

Structure of Nickel Uranyl Acetate Hexahydrate

BY ALLAN ZALKIN, HELENA RUBEN AND DAVID H. TEMPLETON

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

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Abstract. $[\text{Ni}(\text{H}_2\text{O})_6][\text{UO}_2(\text{CH}_3\text{COO})_3]_2$, monoclinic, $P2_1/c$, $a = 13.387$ (3), $b = 14.727$ (3), $c = 15.349$ (3) Å, $\beta = 91.12$ (2)°, $V = 3025.5$ Å³, $Z = 4$, $D_x = 2.329$ Mg m⁻³. The final R was 0.030 for 2507 ($I > 3\sigma$) reflections. The structure consists of octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ cations and hexagonal-bipyramidal $\text{UO}_2(\text{CH}_3\text{COO})_3^-$ anions.

Introduction. As part of a study of uranium salts we prepared bright-green crystals of $[\text{Ni}(\text{H}_2\text{O})_6][\text{UO}_2(\text{CH}_3\text{COO})_3]_2$ from stoichiometric amounts of nickel acetate and uranyl acetate dissolved in a dilute aqueous solution of acetic acid which was allowed to evaporate slowly in air. A crystal, approximately $0.10 \times 0.15 \times 0.20$ mm, was selected for the intensity measurements. Its shape was described by the nine planes (002), $\pm(200)$, $\pm(11\bar{1})$, $\pm(1\bar{1}1)$, $(\bar{1}11)$ and $(\bar{1}\bar{1}\bar{1})$.

A Picker computer-controlled four-circle diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda_{K\alpha_1} = 0.7093$ Å) was used. The setting angles of 12 manually centered reflections, $42^\circ < 2\theta < 52^\circ$, were used to determine the cell parameters. A θ - 2θ scan technique was used to collect the integrated intensities. Each reflection was scanned at a rate of 2° min^{-1} from 0.7° before the $K\alpha_1$ peak to 0.7° beyond the $K\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range. The temperature during data collection was 296 ± 1 K. Three standards were measured after every 250th scan and were used to scale the data. The intensity of the standards decayed about 10% during the 5 d of data collection. The 6021 scans, not including standards, resulted in 3975 unique intensities, 2507 of which were greater than $3\sigma(F^2)$; $\theta_{\text{max}} = 22.5^\circ$. An absorption correction was applied (Templeton & Templeton, 1973), $\mu = 10.8 \text{ mm}^{-1}$; the maximum and minimum corrections were 2.8 and 1.9 respectively. The data were corrected for Lorentz and polarization effects.

A three-dimensional Patterson function was used to derive the atomic positions of the U and Ni atoms. Subsequent least-squares and Fourier calculations revealed the positions of the C and O atoms. A series of least-squares refinements, in which the function $\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2$ was minimized, rapidly converged to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.030$ for the 3σ data, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} =$

0.036; R for all 3975 data was 0.063. Weights were assigned as $w = [S^2 + (pF^2)^2]^{1/2}$ where S is the variance due to counting statistics and p was set at 0.04.

All of the atoms, with the exception of the H atoms which were not included in the least-squares calculations, were given anisotropic thermal parameters. An empirical extinction correction of the type $F_o(\text{corr.})$

