ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 2, pp. 214–218. © Pleiades Publishing, Ltd., 2013.
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Coordination Polymer of Uranyl Nitrate with 4,4,10,10-Tetramethyl-1,3,7,9-Tetraazaspiro[5.5]undecane-2,8-dione (Spirocarbone, Sk): Synthesis and Study of Molecular and Crystal Structures

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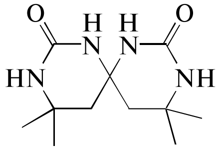
Received April 10, 2012

Abstract—The coordination polymer $\{[UO_2(NO_3)_2(C_{11}H_{20}N_4O_2)] \cdot 2H_2O\}_n$ (**I**) was obtained and examined by X-ray diffraction. The crystals are monoclinic, space group $C2/c$; $a = 23.1386(13)$, $b = 5.41575(15)$, $c = 19.7769(11)$ Å, $\beta = 125.285(8)°$, $V = 2023.01(17)$ Å^3, $\rho_{calcd} = 2.20$ g/cm^3, $Z = 4$. The U atom occupies a special position in the center of inversion. Its coordination polyhedron is a distorted hexagonal bipyramid with axial oxo ligands. In the equatorial plane, the U(1) atom is coordinated by four O atoms of two bidentate nitrate anions and two O atoms of two carbonyl groups of organic spirocarbone (Sk) molecules, which are related by the symmetry operation $(0.5 - x, 0.5 - y, -z)$. In the crystal, polymer chains are parallel to the direction (101). Water molecules are hydrogen-bonded to the N(1) atom of ligand Sk; in addition, they are linked together by the intermolecular hydrogen bonds O(6)–H(6d)···O(6)^i ($^i1/2 - x, -1/2 + y, 1/2 - z$); H···O 2.11 Å angle O–H···O 160°) and to the nitrate anions by the hydrogen bonds O(6)–H(6e)···O(3)^i; H···O 2.29 Å; the angle O–H···O 149°). In the crystal, hydrogen-bonded water molecules form chains along the axis y that are perpendicular to the coordination polymers. To verify the purity of complex **I**, the Rietveld refinement of its X-ray powder diffraction pattern was performed. At room temperature, the unit cell parameters are $a = 23.2965(6)$, $b = 5.51225(15)$, $c = 19.8588(6)$ Å, $\beta = 125.6063(17)°$, $V = 2073.40(10)$ Å^3.

DOI: 10.1134/S1070328413010065

Coordination compounds with cyclic spirobisurea ligands remain poorly studied. One of such ligands is 4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione or spirocarbone (Sk):



This ligand, as a precursor of urea, possesses a number of valuable biological properties: low toxicity (LD_{50} = 3000 mg/kg of white mice weight) [1], membranotropic properties [2], and the ability of penetrate into and accumulate in the cytoplasm of the mouse and human leukemia cell lines L1210 and CEM-T4, respectively [3]. This ligand also favors an increase in the protein content, and a reduction in the starch content, of oats corn [4]. In [5], spirocarbone has been proved to efficiently stimulate callus formation in Forsythia europaea and root formation in Philadelphus coronarius. In addition, spirocarbone is an efficient growth and development stimulator in sheep breeding [6]. That is why the synthesis and study of complexes of this ligand as a hard Lewis acid will help to gain greater insight into the chemism of interactions of Sk with metal ions in high oxidation states and allow one to determine the ligand denticity in nonaqueous media.

The goal of this study was to obtain and structurally characterize a complex of uranyl nitrate (hard Lewis acid) with spirocarbone and water molecules, $\{[UO_2(NO_3)_2(C_{11}H_{20}N_4O_2)] \cdot 2H_2O\}_n$ (**I**).

EXPERIMENTAL

Synthesis. The starting materials were $UO_2(NO_3)_2 \cdot 6H_2O$ (reagent grade) and spirocarbone prepared as described in [7]. Acetone (special purity grade) was used as a solvent. Uranyl nitrate (1.6 g, 3.18 mmol) was dissolved in acetone (15 mL). Then spirocarbone (1.3 g, 5 mmol) was added and the reaction mixture was stirred with a magnetic stirring bar for 5–10 min. The resulting solution was filtered and kept for several hours until 1/3 of the solvent evaporated and crystals began to form. The lemon green crystals were filtered off, washed with acetone, and dried in air. The yield of complex **I** was ~77% (with respect to the ligand).

