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Original Russian Text © 2016 E. E. Netreba, E. A. Sarnit, S. V. Shabanov, A. A. Velikozhon, N. V. Somov.

CRYSTAL STRUCTURE OF A NEW BINUCLEAR COMPLEX bis(2,4,6,8-TETRAMETHYL-2,4,6,8-TETRAAZABICYCLO(3.3.0)OCTANE-3,7-DIONE-O,O′)-TETRAAQUA-hexakis(NITRATO-O,O′)-DIEUROPIUM(III)

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A centrosymmetric binuclear complex of europium(III) nitrate with bicyclic bisurea (2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo(3.3.0)octane-3,7-dione, or mebicar, Mk) $[Eu(C_8H_{14}N_4O_2)(H_2O)_2(NO_3)_3]_2$ (**I**) is synthesized and its atomic structure (CIF file CCDC No. 1451437) is determined. The crystals of **I** are triclinic: space group $P\overline{1}$, $a = 9.8343(4)$ Å, $b = 10.2544(4)$ Å, $c = 10.9411(4)$ Å, $\alpha = 74.366(3)°$, $\beta = 67.734(4)°$, $\gamma = 67.673(4)°$, $V = 934.32(7)$ Å^3, ρ(calc.) = 2.03398 g/cm^3, $Z = 1$. The europium atom is coordinated by two oxygen atoms of two Mk molecules connected by a symmetry operation, three bidentate nitrate anions, and two water molecules. The coordination polyhedron of the europium atom is a 10-vertex polyhedron, the Eu…Eu distance is 9.7433(6) Å.

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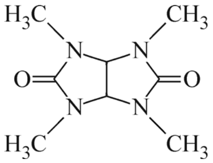
Coordination compounds of lanthanides with ligands of the bicyclic bisurea class of the octane series have been poorly studied so far. One of these ligands is 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo(3.3.0)octane -3,7-dione, or mebicar ($C_8H_{14}N_4O_2$, Mk):



Scheme 1.

Mebicar has the stress-protective, anxiolytic, and nootropic action and is used in medical practice as a commercial drug named Adaptol. It regulates abnormal nocturnal sleep, but does not have a direct sedative effect, does not exhibit the cholinergic and muscle-relaxing action, does not affect the coordination of movements, and weakens nicotine withdrawal symptoms [1-3]. It is known that mebicar improves the oxygen supply of the myocardial tissues, regulates plasma electrolyte

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balance, level of potassium in blood, erythrocytes, and myocardial tissues, helps to enhance protein synthesis and to increase cell energy [4-6].

Previously, A. Yu. Tsivadze with his research team have obtained and described some complexes with mebicar: $[Co(Mk)_2(H_2O)_2Br_2]\cdot 2H_2O$, $[Ni(Mk)_2(H_2O)_2Br_2]$, $[NiMk(H_2O)_4](NO_3)_2$ and $[Cu_2(Mk)_3Br_4]\cdot 2H_2O$, $CdCl_2\cdot Mk\cdot 3H_2O$, $CaCl_2\cdot 2Mk\cdot H_2O$, $Co(NO_3)_2\cdot 2Mk\cdot 4H_2O$, $Ni(NO_3)_2\cdot Mk\cdot 4H_2O$, $CdX_2\cdot Mk$ (X = Br, I, NCS), $Cd(NO_3)_2\cdot 1.5Mk\cdot H_2O$, $ZnCl_2\cdot Mk$, $ZnI_2\cdot Mk$, $Ca(NO_3)_2\cdot 2Mk$, $Cu(NO_3)_2\cdot 0.5Mk$, $[Li_2(Mk)_2(H_2O)_4]Br_2$ [7-10]. The compounds were characterized by the data of elemental analysis, IR and Raman spectroscopy; some of them were also characterized by single crystal XRD. It was shown that Mk coordinates to metals via oxygen atoms of urea moieties, which was confirmed by a decrease in the frequency of amide I C=O and an increase in the frequency of bending vibrations of methyl groups.

Hence, the synthesis and study of coordination compounds of this ligand as a hard Lewis base will help to gain greater insight into the chemistry of its interaction with ions of lanthanides and will determine denticity of the ligand in acetone medium.

The work aims to obtain the coordination compound of europium(III) nitrate, a hard Lewis acid, with mebicar and water molecules, $[Eu(C_8H_{14}N_4O_2)(H_2O)_2(NO_3)_3]_2$ (**I**), and to determine its structure.

EXPERIMENTAL

In the work, chemically pure $Eu(NO_3)_3\cdot 6H_2O$, Mk obtained by the procedures described in [11, 12], and high purity grade acetone were used.

