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Note

# Thermodynamics of complexation of the uranyl(VI) ion with benzoate. The crystal structure of sodium tris(benzoato) dioxouranate dihydrate, $Na[(PhCO_2)_3UO_2]\cdot 2H_2O$

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## Abstract

The stability constant and the enthalpy and entropy changes of formation of the 1:1 complex of uranyl(VI) with benzoate were determined by potentiometric and calorimetric titrations in 1.0 mol $dm^{-3}$ aqueous solution of $NaClO_4$ at 25 °C. The values obtained for the 1:1 complex agree with the general relationship holding for aliphatic monocarboxylato uranyl(VI) complexes. The structure of $Na[UO_2L_3]\cdot 2H_2O$ ($L = PhCO_2^-$) was determined by X-ray crystallography and refined to $R = 0.029$ based on 772 unique observed reflections. The compound is orthorhombic, space group *Pnna*, with $a = 9.387(3)$, $b = 9.576(3)$, $c = 26.491(3)$ Å. Three ligands are equatorially chelated to the uranyl group forming $UO_2L_3^-$ anions with $C_2$ crystallographic symmetry. The $Na^+$ cations, which also lie on two-fold axes, form approximate coordination octahedrons with oxygen atoms of water molecules and neighbouring anions.

*Keywords:* Crystal structures; Thermodynamics; Uranium complexes; Oxo complexes; Carboxylato complexes

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## 1. Introduction

The interaction of the uranyl(VI) ion with monocarboxylic acids in aqueous solution has been extensively investigated, with particular attention to the determination of the stoichiometry and of the stability constants of the resulting complexes [1]. In particular it has been well established that the uranyl(VI) ion forms 1:1 monocarboxylate complexes, the stability (log $\beta_1$) of which strongly depends on the basicity of the ligands (p$K_a$ values). In a previous paper [2] we dealt with the thermodynamic data concerning the formation of the 1:1 uranyl(VI)–phenyl acetate complex and we observed that the calculated log $\beta_1$ agrees with the general relationship. However, under the same experimental conditions, a solid product of formula $NaUO_2L_3$ was also isolated, for which we reported the crystal structure. In order to extend the study to uranyl complexes with other simple organic monocarboxylic acids, we report here the thermodynamic parameters of the uranyl–benzoate system and the crystal structure of the product obtained on reacting benzoic acid with uranyl(VI) diperchlorate in aqueous solution.

## 2. Experimental

Stock solutions of $UO_2(ClO_4)_2$, containing an excess of $HClO_4$, were prepared and standardized as reported [3]. The solutions of benzoic acid were prepared by weight, using commercial products without further purification, and were checked by potentiometry with NaOH solution. The potentiometric and calorimetric measurements on the uranyl(VI) ion were carried out by adding a known amount of a buffered ligand solution to a known volume of a solution containing the metal ion ($C^0_m = 5$–$30$ mmol $dm^{-3}$) and $HClO_4$ ($C^0_H = 15$–$25$ mmol $dm^{-3}$). Buffer solutions were prepared by adding standard NaOH to HL solutions until the required HL/L ratios were reached. Other details on the potentiometric and calorimetric measurements are given in Ref. [3]. All measurements were carried out at 25 °C in 1 M $NaClO_4$ as constant ionic medium. Calculations were performed using the MINIQUAD 75 and LETAGROP KALLE programs [4,5]. The solid compound was prepared by reacting an acidic aqueous solution of $UO_2(ClO_4)_2$ with an excess of a solution of HL ($C_{HL}/C_M$ ratio more than 3) and adding NaOH solution, to

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give a final pH of the reaction medium of about 3.0. Yellow crystals of $NaUO_2L_3$ were obtained by slowly evaporating the solvent at room temperature. The crystals were filtered off, washed and dried in vacuum.

### *2.1. X-ray data*

A crystal of max. dimension 0.2 mm was used for the analysis. Data collection was made with Mo K$\alpha$ radiation on a Philips PW 1100 diffractometer. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and intensity data are reported in Table 1. The crystals are stable under irradiation. Solution of the structure was achieved by standard methods, followed by full-matrix least-squares refinement of the atomic parameters. The H atoms of the phenyl groups were located on the electron density maps but were then introduced in calculated positions with fixed C–H distances and temperature factors (C–H = 1.08 A, $U_{iso} = 0.08$ Å$^2$); those of the water molecules were not located. Anisotropy was introduced for the non-hydrogen atoms.