For $\{[UO_2(NO_3)_2(C_{11}H_{20}N_4O_2)] \cdot 2H_2O\}_n$

anal. calcd. (%):	C, 19.71;	H, 3.61;	N, 12.54;	O, 28.64.
Found (%):	C, 19.83;	H, 3.91;	N, 12.59;	O, 28.33.

Elemental analysis was carried out on an EA-3000 analyzer (EuroVector, Italy). The IR spectra of the starting reagents and polymer **I** were recorded on a Specord-75IR spectrophotometer (Nujol) in the 400–4000 cm^{-1} range.

X-ray diffraction study. Experimental reflection intensities for crystals of complex **I** were collected on an Xcalibur 3 automated four-circle diffractometer. The structure was solved by direct methods with the SHELX-97 program package [8]. The hydrogen atoms were located geometrically and refined using a riding model with $U_{iso} = nU_{equiv}$ of the associated non-hydrogen atom ($n = 1.5$ for water and methyl groups and $n = 1.2$ for other H atoms). The structure was refined on F^2 by the full-matrix least-squares method in the anisotropic approximation for the non-hydrogen atoms.

Selected crystallographic parameters and the data collection and refinement statistics for structure **I** are given in Table 1. Atomic coordinates and other parameters have been deposited with the Cambridge Crystallographic Data Centre (no. 876539; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

X-ray powder diffraction. To verify the purity of polymer **I**, its secondary-beam X-ray powder diffraction pattern (Siemens D500 diffractometer, Cu radiation, graphite monochromator) was refined using the Rietveld method. The single-crystal X-ray diffraction data were employed as an initial model for the FullProf program [9]. To do this, a sample of complex **I** was ground and placed in a glass cell with a working volume of 2 × 1 × 0.1 cm^3 for X-ray powder diffraction experiments.

RESULTS AND DISCUSSION

The IR spectra of complex **I** and spirocarbone are given in Table 2. In the IR spectrum of the complex, the absorption band due to the ν(C=O stretching vibrations of (amide I) is shifted by 30 cm^{-1} to the longer wavelengths because of the coordination of spirocarbone. In addition, the ν_s(N–H) and ν_{as}(N–H) bands are shifted to the shorter wavelengths, which is characteristic of amino groups at coordinated carbonyl [10]. The IR spectrum of complex **I** shows an absorption band ν(O–H) characteristic of water and a set of absorption bands for the coordinated ligand Sk. Note that the spectrum of a free nitrate anion contains a characteristic line at 1800–1700 cm^{-1} [11]. However, this line is absent from the spectrum of the complex, which suggests the chelating bidentate coordination of the nitrate anion to uranyl.

Table 1. Selected crystallographic parameters and the data collection and refinement statistics for structure **I**

Parameter	Value
Empirical formula	$C_{11}H_{24}N_6O_{12}U$
M	670.39
Temperature, K	293(2)
Radiation (λ, Å)	MoK_a (0.71073)
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell parameters	
a, Å	23.1386(13)
b, Å	5.41575(15)
c, Å	19.7769(11)
β, deg	125.285(8)
V, Å^3	2023.01(17)
Z	4
ρ_{calcd}, g/cm^3	2.20
μ(MoK_α), mm^{-1}	8.10
F(000)	1280
Crystal dimensions, mm	0.35 × 0.18 × 0.15
θ scan range, deg	3.52–32.43
$2\theta_{max}$, deg	64.86
Ranges of *h*, *k*, and *l* indices	$-34 \le h \le 34$, $-7 \le k \le 8$, $-29 \le l \le 28$
Number of measured reflections	15017
Number of independent reflections (R_{int})	3395 (0.023)
Number of reflections with $F > 4\sigma(F)$	2781
Number of parameters refined	140
GOOF	1.081
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.017$, $wR_2 = 0.036$
R factors for all reflections	$R_1 = 0.024$, $wR_2 = 0.039$
$\Delta\rho_{max}$, $\Delta\rho_{min}$, *e* Å^{-3}	1.190, –0.994

