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Synthesis and Structure of $[UO_2(C_2O_4)\{CONH_2N(CH_3)_2\}_2]$

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Abstract—The single crystals of $[UO_2(C_2O_4)\{CONH_2N(CH_3)_2\}_2]$ were synthesized and studied by X-ray diffraction. The crystals are monoclinic, $a = 7.461(2)$ Å, $b = 8.828(2)$ Å, $c = 11.756(2)$ Å, $\beta = 107.21(3)°$, space group Pc, $Z = 2$, $R = 2.94\%$. The structure comprises infinite chains $[UO_2(C_2O_4)\{CONH_2N(CH_3)_2\}_2]$ extended along [001] and corresponding to the $AT^{11}M^1_2$ crystallochemical group ($A = UO_2^{2+}$, $T^{11} = C_2O_4^{2-}$, M^1 = N,N–$CONH_2N(CH_3)_2$) of uranyl complexes. The chains are connected into a three-dimensional framework by hydrogen bonds involving the oxygen atoms of oxalate and uranyl ions and the *N,N*-dimethylcarbamide methyl groups.

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Of the known uranyl oxalate complexes with neutral ligands, $UO_2(C_2O_4) \cdot 2N_2H_4 \cdot H_2O$ [1], $UO_2(C_2O_4) \cdot 3L$ (L = H_2O [2], $CO(NH_2)_2$ [3], $HCON(CH_3)_2$ [4]), and $UO_2(C_2O_4) \cdot L$ (L = H_2O [5], $CO(NH_2)_2$ [3], CH_3CONH_2 [3]), only uranyl oxalate trihydrate was structurally studied [2, 6].

This work is devoted to the synthesis and structural study of a new uranyl oxalate complex with *N,N*-dimethylcarbamide (L) as a neutral ligand: $UO_2(C_2O_4)(CONH_2N(CH_3)_2)_2$ (**I**). The yellow crystals of **I** were obtained by slow evaporation of an aqueous solution containing uranyl oxalate and a tenfold excess of *N,N*-dimethylcarbamide at room temperature. A sample for X-ray diffraction analysis was selected from these crystals.

An experimental set of reflection intensities was obtained on an Enraf-Nonius CAD4 diffractometer at room temperature (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by the direct method, all non-hydrogen atoms were located in the difference electron density syntheses and refined on F^2_{hkl} in the anisotropic approximation. The hydrogen atoms were placed in idealized positions and refined in the isotropic approximation in the rigid-body model. All calculations were carried out using SHELXTL software [7].

The atom coordinates and other structural parameters of **I** are deposited with the Cambridge Crystallographic Data Centre (no. 675388).

The crystallographic data and structure refinement details for **I** are summarized in Table 1 and the main geometric characteristics are in Table 2.

The uranium coordination polyhedron is the UO_7 pentagonal bipyramid. The axial positions are occupied by the uranyl oxygen atoms. The UO_2^{2+} group is nearly symmetrical and linear. Of the five oxygen atoms arranged in the equatorial plane, three O atoms belong to two crystallographically equivalent oxalate ions and the other two atoms are parts of the dimethylcarbamide molecules. The volume of the uranium Voronoi–Dirichlet polyhedron (VDP), which is shaped like a pentagonal prism (9.14 Å^3) is consistent with the average value (9.2(3) Å^3) for U(VI) atoms surrounded by oxygen [8]. The oxalate ion is a tridentate chelating-and-bridging ligand (coordination type T^{11}) with respect to uranium, being involved in the formation of a five-membered metal ring. The L molecules are monodentate terminal ligands (M^1 type). The coordination types of the ligands were written down by a known procedure [9]. The oxalate ions are nearly planar (the dihedral angle between the planes through the two carboxyl groups of the anion is 3°). The atoms in the L molecules (without considering hydrogen) also deviate slightly from the corresponding least-mean-squares plane (0.11 and 0.05 Å). The L molecules are in *cis*-positions relative to each other. The main structural unit in the crystal is an infinite chain $[UO_2(C_2O_4)\{CONH_2N(CH_3)_2\}_2]$ (figure) extended along [001] and corresponding to the $AT^{11}M^1_2$ crystallochemical group ($A = UO_2^{2+}$) of uranyl complexes.

