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Acta Cryst. (1985). C**41**, 1439–1441

Redetermination and Absolute Configuration of Sodium Uranyl(VI) Triacetate

BY DAVID H. TEMPLETON, ALLAN ZALKIN, HELENA RUBEN AND LIESELOTTE K. TEMPLETON

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, *USA*

(*Received* 18 *April* 1985; *accepted* 18 *June* 1985)

Abstract. Sodium tris(acetato)dioxouranate(1−), $Na[UO_2(C_2H_3O_2)_3]$, $M_r = 470{\cdot}15$, cubic, $P2_13$, $a = 10{\cdot}689\,(2)$ Å, $V = 1221{\cdot}3$ Å^3, $Z = 4$, $D_m = 2{\cdot}562$, $D_x = 2{\cdot}557\,(2)$ g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 126{\cdot}5$ cm^{-1}, $F(000) = 848$, $T = 294$ K, $R = 0{\cdot}021$ for 1195 unique observed reflections. A determination of the anomalous-scattering term f'' for uranium and Mo $K\alpha$ radiation gives 9·7 (2) e per atom. Each uranyl ion [U—O(av.) = 1·758 (3) Å] lies on a threefold axis and is surrounded equatorially by six O atoms of three acetate groups [U—O(av.) = 2·464 (2) Å]. The absolute configuration determined by the anomalous X-ray scattering is correlated with the sign of the optical activity.

Introduction. The structure of sodium uranyl acetate was studied by Fankuchen (1935) and was determined more completely by Zachariasen & Plettinger (1959). We studied it again to obtain more accurate parameters for use in the analysis of experiments with synchrotron radiation (Templeton & Templeton, 1982). The purpose of these experiments was to measure anomalous-scattering terms and the effect of polarization on them. Incidental to this work we determined that the absolute configuration of the structure, if described in a right-handed coordinate system with the atomic parameters listed in Table 1, is that of a crystal for which the sign of the optical activity is negative.

Experimental. Crystals were made by dissolving reagent-grade uranyl acetate and sodium acetate in water, followed by slow evaporation. Crystal with 18 faces of forms {111}, $\{11\bar{1}\}$ and {110}, 0·11 × 0·11 × 0·23 mm. D_m taken from Fankuchen (1935). Picker FACS-I diffractometer, graphite monochromator, θ–2θ scan; cell dimension from 12 reflections $42 < 2\theta < 48°$; analytical absorption correction, range 2·70 to 3·64; max. $(\sin\theta)/\lambda = 0{\cdot}705$ Å^{-1}, h 0 to 15, k −15 to 15, l −15 to 0; three standard reflections, $\sigma = 1{\cdot}3$, 1·0, 1·4%, no correction for decay; 3922 data, 1207 unique (including 12 observed less than background), $R_{\rm int}(I) = 0{\cdot}030$; structure from Zachariasen & Plettinger (1959) refined on F, 62 parameters including f'' of U, anisotropic thermal parameters for all atoms except H, H atoms found in ΔF map and refined with isotropic thermal parameters and subject to restraints on H—H and C—H distances, $R = 0{\cdot}021$ for 1195 reflections, $wR = 0{\cdot}015$, $S = 1{\cdot}01$, $w = [\sigma(F)]^{-2}$, derived from $\sigma^2(F^2) = [\sigma^2(F^2)$, counting statistics only, $+(0{\cdot}014F^2)^2]$; max. $\Delta/\sigma = 0{\cdot}10$; max. empirical isotropic correction for extinction 10% of F; max. and min. of ΔF synthesis 0·6 and −0·6 e Å^{-3}; atomic f including dispersion for neutral U, Na, O, C and spherical-bonded H from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965). Optical activity (positive rotation of 2 or 3°) was easy to observe in a well formed crystal of thickness 1·5 mm with a polarizing microscope illuminated with white light. This crystal was too large for reliable observation of the signs of Bijvoet differences. A small fragment was broken from a corner. Its diffraction intensities for several Bijvoet pairs, selected to be sensitive to configuration, were consistently reversed from those

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observed and calculated for the crystal used in the structure determination. Thus the latter crystal, for which the atomic parameters are listed in Table 1, has negative optical activity.*

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses)*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
U	0·42935 (1)	0·42935	0·42935	1·89
Na	0·82865 (12)	0·82865	0·82865	2·35
O(1)	0·3343 (2)	0·3343	0·3343	3·33
O(2)	0·5242 (2)	0·5242	0·5242	3·07
O(3)	0·3834 (2)	0·2945 (2)	0·6110 (2)	3·05
O(4)	0·5464 (2)	0·2443 (2)	0·5007 (2)	2·97
C(1)	0·4786 (4)	0·2260 (3)	0·5950 (3)	2·95
C(2)	0·5088 (6)	0·1240 (6)	0·6862 (6)	5·68

