Journal of Structural Chemistry. Vol. 57, No. 3, pp. 542-548, 2016.
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CRYSTAL STRUCTURE OF A NEW COMPLEX bis(4,4,10,10-TETRAMETHYL-1,3,7,9-TETRAAZOSPIRO-[5.5]UNDECANE-2,8-DIONE-O)-DIAQUA-tris(NITRATO-O,O′)-LANTHANUM

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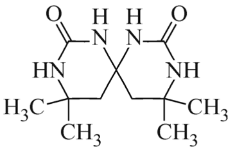
UDC 54.057:548.736.5:546.654

For the first time, a mononuclear biligand complex of lanthanum nitrate with bicyclic bisurea (4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione, or spirocarbon, Sk) $[La(C_{11}H_{20}N_4O_2)_2(H_2O)_2\cdot\cdot(NO_3)_3]$ (**I**) is synthesized and its structure is determined by direct single crystal XRD. The crystals of **I** are monoclinic: space group $P2_1/c$, $a = 11.1989(15)$ Å, $b = 13.015(2)$ Å, $c = 24.153(2)$ Å, $\beta = 101.129(12)°$, $V = 3454.3(8)$ Å^3, $d_{calc} = 1.618$ g/cm^3, $Z = 4$, CCDC 985760. The structure is molecular. The lanthanum cation is coordinated by two oxygen atoms of two organic ligand molecules, two water molecules, and three bidentate nitrate anions. The coordination number of lanthanum is ten; the coordination polyhedron is an irregular 10-vertex polyhedron. The crystal of **I** represents a non-merohedral twin with the components turned by 180° along the *a* axis; the relative weights of the components are 0.76:0.24. To confirm the purity of the sample of **I**, the powder XRD pattern was refined using the Rietveld method; the unit cell parameters at room temperature are as follows: $a = 11.2777(4)$ Å, $b = 13.0774(5)$ Å, $c = 24.3453(9)$ Å, $\beta = 101.129(3)°$, $V = 3523.0(2)$ Å^3.

DOI: 10.1134/S0022476616030173

Keywords: lanthanum, spirocarbon, mononuclear, biligand, complex, structure, IR, single crystal XRD, powder XRD.

Coordination compounds with ligands of the bicyclic bisurea class have been poorly studied so far. One of these ligands is 4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione, or spirocarbon ($C_{11}H_{20}N_4O_2$, Sk):



Scheme.

As a precursor of urea, this bicyclic spirobisurea has a number of valuable biological properties: low toxicity, $LD_{50} = 3000$ mg/kg of a white mouse weight [1]; membranotropic action [2]; the ability to penetrate and accumulate in the cytoplasm of murine and human leukemia cells of L1210 and CEM-T4 lines respectively [3]. It also promotes an increase in

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TABLE 1. Binuclear Complexes of 4,4,10,10-Tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione (Sk) Obtained Previously

Sk Complex	CCDC	Literature
$[Y(C_{11}H_{20}N_4O_2)(H_2O)_3(NO_3)_2]_2(NO_3)_2$	903389	[7]
$[La(C_{11}H_{20}N_4O_2)(H_2O)_2(NO_3)_3]_2$	903388	[8]
$[Pr(C_{11}H_{20}N_4O_2)(H_2O)_3(NO_3)_2]_2(NO_3)_2$	924475	[9]
$[Nd(C_{11}H_{20}N_4O_2)(H_2O)_3(NO_3)_2]_2(NO_3)_2$	876569	[10]
$[Sm(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	924470	[11]
$[Eu(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	924469	[11]
$[Gd(C_{11}H_{20}N_4O_2)(H_2O)_3(NO_3)_2]_2(NO_3)_2$	924472	[11]
$[Tb(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	924473	[11]
$[Dy(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	924474	[11]
$[Ho(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	924467	[12]
$[Er(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	925788	[13]
$[Tm(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	925790	[14]
$[Yb(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	924466	[15]
$[Lu(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_3]_2$	925789	[16]
$[Ce(C_{11}H_{20}N_4O_2)(H_2O)_2(NO_3)_3]_2$	985758	[17]

the amount of proteins and a decrease in the starch content in oat grains [4]. Sk has been proved to efficiently stimulate callusing in *Forsythia europaea* [5] and root formation in *Philadelphos coronarius*. In [6], Sk is shown to be an efficient stimulator for the growth and development in sheep breeding. Therefore, the synthesis and study of coordination compounds of this bicyclic spirobisurea as a hard Lewis base will help to gain greater insight into the chemistry of Sk interactions with different metal atoms.

