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# Single-Crystal Neutron Diffraction: Structure of Sodium Tris(acetato)-dioxouranate(1−)

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**Abstract.** $Na[UO_2(C_2H_3O_2)_3]$, $M_r = 467·09$, cubic, $P2_13$, $a = 10·691$ (8) Å, $V = 1222$ (3) Å³, $Z = 4$, $D_x = 2·562$ g cm⁻³, $\lambda = 0·831$ (1) Å, $\mu = 1·2$ cm⁻¹ (evaluated), $F(000) = 258·9$ fm for cell content, room temperature, $R = 0·037$, $wR = 0·029$ for 452 observed reflections. The structure of the compound determined by neutron diffraction is essentially the same as that obtained by X-ray diffraction, excluding the hydrogen atoms. The uranyl ion lies on the threefold axis surrounded by three symmetrically related acetate groups. The coordination polyhedron of the sodium atom is intermediate between an octahedron and a trigonal prism; six oxygen atoms from six different acetate ligands participate in this coordination. The hydrogen atoms of the methyl group are observed in two positions which do not coincide with those proposed from X-ray studies.

**Introduction.** The crystal structure of $Na[UO_2(C_2H_3O_2)_3]$ was first determined by conventional X-ray methods by Fankuchen (1935), and more completely by Zachariasen & Plettinger (1959). A recent redetermination, including anomalous scattering, by Templeton, Zalkin, Ruben & Templeton (1985) led to more accurate parameters and to the absolute configuration of the structure; the coordinate system corresponds to a crystal with a negative sign for optical activity.

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The compound was also investigated by EXAFS analysis (Charpin, Dejean, Folcher, Rigny & Navaza, 1985) and is now currently used as a standard for many uranyl complexes studied by this technique.

A high-resolution neutron diffraction study was thus undertaken as part of the research program on structural and vibrational properties of the uranyl ion. Atomic parameters are presented here in the same right-handed system as Templeton *et al.* (1985).

**Experimental.** Sodium uranyl triacetate was prepared by slow evaporation of a slightly acidified aqueous solution in molar proportions of uranyl and sodium acetates. Large crystals were grown from small feed specimens suspended in a saturated solution. A complete neutron diffraction data set was obtained at 295 K from a yellow crystal of approximate dimensions $1.6 \times 1.6 \times 2.0$ mm, employing the four-circle diffractometer 5C2 (P110) at the Orphée reactor (CEN Saclay) and using a neutron wavelength of $0.831$ Å. Unit-cell parameters and an orientation matrix for data collection were determined from the refinement of 20 centered reflections in the range $24 < 2\theta < 44°$. Reflection intensities were measured for $4 < 2\theta < 71°$, using the $\omega$-step-scan mode, in the Miller index ranges: $0 \le h,k,l \le 14$. The $\omega$-scan range was adjusted as a function of the scattering angle to match the instrument resolution.

The intensities of two reference reflections (520 and 025), monitored every 50 measured reflections, were essentially constant throughout the data collection period (14 d). Integrated reflection intensities were determined from the $\omega$ scans by profile analysis. Of the 1872 measured reflections, 624 were independent ($R_{sym} = \sum ||F_o| - |F_{oav}||/\sum |F_o| = 0.01$) and 452, having $|F^2| > 2.5\sigma(|F|^2)$, were used in the calculations. Owing to the small absorption effects (small crystal size and evaluated coefficient $\mu = 1.2$ cm$^{-1}$), no correction was applied to the diffraction data. The relatively small $||F_o| - |F_c||$ differences for strong reflections in the final cycles of structure refinement, including an empirical isotropic extinction parameter (maximum correction: 10% on $F$), indicated that no correction for anisotropic extinction effects had to be applied. The full-matrix least-squares refinement of 102 paramteters based on $|F|$'s with weights $w = 1/[\sigma^2(|F_o|) + 0.0002|F_o|^2]$, converged to a final $R = 0.037$, and $wR = 0.029$, $S = 1.10$ and $(\Delta/\sigma)_{max} = 0.02$. Distances C—H and H—H were restrained to $1.045$ and $1.706$ Å respectively, with an estimated e.s.d. of $0.01$ Å. Restrained refinements were chosen as a consequence of an unexpected rise in the number of parameters (doubling of the H-atom positions). Anisotropic temperature factors for all atoms excluding uranium and sodium, which behaved isotropically, were refined.

### Table 1. *Atomic and thermal parameters*

E.s.d.'s are in parentheses and starred atoms were refined isotropically.