Complex **I** is the coordination polymer hydrate $\{[UO_2(NO_3)_2(C_{11}H_{20}N_4O_2)] \cdot 2H_2O\}_n$. The U atom occupies a special position in the center of inversion. Its coordination polyhedron is a distorted hexagonal bipyramid with oxo ligands in the apices (Table 3, Fig. 1).

In the equatorial plane, the U(1) atom is coordinated by four O atoms of two bidentate nitrate anions and two O atoms of two carbonyl groups of two organic molecules Sk, which are related by the symmetry operation $(0.5 - x, 0.5 - y, -z)$. In the crystal, polymer chains are parallel to the direction (101). The equatorial O atoms are coplanar (±0.056 Å). Because of the geometrical restrictions imposed by the bidentate coordination of the nitrate anions, the resulting hexagon is irregular (the angles OUO range from

Table 2. IR spectra of complex **I** and Sk

Assignment	Sk	**I**
	ν, cm^{-1}	
ν_s(H–O–H), ν_{as}(H–O–H)	3480	3550
ν_s(N–H), ν_{as}(N–H)	3320, 3280, 3180 3050	3390, 3250, 3200
ν(C=O, amide I)	1640	1610
ν(C–N) + $\delta(CH_3)$	1450, 1345	1490, 1450, 1375
ν_{as}(C–O) + δ(CH)	1250,1210, 1120	1260, 1200, 1100
ν_γ (ring atom vibrations), $\gamma(CH_2)$ and δ(=CH)	1090, 1010, 820, 770, 750, 620	1040, 1010, 940, 760, 730
δ (amide III) + π(C=O, deviation from the ring plane)	590	580
δ_γ (ring atom vibrations)	490	

Table 3. Bond lengths Å and bond angles (deg) in structure **I***

Bond	d, Å	Angle	ω, deg	Angle	ω, deg
U(1)O(2)	1.7649(15)	O(2)U(1)O(1)	90.39(6)	O(1)C(1)N(1)	120.13(18)
U(1)O(1)	2.3502(15)	O(2)U(1)O(4)	94.30(6)	O(1)C(1)N(2)	119.62(18)
U(1)O(4)	2.5393(15)	O(1)U(1)O(4)	114.86(5)	N(1)C(1)N(2)	120.24(18)
U(1)O(3)	2.5547(16)	O(2)U(1)O(3)	89.93(6)	N(2)C(2)N(2)^{i}	111.0(2)
U(1)N(3)	2.9924(18)	O(1)U(1)O(3)	65.29(5)	N(2)C(2)C(3)^{i}	110.91(10)
O(1)C(1)	1.274(2)	O(4)U(1)O(3)	49.82(5)	N(2)C(2)C(3)	107.29(10)
O(3)N(3)	1.270(2)	C(1)O(1)U(1)	134.46(14)	C(3)C(2)C(3)^{i}	109.5(2)
O(4)N(3)	1.273(2)	N(3)O(3)U(1)	97.22(12)	C(2)C(3)C(4)	115.37(17)
O(5)N(3)	1.214(2)	N(3)O(4)U(1)	97.86(11)	N(1)C(4)C(5)	107.57(16)
N(1)C(1)	1.320(3)	C(1)N(1)C(4)	123.79(17)	N(1)C(4)C(6)	109.51(17)
N(1)C(4)	1.469(3)	C(1)N(2)C(2)	126.18(16)	C(5)C(4)C(6)	108.98(17)
N(2)C(1)	1.351(3)	O(5)N(3)O(3)	122.41(19)	N(1)C(4)C(3)	106.79(16)
N(2)C(2)	1.465(2)	O(5)N(3)O(4)	122.51(18)	C(5)C(4)C(3)	109.69(17)
C(2)C(3)	1.531(3)	O(3)N(3)O(4)	115.08(17)	C(6)C(4)C(3)	114.09(17)
C(3)C(4)	1.534(3)				
C(4)C(5)	1.524(3)				
C(4)C(6)	1.534(3)				

* The symmetry operation code is $-x + 1, y, -z + 1/2$.

