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The Crystal Structure of Sodium Uranyl Triformate Monohydrate, $\text{NaUO}_2(\text{HCOO})_3 \cdot \text{H}_2\text{O}$

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The crystal structure of sodium uranyl triformate monohydrate has been established by X-ray diffraction at room temperature. This compound crystallizes in space group $P2_1/c$, with $a = 6.317$ (2), $b = 24.438$ (3), $c = 6.735$ (3) Å, $\beta = 117.65$ (3)°, $Z = 4$. The structure has been determined by the heavy-atom method from 1244 Mo $K\alpha$ intensities measured on a four-circle diffractometer, and refined by full-matrix least-squares computations. The final weighted R was 0.081 (conventional $R = 0.062$). The U atom is surrounded by a pentagonal bipyramid of O atoms. There appear to be three kinds of bidentate formate groups. The O atoms of the water molecules form distorted squares with the Na atoms. These squares are interconnected by the nearest O atoms of the formate groups. The Na atom is hexacoordinated and with the water molecules forms infinite chains running parallel to the [100] axis. The overall structure appears to be of the $\cdots ABABA \cdots$ sandwich type: a layer of interconnected U polyhedra is stacked between Na– H_2O layers along [010].

Introduction

Claudel, Mentzen, Navarro & Sautereau (1976) reported the preparation and preliminary infrared and X-ray investigations of $\text{NaUO}_2(\text{HCOO})_3 \cdot \text{H}_2\text{O}$. The interpretation of the infrared spectrum led to the following conclusions: (1) There are at least two different types of bridging bidentate formate groups in the solid. (2) The uranyl group is nearly linear with $\text{U}-\text{O} = 1.74$ (2) Å. (3) The water molecule, which is strongly polarized [$\nu_{as}(\text{OH}) = 3585$, $\nu_s(\text{OH}) = 3425$ cm^{-1}], is not coordinated to the U atom.

The crystal structure of $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$ has recently been published (Mentzen, Puaux & Loiseleur, 1977) and it appears that the coordination polyhedron of the U atom is a pentagonal bipyramid (hepta-

coordination). As reported in the same paper, both $\text{NaUO}_2(\text{HCOO})_3 \cdot \text{H}_2\text{O}$ and $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$ are sensitive to visible, ultraviolet and X radiation. The present investigation reveals some similarities in their structures.

Experimental results

Crystals of $\text{NaUO}_2(\text{HCOO})_3 \cdot \text{H}_2\text{O}$ are very fragile and any attempt to shape them into a sphere, or even into a cube, failed because they cleave too easily. A nearly cylindrical crystal, $0.1 \times 0.125 \times 0.125$ mm, was mounted on the four-circle, Enraf–Nonius CAD-4, automatic diffractometer of the Centre de Diffraction Automatique, Lyon. As the crystal was photo-

sensitive, no preliminary X-ray determinations were performed; the orientation matrix was determined and refined as quickly as possible in order to start the data collection. The intensities were collected in the ω - 2θ scan, with $I > 2\sigma(I)$ for $1 < \theta < 28^\circ$, and with a 20 s counting time for each reflexion. After data reduction, 1244 unique reflexions were retained and their intensities corrected for Lorentz and polarization factors as well as for absorption ($\mu R = 2.57$). No decrease of the intensity-control reflexion was observed; however, after the data collection, the crystal suddenly lost its transparency. Inspection of the data collected shows that the conditions limiting possible reflexions are consistent with space group $P2_1/c$, i.e. $h0l: l = 2n, 0k0: k = 2n$.