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

(a) Final atomic coordinates and equivalent isotropic thermal parameters

| | $x$ | $y$ | $z$ | $B_{eq}/B_{iso}$ (Å$^2$) |
|---|---|---|---|---|
| U | 0.4293 (1) | 0.4293 (1) | 0.4293 (1) | 1.56 (3)* |
| Na | 0.8282 (3) | 0.8282 (3) | 0.8282 (3) | 2.18 (9)* |
| O(1) | 0.3342 (2) | 0.3342 (2) | 0.3342 (2) | 2.86 (4) |
| O(2) | 0.5244 (2) | 0.5244 (2) | 0.5244 (2) | 2.94 (4) |
| O(3) | 0.3838 (2) | 0.2920 (2) | 0.6114 (2) | 2.81 (5) |
| O(4) | 0.5464 (2) | 0.2439 (2) | 0.5007 (2) | 2.69 (4) |
| C(1) | 0.4778 (2) | 0.2258 (2) | 0.5943 (2) | 2.50 (5) |
| C(2) | 0.5087 (3) | 0.1246 (3) | 0.6852 (3) | 5.27 (8) |
| H(1) | 0.6054 (8) | 0.115 (4) | 0.694 (3) | 8.1 (7) |
| H(2) | 0.471 (4) | 0.041 (1) | 0.651 (3) | 9.3 (8) |
| H(3) | 0.470 (4) | 0.144 (3) | 0.773 (2) | 8.3 (7) |
| H(4) | 0.564 (5) | 0.167 (2) | 0.756 (4) | 13 (1) |
| H(5) | 0.562 (4) | 0.052 (2) | 0.646 (3) | 9.8 (8) |
| H(6) | 0.429 (2) | 0.087 (3) | 0.729 (4) | 9.1 (8) |

(b) Principal r.m.s. amplitudes of thermal motion

| | Minimum | Intermediate | Maximum |
|---|---|---|---|
| O(1) | 0.137 | 0.212 | 0.212 |
| O(2) | 0.156 | 0.209 | 0.209 |
| O(3) | 0.146 | 0.163 | 0.243 |
| O(4) | 0.148 | 0.152 | 0.239 |
| C(1) | 0.142 | 0.162 | 0.221 |
| C(2) | 0.148 | 0.192 | 0.376 |
| H(1) | 0.197 | 0.253 | 0.450 |
| H(2) | 0.165 | 0.364 | 0.442 |
| H(3) | 0.148 | 0.323 | 0.437 |
| H(4) | 0.169 | 0.453 | 0.507 |
| H(5) | 0.150 | 0.251 | 0.537 |
| H(6) | 0.131 | 0.265 | 0.510 |

12 reflections remained in the last refinement with $||F_o| - |F_c||/\sigma(F_o) > 2$. The residual peaks were uniformly distributed on the final difference map, the absolute value of the largest peak was smaller than $0.05$ of a removed carbon peak, used as a reference. The neutron scattering lengths were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 270). Computer programs used in refinement: *SHELX*76 (Sheldrick, 1976), least-squares planes and torsion angles: unpublished programs (P. Alzari & A. Navaza). Computer used: MicroVAX II.

**Discussion.** The structure analysis of Na[UO$_2$-(C$_2$H$_3$O$_2$)$_3$], based on neutron data, essentially completes the information concerning the hydrogen atoms. The atomic positions and thermal parameters are given in Table 1, bond lengths and angles are in Table 2.*

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Table 2. *Bond distances (Å) and angles (°)*

(a) The acetate ligand

| | | | |
|---|---|---|---|
| O(3)—C(1) | 1·256 (3) | C(2)—H(3) | 1·046 (8)* |
| O(4)—C(1) | 1·256 (3) | C(2)—H(4) | 1·062 (9)* |
| C(2)—C(1) | 1·491 (3) | C(2)—H(5) | 1·047 (8)* |
| C(2)—H(1) | 1·043 (8)* | C(2)—H(6) | 1·049 (8)* |
| C(2)—H(2) | 1·044 (8)* | | |

| | | | |
|---|---|---|---|
| O(3)—C(1)—O(4) | 119·6 (2) | H(1)—C(2)—C(1) | 110 (1) |
| O(3)—C(1)—C(2) | 120·4 (2) | H(2)—C(2)—C(1) | 108 (1) |
| O(4)—C(1)—C(2) | 120·1 (2) | H(3)—C(2)—C(1) | 110 (1) |
| H(1)—C(2)—H(2) | 109 (1) | H(4)—C(2)—C(1) | 106 (1) |
| H(1)—C(2)—H(3) | 110 (1) | H(5)—C(2)—C(1) | 114 (5) |
| H(2)—C(2)—H(3) | 109 (1) | H(6)—C(2)—C(1) | 113 (1) |
| H(4)—C(2)—H(5) | 107 (1) | H(5)—C(2)—H(6) | 109 (1) |
| H(4)—C(2)—H(6) | 107 (1) | | |