Table 1. Positional parameters with e.s.d.'s in parentheses, and B_{eq} values

	x	y	z	B_{eq} (Å ²)*
Ni(1)	0	0	0	2.63 (6)
Ni(2)	0.500	0	0.500	2.47 (6)
U(1)	0.14297 (4)	0.15800 (3)	0.66444 (3)	3.32 (1)
U(2)	0.35693 (4)	-0.16316 (3)	0.16958 (3)	3.19 (1)
O(1)	0.2350 (6)	0.2234 (6)	0.7195 (6)	4.1 (3)
O(2)	0.0506 (7)	0.0948 (7)	0.6110 (7)	5.7 (3)
O(3)	0.2703 (6)	-0.2322 (6)	0.2225 (5)	4.1 (3)
O(4)	0.4448 (8)	-0.0957 (7)	0.1191 (7)	5.9 (3)
O(5)	0.0324 (8)	0.1871 (6)	0.7893 (6)	5.3 (3)
O(6)	0.0271 (6)	0.2882 (6)	0.6866 (6)	4.3 (3)
O(7)	0.1610 (7)	0.2715 (6)	0.5476 (6)	4.6 (3)
O(8)	0.2468 (7)	0.1477 (6)	0.5343 (6)	4.7 (3)
O(9)	0.2684 (7)	0.0318 (6)	0.6768 (7)	4.8 (3)
O(10)	0.1614 (8)	0.0438 (6)	0.7794 (6)	5.1 (3)
O(11)	0.2353 (7)	-0.1683 (6)	0.0447 (6)	4.4 (3)
O(12)	0.3537 (8)	-0.2686 (7)	0.0450 (6)	5.5 (3)
O(13)	0.4756 (6)	-0.2908 (6)	0.1908 (6)	4.1 (3)
O(14)	0.4699 (7)	-0.1915 (6)	0.2948 (6)	4.3 (3)
O(15)	0.3234 (7)	-0.0507 (6)	0.2877 (6)	4.7 (3)
O(16)	0.2367 (7)	-0.0384 (6)	0.1685 (6)	4.8 (3)
O(17)	0.1438 (6)	0.0461 (6)	0.0228 (6)	4.0 (3)
O(18)	0.0351 (6)	-0.1238 (6)	0.0535 (6)	4.2 (3)
O(19)	-0.0440 (7)	0.0526 (6)	0.1166 (6)	5.2 (3)
O(20)	0.4978 (6)	0.1340 (5)	0.5366 (6)	4.0 (3)
O(21)	0.5444 (7)	0.0315 (6)	0.3754 (6)	5.3 (3)
O(22)	0.3546 (7)	0.0088 (7)	0.4595 (7)	6.3 (3)
C(1)	0.003 (1)	0.2661 (9)	0.763 (1)	4.1 (4)
C(2)	-0.053 (1)	0.3256 (9)	0.823 (1)	5.1 (5)
C(3)	0.229 (1)	0.228 (1)	0.5069 (9)	4.3 (4)
C(4)	0.286 (1)	0.270 (1)	0.4338 (9)	5.9 (5)
C(5)	0.243 (1)	0.0104 (9)	0.754 (1)	4.2 (4)
C(6)	0.305 (1)	-0.051 (1)	0.809 (1)	5.9 (5)
C(7)	0.272 (1)	-0.238 (1)	0.0132 (9)	4.2 (4)
C(8)	0.218 (1)	-0.289 (1)	-0.061 (1)	6.2 (5)
C(9)	0.5003 (9)	-0.269 (1)	0.268 (1)	3.9 (4)
C(10)	0.561 (1)	-0.3298 (9)	0.3257 (9)	4.9 (4)
C(11)	0.250 (1)	-0.0160 (9)	0.246 (1)	4.3 (4)
C(12)	0.178 (1)	0.052 (1)	0.289 (1)	6.7 (6)

* $B_{\text{eq}} = \frac{1}{3} \pi^2 \text{ trace } \tilde{U}$.

Table 2. *Interatomic distances (Å), with standard deviations in parentheses*

U(1)—O(1)	1.77 (1)	C(3)—O(7)	1.29 (2)
—O(2)	1.74 (1)	—O(8)	1.27 (2)
—O(5)	2.48 (1)	—C(4)	1.51 (2)
—O(6)	2.49 (1)	C(5)—O(9)	1.27 (2)
—O(7)	2.47 (1)	—O(10)	1.26 (2)
—O(8)	2.46 (1)	—C(6)	1.49 (2)
—O(9)	2.51 (1)	C(7)—O(11)	1.24 (2)
—O(10)	2.45 (1)	—O(12)	1.28 (2)
U(2)—O(3)	1.75 (1)	—C(8)	1.53 (2)
—O(4)	1.73 (1)	C(9)—O(13)	1.27 (2)
—O(11)	2.49 (1)	—O(14)	1.28 (2)
—O(12)	2.46 (1)	—C(10)	1.49 (2)
—O(13)	2.48 (1)	C(11)—O(15)	1.27 (2)
—O(14)	2.46 (1)	—O(16)	1.24 (2)
—O(15)	2.50 (1)	—C(12)	1.55 (2)
—O(16)	2.44 (1)	O(17)—O(7)	2.72 (2)
Ni(1)—2O(17)	2.07 (1)	—O(16)	2.83 (2)
—2O(18)	2.05 (1)	O(18)—O(5)	2.76 (2)
—2O(19)	2.05 (1)	—O(11)	2.77 (2)
Ni(2)—2O(20)	2.05 (1)	O(19)—O(6)	2.74 (2)
—2O(21)	2.07 (1)	—O(10)	2.67 (2)
—2O(22)	2.04 (1)	O(20)—O(12)	2.77 (2)
C(1)—O(5)	1.29 (2)	—O(14)	2.75 (2)
—O(6)	1.27 (2)	O(21)—O(9)	2.81 (2)
—C(2)	1.49 (2)	—O(13)	2.82 (2)
		O(22)—O(8)	2.77 (2)
		—O(15)	2.80 (2)

