{ mM HClO}_4$ ,  $1 \text{ M NaClO}_4$ , in order to determine the constant appearing in the Nernst Equation for the cell (I) through Gran's plot. Once the volume of the Test Solution was doubled, half of it was prelevated and substituted with an equal volume of solution  $T_4 = 10 \text{ mM HClO}_4$ ,  $10 \text{ mM UO}_2(\text{ClO}_4)_2$ ,  $50 \text{ mM Na}_2\text{C}_2\text{O}_4$ ,  $0.9 \text{ M NaClO}_4$  in order to produce a solution of the desired composition  $S_2 = 10 \text{ mM HClO}_4$ ,  $5 \text{ mM UO}_2(\text{ClO}_4)_2$ ,  $25 \text{ mM Na}_2\text{C}_2\text{O}_4$ ,  $0.95 \text{ M NaClO}_4$ . The analytical acidity of this unhydrolyzed solution was stepwise decreased by titrating it with equal volumes of the two solutions  $T_4$  and  $T_5 = 0.1 \text{ NaOH}$ ,  $0.9 \text{ M NaClO}_4$ . In the course of the potentiometric titrations the emf of the cell (I) was monitored, until it remained constant, after each addition, within  $\pm 0.02 \text{ mV}$  for at least 15 min. Solutions with  $[\text{U(VI)}] = 5 \text{ mM}$  and  $[\text{C(III)}] = 25 \text{ mM}$  kept clear up to  $\text{pH}$  about 8, while in the absence of oxalate a solid phase of uranyl hydroxide begins to be formed at  $\text{pH} < 5$ .

The experiments had a duration of about 70 h. A fully automatized data acquisition system, based on Hewlett-Packard components and governed by the software TITPOT<sup>TM</sup> from Inlab Software House (Naples, Italy), allowed to follow the experiments around the clock. An impedance adapter, made by Mr. Luigi Falco (Department of Chemistry, University of Salerno), was used in order to measure emf's with a precision of  $\pm 0.01 \text{ mV}$ .

#### 2.3.2. Thermal analysis

The thermoanalytical curves were obtained using a Perkin Elmer TGA7 thermobalance (range 20–1000  $^\circ\text{C}$ ); the atmosphere was either pure nitrogen or air, at a flow rate of  $100 \text{ ml min}^{-1}$ ; the heating

rate was varied between 5 and 40 °C min<sup>-1</sup>, with the best resolution achieved at a scanning rate of 10 °C min<sup>-1</sup>.

To obtain the IR spectra of the gases evolved during the thermogravimetric analysis, the thermobalance is coupled with a Perkin Elmer FTIR spectrometer, model 1760×. The TGA7 is linked to the heated gas cell of the FTIR instrument by means of a heated transfer line, and the temperatures of the cell and of the transfer line are independently selected.

### 3. Results and discussion

A preliminary evaluation of the primary potentiometric data (volume of titrant, emf) suggests the formation, besides the well known hydrolytic and the binary uranyl-oxalate complexes, of the species (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub><sup>6-</sup> and (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>4-</sup>.

By increasing the pH to 8, the equilibrium shifts from the prevalence of the (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub><sup>6-</sup> complex to the prevalence of the (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>4-</sup> complex with the formation of a solid phase.

Table 1

Analytical data (%) for the complex (calculated)

	C	O	Na (ICP)
Na <sub>4</sub> (UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>4</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	5.8 (5.5)	29.0 (29.2)	10.7 (10.5)

The values resulting from the elemental analysis and the ICP spectroscopy, listed in the Table 1, allow to propose the formula of the precipitated solid as Na<sub>4</sub>(UO<sub>2</sub>)<sub>2</sub>(OH)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.

The IR spectrum of the complex (Fig. 1) shows the typical bands for the coordinated oxalate ion, with the characteristic shift of the band attributed to the stretching vibration of the COO<sup>-</sup> group in the complex, towards lower frequencies when compared with the unionized carbonyl, indicating that the oxalate ion is coordinated to the uranium(VI) atom.

To confirm this hypothesis, a thermogravimetric study of the complex was carried out, and the resulting thermal profile is reported in the Fig. 2.

