



# Maleate ions as ligands in crystal structures of coordination compounds, including two uranyl complexes



Anton V. Savchenkov<sup>a,\*</sup>, Mikhail S. Grigoriev<sup>b</sup>, Pavel A. Udivankin<sup>a</sup>, Denis V. Pushkin<sup>a</sup>, Larisa B. Serezhkina<sup>a</sup>

<sup>a</sup>Samara National Research University, Samara, Russian Federation

<sup>b</sup>Russian Academy of Sciences A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russian Federation

## ARTICLE INFO

### Article history:

Received 6 January 2017

Accepted 7 February 2017

Available online 22 February 2017

### Keywords:

Maleate

Uranyl

Structure elucidation

Coordination modes

Crystal engineering

## ABSTRACT

Synthetic techniques, FTIR spectra and the crystal structures of two new uranyl complexes with maleate ions are reported. The crystal structure of  $(\text{NH}_4)_2[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]$  (**I**) is constructed of chains with the  $[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]^{2-}$  composition. Maleate ions in **I** have the tridentate bridging and chelating  $T^{11-4}$  coordination mode with the formation of 4-membered U-containing rings. The crystal structure of  $\text{Cs}_2[(\text{UO}_2)_3(\text{C}_4\text{H}_2\text{O}_4)_4] \cdot 2\text{H}_2\text{O}$  (**II**) is constructed of layers with the  $[(\text{UO}_2)_3(\text{C}_4\text{H}_2\text{O}_4)_4]^{2-}$  composition. Half of the maleate ions in **II** have the bridging and chelating  $Q^{21-4}$  coordination mode, with the formation of 4-membered rings, while the other half have the  $Q^{21-7}$  coordination mode with the formation of 7-membered rings. The coordination modes of the maleate ions in all the crystal structures of coordination compounds from the CSD were analyzed. The non-planarity of the maleate ions is confirmed by calculation of different geometric parameters. Though in all crystal structures most of the maleate ions tend to realize coordination modes with the formation of 7-membered rings, geometrical difficulties of 7-membered ring formation are shown. The presented data on the coordination modes of the maleate ions in crystal structures are of particular interest for crystal engineering and crystal structure prediction.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

The maleate ion  $\text{C}_4\text{H}_2\text{O}_4^{2-}$  is the ionized form of unsaturated dicarboxylic maleic acid  $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$ . Maleate ions are of particular interest in coordination chemistry due to their diverse coordination modes. In known crystal structures, maleate ions act as terminal [1], bridging [2] and chelating [3] ligands. Structural motifs containing maleate ions can be zero [4], one [5], two [6] and three [7] dimensional. To date, only one crystal structure of a uranyl complex with maleate ions has been reported [8]. It is constructed of 1D bands with the  $[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_4\text{H}_3\text{O}_4)]^-$  composition, bound into a 3D framework by electrostatic interactions with  $\text{K}^+$  cations.

The authors of the cited article [8] note that coordination of maleate ions to U atoms in the structure of  $\text{K}[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_4\text{H}_3\text{O}_4)]$  leads to the formation of 7-membered rings, which are unusual and unstable. They also assumed that “their [7-membered rings] formation could be due to the particular ligand isomer with a *cis* configuration”. Another curious thing mentioned by the

authors [8] is that the maleate ions in  $\text{K}[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_4\text{H}_3\text{O}_4)]$  are not planar. Indeed, although all the C atoms of the maleate ion are  $\text{sp}^2$  hybridized, the maleate ions are not planar due to repulsion of two O atoms of different carboxylate groups. In crystal structures, a planar geometry is typical for hydrogen maleate ions,  $\text{C}_4\text{H}_3\text{O}_4^-$ , in which the H atom prevents repulsion of the two closest O atoms of different carboxylate groups. A planar geometry is also typical for fumarate ions (*trans* isomers of maleate ions), in which the two carboxylate groups are shielded from each other by the carbon skeleton.

In the mentioned  $\text{K}[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_4\text{H}_3\text{O}_4)]$  complex [8], the two carboxylate groups form different angles with the carbon skeleton: 67.5 and 25.7°. The authors [8] suggested that such a distortion of the maleate ions is forced by the necessity of the U atoms to form particular coordination polyhedra. This assumption is supported by the presence of strain in the crystal structure: the five equatorial oxygen atoms of the uranyl ion are rather puckered.

Despite all the mentioned curious facts about the coordination of maleate ions in the described uranyl complex, we were not able to find in the literature any relevant review of the coordination modes of maleate ions. Thus, we intended to perform an analysis of the coordination modes of maleate ions in all coordination

\* Corresponding author.