Here it must be mentioned that Claudel *et al.* (1976) were not able to decide between $P2_1$ and $P2_1/m$. In fact, on the Weissenberg photographs we found the 005 reflexion to be present with medium intensity, and this was for several different crystals. On the other hand, there was no evidence for any twinning (absence of spot doubling), all the unit cells derived from the photographs being consistent with those calculated in previous work and those given by the diffractometer. In any case, even if the crystal investigated was not a proper single crystal, it behaved on the CAD-4 as though it were, with space group $P2_1/c$. The unit-cell parameters are: $a = 6.317(2)$, $b = 24.438(3)$, $c = 6.735(3)$ Å, $\beta = 117.65(3)^\circ$, $Z = 4$, $U = 923$ Å³; $M_r = 446.09$, $D_m = 3.32$, $D_x = 3.21$ g cm⁻³, $F(000) = 792$, $\mu(\text{MoK}\alpha) = 215.5$ cm⁻¹.

Structure determination

The interpretation of the Patterson function gave the atomic coordinates of the heavy atom and a subsequent Fourier synthesis revealed the positions of all but the H atoms. The atomic coordinates and isotropic thermal parameters of the 14 atoms of the asymmetric unit were

Table 1. *Relative atomic coordinates and isotropic thermal parameters with their standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
U	0.7198 (1)	0.34681 (2)	0.4965 (1)	1.2
Na	1.240 (1)	0.5360 (4)	0.977 (1)	3.1 (1)
O(1)	0.829 (3)	0.5117 (6)	0.746 (3)	3.5 (3)
O(2)	0.494 (3)	0.3950 (6)	0.427 (2)	3.2 (3)
O(3)	0.938 (3)	0.2995 (6)	0.559 (2)	2.7 (2)
C(1)	0.830 (3)	0.3455 (8)	0.047 (3)	2.5 (3)
O(4)	0.818 (3)	0.3687 (6)	0.879 (3)	3.2 (3)
O(5)	0.775 (3)	0.3717 (6)	0.181 (2)	2.9 (2)
C(2)	0.407 (3)	0.2446 (7)	0.573 (3)	2.2 (3)
O(6)	0.418 (2)	0.3003 (6)	0.172 (2)	2.9 (3)
O(7)	0.552 (3)	0.2806 (7)	0.639 (3)	3.9 (3)
C(3)	1.219 (4)	0.4175 (9)	0.732 (3)	3.3 (4)
O(8)	0.988 (2)	0.4182 (6)	0.613 (2)	3.1 (3)
O(9)	1.347 (3)	0.4592 (6)	0.825 (2)	3.8 (3)

refined by minimizing $\sum w(|F_o| - |F_c|)^2$, the weighting function being $w = (2|F_o|_{\min} + |F_o| + 2F_o^2/|F_o|_{\max})^{-1}$; after eight iterations the conventional $R (= \sum ||F_o| - |F_c|| / \sum |F_o|)$ was 0.105. Thereafter, the anisotropic thermal parameters and the weighting function $w = (a + b|F_o|)^{-2}$ (Stout & Jensen, 1968) were introduced, and after two iterations $R_w = 0.091$ and $R = 0.067$. On interpreting the standard deviations, we decided to drop the anisotropic thermal parameters for all but the U atoms. Accordingly, the last refinement cycle was run for four iterations by introducing the anomalous-dispersion factors at this stage. The final $R_w = \{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\}$ is 0.081 (conventional $R = 0.062$), which, considering the poor quality of the crystal, is a rather good value.* The anisotropic thermal parameters for the U atom are $\beta_{11} = 0.0230(7)$, $\beta_{22} = 0.00047(2)$, $\beta_{33} = 0.00097(4)$, $\beta_{12} = 0.00006(8)$, $\beta_{23} = 0.01708(3)$, $\beta_{13} = -0.00020(8)$ Å². The refined parameters are listed in Table 1; the atomic scattering factors and anomalous-dispersion factors used were those given in *International Tables for X-ray Crystallography* (1974). For the U atom the equivalent isotropic thermal parameter is calculated according to $B_{\text{eq}} = \frac{4}{3}(\beta_{11}a^2 + \dots - 2\beta_{12}ab - \dots)$.