Previously, we have obtained and characterized binuclear Sk complexes with REE(III) (Table 1), in which the metal:ligand ratio was 1:1. The analysis of the techniques used to synthesize these complexes showed that a preset molar ratio of reagents $n(\text{salt})>n(\text{ligand})$ resulted in the preparation of binuclear 16-membered chelate complexes of Sk where the ligand acted as a chelating bidentate bridge.

In continuation of these studies, the present work describes the synthesis and structure of a new mononuclear biligand complex of Sk and lanthanum(III) nitrate: bis(4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione-O)-diaqua-tris(nitrato-O,O′)-lanthanum. To achieve the goal, in the synthesis, the molar ratio of reagents $n(\text{salt})<n(\text{ligand})$ was set under the same synthesis conditions.

EXPERIMENTAL

Synthesis. To synthesize **I,** chemically pure $La(NO_3)_3\cdot 6H_2O$, Sk obtained by the procedures described in [18, 19], and high purity grade acetone were used. A portion of lanthanum nitrate was dissolved in acetone, then Sk was added in the 1:3 molar ratio, and the mixture was magnetically stirrered for 10 min. The resulting solution was filtered, sealed, and left for several days for crystals to form. The precipitated colorless crystals were filtered, washed with acetone, and dried in the air. Yield was ~61% (with respect to salt).

Elemental analysis. The C, H, N content in **I** was determined on an EA-3000 elemental analyzer (EuroVector, Italy).

Found, %: C 31.43, H 5.31, N 18.30. For $[La(C_{11}H_{20}N_4O_2)_2(H_2O)_2(NO_3)_3]$ calculated, %: C 31.39, H 5.27, N 18.31.

IR spectroscopy. The spectra of the ligand and synthesized **I** were recorded in KBr pellets on a Spectrum ONE Fourier IR spectrometer (PerkinElmer) in the range 400-4000 cm^{-1}.

Single crystal XRD. Experimental material for the crystal of **I** was obtained on an automated four-circle Xcalibur 3 diffractometer (MoK_α radiation, $\lambda = 0.71073$) at 293(2) K. The structure was solved by a direct method using the SHELX-97

TABLE 2. Main Crystallographic Data and the Parameters of the XRD Experiment for Compound **I**

Parameter	Value
Empirical formula	$C_{22}H_{44}LaN_{11}O_{15}$
M	841.59
Measurement temperature, K	293(2)
Radiation (λ, Å)	MoK_α (0.71073)
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
Unit cell parameters: a, b, c, Å; β, deg	11.1989(15), 13.015(2), 24.153(2); 101.129(12)
V, Å^3	3454.3(8)
Z	4
d (calc.), g/cm^3	1.618
μ(MoK_α), mm^{-1}	1.318
F(000)	1720
Crystal size, mm	0.062×0.084×0.152
θ range, deg	2.69-28.99
Intervals of reflection indices	$-15 \le h \le 14$, $-17 \le k \le 17$, $-32 \le l \le 32$
Number of meas. / indep. reflections	8615 / 8615 (R_{int} = 0.0000)
Number of reflections with $I > 2\sigma(I)$	4558
Number of refined parameters	457
R factor for $I > 2\sigma(I)$)	$R_1 = 0.0808$, $wR_2 = 0.1921$
R factor for all reflections	$R_1 = 0.1437$, $wR_2 = 0.2285$
$GOOF$ on F^2	0.907
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$, e/Å^{-3}	2.183 and –2.842

software [20]. The positions of hydrogen atoms were calculated geometrically and refined in the riding model with $U_{\text{iso}} = nU_{\text{eq}}$ of the carrying atom ($n = 1.5$ for water and methyl groups, $n = 1.2$ for the other hydrogen atoms). The structure was refined by full-matrix LSM in the anisotropic approximation for non-hydrogen atoms against F^2. The studied crystal of **I** represents a non-merohedral twin with the components turned by 180° along the a axis; the relative weights of the components are 0.76:0.24. In the structure refinement, we imposed the restrictions on the equality of atomic vibration tensor components along the chemical bonds with an accuracy of 0.003 Å^2.

The main characteristics of the experiment and unit cell parameters are given in Table 2; the bond lengths and angles of the structure are listed in Table 3.

