Structure of Dioxouranium(VI) Formate Hydroxide Monohydrate at 120 K

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Abstract. UO₂(HCOO)(OH).H₂O, orthorhombic, Pbcα, a = 6.3226 (3), b = 10.5320 (6), c = 15.949 (4) Å (120 K) and a = 6.362 (2), b = 10.576 (3), c = 15.999 (5) Å (293 K), Z = 8, Dₘ = 4.38, Dₑ = 4.35 Mg m⁻³ (293 K). The final R_w = 0.07 for 487 reflections. The sevenfold coordination consists of a pentagonal arrangement of O atoms in the equatorial plane perpendicular to the axis of the uranyl group. U-O lengths range from 1.77 (2) to 2.45 (2) Å.

Introduction. An X-ray powder study of precipitates from ammonium diuranate (ADU) solutions led to the identification of a compound which was originally prepared by Bideau et al. (1970). The latter investigators reported Dₘ = 3.45 Mg m⁻³ and b = 13.52 Å, which are not in agreement with our values.

Single crystals for the present investigation were obtained by dissolving 1.0 g ADU in 2 ml 25% aqueous HCOOH and diluting with 50 ml CH₃OH and 50 ml HOC₂H₄OH. The methanol and excess formic acid were slowly removed by a water pump. Suitable orthorhombic greenish-yellow crystals were obtained after 38 days by partial precipitation. They were washed several times with water, methanol and ether, in that order, before drying.

A powder diffractogram taken on an IRDAB XDC700 Guinier camera (114.6 mm diameter) with quartz-monochromated Cu Kα₁ radiation yielded d values in agreement with those reported by Bideau et al. (1970). The room-temperature cell constants were refined from the first 15 powder lines.

A crystal 0.1 x 0.07 x 0.04 mm was mounted on a Stoe reciprocal-lattice explorer with the long axis of the crystal parallel to the rotation axis. From a rotation photograph the lattice constant which corresponded to the crystal rotation axis turned out to be a = 6.35 (6) Å. A De Jong-Bouman zero-layer exposure supplied the other lattice constants and from higher-layer photographs, as well as Buerger precession exposures, the space group was determined unambiguously. The crystal faces were found to be the major crystallographic faces {100}.

A method based on Boyle's law was used for density measurements. 893 reflections with sin θ/λ ≤ 0.71 Å⁻¹ were measured on a Philips PW 1100 automatic diffractometer with graphite-monochromated Mo Kα₁ radiation. The thermal background was reduced by cooling the sample to 120 (2) K with an Enraf-Nonius universal low-temperature device. The low-temperature cell constants were refined from 15 non-axial reflections with diffractometer 2θ values.

A set of 487 contributing reflections (I > 3σ) formed the basis for the data reduction which included crystallographic orientation corrections and Lorentz-polarization corrections.

Table 1. Atomic parameters (×10⁴) at 120 K

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>1479 (2)</td>
<td>589 (1)</td>
<td>1011 (1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>417 (42)</td>
<td>5756 (22)</td>
<td>6533 (14)</td>
</tr>
<tr>
<td>O(2)</td>
<td>2621 (32)</td>
<td>3141 (19)</td>
<td>5427 (13)</td>
</tr>
<tr>
<td>O(3)</td>
<td>1703 (28)</td>
<td>5664 (16)</td>
<td>4758 (10)</td>
</tr>
<tr>
<td>O(4)</td>
<td>835 (32)</td>
<td>7750 (18)</td>
<td>8424 (11)</td>
</tr>
<tr>
<td>O(5)</td>
<td>1976 (34)</td>
<td>8731 (20)</td>
<td>7307 (12)</td>
</tr>
<tr>
<td>O(6)</td>
<td>108 (34)</td>
<td>4687 (18)</td>
<td>1011 (13)</td>
</tr>
<tr>
<td>C</td>
<td>3019 (44)</td>
<td>2823 (25)</td>
<td>7796 (17)</td>
</tr>
</tbody>
</table>

*Anisotropic parameters: U₁₁ = 76 (13), U₁₂ = 200 (13), U₁₃ = 143 (12), U₂₂ = −6 (6), U₂₃ = 3 (5), U₃₃ = −6 (6).

dispersion correction for U (Cromer & Liberman, 1970), absorption ($\mu = 2.89 \text{ m}^{-1}$) and $L_p$ corrections. The absorption correction factors applied to the $F^2$ data ranged from 31.6 to 8.4.

The Patterson function gave the U positions and the O and C positions were revealed by a difference map. Only the temperature factor of the U atom was refined anisotropically. Without absorption correction the C-atom temperature factor was negative and the U atom exhibited extreme anisotropic behaviour. The final full-matrix least-squares refinement for 38 parameters gave $R = 0.051$ and $R_w = 0.070$ [$w = 1/\sigma(I)$]. Atomic parameters are presented in Table 1. XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the calculations and ORTEP (Johnson, 1965) for the drawings.

Discussion. The U atom has a pentagonal-bipyramidal coordination. A stereoview of the crystal structure is shown in Fig. 1. Interatomic distances and angles are given in Table 2.

The O atoms are at the corners and the U atom at the centre of a bipyramid, the axis of the latter being formed by the uranyl group. On one side, a U atom is doubly bridged to its centroymetrically related nearest neighbour by the O(3) atoms, and on the other side the U atom links to its two second-nearest U neighbours via the formate groups. The C atom lies about 10° out of the equatorial plane. The formate group has an O(4)–C–O(5) angle of 124 (3)°, close to the characteristic value of 120°.

On account of its shorter bond length compared to O(6), O(3) probably belongs to the hydroxyl group and O(6) to the crystal water. O(3) has a somewhat smaller temperature factor than the rest of the O atoms which seems reasonable in the light of the double U bonding.

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References