## COORDINATION COMPOUNDS

# **Conformation of Diethylglyoxime in Uranyl Complexes**

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**Abstract**—New complexes of uranyl with diethylglyoxime have been synthesized and studied. A feature of these complexes is the tetradentate bridging coordination of the ligand in both *cis*- and *trans*-conformations. The structure of organic ligand  $C_6H_{12}N_2O_2$  and binuclear complex  $(CN_3H_6)_4[(UO_2)_2(C_6H_{10}N_2O_2)(CO_3)(C_2O_4)_2] \cdot H_2O$  have been determined by X-ray diffraction.

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It is known that the molecule of  $\alpha$ -dioxime in the *anti*-isomer form can exist in two flat conformations depending on the position of oxime groups relative to the C–C bond, namely *cis* and *trans*:



In the crystal structures of  $\alpha$ -dioximes having noncyclic aliphatic substituents, molecules have the *trans*conformation [1, 2], whereas  $\alpha$ -dioximes in *d*-transition metal complexes are coordinated only in the *cis*conformation [3].

Previously, we have shown that the feature of uranyl complexes with  $\alpha$ -dioximes is that the ligand is coordinated both in the *cis*- and in *trans*-conformations [4]:



trans-conformation

cis-conformation

Continuing this topic, we studied new complexes of uranyl with diethylglyoxime.

#### EXPERIMENTAL

3,4-Hexanedione (Acros Organics) and guanidinium carbonate (Fluka) were used in the study. The other reagents were chemically pure or pure for analysis.

**Diethylglyoxime (I)** was prepared from 3,4-hexanedione by a procedure slightly modified from that reported in [5]. 3,4-Hexanedione (6.3 g), hydroxylamine hydrochloride (12.0 g), and NaOH (22.0 g) were placed into a round-bottomed flask. Dilute ethanol (25 mL, 1:0.25) was added, and the resulting mixture was heated for 30 min with a refluxer. The molar ratio 3,4-hexanedione :  $NH_2OH \cdot HCl$  : NaOH = 1 : ~3 : ~10. After cooling, 1.5 M HCl (250 mL) was added to the mixture. The white precipitate was filtered and recrystallized from water—ethanol (1 : 1) solution. The resulting colorless crystals were dried on the filter in an air flow and then in a vacuum desiccator. Yield, 5.6 g (70%); mp 85–186°C.

IR (KBr, cm<sup>-1</sup>): 3280, 3220 v(OH); 1629 v(C=N); 965, 884 v(NO).

**Uranyl diaquadiethylglyoximate dihydrate (II).** A solution of 2.0 g of complex I in 40 mL of ethanol was added to a suspension of uranium trioxide (2 g in 20 mL of water). The reaction mixture was stirred for 12 h at

40°C (the molar ratio U :  $C_6H_{12}N_2O_2$  was 1 : 2). The resulting yellow precipitate was filtered off, washed with water and several times with alcohol and ether, and dried on the filter in the air flow. Yield, 2.7 g (80%).

For  $[UO_2(C_6H_{10}N_2O_2)(H_2O)_2] \cdot 2H_2O$  anal. calcd. (%):  $UO_2$ , 55.76; N, 5.78; C, 14.88.

Found (%): UO<sub>2</sub>, 55.26, 55.38; N, 5.25, 5.46; C, 14.37, 14.29.

**Uranyl bis(dimethylsulfoxide)diethylglyoximate (III).** A suspension of complex **II** (1 g) in DMSO (10 mL) was stirred under heating for 6 h. The precipitate of dark yellow color was filtered off, washed with water, and dried on the filter in an air flow. Yield, 0.85 g (72%).

For  $[UO_2(C_6H_{10}N_2O_2)(H_2O)_2] \cdot 2H_2O$  anal. calcd. (%): UO<sub>2</sub>, 47.50; N, 4.93; C, 21.13.

Found (%): UO<sub>2</sub>, 47.18, 47.21; N, 5.08, 5.16; C, 20.87, 20.79.

Guanidinium dioxalato- $\mu$ -diethylglyoximato- $\mu$ -carbonatodiuranilate monohydrate (IV). Uranyl nitrate hexahydrate (2 g) and guanidinium oxalate (1 g) were stirred on heating in 40 mL of water. Complex I (0.3 g) in ethanol (20 mL) was added to the resulting light yellow hot suspension, and solid guanidinium carbonate (0.72 g) was added slowly (with stirring and heating) until the precipitate completely dissolved (molar ratio

U :  $C_2O_4^{2-}$ :  $C_6H_{12}N_2O_2$  :  $CO_3^{2-} = 1 : 1.2 : 1 : 1.0$ ). The resulting red solution was filtered off and allowed to crystallize in air. After 2–3 h, orange platelike crystals were filtered and dried on the filter in an air flow. Yield, 1.8 g (76%).

