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Structure of Bis(ε-caprolactam)dinitratodioxouranium(VI)

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Abstract

The results of the structure determination of the title compound, bis(hexahydro-2*H*-azepin-2-one-*O*)di(nitrato-*O*,*O'*)dioxouranium(VI), revealed that the uranyl ion is coordinated to six O atoms, two of which are from the carbonyl groups of the caprolactams and the other four are from the two nitrate groups. Average U—O distances are 2.531 (7) (nitrate) and 2.360 (5) Å (carbonyl).

Comment

It has been reported that *N*,*N*-dialkylamides are effective reagents for the extraction and separation of actinides (Musikas, 1988). We have found recently that *N*-alkylcaprolactams are even more effective for this purpose. As knowledge of the molecular and crystal structure of the extraction complex is useful for investigating the extraction mechanism of the corresponding extractant, we discuss here the crystal structure of the title complex which has not been reported previously.

The molecular structure consists of a U atom on a centre of symmetry coordinated to eight O atoms. The two O atoms of the uranyl group are perpendicular to the plane of the remaining coordinating O atoms and with them form an approximate hexagonal bipyramid about the U atom. This coordination geometry is typical of uranyl nitrates and is the same as that found in $UO_2(NO_3)_2.6H_2O$ (Hall, Rac & Waters, 1965), $UO_2(NO_3)_2.2[OP(OC_2H_5)_3]$ (Fleming & Lynton, 1960) and $UO_2(NO_3)_2.2C_4H_4O$ (Reynolds, Zalkin & Templeton, 1977).

The U—O(caprolactam) bond distance [2.360 (5) Å] is shorter than 2.442 (7) Å found in $UO_2(NO_3)_2.2C_4H_4O$ (C_4H_4O is tetrahydrofuran). This indicates that the U—O bond is stronger than that in the latter compound. The axial U—O(oxo) distance [1.752 (7) Å] is similar to that (1.75 Å) in $UO_2(NO_3)_2.2C_4H_4O$.

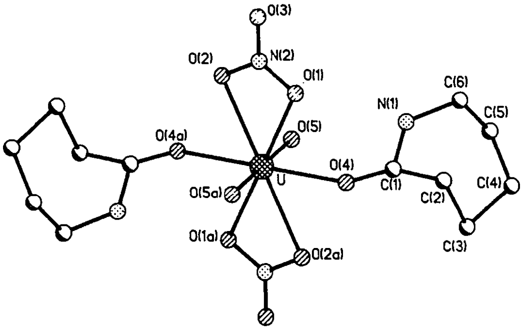

Fig. 1. Molecular configuration of the title complex.

Experimental

Crystal data

$[UO_2(NO_3)_2(C_6H_{11}NO)_2]$
$M_r = 618.3$
Monoclinic
$P2_1/n$
$a = 7.453$ (2) Å
$b = 17.238$ (4) Å
$c = 8.139$ (2) Å
$\beta = 106.40°$
$V = 1003.1$ (4) Å^3
$Z = 2$
$D_x = 2.07$ Mg m^{-3}

Graphite-monochromated Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 4.04$- 12.17°
$\mu = 7.722$ mm^{-1}
$T = 293.0$ (1.5) K
Transparent
0.40 × 0.40 × 0.24 mm
Yellowish

Data collection

Modified *R3m/E* diffractometer
θ-2θ scans
Absorption correction: empirical
$T_{\min} = 0.415$, $T_{\max} = 0.977$
1996 measured reflections
1231 observed reflections [$I > 1.5\sigma(I)$]

$R_{\rm int} = 0.137$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 21$
$l = -10 \rightarrow 10$
2 standard reflections monitored every 9.8 reflections
intensity variation: 0.012%

Refinement

Refinement on F
Final $R = 0.034$
$wR = 0.0288$
$S = 1.171$
1231 reflections
125 parameters
H atoms not located
$w = (\sigma^2F + |10^{-5}F^2|)^{-1} \times \{1-\exp[-5(\lambda/\sin\theta)^2]\}$
$(\Delta/\sigma)_{\max} = -0.171$

$\Delta\rho_{\max} = 1.154$ e Å^{-3}
$\Delta\rho_{\min} = -0.547$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 0.00239
Atomic scattering factors from *SHELXTL* (Sheldrick, 1986)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
U	0.5000	0.0	0.5000	0.039 (1)
N(1)	0.1030 (11)	−0.0944 (6)	0.1453 (10)	0.067 (3)
N(2)	0.1523 (10)	0.0760 (4)	0.5187 (10)	0.051 (3)
O(1)	0.1752 (8)	0.0522 (4)	0.3823 (7)	0.059 (2)
O(2)	0.2862 (9)	0.0671 (4)	0.6525 (7)	0.056 (2)
O(3)	0.0062 (11)	0.1081 (5)	0.5269 (9)	0.073 (3)
O(4)	0.3660 (8)	−0.0248 (4)	0.2057 (7)	0.054 (2)
O(5)	0.4168 (9)	−0.0900 (4)	0.5466 (8)	0.053 (2)
C(1)	0.2481 (12)	−0.0666 (5)	0.1034 (10)	0.048 (3)
C(2)	0.2769 (14)	−0.0866 (6)	−0.0673 (11)	0.058 (3)
C(3)	0.317 (2)	−0.1718 (9)	−0.0862 (16)	0.095 (6)
C(4)	0.132 (3)	−0.2229 (8)	−0.1359 (19)	0.109 (7)
C(5)	0.026 (3)	−0.2227 (8)	0.003 (2)	0.119 (8)
C(6)	−0.0473 (19)	−0.1450 (9)	0.0391 (14)	0.090 (5)

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

The geometry of caprolactam is given in square brackets (Oya & Myasnikova, 1974).