The uranium-containing chains are combined into a framework by hydrogen bonds (Table 3), formed with participation of oxalate ions and L molecules. The ura-

Table 1. Crystal data, X-ray experiment details, and structure refinement parameters for I

Parameter	Value
Molecular formula	$C_8H_{16}N_4O_8U$
M	534.28
System	Monoclinic
Space group	*Pc*
Z	2
a, Å	7.4608(15)
b, Å	8.8283(18)
c, Å	11.756(2)
β, deg	107.21(3)
V, Å^3	739.7(3)
ρ(calcd), g/cm^3	2.399
μ, mm^{-1}	11.016
F(000)	496
Crystal size (mm)	0.40 × 0.20 × 0.02
Data collection range for θ, deg	2.86–27.87
Range of reflection indices	$0 \le h \le 9$, $-2 \le k \le 11$, $-15 \le l \le 14$
The number of measured reflections	1918
The number of independent reflections	1894 (R_{int} = 0.0202)
The number of reflections with $I > 2\sigma(I)$	1780
The number of refined parameters	194
GOOF	1.035
R_1 ($I > 2\sigma(I)$)	0.0294
wR_2 (all reflections)	0.0768
Residual electron density (min/max), *e* Å^{-3}	–1.415/2.409

Table 2. Selected geometric parameters of structure **I**

Pentagonal bipyramid UO_7

Bond	*d*, Å	Ω(U–O), %*	Angle	ω, deg
U–O(1)	1.775(8)	21.5	O(1)UO(2)	177.8(4)
U–O(2)	1.760(7)	21.6	O(3)UO(4)	72.9(3)
U–O(3)	2.320(9)	12.4	O(4)UO(5)	64.6(2)
U–O(4)	2.464(7)	10.1	O(5)UO(6)	71.3(3)
U–O(5)	2.394(8)	10.8	O(6)UO(7)	76.0(3)
U–O(6)	2.406(8)	11.3	O(7)UO(3)	75.3(3)
U–O(7)	2.345(8)	12.3		

Oxalate ion

Bond**	*d*, Å	Angle	ω, deg
C(1a)–O(5)	1.271(13)	O(5b)C(1)O(8)	126.6(9)
C(1)–O(8)	1.215(15)	O(5b)C(1)C(2)	112.7(9)
C(1)–C(2)	1.556(12)	O(8)C(1)C(2)	120.7(9)
C(2)–O(4b)	1.245(12)	O(4b)C(2)O(6)	127.6(8)
C(2)–O(6)	1.261(12)	O(4b)C(2)C(1)	116.1(8)
		O(6)C(2)C(1)	116.3(9)

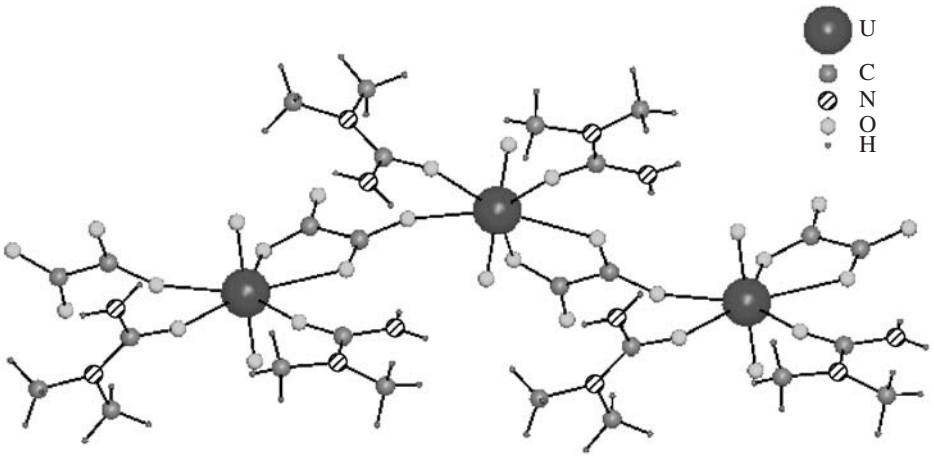
Dimethylcarbamide molecules

Bond	*d*, Å	Angle	ω, deg
C(3)–O(3)	1.236(13)	O(3)C(3)N(1)	122.2(10)
C(3)–N(1)	1.337(14)	O(3)C(3)N(2)	118.4(10)
C(3)–N(2)	1.351(14)	C(3)N(2)C(4)	119.7(10)
N(2)–C(4)	1.463(18)	C(3)N(2)C(5)	123.6(12)
N(2)–C(5)	1.450(18)	C(4)N(2)C(5)	116.7(13)
C(6)–O(7)	1.264(13)	O(7)C(6)N(3)	120.6(9)
C(6)–N(3)	1.335(14)	O(7)C(6)N(4)	119.2(10)
C(6)–N(4)	1.348(14)	C(6)N(4)C(7)	120.2(11)
N(4)–C(7)	1.459(17)	C(6)N(4)C(8)	123.3(11)
N(4)–C(8)	1.457(17)	C(7)N(4)C(8)	115.9(12)

Notes: * Ω is the solid angle (in percent of the total solid angle equal to 4π steradian) under which common faces of the Voronoi–Dirichlet polyhedra of neighboring atoms are seen from any of their nuclei.