49.82(5)°–65.29(5)°. The geometry of the coordinated nitrate anions is also distorted: the bond angle O(3)N(3)O(4) is substantially smaller (115.08(17)°), the N(3)–O(3) and N(3)–O(4) bonds are longer (1.270(2) and 1.273(2) Å), and the N(3)–O(5) bond is shorter (1.214(2) Å) than the average bond length in nitrate anions (1.24 Å) [12].

The organic ligand Sk occupies a special position on axis 2 passing through the spiro atom C(2). The conformation of the six-membered ring of the Sk molecule is a distorted sofa, with the C(3) atom deviating by 0.58 Å from the mean-square plane of the other ring atoms. The dihedral angle between the mean-square planes of the two rings of the Sk molecule is 80°. Such a conformation gives rise to a strongly shortened intramolecular contact H(2)···H(16c) 1.97 Å against 2.32 Å for the doubled van der Waals radius of the H atom [13].

The C(1)–O(1) bond (1.274(2) Å) is longer than the average bond length in such urea fragments (1.24 Å) [12], which is due to the coordination of the O atom to the metal atom. It is also worth noting that the N(1)–C(1) is shortened (1.320(3) Å), which suggests a stronger conjugation of the N(1) atom with the carbonyl group and localization of a partial positive charge on this atom. Such a charge redistribution can

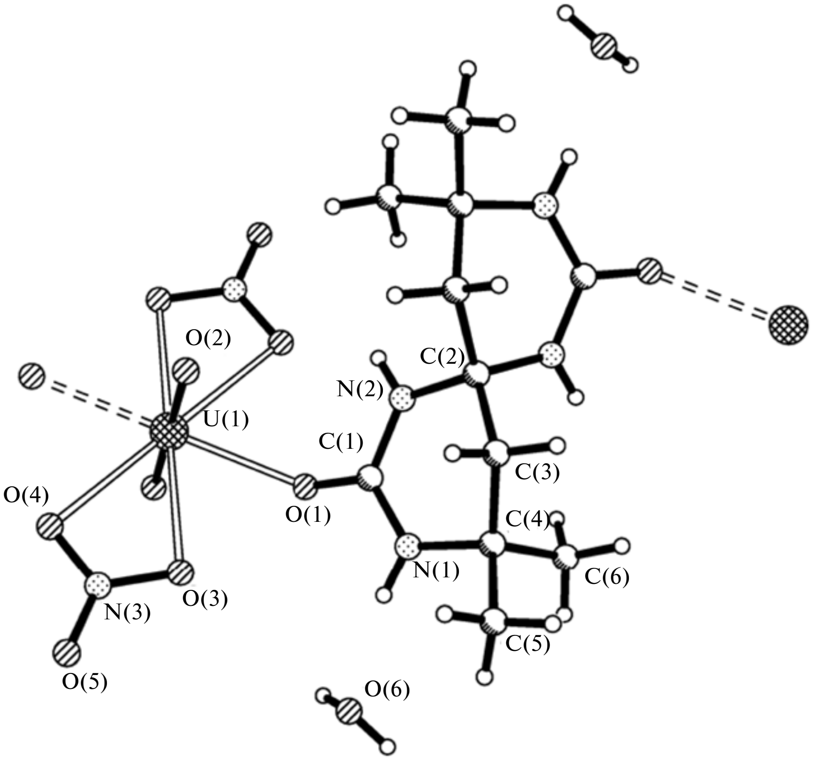


Fig. 1. Structure **I**.