The decomposition curve (air flow) shows the release of hygroscopic water at very low temperatures, followed by the main steps related to the loss of the

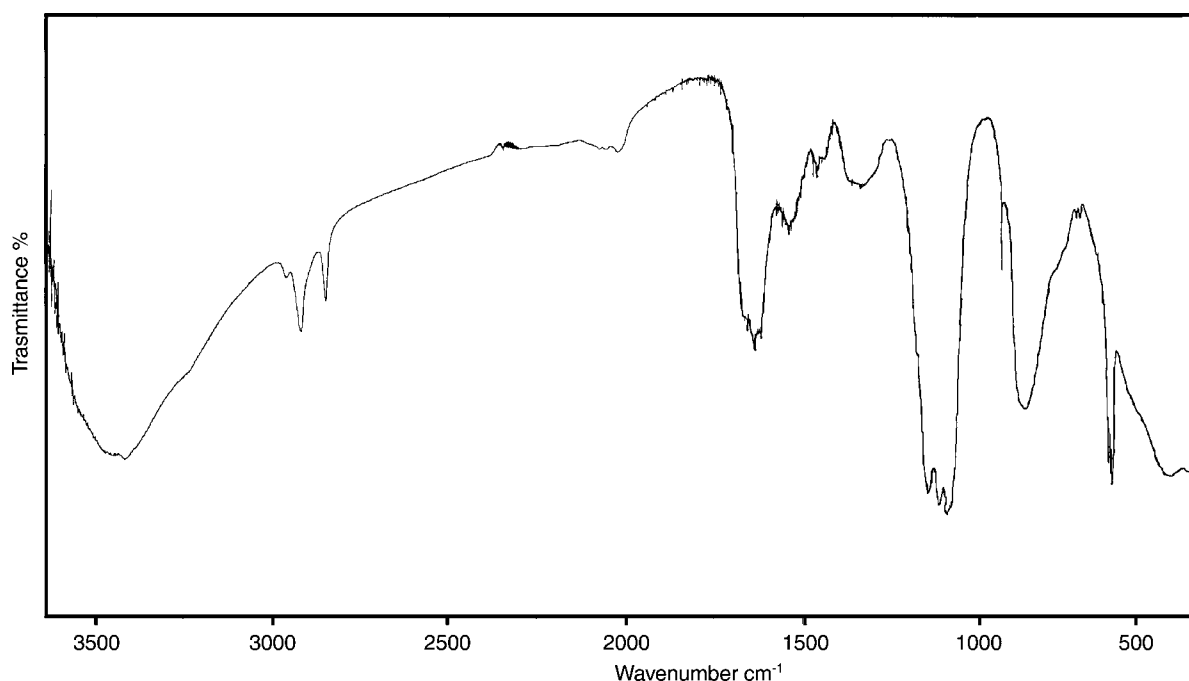


Fig. 1. Infrared spectrum of the Na<sub>2</sub>(UO<sub>2</sub>)<sub>2</sub>(OH)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> complex KBr disk-resolution: 4 cm<sup>-1</sup>-20 scans.

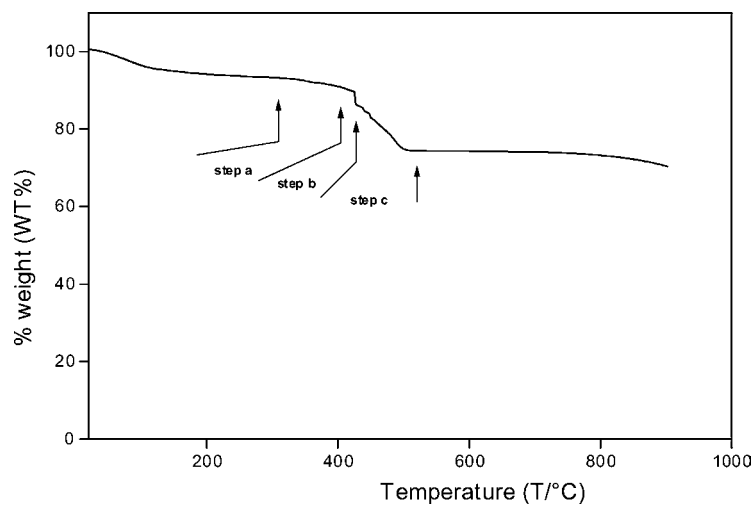


Fig. 2. Thermogravimetric profile of the  $\text{Na}_2(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2$  complex. Scanning rate:  $10^\circ\text{C min}^{-1}$ . Air flow at  $100\text{ ml min}^{-1}$  rate.