Description of the structure

The principal bond distances and bond angles are given in Table 2. This structure is built up from two distinct

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32515 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

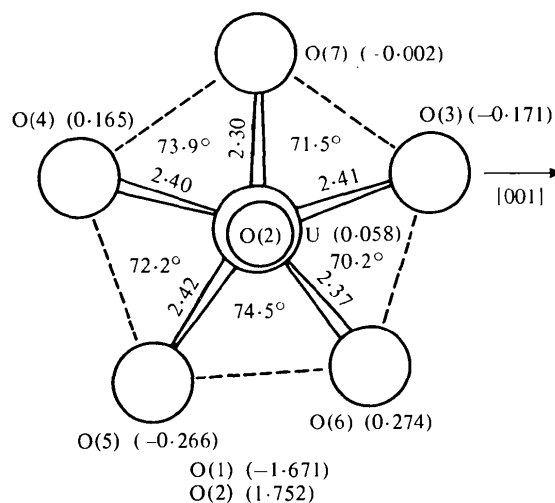


Fig. 1. The mean equatorial plane of the pentagonal bipyramid about the U atom. Numbers in parentheses indicate the distances of the atoms to the mean plane in Å.

have their centres located on inversion centres. These squares are interconnected through the O(8) atoms, thus forming infinite chains of Na–H₂O squares running parallel to the [100] axis (Fig. 2); these chains constitute a second type of layer represented in Fig. 3, where they run normal to the figure plane.

Finally, the U polyhedra and the Na–H₂O layers are linked by the bridging bidentate type III formate group [C(3), O(7) and O(8)].

Discussion

It appears, from the above description, that the conclusions reported in the former infrared study (Claudel *et al.*, 1976) are consistent with the outline of the present structure.

The heptacoordination (pentagonal bipyramid) of the U atom in uranyl compounds is met more and more often in the literature (Howatson, Grev & Morosin, 1975; Legros & Jeannin, 1976; Mentzen, Puaux & Loiseleur, 1977). In the present study the uranyl group appears to be nearly linear [OUO angle = 178.8 (6)°, and U–O bond lengths of 1.70 (2) and 1.74 (2) Å]. As the standard deviations are relatively high for all the distances reported in this structure, we consider that the two primary U–O distances are not significantly different, the mean distance being 1.72 (2) Å. The secondary U–O bond lengths all range between 2.42 (2) and 2.37 (2) Å, except for U–O(7) which seems to be shorter [2.30 (2) Å]. In the case of uranyl diformate monohydrate the shortest secondary U–O bond is 2.38 (1) Å, and the fact that NaUO₂(HCOO)₃·H₂O is more photosensitive than UO₂(HCOO)₂·H₂O could possibly be connected with this shorter U–O bond.

In the first stages of the structure determination, the most surprising feature found was the distorted Na–H₂O squares, with a Na–O(*W*) bond length of 2.40 (2) Å. This distance is almost the same as the shortest Na–OH distances in solid sodium hydroxide (Wells,

1967). Hereafter, the $\nu(\text{OH})$ infrared band at 3585 cm⁻¹ is interpreted as a result of the strong polarization of the Na–O(*W*) bond; in fact, the IR spectrum of solid LiOH·H₂O presents the same type of $\nu(\text{OH})$ band at 3574 cm⁻¹ (Nakamoto, 1970).

The cleavability of NaUO₂(HCOO)₃·H₂O may be interpreted by considering the ...*ABABA*... type stacking (along the [010] axis) of alternate U polyhedra and Na–H₂O layers running in two different directions, parallel to [001] and [100] respectively.

Concerning the formate groups (types I, II and III), all the C–O bond distances are comparable with those reported for similar structures. Types I and III appear to be nearly symmetric, type II possibly being asymmetric, since its C–O distances are 1.20 (3) and 1.27 (2) Å.

All the computations have been performed on an IBM 370-168 computer at Orsay (CIRCE), through the terminal of the Institut de Recherches sur la Catalyse, Lyon, and by means of a program library available at the Laboratoire de Chimie Analytique II, Université Claude Bernard, Lyon I.

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