E-mail address: [anton.savchenkov@gmail.com](mailto:anton.savchenkov@gmail.com) (A.V. Savchenkov).

compounds from the CSD. We also report the crystal structures of two new uranyl complexes,  $(\text{NH}_4)_2[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]$  (**I**) and  $\text{Cs}_2[(\text{UO}_2)_3(\text{C}_4\text{H}_2\text{O}_4)_4] \cdot 2\text{H}_2\text{O}$  (**II**), with three different coordination modes of the maleate ions.

## 2. Experimental

**Caution!** Although depleted uranium was used in the following experiments, all uranium containing samples must be handled with suitable care and protection.

### 2.1. Synthesis

Yellow crystals of **I** and **II** were obtained after a few days of isothermal evaporation of the reaction mixtures at ambient conditions.  $\text{UO}_2(\text{NO}_3)_2 \cdot 3.23\text{H}_2\text{O}$  was synthesized according to the reported procedure [9] and the hydration number was calculated through gravimetric analysis. Maleic acid ( $\text{C}_4\text{H}_4\text{O}_4$ ), ammonium hydroxide solution (28%  $\text{NH}_3$  in  $\text{H}_2\text{O}$ ) and cesium hydroxide ( $\text{CsOH} \cdot \text{H}_2\text{O}$ ) of reagent grade were obtained commercially (ALDRICH).

$(\text{NH}_4)_2[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]$  (**I**).  $\text{UO}_2(\text{NO}_3)_2 \cdot 3.23\text{H}_2\text{O}$  (200 mg, 0.44 mmol) and  $\text{C}_4\text{H}_4\text{O}_4$  (205 mg, 1.77 mmol) were dissolved in distilled water (10 ml). Ammonium hydroxide solution was added to the reaction mixture to give a pH value of 4 (approximately 107 mg of solution, 1.77 mmol of  $\text{NH}_3$ ). The final molar ratio of the reagents was 1:4:4 respectively. Yield: ~70%. Gravimetric analysis on uranium: 44.4% (calculated 44.6%).

$\text{Cs}_2[(\text{UO}_2)_3(\text{C}_4\text{H}_2\text{O}_4)_4] \cdot 2\text{H}_2\text{O}$  (**II**).  $\text{UO}_2(\text{NO}_3)_2 \cdot 3.23\text{H}_2\text{O}$  (200 mg, 0.44 mmol) and  $\text{C}_4\text{H}_4\text{O}_4$  (103 mg, 0.88 mmol) were dissolved in distilled water (10 ml).  $\text{CsOH} \cdot \text{H}_2\text{O}$  (149 mg, 0.88 mmol) was added to the reaction mixture. The pH of the final solution was equal to 4. The final molar ratio of the reagents was 1:2:2 respectively. Yield: ~75%. Gravimetric analysis on uranium: 45.2% (calculated 45.5%).

**Table 1**

Details of data collection and structure refinement parameters for  $(\text{NH}_4)_2[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]$  (**I**) and  $\text{Cs}_2[(\text{UO}_2)_3(\text{C}_4\text{H}_2\text{O}_4)_4] \cdot 2\text{H}_2\text{O}$  (**II**).

Compound	<b>I</b>	<b>II</b>
Chemical formula	$(\text{NH}_4)_2[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]$	$\text{Cs}_2[(\text{UO}_2)_3(\text{C}_4\text{H}_2\text{O}_4)_4] \cdot 2\text{H}_2\text{O}$
Crystal system, space group, Z	monoclinic, C2/c, 4	triclinic, P1, 2
a, b, c (Å)	12.9752(3), 7.52160(10), 13.5419(3)	6.8275(2), 14.5728(4), 16.2015(4)
$\alpha, \beta, \gamma$ (°)	90, 100.415(1), 90	63.753(1), 78.631(1), 82.326(1)
V (Å <sup>3</sup> )	1299.84(5)	1415.44(7)
D <sub>x</sub> (g/cm <sup>3</sup> )	2.730	3.679
Radiation, λ (Å)	Mo K $\alpha$ , 0.71073	Mo K $\alpha$ , 0.71073
μ (mm <sup>-1</sup> )	12.544	19.758
T (K)	100(2)	100(2)
Crystal size (mm)	0.20 × 0.16 × 0.10	0.12 × 0.04 × 0.03
θ range (°)	4.182–34.997	4.248–29.996
h, k, l range	–20 ≤ h ≤ 20, –12 ≤ k ≤ 12, –21 ≤ l ≤ 18	–9 ≤ h ≤ 9, –19 ≤ k ≤ 20, –22 ≤ l ≤ 22
Reflections	10244/2839, 0.0213/2134	14668/8221, 0.0255/6501
number: collected/unique (N <sub>1</sub> ), R <sub>int</sub> /with I > 2σ (I) (N <sub>2</sub> )		
Parameters refined	110	406
wR <sub>2</sub> on N <sub>1</sub>	0.0319	0.0765
R <sub>1</sub> on N <sub>2</sub>	0.0151	0.0339
S	1.012	1.040
Δρ <sub>maximum</sub> /Δρ <sub>minimum</sub> (e Å <sup>-3</sup> )	0.765/–0.677	3.602/–2.094