** The atom coordinates were derived from the basis set by the symmetrical transformation:(a) x, $-y + 2$, $z + 1/2$; (b) x, $-y + 2$, $z - 1/2$.

nium-uncoordinated O(8) atom of the oxalate ligand is connected by hydrogen bonds to H(14) and H(16) atoms of the amino groups of two L molecules of a neighboring uranium chain. Another oxalate oxygen O(4), which is a part of uranium coordination sphere, forms an intrachain H-bond with the H(13) atom of L; this closes a six-membered metal ring. The uranyl O(1) atom forms two intrachain H-bonds (with amino-group H(13) and methyl H(12)). The U=O(1) distance is increased to 1.775 Å compared to U=O(2) (1.760 Å).



Structure of the uranium-containing chain $[UO_2(C_2O_4)\{CONH_2N(CH_3)_2\}_2]$

According to a known classification [10], the H-bonds in **I** are medium-strength bonds.

The coordination type T^{11} of oxalate ions is found rather frequently in crystal structures. However, among U(VI) compounds, only one uranyl complex, $(NH_4)_2[UO_2(C_2O_4)_2]$ (**II**) [12], in which the oxalate group is coordinated to uranium in this way is known apart from **I**. The structure of **II** composed of $[UO_2(C_2O_4)_2]^{2-}$ chains comprises two crystallographically different oxalate ions with T^{11} and B^{01} types of coordination. The U–U distances in the chains of **I** and **II** are similar, being equal to 6.22 and 6.31 Å. The dihedral angle in the oxalate ion with T^{11} coordination is 3° and 16° for **I** and **II**, respectively, and the planes of the oxalate ions coordinated by the same U(VI) are arranged at 75° and 0° angles with respect to each other. In the chains of structure **II**, neighboring uranyl groups are parallel, while in structure **I**, they are rotated with respect to each other by 51°. As regards these parameters, structure **I** resembles more closely the chain complex group in the crystals of $[UO_2(C_2O_4)(H_2O)] \cdot 2H_2O$ (**III**) [6] in which the U–U distance is 6.27 Å and the oxalate ions are planar. Presumably, the structural units in **I** are formed upon replacement of water in the uranium coordination sphere in **III** by a dimethylcarbamide molecule. The second molecule of neutral organic ligand L displaces the oxalate oxygen atom from this sphere and, hence, the oxalate changes the type of coordination from K^{02} in **III** to T^{11} in **I**.

Table 3. Geometric parameters of hydrogen bonds and shortened contacts (H···O < 3 Å) in the structure of complex **I***

D–H···O**	Distance, Å			DHO angle, deg	Ω, %	
	D–H	H···O	D···O		D–H	H···O
N(1)–H(13)···O(4)	0.86	2.27	2.99(1)	141	33.1	18.3
N(1)–H(13)···O(1a)	0.86	2.40	3.00(1)	126	33.1	15.1
N(1)–H(14)···O(8Ò)	0.86	2.17	2.91(1)	145	33.4	16.0
N(3)–H(15)···O(5d)	0.86	2.36	3.18(1)	160	33.6	17.2
N(3)–H(16)···O(8b)	0.86	2.21	3.03(1)	161	33.6	17.2
C(5)–H(5)···O(2)	0.96	2.90	3.64(2)	134	26.7	12.3
C(7)–H(7)···O(6)	0.96	2.71	3.47(1)	137	26.8	10.0
C(7)–H(8)···O(2)	0.96	2.59	3.54(2)	171	26.8	11.7
C(8)–H(12)···O(1)	0.96	2.30	3.19(1)	153	26.7	17.4

Notes: * All contacts with r(H···O) < 3 Å and Ω(H···O) ≥ 10% were taken into account.

** The atom coordinates were derived from the basis set by the symmetrical transformations. For (*a*) and (*b*), see Table 2; (*c*) $x + 1, y, z + 1$; (d) $x + 1, y, z$.

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