Refinement of scale factor, and positional and thermal parameters, were accomplished by minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. Refinement using a sigma weighting resulted in a final $R$ of 0.032 with no significant differences in atomic coordinates. At convergence, the largest shift on the refined parameters was 0.07 times the standard deviation, and the highest map residual in the final electron density map was 0.8 e/Å$^3$. Form factors for the atoms were supplied internally by the SHELX program system [7].

Final atomic parameters are listed in Table 2; bond distances and angles are reported in Table 3.

Table 1
Crystal and intensity data

| | |
|---|---|
| Formula | $C_{21}H_{19}O_{10}NaU$ |
| Formula weight | 692 |
| $F(000)$ | 1312 |
| $a$ (Å) | 9.387(3) |
| $b$ (Å) | 9.576(3) |
| $c$ (Å) | 26.491(5) |
| $V$ (Å$^3$) | 2381(1) |
| Molecules/cell ($Z$) | 4 |
| Crystal system | orthorhombic |
| Space group | *Pnna* |
| Scan method | $\theta/2\theta$ |
| $\theta_{max}$ (°) | 50 |
| Scan speed (°/min) | 2 |
| Index range | $0<h<10$; $0<k<10$; $0<l<31$ |
| Recorded intensities | 803 |
| Observed intensities | 772 |
| Wavelength (Mo K$\alpha$) (Å) | 0.7107 |
| Corrections | Lp, absorption [6] |
| $\mu$ (Mo K$\alpha$) (cm$^{-1}$) | 66 |
| Final $R$ factor | 0.029 |
| GOF | 0.974 |

Table 2
Fractional coordinates with equivalent isotropic thermal parameters (Å$^2$)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| U(1) | 0.250 | 0.000000 | 0.32336(3) | 0.0511(2) |
| O(1) | 0.347(1) | 0.165(1) | 0.3219(5) | 0.073(4) |
| C(1) | 0.250000 | 0.000000 | 0.2130(6) | 0.063(8) |
| C(2) | 0.250000 | 0.000000 | 0.1588(6) | 0.052(6) |
| C(3) | 0.126(2) | 0.043(2) | 0.1327(5) | 0.071(7) |
| C(4) | 0.127(2) | 0.041(2) | 0.0804(6) | 0.081(9) |
| C(5) | 0.250000 | 0.000000 | 0.0548(8) | 0.10(1) |
| O(2) | 0.151(1) | 0.058(1) | 0.2387(3) | 0.071(5) |
| O(3) | 0.019(1) | 0.124(1) | 0.3269(4) | 0.063(4) |
| O(4) | 0.117(1) | 0.061(1) | 0.3982(3) | 0.063(4) |
| C(6) | 0.010(2) | 0.115(2) | 0.3740(5) | 0.059(6) |
| C(8) | −0.232(2) | 0.218(1) | 0.3742(3) | 0.083(8) |
| C(9) | −0.354(2) | 0.262(1) | 0.3994(3) | 0.11(1) |
| C(10) | −0.364(2) | 0.249(1) | 0.4517(3) | 0.086(9) |
| C(11) | −0.250(2) | 0.192(1) | 0.4789(3) | 0.075(6) |
| C(12) | −0.128(2) | 0.148(1) | 0.4537(3) | 0.057(6) |
| C(7) | −0.119(2) | 0.161(1) | 0.4013(3) | 0.054(6) |
| O(7) | −0.193(3) | 0.103(4) | 0.234(1) | 0.15(2) |
| Na(1) | −0.010(1) | 0.250000 | 0.250000 | 0.058(3) |

[a] $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 3
Bond distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| U–O(1) | 1.83(1) | U–O(2) | 2.49(1) |
| U–O(3) | 2.47(1) | U–O(4) | 2.42(1) |
| O(2)–C(1) | 1.28(1) | C(6)–C(7) | 1.48(2) |
| C(1)–C(2) | 1.43(2) | C(7)–C(8) | 1.39(2) |
| C(2)–C(3) | 1.42(2) | C(8)–C(9) | 1.39(2) |
| C(3)–C(4) | 1.39(2) | C(9)–C(10) | 1.40(1) |
| C(4)–C(5) | 1.40(2) | C(10)–C(11) | 1.40(2) |
| O(3)–C(6) | 1.26(2) | C(11)–C(12) | 1.39(2) |
| O(4)–C(6) | 1.30(2) | C(12)–C(7) | 1.40(1) |
| Na···O(2) | 2.40(1) | Na···O(3) | 2.38(1) |
| Na···O(7) | 2.26(3) | O(7)···O(7$^{I}$) | 2.25(3) |
| O(2)–U–O(2$^{II}$) | 51.6(3) | O(3)–U–O(4) | 53.1(3) |
| U–O(2)–C(1) | 96.3(5) | U–O(3)–C(6) | 93.6(9) |
| U–O(4)–C(6) | 95.2(8) | O(2)–C(1)–O(2$^{II}$) | 116(1) |
| O(3)–C(6)–O(4) | 118(1) | O(2)–C(1)–C(2) | 122(1) |
| O(3)–C(6)–C(7) | 121(1) | O(4)–C(6)–C(7) | 121(1) |

Symmetry code: $^{I} = -1+x, \frac{1}{2}-y, \frac{1}{2}-z$; $^{II} = \frac{1}{2}-x, 1-y, z$.