Synthesis of I. A portion of europium nitrate was dissolved in acetone, then mebicar was added in the 1:0.5 molar ratio, and the mixture was magnetically stirred for 5-10 min. The resulting solution was filtered and left for several days for crystals to form in a sealed vessel. The precipitated white crystals were filtered, washed with acetone, and dried in the air. Yield was ~89% (with respect to ligand). Complex **I** is stable in the air.

Elemental analysis. The C, H, N content in **I** was determined on a EuroVector EA-3000 elemental analyzer (Italy). Found, %: C 16.81, H 3.19, N 17.11. For $[Eu(C_8H_{14}N_4O_2)(H_2O)_2(NO_3)_3]_2$ calculated, %: C 16.79, H 3.17, N 17.13.

IR spectroscopy. The spectra of mebicar and **I** were recorded on a Bruker Vertex 70 Fourier IR spectrometer with a FTIR module in a diamond crystal (4 cm^{-1} resolution, 20 scans, 350-4500 cm^{-1} range).

Single crystal XRD. Experimental material for the crystal of **I** was obtained on an automated Oxford Diffraction Gemini S diffractometer with a Sapphire III CCD detector (MoK_α radiation, $\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by a direct method using the SHELX software [13] in the integrated WINGX system [14]. The positions of hydrogen atoms were determined from difference electron density maps. The structure was refined by full-matrix LSM in the anisotropic approximation for non-hydrogen atoms against F^2; we imposed the restrictions on the values of some parameters of hydrogen atoms.

The main characteristics of the experiment and unit cell parameters are given in Table 1; the bond lengths and angles of the structure of **I** are listed in Table 2.

The results of single crystal XRD of **I** have been deposited with the Cambridge Structural Database (CCDC No. 1451437; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The IR spectra of **I** and mebicar are observed to have the following characteristic bands (ν, cm^{-1}) for Mk: 2926, 2884, 2831, 2804 (CH_3, CH_2); 1701 (C=O, amide I); 1454, 1367 (C–N); for **I**: 3400, 3243 (H_2O); 2940, 2891 (CH_3, CH_2); 1655 (C=O, amide I); 1437, 1367 (C–N); 1548, 1285, 1027, 835 (NO_3).

The IR spectrum of **I** are observed to have a shift of 46 cm^{-1} to the far region of the absorption band corresponding to the ν(C=O, amide I) stretching vibrations suggesting the coordination of Mk molecules with the Eu atom via oxygen atoms

TABLE 1. Crystallographic Data, the Parameters of the Experiment and Refinement of the Structure of **I**

Parameter	Value
M	1144.51
Crystal symmetry	Triclinic
Space group	$P\overline{1}$
Unit cell parameters: a, b, c, Å	9.8343(4), 10.2544(4), 10.9411(4)
α, β, γ, deg	74.366(3), 67.734(4), 67.673(4)
V, Å^3	934.32(7)
Z	1
ρ(calc.), g/cm^3	2.03398
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	3.438
F(000)	564
Crystal size, mm	0.22×0.14×0.09
θ range, deg	3.559–33.071
Intervals of reflection indices	$-15 \leq h \leq 14$, $-15 \leq k \leq 14$, $-16 \leq l \leq 15$
Number of meas. / indep. reflections (R_{int})	18470 / 6374 (0.0499)
Number of reflections with $I > 2\sigma(I)$	5938
Number of refined parameters	278
Number of reflections	6
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0337$, $wR_2 = 0.0825$
R factor for all reflections	$R_1 = 0.0361$, $wR_2 = 0.0841$
$GOOF$ on F^2	1.084
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$, e/Å^3	2.768 and –2.513

TABLE 2. Selected Bond Lengths (Å) and Bond Angles (deg) in the Structure of **I**