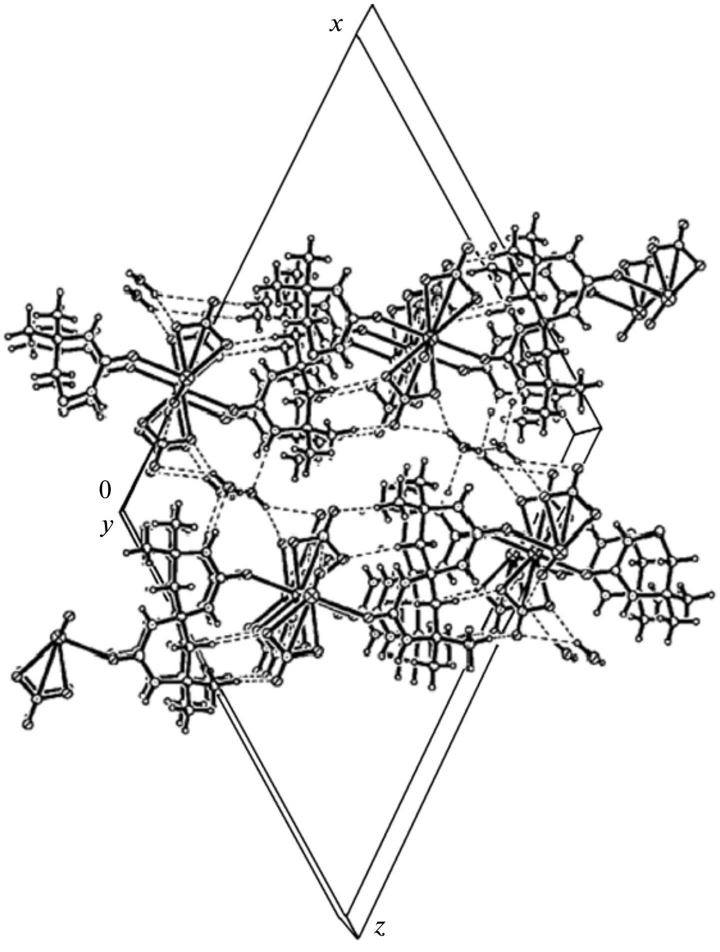


Fig. 2. General view of structure **I** along the direction [101].

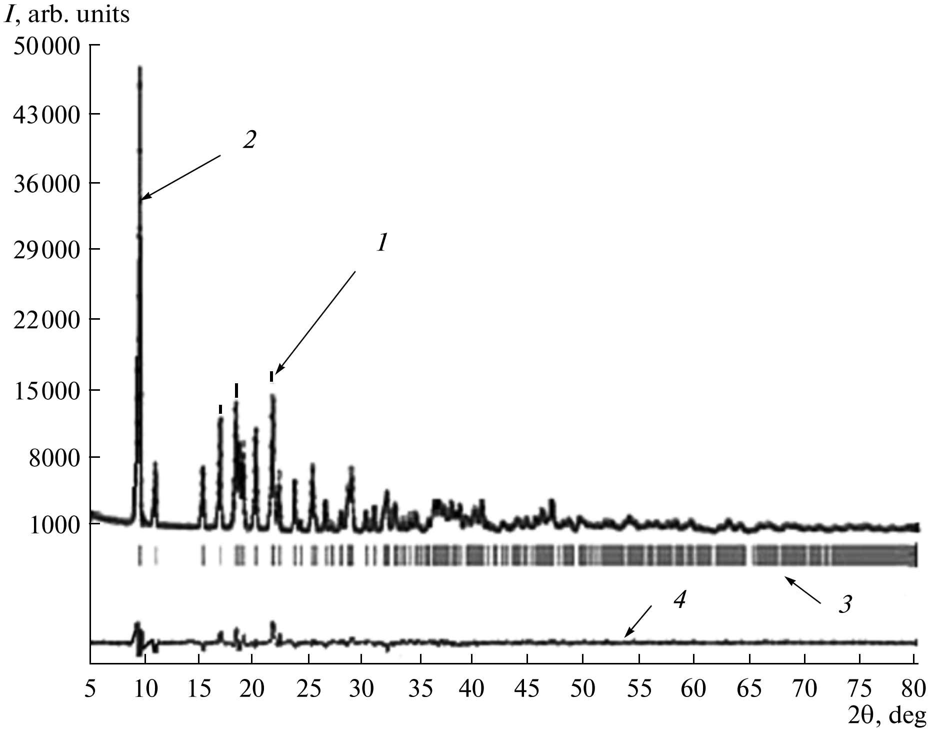


Fig. 3. Rietveld refinement of the X-ray powder diffraction pattern of complex **I**: (*1*) experimental pattern, (*2*) calculated pattern, (*3*) line positions, and (*4*) difference curve ($I_{exp} - I_{calcd}$).