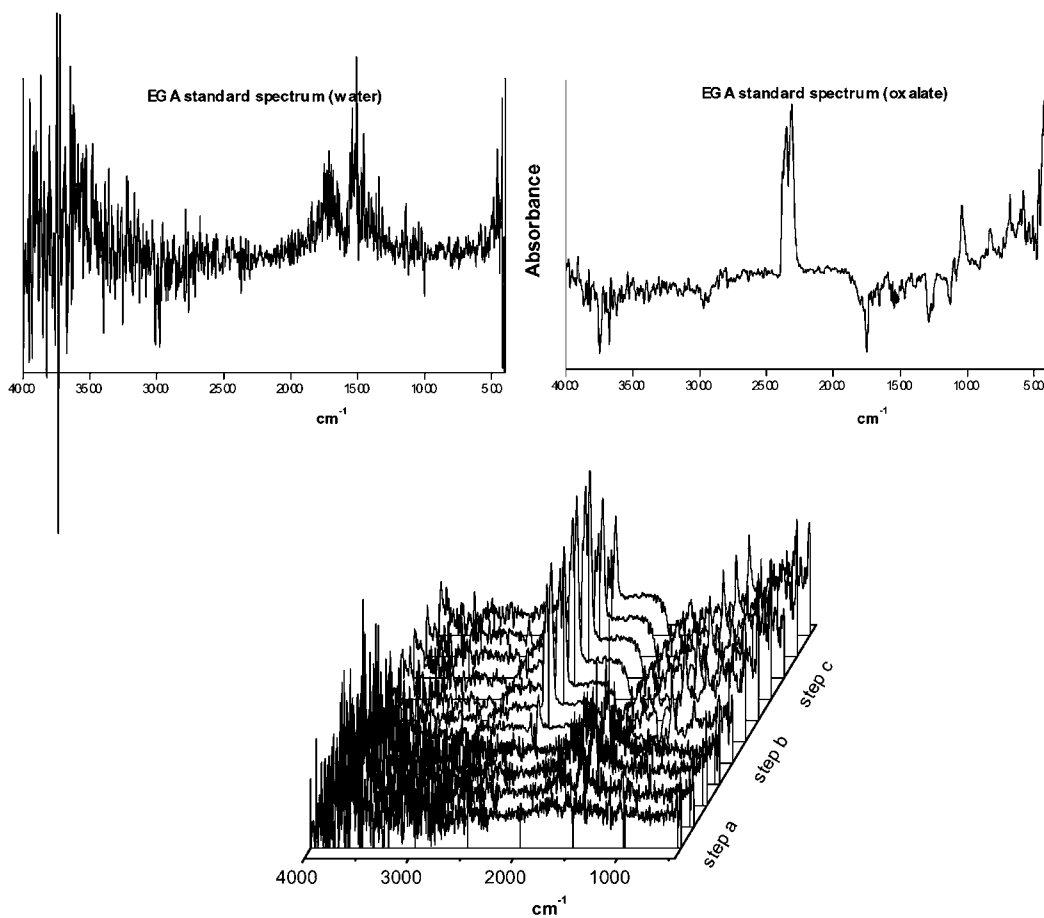
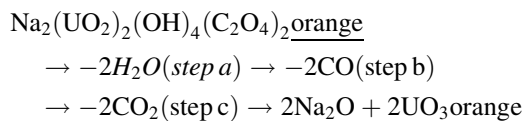


Fig. 3. Infrared spectra of the TG evolved gases in the temperature range  $250\text{--}450^\circ\text{C}$ . Resolution:  $8\text{ cm}^{-1}$ –10 scans per spectrum.

four –OH groups and of the two oxalate ions, to obtain an orange mixture of composition ( $2 \text{Na}_2\text{O} + 2 \text{UO}_3$ ); this mixture is stable until  $700^\circ\text{C}$ , with the successive reaction  $3 \text{UO}_3 \rightarrow \text{U}_3\text{O}_8$  that is not yet completed at  $900^\circ\text{C}$ . This behavior is typical of the uranyl-oxalate complexes [11].

On the base of the experimental data, the following mechanism can be proposed:



with the difference between the experimental and the theoretic values being  $< 1\%$ .

The evolved gas analysis, performed by coupling the thermobalance to a FTIR spectrometer through an heated transfer line, prove the releasing processes: the IR spectra recorded as function of the increasing temperature shows bands related to the water (step a) and then to the  $\text{CO}_2$  release (steps b and c). The  $\text{CO}_2$  bands related to the step b can be explained by considering that the air flow purging the thermobalance and acting as carrier gas enhances the parallel gas-phase reaction  $\text{CO} + (1/2) \text{O}_2 \rightarrow \text{CO}_2$ . The TG–IR spectra are collected in the stacked plot of the Fig. 3.

These results enhance how the presence of oxalate in natural waters may increase the solubility of uranyl up to pH about 8 before the precipitation of a solid phase. It looks however reliable that a similar behavior may be expected with ligands containing many carboxylic groups. This implies that in a real system, like for instance in the fallout of radioactive materials

from deep repositories for the disposal of nuclear wastes, the environmental contamination could be more serious than expected. Once more it appears evident how collecting accurate thermodynamic data on the coordination behavior of radionuclides may contribute to properly model their migration in the environment.

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