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The Crystal and Molecular Structure of the Bis(4-N,N′-dimethylaminopyridine) Solvate of Di-μ-Salicylicacidato Bis{nitratodioxouranium(VI)}

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The structure of the title compound $[(C_7H_4NO_8U)(C_7H_{11}N_2)]_2$ *has been determined by Patterson and Fourier methods from single crystal X-ray diffraction data collected on a four-circle diffractometer. Full-matrix least-squares refinement yielded a final conventional R of 0.041 for 2189 reflections. The complex crystallizes in the space group* $P\bar{1}$ *with* $a = 11.004(5)$, $b = 9.981(5)$, $c = 9.928(5)$ Å, $\alpha = 119.6(3)$, $\beta = 107.7(3)$, $\gamma = 81.9(3)^\circ$, $D_m = 2.17$, $D_c = 2.173$ *g cm*$^{-3}$.

The structure is dimeric. The uranium atoms are eight-coordinate and are bridged via centrosymmetrically related carboxylic oxygen atoms. The nitrate group is bidentate and the average U–O (ligand) distance is 2.463 Å. Hydrogen bonding of the type N–H···O links two dimethyl-aminopyridine molecules to the dimer.

Introduction

The X-ray structural determination of the title compound was undertaken as part of a general program investigating pyridine adducts of uranyl complexes.

Experimental

Preparation of the Complex

Solutions containing 1 g $UO_2(NO_3)_2 \cdot 6H_2O$ dissolved in 10 g methanol and 0.6 g salicylic acid dissolved in 20 ml methanol were mixed. To this was added a solution containing 0.2 g 4-dimethylaminopyridine dissolved in 10 ml methanol. After allowing to stand at room temperature for 2 days, deep red crystals were precipitated. These were washed with methanol and air dried. *Anal.* calculated for $[C_{14}H_{15}N_3O_8U]_2$: C 28.42, H 2.53, N 7.10; experimentally found: C 28.5, H 2.6, N 7.0%. The figures agreed closely enough to suggest the formulation $[UO_2NO_3$(salicylic acid)·(dimethylaminopyridine)$]_2$ which was subsequently confirmed in the X-ray determination.

Crystal Data

The density was determined by flotation in a mixture of *m*-xylene (ρ = 0.86 g cm^{-3}) and diiodomethane (ρ = 3.31 g cm^{-3}). Preliminary oscillation and Weissenberg photographs gave P1 or $P\bar{1}$ as the possible space group with the latter being confirmed by the successful structural analysis. A single crystal was ground into a sphere of radius 0.18 mm using a device similar to that described by Bond [1]. This crystal was used for the data collection. The lattice constants were obtained from a least squares analysis of the settings of 25 reflections measured on a four-circle diffractometer with MoKα radiation (λ = 0.71069 Å).

Molecular formula:	$[(C_7H_4NO_8U)(C_7H_{11}N_2)]_2$
Molecular weight:	1182
Asymmetric unit:	$[(C_7H_4NO_8U)(C_7H_{11}N_2)]$
a: 11.004(5) Å	D_m: 2.17 g cm^{-3}
b: 9.981(5) Å	D_c: 2.173 g cm^{-3} for Z = 1 dimer
c: 9.928(5) Å	μ(MoKα): 86.08 cm^{-1}
α: 119.6(3)°	V: 903.25 Å^3
β: 107.7(3)°	F(000): 552
γ: 81.9(3)°	Space Group: $P\bar{1}$ after structure determination

Figures in parentheses are the e.s.d's calculated from several measured values of the parameters.

Intensity Data

The intensity data were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the ω–2θ scan mode (scan width = 1.50°θ and scan speed = 0.05°θ s^{-1}). The background and scan times were both 30 seconds. Using graphite-monochromated MoKα radiation, 2214 reflections up to $2\theta = 44°$ were measured. Of these 25 were omitted as they did not satisfy the condition $I_{rel} > 3\sigma(I_{rel})$ for an observed reflection.

Throughout the course of the data collection process three standard reflections were measured after every 56 reflections to ensure stability of operation and to monitor any crystal decomposition. These remained constant to within ±4%. Lorentz-polarization corrections were applied to the data. Absorption corrections [2] were carried out with A* for a sphere with $\mu R = 1.55$.