be explained by the fact that the hydrogen bond N(2)–H(2)···O(4) between the N(2) atom and the nitrate anion (H···O 2.29 Å; the angle N–H···O 139°) is much weaker than the bond N(1)–H(1)···O(6) between the N(1) atom and a water molecule (H···O, 2.06 Å; the angle N–H···O, 164°).

Apart from the hydrogen bonds to the N(1) atom, water molecules are linked together by the intermolecular hydrogen bonds O(6)–H(6d)···O(6)^{i} ($^{i}1/2 - x$, $-1/2 + y$, $1/2 - z$); H···O 2.11 Å; the angle O–H···O 160°) and to the nitrate anions by the hydrogen bonds O(6)–H(6e)···O(3)^{i}; H···O 2.29 Å, O–H···O 149°. Thus, hydrogen-bonded water molecules form chains in the crystal along the axis *y* that are perpendicular to the coordination polymers (Fig. 2).

X-ray powder diffraction data confirmed the absence of any impurities in complex **I** (Fig. 3). The Rietveld refinement of its X-ray powder diffraction pattern gave the exact unit cell parameters of the complex at room temperature: $a = 23.2965(6)$ Å, $b = 5.51225(15)$ Å, $c = 19.8588(6)$ Å, $\beta = 125.6063(17)°$, $V = 2073.40(10)$ Å^3.

REFERENCES

1. Tribrat, T.P. and Eres'ko, V.A., *Vseukr. Nauch.-Prakt. Konf.* (All-Ukraininan Scientific and Pract. Conf.), 1994, p. 101.
2. Starikovich, L.S., Starikovich, M.A., Rechitskii, A.N., et al., *Studia Biologica,* 2009, vol. 3, no. 2, p. 93.
3. Starikovich, L.S., Dudok, E.P., Sibirnaya, N.A., et al., *Medichna Khimiya,* 2009, vol. 11, no. 1, p. 57.
4. Musatov, A.G., Semyashkina, A.A., and Dashevskii, R.F., *Khranenie i Pererabotka Zerna*, 2003, p. 16.
5. Gurevich, A.S., Titov, V.A., Babaeva, E.V., et al., *Introduktsiya, Akklimatizatsiya i Kul'tivatsiya Rastenii: Sb. Nauch. Trud.*, 1998, p. 30.
6. Kozichar, M.V., *Extended Abstract of Candidate Sci. (Biol.) Dissetation*, Kherson: Kherson National Technical Univ., 1999.
7. Netreba, E.E., Fedorenko, A.M., and Pavlov, A.A., *Nauk. Visnik Uzhgorod. Un-tu, Ser. Khim.,* 2011, no. 1(25), p. 107.
8. Sheldrick, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
9. Rodriguez-Carvajal, J. and Roisnel, T., *FullProf.98 and WinPLOTR: New Windows 95/NT Applications for Diffraction. Commission for Powder Diffraction, International Union of Crystallography*, 1998, no 20.
10. Grigor'ev, A.I., *Vvedenie v kolebatel'nuyu spektroskopiyu neorganicheskikh soedinenii* (Introduction to Vibrational Spectroscopy of Inorganic Compounds), Moscow: MGU, 1977.
11. Nakanishi, K., *Infrared Absorption Spectroscopy, Practical*, San-Francisco: Holden-Day, 1962.
12. Burgi, H.B. and Dunitz, J.D., *Structure Correlation,* Weinheim: VCH, 1994. vol. 2, P. 741.
13. Zefirov, Yu.V. and Zorkii, P.M., *Usp. Khim.,* 1989, vol. 58, no. 5, p. 713.