**Table 2**

Assignment of absorption bands in the FTIR spectra of  $(\text{NH}_4)_2[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]$  (**I**) and  $\text{Cs}_2[(\text{UO}_2)_3(\text{C}_4\text{H}_2\text{O}_4)_4] \cdot 2\text{H}_2\text{O}$  (**II**).

Wavenumber, cm <sup>-1</sup>		Assignment
<b>I</b>	<b>II</b>	
–	3519 m., br. 3445 m., br.	ν(OH)
3168 s.	–	ν(NH)
3035 s.	3036 w.	ν(CH)
2928 m.	2925 w.	
2892 m.		
2858 m.	2854 w.	
1651 s.	1648 m.	ν(C=C)
1587 v.s.	1589 s.	ν <sub>as</sub> (COO)
1547 v.s.	1541 v.s.	
1534 v.s.	1520 v.s.	
1453 v.s.	1448 s.	δ <sub>in-plane</sub> (CH), δ(NH), ν <sub>s</sub> (COO)
1416 v.s.	1411 s.	
1388 v.s.	1385 m.	δ <sub>in-plane</sub> (CH)
1308 v.s.	1314 s.	
1200 s.	1205 w.	ν(C–O)
935 v.s.	926 s.	ν <sub>as</sub> (UO <sub>2</sub> )
911 s.	917 s.	
851 s.	856 m.	δ <sub>out-of-plane</sub> (CH)
832 s.	840 w. 828 w.	
744 m.	746 w.	
697 s.	694 m. 631 m.	δ(COO) γ(COO)
617 s.	621 m. 583 w.	
549 s.	545 w.	ω(COO)

v.s. – very strong, s. – strong, m. – medium, w. – weak, br. – broad, γ – rocking, ω – wagging.

### 2.2. X-ray diffraction analysis

An automatic four-circle diffractometer with the area detector Bruker KAPPA APEX II was used for the X-ray experiments. Unit cell parameters were refined over the whole dataset [10]. Experimental intensities were corrected for absorption using the SADABS program [11]. The structures were solved using the direct method (SHELXS97) [12] and refined using the full-matrix least-squares method (SHELXL-2014) [13] on F<sup>2</sup> over the whole dataset. All non-hydrogen atoms in **I** and **II** were refined in an anisotropic approximation. H atoms of maleate anions were placed in geometrically calculated positions with U<sub>iso</sub> = 1.2U<sub>eq</sub>(C). H atoms of the NH<sub>4</sub><sup>+</sup> cation in **I** were located from the difference Fourier map and refined with equal N–H and equal H...H distances, and U<sub>iso</sub> = 1.2U<sub>eq</sub>(N). Two out of three independent Cs atoms and two water molecules in **II** are disordered over two positions. Details of the data collection and structure refinement parameters are provided in Table 1.

### 2.3. FTIR spectroscopy

FTIR spectra of **I** and **II** (provided in the Supplementary Material) were measured in the range 400–4000 cm<sup>-1</sup> from pressed KBr pellets using a Perkin Elmer Spectrum 100 spectrometer. Assignment of bands (Table 2) was performed in accordance with the established data for other maleate containing compounds [14–16] and other reliable sources [17–19]. Due to the variable coordination modes of the carboxylate groups (see further discussion) we were unable to accurately assign all the bands in the region 1600–1400 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Description of the crystal structures

$(\text{NH}_4)_2[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)_2]$  (**I**) crystallizes in the monoclinic crystal system (space group C2/c) with Z = 4 and Z' = 0.5. The only atom

Download English Version:

<https://daneshyari.com/en/article/5154533>

Download Persian Version:

<https://daneshyari.com/article/5154533>

[Daneshyari.com](https://daneshyari.com)