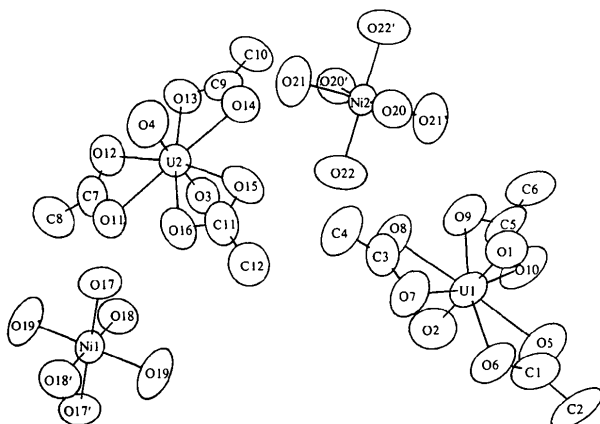


Fig. 1. View of the structure showing the atomic numbering.

$= F_o(1 + kI)$ (Zachariasen, 1967), in which $k = 2.0 \times 10^{-7}$, was applied. For 337 parameters and 2507 data the goodness-of-fit value was 1.25. The largest final shift of any parameter was 0.05σ . The largest peak in the final difference Fourier map, $1.2 \text{ e } \text{Å}^{-3}$, was near a U atom. Several smaller peaks could be related to H atoms, but were poorly resolved.

Positional parameters are given in Table 1.* Dis-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36284 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected angles (°)*