U—O(1)	2.506 (6)	U—O(2)	2.556 (7)
U—O(4)	2.360 (5)	U—O(5)	1.752 (7)
N(2)—O(1)	1.239 (11)	N(2)—O(2)	1.262 (8)
N(2)—O(3)	1.239 (12)	N(1)—C(6)	1.490 (15) [1.48]
N(1)—C(1)	1.313 (13) [1.23]	O(4)—C(1)	1.253 (10) [1.25]
C(1)—C(2)	1.504 (13) [1.51]	C(2)—C(3)	1.514 (19) [1.52]
C(3)—C(4)	1.59 (2) [1.53]	C(4)—C(5)	1.55 (3) [1.53]
C(5)—C(6)	1.51 (2) [1.50]		
O(1)—U—O(2)	49.9 (2)	O(2)—U—O(4)	115.6 (2)
O(1)—U—O(4)	65.8 (2)	O(2)—U—O(5)	89.3 (3)
O(1)—U—O(5)	92.2 (2)	O(2)—U—O(2*a*)	180.0 (1)
O(1)—U—O(1*a*)	180.0 (1)	O(4)—U—O(5)	89.1 (2)
O(4)—U—O(4*a*)	180.0 (1)	O(5)—U—O(5*a*)	180.0 (1)
O(1)—N—O(3)	122.7 (7)	O(1)—N(2)—O(2)	117.2 (8)
U—O(1)—N(2)	98.0 (4)	O(2)—N(2)—O(3)	120.0 (8)
U—O(4)—C(1)	142.7 (6)	U—O(2)—N(2)	94.9 (5)
C(1)—N(1)—C(6)	127.1 (9) [125.0]	O(4)—C(1)—C(2)	119.3 (9)
N(1)—C(1)—C(2)	119.9 (9) [119.5]	N(1)—C(1)—O(4)	120.7 (8) [121.0]
C(1)—C(2)—C(3)	113.6 (9) [112.5]	C(2)—C(3)—C(4)	112.3 (12) [114]
C(3)—C(4)—C(5)	113.3 (12) [114.5]	C(4)—C(5)—C(6)	115.5 (13) [114.5]
N(1)—C(6)—C(5)	112.3 (12) [114]		

An HNO_3 solution (3 *M*) of $UO_2(NO_3)_2$ was extracted by caprolactam dissolved in petroleum ether (b.p. 333-363 K) at room temperature until the organic phase was saturated by the compound. The yellowish precipitate formed was washed with deionized water and petroleum ether successively. A crystal suitable for X-ray diffraction studies was obtained by recrystallization from toluene solution. Seven reflections with $I \geq 15000$ in the range $10 < \theta < 45°$ were selected to collect azimuthal (ψ scan) data. The increment in the azimuthal angle ψ was 10° each time so that 36 data were collected for each reflection and the total 252 data were used to model and define the pseudo ellipsoid which was then used to calculate the absorption corrections; maximum $(\sin\theta/\lambda) = 0.596$ Å^{-1}. The crystal structure was solved by the heavy-atom method and developed from electron-density syntheses. The coordinates of non-H atoms and isotropic thermal vibration parameters were then refined by least squares. Anisotropic thermal vibration parameters were then introduced. All the above calculations were performed on an Eclipse/S140 computer using the *SHELXTL* program (Sheldrick, 1986). The least-squares method used was the block-diagonal matrix approximation.

Lists of structure factors and anisotropic thermal parameter have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71305 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1002]

References

Fleming, J. E. & Lynton, H. (1960). *Chem. Ind.* (*London*), pp. 1415-1416.

Hall, D., Rac, A. D. & Waters, T. N. (1965). *Acta Cryst.* **24**, 389-391.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664-665.

Musikas, C. (1988). *Sep. Sci. Technol.* **22**, 1211-1218.

Oya, Kh. P. & Myasnikova, P. M. (1974). *Zh. Strukt. Khim.* **15**, 680-685.

Reynolds, J. G., Zalkin, A. & Templeton, D. H. (1977). *Inorg. Chem.* **16**, 3357-3359.

Sheldrick, G. M. (1985). *SHELXTL User's Manual.* Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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Structure of Dibenzylchlorotin(IV) Thiooxinate

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Abstract

The structure of dibenzylchloro(8-quinolinethiolato-*N,S*)tin(IV) consists of monomeric trigonal bipyramidal chelate molecules. The two benzyl C atoms and the thiooxinate S atom occupy equatorial sites; the N atom of the bidentate thiooxinate group [Sn—N 2.367 (4) Å] and the Cl atom [Sn—Cl 2.475 (2) Å] are axial. The strong Sn—N bond causes deformation of the coordination polyhedron and is a consequence of electronic effects of the thiooxinate group and steric effects of the benzyl substituents.

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