The atomic coordinates and other parameters of the structure of **I** have been deposited with the Cambridge Structural Database (CCDC 985760, deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Powder XRD. To confirm the purity of the synthesized powder portion of **I** and its single phase state, we refined the powder XRD pattern by the Rietveld method using the FullProf software [21]. The analysis was performed on a Siemens D500 powder diffractometer with copper radiation (Ni filter). A sample for the XRD measurement was first ground and then placed in a glass cuvette with a working volume of 2×1×0.1 cm. The XRD pattern was measured in the angle range of $5° < 2\theta < 75°$ with a step of 0.02° and an acquisition time of 100 s in each point. The XRD pattern of lanthanum hexaboride was used as the external standard.

RESULTS AND DISCUSSION

The IR spectra of **I** and Sk are observed to have the following characteristic bands ($\bar{\nu}$, cm^{-1}) for Sk: 3416 (H_2O); 3335, 3293, 3218 (HN); 3075, 2991, 2978 (CH_3, CH_2); 1653 (C=O, amide I); 1418 (C–N); for **I**: 3788, 3726 (H_2O); 3415,

TABLE 3. Bond Angles (deg) and Bond Lengths (Å) in the Structure of **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
La(1)–O(1)	2.514(9)	La(1)–O(8)	2.685(8)	La(1)–O(14)	2.512(8)
La(1)–O(3)	2.467(8)	La(1)–O(9)	2.657(8)	La(1)–O(15)	2.578(8)
La(1)–O(5)	2.617(8)	La(1)–O(11)	2.592(9)	La(1)–N(11)	3.067(11)
La(1)–O(6)	2.666(9)	La(1)–O(12)	2.683(9)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)La(1)O(5)	96.0(3)	O(5)La(1)N(11)	155.0(3)	O(14)La(1)O(11)	75.5(3)
O(1)La(1)O(6)	134.0(3)	O(6)La(1)O(8)	73.5(3)	O(14)La(1)O(12)	113.0(3)
O(1)La(1)O(8)	68.2(3)	O(6)La(1)O(12)	140.3(3)	O(14)La(1)O(15)	66.7(3)
O(1)La(1)O(9)	87.3(3)	O(6)La(1)N(11)	151.2(3)	O(14)La(1)N(11)	95.2(3)
O(1)La(1)O(11)	81.1(3)	O(8)La(1)N(11)	119.8(3)	O(15)La(1)O(5)	116.4(3)
O(1)La(1)O(12)	71.2(3)	O(9)La(1)O(6)	84.7(3)	O(15)La(1)O(6)	69.9(3)
O(1)La(1)O(15)	144.3(3)	O(9)La(1)O(8)	46.9(3)	O(15)La(1)O(8)	105.2(3)
O(1)La(1)N(11)	73.1(3)	O(9)La(1)O(12)	63.8(3)	O(15)La(1)O(9)	66.7(3)
O(3)La(1)O(1)	72.0(3)	O(9)La(1)N(11)	88.0(3)	O(15)La(1)O(11)	85.8(3)
O(3)La(1)O(5)	66.1(3)	O(11)La(1)O(5)	134.5(3)	O(11)N(11)La(1)	56.3(6)
O(3)La(1)O(6)	107.1(3)	O(11)La(1)O(6)	143.4(3)	O(12)N(11)La(1)	60.7(6)
O(3)La(1)O(8)	118.9(3)	O(11)La(1)O(8)	141.2(3)	O(13)N(11)La(1)	173.9(10)
O(3)La(1)O(9)	159.1(3)	O(11)La(1)O(9)	110.9(3)	C(12)O(3)La(1)	130.5(8)
O(3)La(1)O(11)	69.9(3)	O(11)La(1)O(12)	47.9(3)	N(9)O(5)La(1)	98.6(7)
O(3)La(1)O(12)	110.6(3)	O(11)La(1)N(11)	23.7(3)	N(9)O(6)La(1)	96.6(7)
O(3)La(1)O(14)	68.7(3)	O(12)La(1)O(8)	98.2(3)	N(10)O(8)La(1)	96.9(6)
O(3)La(1)O(15)	133.2(3)	O(12)La(1)N(11)	24.4(3)	N(10)O(9)La(1)	98.5(7)
O(3)La(1)N(11)	89.0(3)	O(14)La(1)O(1)	139.2(3)	N(11)O(11)La(1)	100.0(8)
O(5)La(1)O(6)	48.4(3)	O(14)La(1)O(5)	78.2(3)	N(11)O(12)La(1)	94.9(7)
O(5)La(1)O(8)	74.0(3)	O(14)La(1)O(6)	70.0(3)	O(15)La(1)O(12)	75.4(3)
O(5)La(1)O(9)	114.3(3)	O(14)La(1)O(8)	143.2(3)	O(15)La(1)N(11)	81.7(3)
O(5)La(1)O(12)	166.9(3)	O(14)La(1)O(9)	132.2(3)	C(1)O(1)La(1)	134.6(8)

3366, 3322, 3254 (NH); 2978, 2935, 2873 (CH_3, CH_2); 1710, 1644, 1622 (C=O, amide I); 1463, 1452, 1435 (C–N); 1514, 1503, 1253, 1036, 817, 741, 711, 667 (NO_3).