O(1)—U(1)—O(2)	179.0 (5)	O(3)—U(2)—O(4)	178.6 (4)
O(5)—U(1)—O(6)	51.7 (3)	O(11)—U(2)—O(12)	51.9 (3)
O(7)—U(1)—O(8)	52.2 (3)	O(13)—U(2)—O(14)	52.1 (3)
O(9)—U(1)—O(10)	51.6 (3)	O(15)—U(2)—O(16)	51.7 (3)
O(6)—U(1)—O(7)	69.4 (3)	O(12)—U(2)—O(13)	68.0 (3)
O(8)—U(1)—O(9)	68.2 (3)	O(14)—U(2)—O(15)	70.3 (3)
O(10)—U(1)—O(5)	67.4 (3)	O(16)—U(2)—O(11)	66.2 (3)
O(1)—U(1)—O(5)	87.5 (4)	O(3)—U(2)—O(11)	84.9 (3)
O(1)—U(1)—O(6)	86.9 (4)	O(3)—U(2)—O(12)	89.6 (4)
O(1)—U(1)—O(7)	84.3 (4)	O(3)—U(2)—O(13)	85.8 (4)
O(1)—U(1)—O(8)	91.3 (4)	O(3)—U(2)—O(14)	86.7 (3)
O(1)—U(1)—O(9)	84.8 (4)	O(3)—U(2)—O(15)	85.4 (4)
O(1)—U(1)—O(10)	88.3 (4)	O(3)—U(2)—O(16)	89.9 (4)
O(2)—U(1)—O(5)	91.6 (4)	O(4)—U(2)—O(11)	96.4 (4)
O(2)—U(1)—O(6)	92.2 (4)	O(4)—U(2)—O(12)	90.9 (4)
O(2)—U(1)—O(7)	95.7 (4)	O(4)—U(2)—O(13)	93.1 (4)
O(2)—U(1)—O(8)	89.5 (4)	O(4)—U(2)—O(14)	92.0 (4)
O(2)—U(1)—O(9)	96.2 (4)	O(4)—U(2)—O(15)	94.4 (4)
O(2)—U(1)—O(10)	91.9 (4)	O(4)—U(2)—O(16)	91.1 (4)
O(17)—Ni(1)—O(17)'	180.0	O(20)—Ni(2)—O(20)'	180.0
O(17)—Ni(1)—O(18)	91.1 (3)	O(20)—Ni(2)—O(21)	92.5 (4)
O(17)—Ni(1)—O(18)'	88.9 (3)	O(20)—Ni(2)—O(21)'	87.5 (4)
O(17)—Ni(1)—O(19)	90.6 (4)	O(20)—Ni(2)—O(22)	90.2 (4)
O(17)—Ni(1)—O(19)'	89.4 (4)	O(20)—Ni(2)—O(22)'	89.8 (4)
O(18)—Ni(1)—O(18)'	180.0	O(21)—Ni(2)—O(21)'	180.0
O(18)—Ni(1)—O(19)	86.9 (4)	O(21)—Ni(2)—O(22)	89.7 (4)
O(18)—Ni(1)—O(19)'	93.1 (4)	O(21)—Ni(2)—O(22)'	90.3 (4)
O(19)—Ni(1)—O(19)'	180.0	O(22)—Ni(2)—O(22)'	180.0
C(2)—C(1)—O(5)	119.8 (14)	C(8)—C(7)—O(11)	121.1 (14)
C(2)—C(1)—O(6)	124.0 (14)	C(8)—C(7)—O(12)	120.0 (14)
O(5)—C(1)—O(6)	116.3 (12)	O(11)—C(7)—O(12)	118.9 (13)
C(4)—C(3)—O(7)	121.5 (13)	C(10)—C(9)—O(13)	121.9 (14)
C(4)—C(3)—O(8)	122.6 (13)	C(10)—C(9)—O(14)	121.2 (14)
O(7)—C(3)—O(8)	115.8 (13)	O(13)—C(9)—O(14)	116.9 (13)
C(6)—C(5)—O(9)	121.2 (13)	C(12)—C(11)—O(15)	121.6 (14)
C(6)—C(5)—O(10)	122.5 (13)	C(12)—C(11)—O(16)	120.0 (13)
O(9)—C(5)—O(10)	116.3 (13)	O(15)—C(11)—O(16)	118.4 (14)
O(7)—O(17)—O(16)	106.8 (4)	O(12)—O(20)—O(14)	99.5 (4)
O(5)—O(18)—O(11)	107.3 (4)	O(9)—O(21)—O(13)	106.5 (4)
O(6)—O(19)—O(10)	115.1 (4)	O(8)—O(22)—O(15)	123.5 (4)

tances and angles are given in Tables 2 and 3, with atom numbers as in Fig. 1.

Discussion. The unit cell and space group of this salt were reported by Tani (1958) and are similar to the present results except for a typographical error in the value of the b axis. The structure consists of packing of octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ cations and hexagonal-bipyramidal $(\text{CH}_3\text{COO})_3\text{UO}_2^-$ anions. Although there are two crystallographically different formula units in the asymmetric unit, their geometry is nearly the same. With some small shifts in the positional parameters, most of the structure could be described in the orthorhombic space group $Pbca$ with only one formula unit per asymmetric unit; the monoclinic angle is only 1.12° from orthogonality. Only the water molecules deviate more than 0.34 Å from this orthorhombic symmetry, but this is enough to introduce gross deviations from mmm symmetry in the intensity data.

All of the H atoms of the water molecules are involved in hydrogen bonds with $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond lengths ranging from 2.67 to 2.83 Å (Table 2) and $\text{O}-\text{H}_2\text{O}-\text{O}$ angles ranging from 100 to 124° (Table 3).

The structure of the $\text{UO}_2(\text{CH}_3\text{COO})_3^-$ anion is the same as was found in sodium uranyl acetate (Zachariassen & Plettinger, 1959).