For  $(CN_3H_6)_4[(UO_2)_2(C_6H_{10}N_2O_2)(CO_3)(C_2O_4)_2] \cdot H_2O$  anal. calcd. (%): UO<sub>2</sub>, 45.90; N, 16.67; C, 15.31.

Found (%): UO<sub>2</sub>, 45.89, 46.01; N, 16.89, 16.27; C, 16.10, 16.05.

Guanidinium ethylenediammonium dioxalato- $\mu$ diethylglyoximato- $\mu$ -carbonatodiuranylate trihydrate (V). Uranyl nitrate hexahydrate (2 g) and ethylenediammonium oxalate (0.72 g) were stirred with heating in 60 mL of water. Complex I (0.3 g) in ethanol (20 mL) was added to the light yellow hot suspension, and solid guanidinium carbonate (0.72 g) was added slowly (with stirring and heating) until the precipitate com-

pletely dissolved (molar ratio  $U : C_2O_4^{2-}: C_6H_{12}N_2O_2:$ 

 $CO_3^{2-} = 1 : 1.2 : 1 : 1.0$ ). The resulting red solution was filtered off and allowed to crystallize in air. After 2–3 h, the orange plate-like crystals were filtered off and dried on the filter in an air flow. Yield, 1.6 g (69%).

For

 $(CN_3H_6)_2(C_2H_{10}N_2)[(UO_2)_2(C_6H_{10}N_2O_2)(CO_3)(C_2O_4)_2] \cdot 3H_2O$  anal. calcd. (%): UO<sub>2</sub>, 46.78; N, 12.13; C, 15.60.

Found (%): UO<sub>2</sub>, 46.30, 46.30; N, 12.54, 12.67; C, 16.23, 16.19.

**Elemental analysis** for carbon, hydrogen, and nitrogen was carried out on a Carlo Erba CHN analyzer at the Shared Facility Center of the Kurnakov Institute.

**IR spectra** of the samples were recorded on a Lumex Infralum FT-02 Fourier-transform spectro-photometer in the range of  $4000-400 \text{ cm}^{-1}$  at a resolution of 1 cm<sup>-1</sup>. Samples were prepared as Nujol (Aldrich) mulls.

**X-ray diffraction.** The sets of diffraction reflections for the structure of I were collected on an Enraf-Nonius CAD4 four-circle automatic diffractometer at ambient temperature (Cu $K_{\alpha}$  radiation,  $\lambda = 1.54178$  Å, graphite monochromator); those for complex IV were collected on a SMART APEX II automatic diffractometer at 150 K (Mo $K_{\alpha}$ -radiation,  $\lambda = 0.71073$  Å, graphite monochromator) at the Shared Facility Center of the Kurnakov Institute. The data were corrected for absorption based on equivalent reflections.

The structures were solved by direct methods and refined by the full-matrix least-squares method for all non-hydrogen atoms in the anisotropic approximation. All hydrogen atoms in both structures, except of H(1) in I as well as H(1) and H(2) in IV, were calculated geometrically and refined within the riding model. The hydroxyl hydrogen atom in I and hydrogen atoms of the water molecule in IV were located from difference electron density syntheses and refined using the least-squares method in the isotropic approximation. The structures were solved using the SHELXS and SHELXL software [6].

Selected crystal data, details of data collection, and characteristics of structure refinement for complexes I and IV are listed in Table 1, bond lengths and bond angles are presented in Table 2, and parameters of hydrogen bonds are shown in Table 3. The crystallographic data were deposited with the Cambridge Structural Database, CCDC nos. 1485431 (I) and 1485432 (IV).

#### **RESULTS AND DISCUSSION**

Centrosymmetric diethylglyoxime molecules in the structure of I are in the *trans*-conformation. The interatomic distances and angles (Table 2) in I almost coincide with those in the structures of dimethylglyox-ime [1] and methylethylglioxime [2].

In the structure of I, diethylglyoxime molecules are joined by  $O-H\cdots N$  intermolecular hydrogen bonds (2.80 Å) to form a chain along the *a* axis (Fig. 1).

Similar fragments with hydrogen bonds are typical of other non-alicyclic  $\alpha$ -dioximes [1, 2]; therefore we can assume that the presence of double hydrogen bonds O–H···N is crucial for the flat *trans*-conformation of molecules of these compounds.