Structure Determination and Refinement

The uranium atom was located from a Patterson map. A difference map was calculated with the weighting scheme $w = \exp(-g\sin^2\theta/\lambda^2 s^2)$ in which s is the value of $\sin\theta/\lambda$ for which the weight is half that at $\theta = 0$. With a value of s = 0.5 the difference map yielded the positions of all the non hydrogen atoms and a residual index value of $R = \Sigma\,(||F_o| - |F_c||)/\Sigma|F_o| = 0.166$. Full-matrix least-squares refinement (SHEL-X program system [3]) with the uranium atom anisotropic and the remaining non hydrogen atoms isotropic yielded an R of 0.041. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is the weight of a reflection. At this stage a difference map showed the positions of nine hydrogen atoms, including H(1) which is involved in hydrogen bonding. Accordingly the positional parameters of H(1) were refined independently of the other hydrogen atoms which in turn were constrained to be 1.08 Å from their corresponding parent atoms, their positions being dictated by the geometry of the molecule. The methyl hydrogens were refined as rigid groups. The isotropic temperature factors of the hydrogen atoms were refined as four single parameters, one for the salicylic acid hydrogens, one for the pyridine ring hydrogens, one for the methyl hydrogens and one for H(1). This technique of constrained least-squares refinement using bond length constraints and location and refinement of hydrogen atoms is discussed by Sheldrick [3].

The weighting scheme adopted was of the form $w = 1/(\sigma^2 F + gF)$. The final value of g = 0.00029 was chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F. After several cycles of refinement, $R_w = \Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o|$ converged to 0.046 with a corresponding unweighted R of 0.041. In the final cycle the average shift-to-error ratio was 0.15 indicating satisfactory convergence while a final difference electron density map had no peaks > 0.64 eÅ^{-3}. Table I shows an analysis of variance computed after the refinement process had been completed. Atomic scattering factors for the heavy atoms were those from Cromer and Mann [4] and those for hydrogen were from Stewart *et al.* [5]. The scattering curve for uranium was corrected for anomalous dispersion ($\Delta f' = -10.673$, $\Delta f'' = 9.654$, for MoKα).

The final atomic positional and thermal parameters for the non hydrogen atoms are given in Table II while Table III lists those of the hydrogen atoms. The observed and calculated structure factors are available from the Editor.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1106 computer with the program system SHEL-X written by G. M. Sheldrick [3].

Description of the Structure and Discussion

The structure of the dimer is shown in Figure 1 (Program: Pluto) [6]. The intramolecular bond lengths and angles and their associated e.s.d's are given in Tables IV and V respectively (SHEL-X). Table VI lists computed least-squares planes with their equations and the distances of various atoms from these planes. In all cases the superscripted atoms are centrosymmetrically related to the corresponding atoms without superscripts.

The structure is dimeric and centrosymmetric. The two uranium atoms are bonded to two salicylic acid ligands through their carboxylic [O(6) and O(7)] and phenolic [O(8^1)] oxygen atoms (2.467(7), 2.563(7) and 2.287(7) Å respectively). The U–O(8^1)

TABLE I. Analysis of Variance.

(a) As a function of $\sin\theta$

$\sin\theta$	0.00–0.18	–0.22	–0.26	–0.28	–0.30	–0.32	–0.34	–0.35	–0.37	–0.38
N	230	211	290	178	234	208	285	144	344	65
V	208	180	159	193	196	198	197	242	219	185

(b) As a function of $(F/F_{max})^{1/2}$

$(F/F_{max})^{1/2}$	0.00–0.22	–0.29	–0.34	–0.38	–0.41	–0.44	–0.48	–0.53	–0.59	–1.00
N	237	220	223	249	199	211	232	221	192	205
V	270	333	215	178	172	149	140	126	133	143

TABLE II. Non Hydrogen Atoms. Fractional Atomic Parameters (× 10^4) and Thermal Parameters (Å^2 × 10^3) and Their Respective e.s.d's.

Atom	X	Y	Z	U
U	1898(0)	880(0)	1284(0)	a
C(1)	198(11)	1374(12)	−1402(13)	42(2)
C(2)	−602(10)	1420(11)	−2815(12)	42(2)
C(3)	−65(13)	1926(14)	−3598(15)	52(3)
C(4)	−762(12)	1856(14)	−5048(15)	58(3)
C(5)	−1999(13)	1271(15)	−5740(16)	60(3)
C(6)	−2533(12)	757(13)	−4984(14)	54(3)
C(7)	−1859(10)	834(11)	−3485(12)	41(2)
C(8)	−5006(14)	2849(16)	−3214(18)	65(4)
C(9)	−6102(14)	3756(16)	−3147(17)	65(4)
C(10)	−6740(12)	4090(12)	−1997(12)	46(2)
C(11)	−6260(13)	3450(15)	−964(17)	62(3)
C(12)	−5159(12)	2539(14)	−1080(16)	61(3)
C(13)	−8384(15)	5512(18)	−625(19)	72(4)
C(14)	−8295(15)	5608(17)	−3037(19)	74(4)
N(1)	−4600(10)	2243(13)	−2236(12)	49(3)
N(2)	−7776(11)	4991(12)	−1908(13)	59(3)
N(3)	4406(11)	2395(13)	2626(14)	69(3)
O(1)	1309(9)	2460(10)	2776(11)	61(2)
O(2)	2516(9)	−682(10)	−206(11)	59(2)
O(3)	4197(9)	1439(10)	3010(11)	66(2)
O(4)	5450(18)	3096(20)	3271(22)	132(6)
O(5)	3503(11)	2661(13)	1669(14)	77(3)
O(6)	−131(8)	670(9)	−756(10)	55(2)
O(7)	1275(8)	2036(9)	−633(9)	57(2)
O(8)	−2430(7)	390(9)	−2760(8)	38(2)