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catena- μ -Acetato- N,N' -ethylenebis[(2-hydroxy-1-naphthyl)methaniminato]manganese(III)

BY FARIDA AKHTAR AND MICHAEL G. B. DREW

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, England

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Abstract. $\text{C}_{26}\text{H}_{21}\text{MnN}_2\text{O}_4$, orthorhombic, $a = 20.30$ (1), $b = 6.609$ (7), $c = 15.24$ (1) Å, $U = 2045$ (1) Å³, $D_m = 1.54$, $D_c = 1.56$ Mg m⁻³, $F(000) = 1800$, $Z = 4$, Mo K radiation, $\lambda = 0.7107$ Å, $\mu = 0.462$ mm⁻¹; space group $Pccn$ from the systematic absences $hk0$, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$, $0kl$, $l = 2n + 1$; 886 independent reflections; $R = 0.079$. The structure is made up of N,N' -ethylenebis[(2-hydroxy-1-naphthyl)methaniminato]manganese moieties with imposed C_2 symmetry [Mn–N, Mn–O 2.006 (9), 1.885 (7) Å] bridged by single acetate groups [Mn–O 2.220 (7) Å] in an *anti-anti* configuration to form a one-dimensional polymer.

Introduction. The crystal structure of the 1:1 molecular complex of nickel and N,N' -ethylenebis[(2-hydroxy-1-naphthyl)methanimine] (=L) and its characteristics compared to those of the corresponding salicylideneimine complex have been reported previously (Akhtar, 1981). We now report the structure of the complex [MnL(acetate)] (I). These structures can be compared to those containing the analogous trimethylene ligand L^1 {*viz* N,N' -propylenebis[(2-hydroxy-1-naphthyl)methanimine]}, namely [NiL¹] and [CuL¹(dms)_{0.5}] (dms = dimethyl sulphoxide) (Akhtar & Drew, 1982).

The compound MnL was prepared by refluxing an equimolar mixture of manganese acetate dihydrate and the ligand N,N' -ethylenebis[(2-hydroxy-1-naphthyl)methanimine] (Hussain, 1978). Dark purple-brown elongated prisms were obtained on slow recrystallization from methanol. A crystal of approximate size 0.4 × 0.3 × 0.1 mm was mounted along *c* in a Lindemann tube and intensities were measured on a

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Stoe STADI2 diffractometer equipped with a graphite monochromator. 1950 reflections with a 2θ maximum of 50° were measured by ω scans with a scan speed of 0.0333° s⁻¹ and a background count of 20 s. Of these, 886 independent reflections with $I > 2\sigma(I)$ were used in subsequent calculations. Neither absorption nor extinction corrections were applied. The positions of the Mn atoms in (I) were obtained from the Patterson function and the positions of the remaining non-hydrogen atoms were obtained from Fourier maps. Atoms were refined anisotropically. H atoms were fixed in trigonal and

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å² $\times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mn	2500	2500	4022 (1)	34 (2)
O(1)	1805 (3)	2377 (14)	3203 (4)	43 (9)
N(1)	1844 (5)	2653 (16)	5004 (5)	37 (10)
C(1)	841 (5)	2355 (21)	4160 (6)	40 (12)
C(2)	1170 (6)	2091 (14)	3348 (7)	38 (12)
C(3)	793 (6)	1462 (20)	2609 (8)	46 (14)
C(4)	119 (6)	1287 (21)	2655 (8)	45 (15)
C(5)	-236 (6)	1686 (18)	3469 (8)	50 (12)
C(6)	-928 (6)	1557 (21)	3489 (10)	66 (16)
C(7)	-1247 (6)	1931 (19)	4245 (11)	68 (16)
C(8)	-895 (6)	2467 (22)	4998 (8)	63 (17)
C(9)	-224 (5)	2590 (22)	4981 (7)	54 (14)
C(10)	140 (6)	2195 (19)	4207 (7)	46 (12)
C(11)	1215 (5)	2650 (20)	4941 (7)	45 (13)
C(12)	2176 (6)	3067 (19)	5863 (7)	49 (13)
O(2)	2505 (5)	-834 (11)	4202 (5)	53 (10)
C(21)	2500	7500	3803 (10)	42 (12)
C(22)	2500	7500	2807 (11)	64 (18)