The main fragment of molecule **I**, with the exception of methyl groups and hydrogen atoms, is planar (Fig. 2). Methyl groups are in *trans*-position relative to

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Table 1. Selected crystallographic data, details of experiment	t, and refinement factors for compounds I and IV
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Compound	I	IV		
Formula	$C_6H_{12}N_2O_2$	$C_{15}H_{36}N_{14}O_{18}U_2$		
FW	144.17	1176.59		
Crystal size, mm	$0.25\times0.08\times0.01$	$0.40\times0.20\times0.15$		
Crystal system	Orthorhombic	Monoclinic		
Space group	Pbca	$P2_{1}/n$		
Т, К	293(2)	150(2)		
$a, \text{\AA}$ $b, \text{\AA}$ $c, \text{\AA}$ $\beta, \text{deg}$ $V, \text{\AA}^3$	6.393(2) 7.773(3) 15.678(5) 90 779.0(5)	7.6140(3) 15.4388(6) 28.0097(11) 95.99(1) 3274.6(2)		
Ζ	4	4		
$\rho_{calc}$ , g/cm <sup>3</sup>	1.298	2.387		
$\mu$ , mm <sup>-1</sup>	0.774	9.974		
<i>F</i> (000)	344	2208		
$\theta$ range, deg	5.64-64.26	2.56-27.00		
Ranges of indexes	$-7 \le h \le 3$ $-9 \le k \le 9$ $-18 \le l \le 18$	$-9 \le h \le 9$ $-19 \le k \le 19$ $-35 \le l \le 35$		
Number of reflections				
Measured	3116	27292		
Unique ( $N$ ) [ $R_{int}$ ]	649 ( $R_{\rm int} = 0.054$ )	7122 ( $R_{\rm int} = 0.029$ )		
observed $(I \ge 2\sigma(I)) (N_o)$	446	6790		
Number of parameters to be refined	51	451		
GOOF	0.993	1.089		
$R_1, wR_2$ for $N_0$ $R_1, wR_2$ for $N$	$R_1 = 0.043$ $wR_2 = 0.1405$	$R_1 = 0.0213$ $wR_2 = 0.0460$		
$\Delta\rho_{min}/\Delta\rho_{max},e/\AA^3$	-0.119/0.184	-0.865/1.198		

I					
Bond	d, Å		d, Å		
C(1)–C(1A)*	1.477(4)	C(1)–C(2)	1.494(3)		
C(1)–N(1)	1.291(2)	C(2)–C(3)	1.507(4)		
Angle	ω, deg	Angle	ω, deg		
C(1)C(1A)N(1)	114.1(2)	C(1)N(1)O(1)	112.41(16)		
C(1)C(1A)C(2)	122.1(2)				
C(1)C(2)C(3)	111.6(2)				
	I	V	I		
Bond	d, Å	Bond	d, Å		
U(1)–O(1)	1.791(2)	U(2)–O(5)	1.792(3)		
U(1)–O(2)	1.804(2)	U(2)–O(4)	1.799(3)		
U(1)–O(3)	2.312(2)	U(2)–O(6)	2.305(2)		
U(1)–O(7)	2.415(2)	U(2)–O(7)	2.402(2)		
U(1)–O(13)	2.422(2)	U(2)–O(16)	2.415(2)		
U(1)–O(14)	2.425(3)	U(2)–O(15)	2.419(2)		
U(1)–N(1)	2.430(3)	U(2)–N(2)	2.424(3)		
U(1)–O(8)	2.510(2)	U(2)–O(9)	2.514(2)		
N(1)–C(7)	1.293(4)	C(1)–C(2)	1.541(5)		
N(1)–O(3)	1.370(3)	C(2)–O(12)	1.239(4)		
N(2)–C(8)	1.286(4)	C(2)–O(14)	1.277(4)		
N(2)–O(6)	1.376(3)	C(3)–O(17)	1.233(4)		
C(20)–O(8)	1.252(4)	C(3)–O(15)	1.260(4)		
C(20)–O(9)	1.274(4)	C(3)–C(4)	1.554(5)		
C(20)–O(7)	1.316(4)	C(4)–O(18)	1.233(5)		
C(1)–O(11)	1.232(4)	C(4)–O(16)	1.274(4)		
C(1)–O(13)	1.276(4)	C(5)–C(6)	1.526(5)		
C(5)–C(6)	1.526(5)	C(8)–C(9)	1.504(5)		
C(7)–C(8)	1.489(5)	C(9)-C(10)	1.529(5)		
Angle	ω, deg	Angle	ω, deg		
O(1)U(1)O(2)	179.69(13)	O(5)U(2)O(4)	178.11(12)		
O(13)U(1)O(14)	64.61(8)	64.61(8) O(16)U(2)O(15)			
O(3)U(1)N(1)	33.48(8)	3) O(6)U(2)N(2) 33.7			
O(7)U(1)O(8)	)O(8) 52.90(8) O(7)U(2)O(9)		52.83(8)		
O(8)C(20)O(9)	127.1(3)	C(7)N(1)O(3)	117.5(3)		
O(8)C(20)O(7)	117.4(3)	C(8)N(2)O(6)	118.2(3)		
O(9)C(20)O(7)	115.4(3)	N(2)C(8)C(7)	120.1(3)		
C(7)C(6)C(5)	112.2(3)	N(2)C(8)C(9)	120.9(3)		
N(1)C(7)C(8)	119.8(3)	C(7)C(8)C(9)	118.9(3)		
N(1)C(7)C(6)	120.1(3)	C(8)C(9)C(10)	113.4(3)		
C(8)C(7)C(6)	120.0(3)				