[a] The anisotropic temperature factors are of the form: T = exp[$-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)$] and have values U_{11} = 36(0), U_{22} = 51(0), U_{33} = 42(0), U_{23} = 28(0), U_{13} = 9(0), U_{12} = 2(0).

TABLE III. Hydrogen Atoms. Fractional Atomic Coordinates (× 10^3) and Thermal Parameters (Å^2 × 10^2) and Their e.s.d's.

Atom	X	Y	Z	U
H(1)[b]	−416(12)	136(15)	−266(13)	5(3)
H(3)[b]	90(1)	237(1)	−307(2)	8(2)
H(4)[b]	−36(1)	227(1)	−564(2)	
H(5)[b]	−254(1)	120(2)	−688(2)	
H(6)[b]	−349(1)	28(1)	−554(1)	
H(8)[b]	−452(1)	261(2)	−411(2)	17(6)
H(9)	−644(1)	422(2)	−397(2)	
H(11)	−671(1)	369(2)	−4(2)	
H(12)	−479(1)	205(1)	−28(2)	
H(131)	−912(2)	634(2)	−68(2)	20(4)
H(132)[b]	−768(2)	603(2)	53(2)	
H(133)	−880(2)	452(2)	−77(2)	
H(141)[b]	−910(2)	637(2)	−287(2)	
H(142)[b]	−825(2)	512(2)	−426(2)	
H(143)[b]	−743(2)	625(2)	−222(2)	

[b] Hydrogen atoms which were found in difference syntheses.

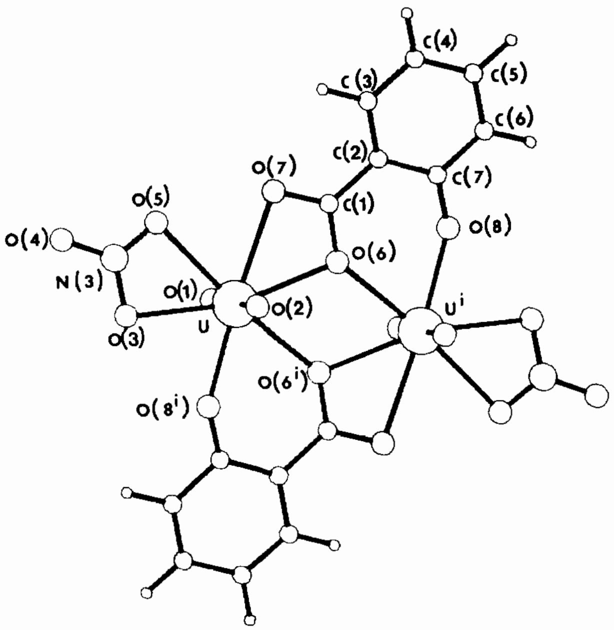

Fig. 1. Structure of the dimer viewed perpendicular to U, O(7), C(5). The solvate molecules have been omitted for clarity.

distance (2.287(7) Å) is somewhat shorter than the U–O bond lengths normally found in uranyl complexes containing 6 oxygen atoms in the equatorial plane [7–9]. Nevertheless it is in agreement with the sum of the Pauling crystal radii (0.87 + 1.40 Å) [10] as well as with U–O phenolic bond lengths reported for [N-N'-Ethylenebis(salicylideneiminato)](methanol)dioxouranium (2.25 and 2.33 Å) [11] and [bis(N-ethylenedimethylaminesalicylaldiminato)dioxouranium(VI)] (2.24 and 2.34 Å) [12].