As seen from the comparison of the ν(C=O, amide I) stretching vibrations there is a shift of 9 cm^{-1} to the far region due to the coordination of Sk molecules and the singlet is split because the complex contains free C=O groups and a shift of ν_s(NH), ν_{as}(NH) to the near region, which is typical of amino groups at coordinated carbonyl [22]. The IR spectrum of **I** has the ν_{s+as}(HOH) absorption bands of the water contained and a set of absorption bands of the coordinated Sk ligand. A free nitrate anion, as a planar ion belonging to the point group D_{3h}, has four different main vibrational frequencies: the frequency of symmetric stretching vibrations $\nu_s(NO) \approx 1050\text{-}1060$ cm^{-1}, the frequency of asymmetric doubly degenerate stretching vibrations $\nu_e(NO) \approx 1350\text{-}1400$ cm^{-1}, and two bending vibrational frequencies $\delta(NO_3) \approx 810\text{-}840$ cm^{-1} and ~710-730 cm^{-1}. Only three frequencies are usually active in the IR spectrum: ν_e(NO) and two $\delta(NO_3)$ [23]. In the coordination of the nitrate ion, its symmetry can decrease to C_s and C_{2v}. As a result, six intense lines appear in the IR spectrum [24]: a totally symmetric vibration in the range 970-1040 cm^{-1}; a stretching antisymmetric vibration splitting into two intense lines in the range 1550-1410 cm^{-1} and 1290-1250 cm^{-1}; a non-planar vibration in the range 830-800 cm^{-1}; a planar bending vibration appearing as two bands at 780-700 cm^{-1} and about 680 cm^{-1} [25]. The IR spectrum of **I** has the lines at 1514 cm^{-1}, 1503 cm^{-1}, 1253 cm^{-1}, 1036 cm^{-1}, 817 cm^{-1}, 741 cm^{-1}, 711 cm^{-1}, 667 cm^{-1}. This confirms that nitrate anions are coordinated in a bidentate-chelate mode.

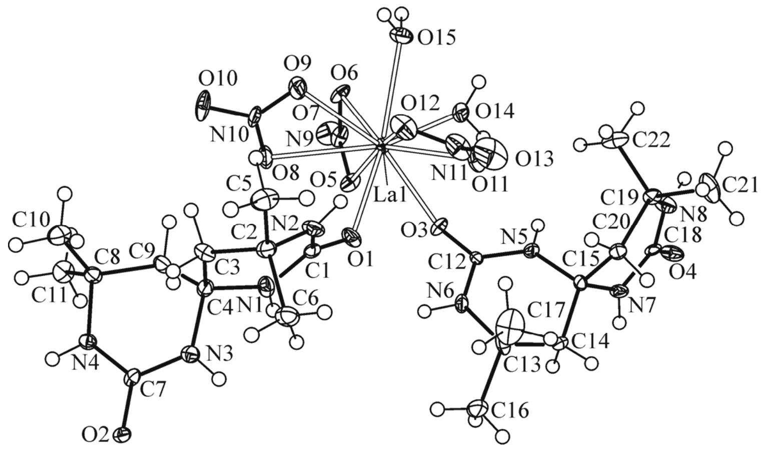

Fig. 1. Molecular structure of **I** according to the single crystal XRD data (thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level).

According to the single crystal XRD data, compound **I** is a molecular complex in which a lanthanum(III) cation is coordinated by two oxygen atoms of two Sk molecules, two water molecules, and three bidentate nitrate anions. The coordination polyhedron is an irregular 10-vertex polyhedron (Fig. 1).

Two Sk molecules have different conformations. The six-membered heterocycle containing the N(1) atom is in an intermediate conformation between *half-sofa* and *twist-boat* with a flattened N(1)–C(1)–N(2)–C(2) fragment (the torsion angle is 6.7(18)°) and a deviation of C(3) and C(4) atoms from the mean plane of this fragment by –0.85(2) Å and –0.59(2) Å respectively. The cycles containing the N(3), N(5), and N(7) atoms are in a *sofa* conformation with a deviation of the C(9), C(14), and C(15) atoms from the planes of other atoms of the cycle by –0.61(2) Å, –0.54(2) Å, and –0.60(2) Å respectively.