(b) The uranium atom environment

| | | | |
|---|---|---|---|
| U—O(1) | 1·761 (2) | U—O(3) | 2·486 (2) |
| U—O(2) | 1·761 (2) | U—O(4) | 2·466 (2) |

| | | | |
|---|---|---|---|
| O(1)—U—O(2) | 180 | O(3)—U—O(4) | 51·9 (7) |
| O(1)—U—O(3) | 89·9 (1) | O(3)—U—Oⁱ(4) | 68·2 (8) |
| O(1)—U—O(4) | 90·4 (1) | | |

(c) The sodium atom environment

| | | | |
|---|---|---|---|
| Na—O(3ⁱⁱ,ⁱⁱⁱ,ⁱᵛ) | 2·388 (4) | Na—O(4⁰,ᵛ,ᵛⁱ) | 2·407 (4) |

| | | | |
|---|---|---|---|
| O(3ⁱⁱ)—Na—O(3ⁱⁱⁱ) | 98·4 (1) | O(3ⁱⁱⁱ)—Na—O(4ᵛⁱ) | 105·6 (1) |
| O(3ⁱⁱ)—Na—O(4⁰) | 70·7 (1) | O(4⁰)—Na—O(4ᵛ) | 89·8 (1) |
| O(3ⁱⁱ)—Na—O(4ᵛ) | 154·7 (1) | | |

Symmetry code: (0) x, y, z; (i) y, z, x; (ii) z, x, y; (iii) 0·5 + x, 0·5 − y, 1 − z; (iv) 1 − y, 0·5 + z, 0·5 − x; (v) 0·5 + y, 0·5 − z, 1 − x; (vi) 1 − z, −0·5 + x, 0·5 − y.

* Without correction for thermal motion according to the riding model.

The structure (Fig. 1) is in reasonable agreement with that determined by Templeton *et al.* (1985) from X-ray data. All distances and angles between uranyl and acetate non-hydrogen atoms are not significantly different from those determined by X-ray diffraction. However, the equivalent isotropic thermal parameters are 10% lower, on average. All acetate atoms exhibit the largest amplitude of their thermal motion almost perpendicular to the equatorial plane of the uranyl ion, while the uranyl oxygens vibrate in a parallel direction. Due to the high anisotropy of the methyl C2 (Table 1b), the hydrogen atoms were also anisotropically refined.

The main information concerns hydrogen-atom locations: two positions, with 50% probability, for each hydrogen of the CH₃ groups were observed. These positions are related by a non-crystallographic local binary axis perpendicular to the uranyl ion, passing through C1 and C2. Torsion angles (Table 3a) demonstrate their equivalence in the acetate ligand; the absence of short intermolecular H···O distances shows their equivalence in the crystal packing. The angle between the two planes containing H1, H2, H3 and H4, H5, H6 is 6°. The probable coordinates of hydrogen atoms given by Zachariasen & Plettinger (1959) and refined by Templeton *et al.*

Table 3. *Selected torsion angles (°) and the least-squares plane through the equatorial oxygen atoms (Å)*

(a) Torsion angles

| | | | |
|---|---|---|---|
| O(3)—C(1)—C(2)—H(1) | 144·8 | O(4)—C(1)—C(2)—H(6) | 150·5 |
| O(3)—C(1)—C(2)—H(2) | −95·8 | O(4)—C(1)—C(2)—H(4) | −92·8 |
| O(3)—C(1)—C(2)—H(3) | 23·3 | O(4)—C(1)—C(2)—H(5) | 25·2 |
| O(3)—C(1)—C(2)—H(4) | 86·6 | O(4)—C(1)—C(2)—H(2) | 84·9 |
| O(3)—C(1)—C(2)—H(5) | −155·5 | O(4)—C(1)—C(2)—H(3) | −156·0 |
| O(3)—C(1)—C(2)—H(6) | −30·2 | O(4)—C(1)—C(2)—H(1) | −34·6 |

(b) Least-squares plane

Equation of the plane (orthogonalized system):

$$-0.5774\,x - 0.5774\,y - 05774\,z + 7.9637 = 0$$

| Atoms in the plane | Distance | Other atoms | Distance |
|---|---|---|---|
| O(3) | 0·005 (2) | U | 0·014 (1) |
| O(4) | −0·005 (2) | C(1) | −0·048 (2) |
| O(3ⁱ) | 0·005 (2) | C(2) | −0·175 (3) |
| O(4ⁱ) | −0·005 (2) | | |
| O(3ⁱⁱ) | 0·005 (2) | | |
| O(4ⁱⁱ) | −0·005 (2) | | |