Bridging of the two uranium atoms is effected via O(6) and O(6^i), where the U–O(6^i) bond distance is 2.425(8) Å. The bidentate nitrate ligand together with the two uranyl oxygen atoms O(1) and O(2) make each uranium atom eight-coordinate. The two U–O(nitrate) distances 2.542(7) and 2.496 (9) Å may be compared with the 2.53 Å reported for bis(ethyl carbamate)dinitratodioxouranium(VI) [13] and the two distances 2.56 and 2.60 Å in dioxodinitratobis(triphenylarsineoxide)uranium(VI) [14].

The U–O distances within the bridge formed by O(6) and O(6^i) are 2.467(7) and 2.425(8) Å respectively. These are somewhat shorter than the other U–O(ligand) bonds in which the oxygen atoms are coordinated to one uranium atom only. The latter U–O distances have values 2.542(7), 2.496(9) and 2.563(7) Å. This same feature is displayed in the molecular structure of [$(UO_2)_2(OH)_2Cl_2(H_2O)_4$] in which the bridging U–O distances have a mean value of 2.37 Å while the remaining U–O(ligand) bond lengths vary between 2.37 and 2.53 Å [15].

TABLE IV. Intramolecular Bond Lengths (Å) and Their e.s.d's.

U–O(1)	1.758(7)	C(2)–C(3)	1.40(1)
U–O(2)	1.766(7)	C(3)–C(4)	1.38(2)
U–O(3)	2.542(7)	C(4)–C(5)	1.39(2)
U–O(5)	2.496(9)	C(5)–C(6)	1.38(1)
U–O(6)	2.467(7)	C(6)–C(7)	1.42(1)
U–O(7)	2.563(7)	C(7)–O(8)	1.32(1)
U–O(6^i)	2.425(8)	N(1)–C(8)	1.32(1)
U–O(8^i)	2.287(7)	C(8)–C(9)	1.40(2)
O(3)–N(3)	1.26(1)	C(9)–C(10)	1.40(1)
O(4)–N(3)	1.25(2)	C(10)–C(11)	1.40(2)
O(5)–N(3)	1.25(1)	C(11)–C(12)	1.41(2)
C(1)–O(6)	1.30(1)	C(12)–N(1)	1.36(1)
C(1)–O(7)	1.26(1)	C(10)–N(2)	1.34(1)
C(1)–C(2)	1.43(1)	N(2)–C(13)	1.45(2)
		N(2)–C(14)	1.47(2)

TABLE V. Intramolecular Bond Angles (°) and Their e.s.d's.

O(1)–U–O(2)	178.7(3)
O(3)–U–O(5)	50.2(3)
O(6)–U–O(7)	50.3(2)
O(6)–U–O(6^i)	58.6(6)
O(6^i)–U–O(8^i)	68.3(5)
U–O(3)–N(3)	95.2(6)
O(3)–N(3)–O(5)	116.9(9)
O(3)–N(3)–O(4)	120 (1)
N(3)–O(5)–U	97.7(7)
U–O(6)–C(1)	99.6(5)
U–O(6)–U^i	121.4(5)
U–O(7)–C(1)	96.0(5)
O(6)–C(1)–O(7)	113.2(8)
C(2)–C(3)–C(4)	120.5(9)
C(3)–C(4)–C(5)	120 (1)
C(4)–C(5)–C(6)	120 (1)
C(5)–C(6)–C(7)	121.7(9)
C(6)–C(7)–C(2)	117.0(8)
C(6)–C(7)–O(8)	119.9(8)
C(7)–O(8)–U^i	138.2(7)
N(1)–C(8)–C(9)	121 (1)
C(8)–C(9)–C(10)	120 (1)
C(9)–C(10)–C(11)	117.5(9)
C(10)–C(11)–C(12)	120 (1)
C(11)–C(12)–N(1)	119 (1)
C(8)–N(1)–C(12)	122 (1)
C(9)–C(10)–N(2)	120.4(9)
C(10)–N(2)–C(14)	121.5(9)
C(10)–N(2)–C(13)	122.4(9)
C(13)–N(2)–C(14)	115.9(9)

The present uranyl U=O distances are 1.758(7) and 1.766(7) Å which compare favourably with the mean U=O distance of 1.79 Å in $[(UO_2)_2(OH)_2Cl_2(H_2O)_4]$ and with the 1.78 Å reported for another dimeric uranyl complex, di-μ-acetato-bis(dioxotriphenylphosphine oxide acetate)dioxouranium(VI) [16].

TABLE VI. Least Squares Planes. Deviations (Å) of various atoms from the planes are listed in square brackets. The equations of the planes are expressed in direct space as PX + QY + RZ = S.