## 3. Results and discussion

The potentiometric and calorimetric data obtained for the uranyl(VI)–benzoate system are consistent, probably because of the very low solubility of the ligand in water, with the model corresponding to the formation of only a 1:1 mononuclear complex.

The following stability constants and changes in enthalpy and entropy were observed for the formation of proton– and uranyl–benzoate complexes at 25 °C in 1 M $NaClO_4$ solution.

The thermodynamic values for the formation of the uranyl(VI)–benzoate complex are not affected by the

| Reaction | Log $\beta_1$ | $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| $H+L=HL$ | 4.03(1) | −1.3(3) | 73 |
| $UO_2+L=UO_2L$ | 2.10(4) | 10.5(6) | 75 |

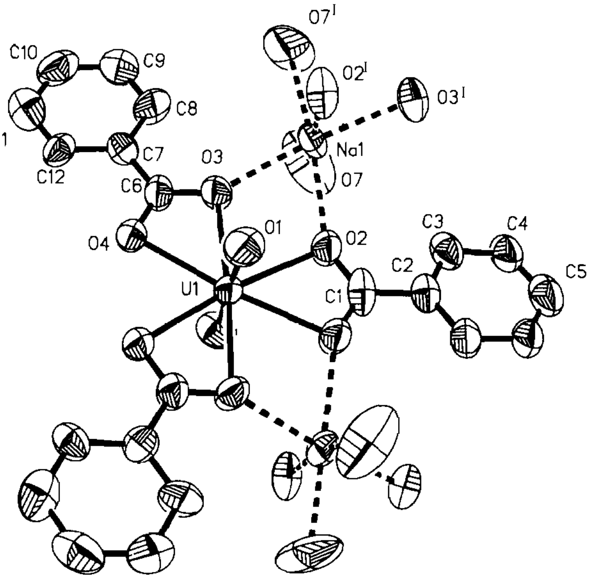

Fig. 1. Crystal structure of $Na[UO_2L_3]\cdot 2H_2O$.

presence of the phenyl ring of the benzoic acid and follow the trend observed for the formation of the parent complexes with aliphatic monocarboxylic acids. Also in this case, in apparent disagreement with the presence of a 1:1 complex in solution, a solid compound of formula $NaUO_2L_3$ was obtained, which is probably the least soluble species formed in the reaction.

### 3.1. X-ray structure of $Na[UO_2L_3]\cdot 2H_2O$

The crystal structure of $Na[UO_2L_3]\cdot 2H_2O$ is shown in Fig. 1 together with its numbering scheme. Space group *Pnna* has 8 general positions. In this case the U, C(1), C(2) and C(5) atoms lie on the two-fold axis at $\frac{1}{4}$, 0, $z$ (special positions of equipoint 4 c) whereas Na lies on the two-fold axis at $x$, $\frac{1}{4}$, $\frac{1}{4}$ (equipoint 4 d). Thus, only 4 formula units of the compound are present in the elementary cell and the asymmetric unit is one half of the formula unit.

Three bidentate ligands are equatorially bonded to the uranyl ion; the six oxygen atoms are only roughly coplanar being alternatively displaced by ±0.1 to ±0.2 Å with respect to the base plane in the usual puckered configuration. The phenyl rings are essentially coplanar with the equatorial plane. U–O(L) bond lengths (mean 2.46 Å) and O–U–O chelation angles (mean 52.4°) agree with corresponding values found in other uranyl complexes with six equatorial oxygen donor atoms [8,9] and particularly with those found in $Na[UO_2(PhCH_2CO_2^-)_3]$ [2] which is structurally similar.

As shown in the Figure the $UO_2L_3^-$ anions are held together in polymeric chains by strong interactions of the ligand oxygens O(2) and O(3) (and of the corresponding two oxygens related by two-fold symmetry) with the neighbouring $Na^+$ cations. These are also involved in strong interactions with the two water molecules in a roughly octahedral environment.

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