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

U–O(1)	1·759 (4)	1·774*	O(1)–U–O(2)	180
U–O(2)	1·756 (4)	1·769*	O(1)–U–O(3)	90·12 (6)
U–3 O(3)	2·467 (2)	2·475*	O(1)–U–O(4)	90·48 (7)
U–3 O(4)	2·462 (2)	2·469*	O(3)–U–O(4)	52·24 (8)
C(1)–O(3)	1·264 (4)	1·268*	O(3)–C(1)–O(4)	118·9 (3)
C(1)–O(4)	1·256 (4)	1·258*	O(3)–C(1)–C(2)	120·4 (3)
C(1)–C(2)	1·498 (5)	1·530*	O(4)–C(1)–C(2)	120·7 (4)
Na–3 O(3)	2·385 (3)		U–C(1)–C(2)	176·8 (4)
Na–3 O(4)	2·403 (3)			

* Corrected for thermal motion according to the riding model.

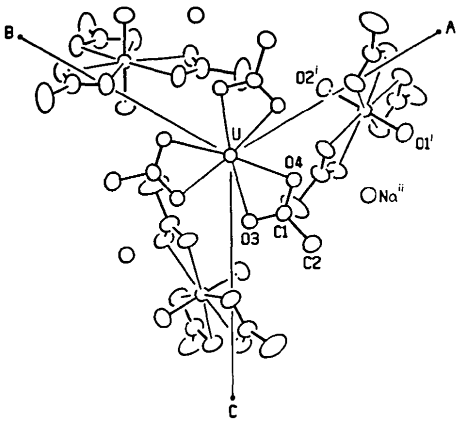

Fig. 1. View of the structure down [111]. O(1) is below the central U atom, while O(2) and Na are above it. The central molecule has three more neighbors above it, generated by unit translations of the three depicted below it; *e.g.* the upper-left molecule shifted by **c**. Symmetry code: (i) $1-x, -\frac{1}{2}+x, \frac{1}{2}-x$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-x, 1-x$.

Discussion. This work confirms, with about a tenfold improvement of precision, the structure which was determined in projection by Zachariasen & Plettinger (1959). Each uranyl is complexed with six O atoms from three acetate ions (Fig. 1 and Table 2), giving the U atom the hexagonal-bipyramidal coordination which is commonplace for uranyl salts. The thermal motion of the methyl atom, C(2), is quite anisotropic, with principal r.m.s. amplitudes of 0·18, 0·21 and 0·38 Å. The largest amplitude is nearly perpendicular to the plane of the acetate ion. The other acetate atoms exhibit excess motion in the same direction, but to a lesser extent. This motion explains the short C(1)–C(2) bond length; after correction according to the riding model, it is quite normal (Table 2).

Zachariasen & Plettinger (1959) used the uranyl bond distance in this compound [1·71 (4) Å] to revise upward to 1·70 Å the end point of a curve of uranium–oxygen bond lengths *vs* bond strength. The present results [ave. = 1·758 (3) Å] are more in line with other recent values for 'bond strength = 2·00' structures, and some further revision of the curve is suggested. A few examples are 1·75 (2) Å in dioxobis(tetrahydrofuran)uranium(IV) nitrate (Reynolds, Zalkin & Templeton, 1977), 1·76 (1) Å in dioxopentakis(urea)uranium(VI) nitrate (Zalkin, Ruben & Templeton, 1979), and 1·746 (4) Å in rubidium uranyl nitrate (to be reported elsewhere). All these values are listed without any correction for thermal motion.

The chiral nature of the molecular environment in this crystal is evident in Fig. 1, which depicts the absolute configuration which produces negative optical rotation. To associate the present atomic coordinates with another specimen, two steps are required: correct designation of axes *a*, *b*, and *c*, and determination of the enantiomer. There are two distinct ways in which right-handed axes can be assigned to a specimen. They can be distinguished by the relative intensities of reflection pairs *hk*0, *h*0*k* [*e.g.* $I(720)/I(702) = 52$ for our setting] which are independent of the enantiomer. This ratio is inverted for the other setting. Then the handedness can be determined by Bijvoet pairs such as $I(712)/I(7,1,-2) = 1·58$, $I(721)/I(7,2,-1) = 1·26$ (for coordinates of Table 1), or by observation of optical rotation.