Plane 1:	U, O(3), O(5), O(6), O(7), O(6^i), O(8^i) $-5.3875X + 4.3066Y + 5.0968Z = -0.02585$ [U 0.04, O(3) –0.08, O(5) 0.14, O(6) 0.0, O(7) –0.11, O(6^i) 0.06, O(8^i) –0.04, O(1) 1.79, O(2) –1.73]
Plane 2:	U, O(3), N(3), O(5) $-5.2912X + 3.4961Y + 5.9287Z = 0.0652$ [U 0.0, O(3) 0.0, N(3) 0.0, O(5) 0.0, O(1) 1.75, O(2) –1.76, U^i –0.13]
Plane 3:	U, O(6), C(1), O(7) $-5.2378X + 4.9876Y + 4.3966Z = 0.0287$ [U –0.02, O(6) 0.04, C(1) –0.06, O(7) 0.04, O(1) 1.73, O(2) –1.78, U^i –0.04]
Plane 4:	U^i, O(6), C(1), C(2), C(7), O(8) $-4.7903X + 5.4875Y + 3.9693Z = 0.0567$ [U^i –0.14, O(6) 0.07, C(1) 0.05, C(2) –0.11, C(7) –0.09, O(8) 0.22, O(1) 1.77, O(2) –1.72, U 0.03]
Plane 5:	C(1), C(2), C(3), C(4), C(5), C(6), C(7), O(6), O(7), O(8) $-4.2999X + 6.9379Y + 2.0965Z = 0.5976$ [C(1) –0.02, C(2) 0.06, C(3) 0.01, C(4) –0.04, C(5) –0.06, C(6) –0.03, C(7) 0.05, O(6) –0.23, O(7) 0.13, O(8) 0.13, U –0.53, U^i –0.66]
Plane 6:	C(8), C(9), C(10), C(11), C(12), C(13), C(14), N(1), N(2) $5.7558X + 6.4458Y + 1.0170Z = -2.1151$ [C(8) 0.05, C(9) 0.01, C(10) –0.02, C(11) –0.05, C(12) –0.02, C(13) 0.09, C(14) –0.04, N(1) 0.00, N(2) –0.03, O(8) 0.69]

Angles between planes (°):
2–3 10.4, 2–4 13.2, 3–4 3.5, 1–5 19.0, 1–6 61.2

The angles subtended at the uranium atom in the equatorial plane have values ranging from 50.2 to 68.9°. The uranyl group may be regarded as linear and normal to the equatorial plane.

The largest deviation of any atom in the equatorial plane (plane 1, Table VI) is that of O(7) at a distance of 0.11 Å. The two 4-membered and one 6-membered chelate rings are all planar (planes 2, 3 and 4) and intersect at angles of 10.4, 13.2 and 3.5°. The salicylic acid ligand, however, is not planar (plane 5) as O(8) is significantly out of the plane (0.22 Å). Indeed this is to be expected if the O(6)–O(8) "bite" is suited to chelation.

Two dimethylaminopyridine molecules are associated with the dimer via N(1)–H(1)···O(8) hydrogen bonds (Figure 2). For hydrogen bonding we adopt the criterion $d(H–B) < W_H + W_B - 0.2$ Å [17] where W_H and W_B are the van der Waals radii for hydrogen (1.2 Å) and the acceptor B (O: 1.4 Å). In the present study the N···O and H···O separa-

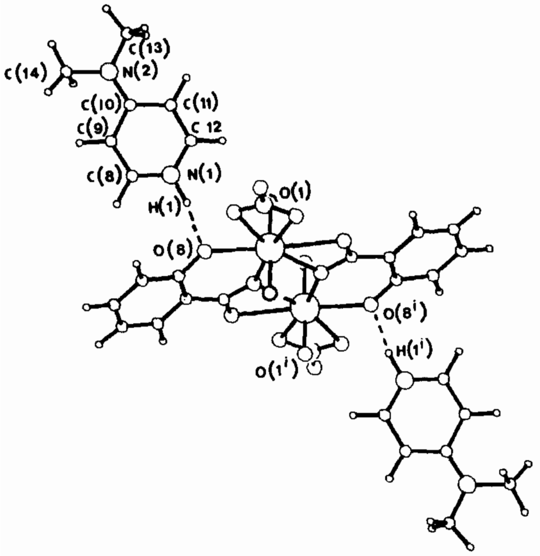

Fig. 2. Hydrogen bonding of the dimethylaminopyridine molecule to the dimer.

tions are 2.819 and 2.018 Å respectively while the N–H···O angle is 146.2°. The hydrogen bond interaction occurs on the O(1) side of the equatorial plane. Approach of the pyridine on the opposite side of this plane is not possible because of the proximity of neighbouring dimers. The pyridine molecule is itself planar (plane 6) and makes an angle of 61.2° with plane 1.

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