Multiple intermolecular hydrogen bonds form in the crystal (Table 4) linking the complex molecules with each other (Fig. 2).

The indexation of the powder XRD pattern confirmed that the sample of **I** crystallizing in the space group $P2_1/c$ was single phase. By the calculation using the Rietveld method, the unit cell parameters, profile parameters, background, and total thermal correction were refined. The following unit cell parameters at $T = 293$ K were obtained: $a = 11.2777(4)$ Å, $b = 13.0774(5)$ Å, $c = 24.3453(9)$ Å, $\beta = 101.129(3)°$, $V = 3523.0(2)$ Å^3. The average crystallite size in the powder sample was 69 nm; microtensions were almost absent. All lines observed in the XRD pattern correspond to the main phase of **I**.

TABLE 4. Hydrogen Bonds in the Structure of **I**

(D–H…A) bond	Symmetry operation	*d*(H…A), Å	*d*(D–H), Å	*d*(D…A), Å	ω(D–H…A), deg
O(14)–H(14A)…O(2)	*x*, 1/2–*y*, 1/2+*z*	1.90	0.85	2.728(12)	163
O(14)–H(14B)…O(2)	–*x*, –1/2+*y*, 1/2–*z*	1.92	0.85	2.745(12)	164
O(15)–H(15A)…O(4)	–*x*, –*y*, 1–*z*	1.92	0.85	2.756(14)	166
O(15)–H(15B)…O(4)	1+*x*, *y*, *z*	1.87	0.85	2.668(13)	156
N(2)–H(2)…O(12)	–	2.28	0.86	3.030(15)	145
N(3)–H(3)…O(3)	–*x*, 1/2+*y*, 1/2–*z*	2.45	0.86	3.177(14)	142
N(4)–H(4)…O(15)	*x*, 1/2–*y*, –1/2+*z*	2.19	0.86	3.038(13)	171
N(5)–H(5)…O(2)	–*x*, –1/2+*y*, 1/2–*z*	1.96	0.86	2.791(14)	162
N(6)–H(6)…O(1)	–	2.48	0.86	3.033(15)	123
N(7)–H(7)…O(9)	–1+*x*, *y*, *z*	2.19	0.86	3.012(14)	160
N(8)–H(8)…O(6)	–*x*, –*y*, 1–*z*	2.20	0.86	3.061(14)	174

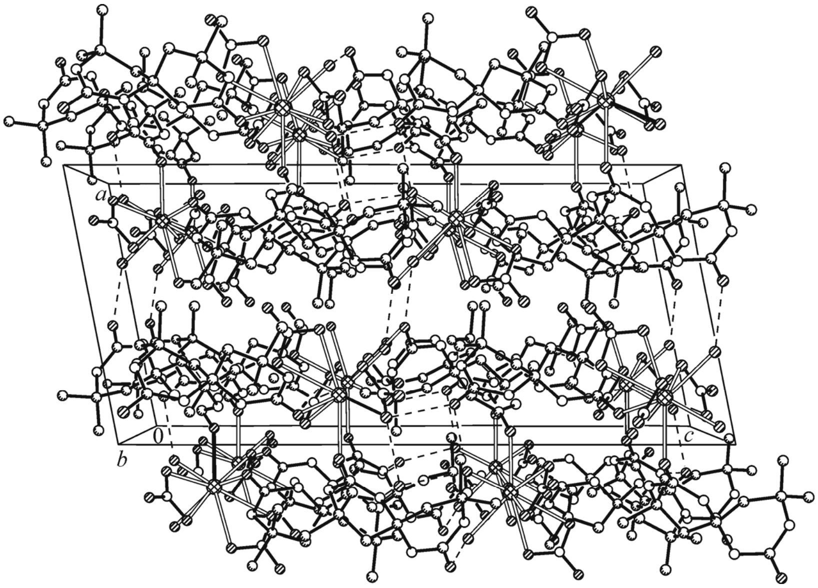

Fig. 2. Crystal structure of **I** according to the single crystal XRD data.

The study shows that at a given molar ratio between lanthanum nitrate and 4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione *n*(salt)<*n*(ligand), a molecular mononuclear biligand complex bis(4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione-O)-diaqua-tris(nitrato-O,O′)-lanthanum forms. The composition and structure of this complex are confirmed by the elemental analysis data and IR spectroscopy, single crystal and powder XRD. The ligand is proved to exhibit a terminal function and is coordinated via the oxygen atoms of carbamide fragments in the acetone medium.

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