**Table 2.** Selected bond lengths (*d*) and bond angles ( $\omega$ ) in the structures of I and IV

\* Symmetry transformations used to generate equivalent atoms: -x, -y, -z.

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D-H···A	Position of atom A	<i>d</i> (D–H), Å	<i>d</i> (H⋯A), Å	<i>d</i> (D···A), Å	Angle (DHA), deg	
I						
O(1)-H(1)····N(1)	-x, -y, -z	0.94(4)	1.91(4)	2.800(2)	158(3)	
IV						
N(12)-H(12A)····O(11)	<i>x</i> , <i>y</i> , <i>z</i>	0.88	2.00	2.848(4)	163	
N(13)-H(13A)···O(12)	<i>x</i> , <i>y</i> , <i>z</i>	0.88	2.07	2.928(4)	166	
N(21)-H(21A)····O(13)	<i>x</i> , <i>y</i> , <i>z</i>	0.88	2.20	3.018(4)	155	
N(23)-H(23A)···O(11)	<i>x</i> , <i>y</i> , <i>z</i>	0.88	1.99	2.864(4)	173	
N(32)-H(32B)····O(15)	<i>x</i> , <i>y</i> , <i>z</i>	0.88	2.15	2.955(4)	151	
N(33)-H(33A)····O(9)	<i>x</i> , <i>y</i> , <i>z</i>	0.88	1.97	2.833(4)	165	
O(20)-H(1)···O(14)	<i>x</i> , <i>y</i> , <i>z</i>	0.87(6)	1.94(6)	2.768(4)	157(5)	
O(20)-H(2)···O(17)	1/2 + x, $1.5 - y$ , $1/2 + z$	0.82(6)	2.01(6)	2.774(4)	157(6)	
N(11)-H(11B)…O(6)	-1/2 + x, $1.5 - y$ , $1/2 + z$	0.88	2.07	2.942(4)	170	
N(13)-H(13B)···O(16)	-1/2 + x, $1.5 - y$ , $1/2 + z$	0.88	2.32	3.000(4)	134	
N(22)-H(22B)····O(2)	1/2 - x, $-1/2 + y$ , $1/2 - z$	0.88	2.39	3.034(4)	130	
N(31)-H(31B)···O(2)	1/2 - x, $-1/2 + y$ , $1/2 - z$	0.88	2.23	3.048(4)	154	
N(33)-H(33B)····O(3)	1/2 - x, $-1/2 + y$ , $1/2 - z$	0.88	2.21	2.887(4)	134	
N(31)-H(31A)···O(18)	1 - x, 1 - y, -z	0.88	2.02	2.888(4)	168	
N(32)-H(32A)····O(17)	1 - x, 1 - y, -z	0.88	1.99	2.864(4)	174	
N(43)-H(43B)····O(5)	1 + x, y, z	0.88	2.06	2.930(4)	169	
N(41)-H(41B)…O(17)	1 - x, 1 - y, -z	0.88	2.15	3.006(4)	166	
N(43)-H(43A)····O(12)	1/2 + x, $1.5 - y$ , $-1/2 + z$	0.88	2.03	2.869(4)	159	
N(42)-H(42A)····O(20)	1.5 - x, -1/2 + y, 1/2 - z	0.88	2.09	2.871(5)	147	
N(41)-H(41A)···O(20)	1/2 + x, $1.5 - y$ , $-1/2 + z$	0.88	2.46	2.972(5)	118	