Symmetry code: (i) y, z, x; (ii) z, x, y.
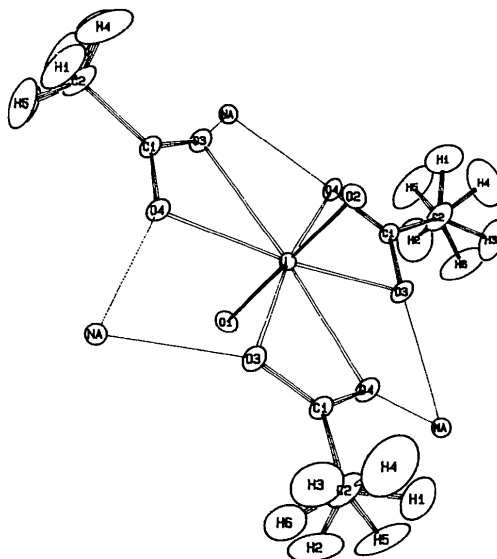


Fig. 1. *ORTEP* (Johnson, 1976) plot of Na[UO₂(C₂H₃O₂)₃] with atomic numbering. The thermal ellipsoids enclose 50% probability.
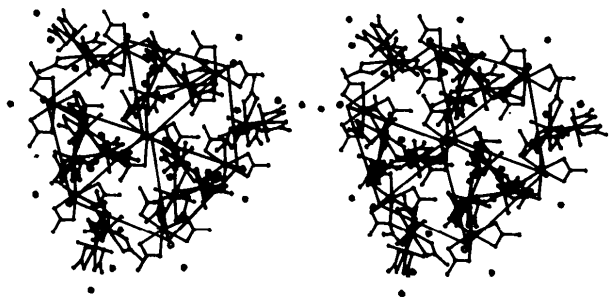


Fig. 2. Stereoscopic *ORTEP* view (Johnson, 1976) of the crystal packing.

(1985), are intermediate between the locations derived from neutron data.

The uranium atom presents a hexagonal-bipyramidal coordination (Table 2). The uranyl ion lies on a threefold axis imposing an uncommon exact linear configuration. It is surrounded by six coplanar oxygen atoms of three acetate ligands. Table 3(*b*) shows the quasi-planarity of the uranyl equatorial plane and a small shift of the uranium and carbon atoms on both sides of this plane.

The six-coordination polyhedron around sodium, based on the site symmetry $C_3$, is formed by two independent triangles of oxygen atoms, O3 and O4. It can be considered as intermediate between an octahedron and a trigonal prism (the rotation angle around the threefold axis between the two triangles is 30°). The six oxygen atoms belong to six different

acetate ligands and each of them is shared between two sodium atoms. Fig. 2 shows the crystal packing.

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# Dichloro{1-[(2-methylphenylimino)methyl]-2-naphtholato}diphenyltin(IV): a 1:1 Molecular Adduct Formed by the Interaction of Diphenyltin(IV) Dichloride with *N*-(*o*-Substituted phenyl)-2-hydroxynaphthylmethyleneamine

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**Abstract.** [Sn(Cl)$_2$(C$_6$H$_5$)$_2$(C$_{18}$H$_{15}$NO)], $M_r = 605 \cdot 13$, monoclinic, $P2_1$, $a = 9 \cdot 586$ (2), $b = 14 \cdot 269$ (2), $c = 9 \cdot 765$ (3) Å, $\beta = 97 \cdot 53$ (1)°, $V = 1324 \cdot 2$ (6) Å$^3$, $Z = 2$, $D_x = 1 \cdot 518$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 1 \cdot 085$ mm$^{-1}$, $F(000) = 608$, $T = 298$ K, $R = 0 \cdot 0700$ for 2447 observed reflections. The compound crystallizes in the form of an adduct with the organotin and ligand in a 1:1 stoichiometry. The Sn atom in the title compound possesses trigonal bipyramidal geometry, with the phenolic O atom of the Schiff base and one Cl atom occupying the axial positions. The other Cl atom and the two phenyl rings occupy the equatorial positions.

**Introduction.** Whilst a large number of molecular adducts of organotin halides and 2-hydroxynaphthylmethyleneanilines, having different substituents

in the aniline fragment, have been synthesized, crystallographic studies on the compounds have only recently been carried out (Charland, Lee, Gabe, Khoo & Smith, 1987; Khoo, Charland, Gabe & Smith, 1987). These studies, however, involve adducts with *para*-substituted anilines. To date there has been no known report on the corresponding molecular adducts with Schiff bases having *ortho*-substituted anilines. In view of the above, the 1:1 molecular adduct of diphenyltin(IV) dichloride and *N*-(*o*-substituted phenyl)-2-hydroxynaphthylmethyleneamine was synthesized and a full X-ray structural investigation carried out.

**Experimental.** *o*-Toluidine was purified before being used. The other reagents, 2-hydroxy-1-naphthaldehyde and diphenyltin(IV) dichloride, were utilized without further purification.

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