This data set permits a good determination of f'' for uranium at Mo $K\alpha$; the result 9·7 (2) e per atom is in agreement with 9·654 e per atom calculated by Cromer & Liberman (1970) for Mo $K\alpha_1$.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under grant No. CHE-8217443.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42306 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1985). C**41**, 1441–1444

Structure of Tris-μ-[bis(8-quinolinolato)hydrogen(I)-*N*,*O*]-dinickel(II) Triiodide

BY HIDEKO KIRIYAMA, TOMIYO FUKUDA, YURIKO YAMAGATA AND EIICHI SEKIDO

Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657, *Japan*

(*Received* 10 *May* 1985; *accepted* 26 *June* 1985)

Abstract. $[Ni_2\{H(C_9H_6NO)_2\}_3]I_3$, $M_r = 1366{\cdot}04$, monoclinic, $P2_1/c$, $a = 21{\cdot}151$ (10), $b = 15{\cdot}231$ (3), $c = 15{\cdot}993$ (6) Å, $\beta = 98{\cdot}75$ (2)°, $V = 5092$ (3) Å^3, $Z = 4$, $D_m = 1{\cdot}76$ (1), $D_x = 1{\cdot}78$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}60$ mm^{-1}, $F(000) = 2672$, $T = 298$ K, $R = 0{\cdot}096$ for 3029 observed reflections. Each Ni^{II} atom is surrounded by three bidentate 8-quinolinol ligands with facial conformation in a distorted octahedral coordination. Two such facial isomers form a dinuclear cation of $[Ni_2\{H(C_9H_6NO)_2\}_3]^+$ joined face to face by three strong O···H···O hydrogen bonds with an average distance of 2·45 (3) Å. Counteranions exist as I_3^- with I(1)–I(2) 2·921 (3) Å and I(2)–I(3) 2·897 (3) Å, and I(1)–I(2)–I(3) 176·9 (1)°.

Introduction. 8-Quinolinol is a useful analytical reagent, which forms neutral bidentate chelates with many metal ions. Recently, nickel 8-quinolinol complexes containing anions such as iodide, perchlorate or thiocyanate were obtained from ethanol solution (Sekido & Fukuyori, 1984, unpublished), but their chemical compositions have been ambiguous from the chemical and spectroscopic analyses. In this study the crystal structure of the nickel 8-quinolinol complex with iodide anions was determined by means of X-ray diffraction in order to make clear its stoichiometry and structural details.

Experimental. Nickel(II) chloride hexahydrate (10 mmol in 20 ml of ethanol) and 8-quinolinol (60 mmol in 100 ml of ethanol) were added dropwise into a sodium iodide solution (20 mmol in 30 ml ethanol). The mixture was stirred and filtered. The filtrate was allowed to stand in air to evaporate for several days, during which time the color of the solution changed from yellow to brown and then dark-brown crystals were obtained. Density measured by flotation (*m*-xylene–1,2-dibromoethylene mixture); crystal 0·2 × 0·15 × 0·15 mm; Rigaku AFC-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 40 kV–200 mA; unit-cell parameters determined from least squares of setting angles of 30 reflections in 2θ range 20–24°; 7334 reflections measured, 7020 unique reflections, $R_{\rm int} = 0{\cdot}052$, ω–2θ scan technique, ω scan width $(0{\cdot}8 + 0{\cdot}35\tan\theta)°$, $2\theta_{\max} = 50°$ (h −25→25, k 0→18, l 0→19), 3029 (43%) with $|F_o| > 3\sigma(F_o)$; standard reflections 040, 815 and 400, intensity variation <2·2%; corrections for Lorentz–polarization and absorption (North, Phillips & Mathews, 1968) (min. = 1·006, max. = 1·138); structure solved by heavy-atom method and refined by block-diagonal least squares on F with anisotropic thermal parameters for I, Ni, O and N atoms and isotropic thermal parameters for C atoms; H atoms included in fixed theoretical positions (C—H = 1·0 Å and O—H = 1·0 Å) with an isotropic temperature factor of 5·0 Å^2; $\sum w(|F_o| - |F_c|)^2$ minimized for 371 parameters. Final $R = 0{\cdot}096$, $wR = 0{\cdot}061$, $S = 1{\cdot}38$; $w = 1/\sigma^2(F_o)$, which was the best weighting scheme among various ones tested such as $w = 1{\cdot}0$, $w = [\sigma^2(F_o) + 0{\cdot}051|F_o|]^{-1}$ and $w = [\sigma^2(F_o) + 4{\cdot}626|F_o| - 0{\cdot}0304|F_o|^2]^{-1}$ derived from an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$; $(\Delta/\sigma)_{\max} = 0{\cdot}47$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}03$. The ensuing refinement with anisotropic thermal parameters of all non-H atoms was unsuccessful in that anisotropic thermal parameters of five C atoms became unreasonable.

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