Table 3. Parameters of hydrogen bonds in compounds  ${\bf I}$  and  ${\bf IV}$ 

**Table 4.** Selected absorption bands  $(cm^{-1})$  in IR spectra of compounds I–V

Compound	ν(U=O)	ν(C=N)	ν(NO)	ν(OH)	v(C=O)	v(CO)CO <sub>3</sub>	v(S=O)
I	_	1629	965 884	3280 3220	_	_	_
II	905	1625	965 884	3275 3205	_	-	_
III	905	1669	956 876	_	_	_	998
IV	892	1697	867	~3350	1654 1578	1509	_
V	895	1693	865	~3350	1660	1548	—

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Fig. 1. Fragment of the chain structure of  $C_6H_{12}N_2O_2$  (I). Hydrogen atoms are shown with dashed lines.



Fig. 2. Flat fragment of the structure of diethylglyoxime molecule in the structure of I.

the plane of the main fragment and are out of the plane by 1.40 Å.

The reaction of  $\alpha$ -dioximes with uranyl compounds results in their deprotonation. Synthesis conditions and the compositions of the resulting complexes have a pronounced effect on the conformation of  $\alpha$ -dioximes.

The polynuclear structure with the *trans*-bridged position of dioximate ligands can be assumed for complexes II and III (U : L = 1: 1) (Fig. 3). This is confirmed by the presence of bands of stretching vibrations v(C=N) in the 1625–1670 cm<sup>-1</sup> region and two bands of stretching vibrations v(NO) at 880–884 cm<sup>-1</sup> and 956–965 cm<sup>-1</sup> in the IR spectra of complexes I–III (Table 4).

Under the action of dimethylsulfoxide, only coordinated water molecules in complex **II** are substituted to form  $[UO_2(C_6H_{10}N_2O_2)\{(CH_3)_2SO\}_2]$  (III), which retains polynuclear structure with the bridged *trans*-coordination of the diethylglyoximate ligand.

The presence of the carbonate group in complex IV (U: L = 1: 0.5) favors the bridged *cis*-coordination of diethylglyoxime.



Fig. 3. Structural scheme of complexes II and III (L =  $H_2O$  and DMSO).

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Fig. 4. Asymmetric unit of the structure of IV.

The main structural units of crystal **IV** are guanidinium cations, a hydrated water molecule, and complex anion  $[(UO_2)_2(C_6H_{10}N_2O_2)(CO_3)(C_2O_4)_2]^{4-}$ (Fig. 4).

In the binuclear complex anion, the composition of the equatorial plane of uranium atoms is (50 + N)and for each uranyl group it is supplemented with oxygen atoms of the bridging carbonate group, two oxygen atoms of the bidentate chelate oxalate group, and nitrogen and oxygen atoms of the cis-tetradentate bridged diethylglyoxime ligand. The U(1)-U(2) distance in the binuclear fragment of IV is 4.7506(2) Å (the U(1)O(7)U(2) angle is  $160.87(13)^{\circ}$ ) and is comparable with the U–U distances in structurally similar complexes with methylglyoxime (4.834 Å) [7], methylethylglyoxime (4.784 Å) [8], and methyl derivatives of alicyclic dioximes (4.847 and 4.735 Å) [9]. The diethylglyoximate group is in the planar *cis*-conformation. The plane of the main fragment consists of six atoms (O(3), N(1), C(7), O(6), N(2), and C(8)) in contrast to the plane of the main fragment of the free ligand, which consists of eight atoms. Methylene carbon atoms C(6) and C(9) are out of the plane (by -0.19and 0.37 Å, respectively) as well as the atoms C(5) and C(10) (1.1 and -0.86 Å, respectively) of methyl groups (Fig. 5).

In the structure of **IV**, the O(8)C(20)O(9) bond angle in the bridging carbonate group is  $127.1(3)^{\circ}$  and two other angles O(9)C(20)O(7) and O(8)C(20)O(7) are substantially less and equal to  $115.4(3)^{\circ}$  and 117.4(3)°, respectively. This repeats completely the distribution pattern of bond angles in the carbonate group in all previously studied structures of uranyl complexes with carbonate bridging ligands [7–11]. Guanidinium cations and water molecules in the structure of **IV** are involved in the extensive system of intramolecular and intermolecular hydrogen bonds consisting of oxygen uranyl groups (Table 3).

In view of the virtual coincidence of the IR spectra of IV and V (Table 4), their anionic complexes can be assumed to be structural analogues with the *cis*-conformation of the diethylglyoximate bridging ligand.



Fig. 5. Flat structure fragment of the diethylglyoxime group in the structure of IV.

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