Bond	d, Å	Bond	d, Å	Bond	d, Å
O(1)–Eu(1)	2.503(2)	O(7)–Eu(1)	2.593(2)	O(11w)–Eu(1)	2.442(2)
O(3)–Eu(1)	2.569(2)	O(9)–Eu(1)	2.594(3)	O(12)–Eu(1)	2.385(2)
O(4)–Eu(1)	2.4875(2)	O(10w)–Eu(1)	2.488(2)	O(13)–Eu(1)	2.3350(2)
O(6)–Eu(1)	2.584(2)				
Bond	ω, deg	Bond	ω, deg	Bond	ω, deg
O(13)Eu(1)O(12)	70.49(7)	O(13)Eu(1)O(3)	116.74(8)	O(12)Eu(1)O(9)	115.41(8)
O(13)Eu(1)O(11w)	76.93(9)	O(12)Eu(1)O(3)	70.58(7)	O(11w)Eu(1)O(9)	67.30(8)
O(12)Eu(1)O(11w)	143.64(8)	O(11w)Eu(1)O(3)	112.29(7)	O(4)Eu(1)O(9)	106.49(7)
O(13)Eu(1)O(4)	144.04(8)	O(4)Eu(1)O(3)	67.38(7)	O(10w)Eu(1)O(9)	108.93(8)
O(12)Eu(1)O(4)	78.75(7)	O(10w)Eu(1)O(3)	63.65(8)	O(1)Eu(1)O(9)	134.61(8)
O(11w)Eu(1)O(4)	137.05(8)	O(1)Eu(1)O(3)	50.09(7)	O(3)Eu(1)O(9)	171.08(8)
O(13)Eu(1)O(10w)	141.46(8)	O(13)Eu(1)O(6)	100.97(8)	O(6)Eu(1)O(9)	67.24(8)
O(12)Eu(1)O(10w)	132.85(7)	O(12)Eu(1)O(7)	137.44(7)	O(7)Eu(1)O(9)	48.82(7)
O(11w)Eu(1)O(10w)	68.99(8)	O(11w)Eu(1)O(7)	73.80(8)	O(12)Eu(1)O(6)	70.73(7)
O(4)Eu(1)O(10w)	74.05(7)	O(4)Eu(1)O(7)	72.10(7)	O(11w)Eu(1)O(6)	132.65(8)
O(13)Eu(1)O(1)	79.45(8)	O(10w)Eu(1)O(7)	66.89(7)	O(4)Eu(1)O(6)	50.02(7)
O(12)Eu(1)O(1)	85.99(7)	O(1)Eu(1)O(7)	134.89(7)	O(10w)Eu(1)O(6)	115.14(7)
O(11w)Eu(1)O(1)	72.36(8)	O(3)Eu(1)O(7)	122.26(7)	O(1)Eu(1)O(6)	154.75(8)
O(4)Eu(1)O(1)	117.13(6)	O(6)Eu(1)O(7)	66.81(7)	O(3)Eu(1)O(6)	110.52(7)
O(10w)Eu(1)O(1)	73.61(7)	O(13)Eu(1)O(9)	72.10(8)		

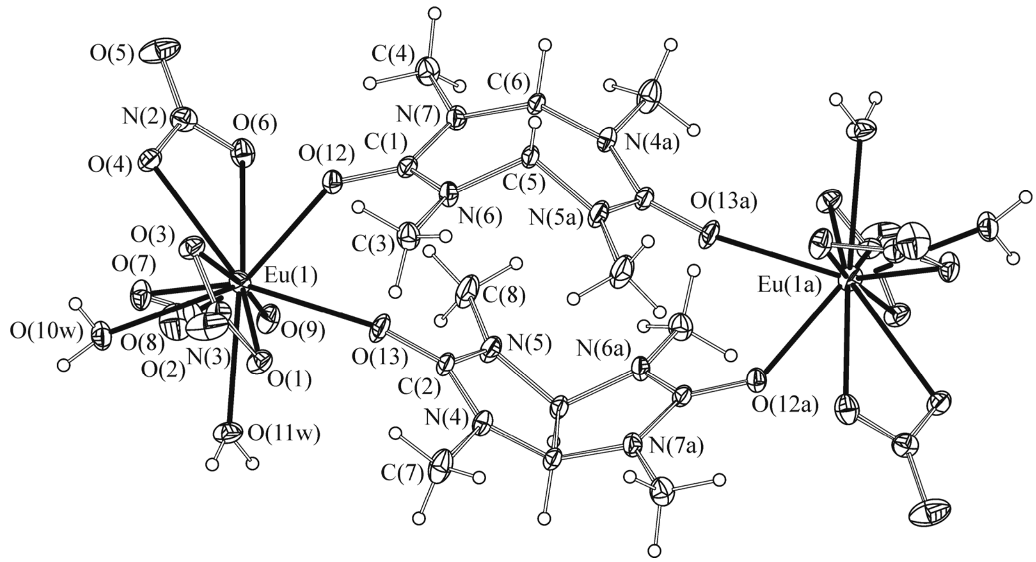

Fig. 1. Fragment of the atomic structure of **I**. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level.

[15]. The IR spectrum also has the ν_{s+as}(HOH) absorption bands of the water contained and a set of absorption bands of the Mk cycles. A free nitrate anion, as a planar ion (point group D_{3h}), has four main vibrational frequencies: the frequency of symmetric stretching vibrations ν_s(NO) (1050-1060 cm^{-1}), the frequency of asymmetric doubly degenerate stretching vibrations ν_e(NO) (1350-1400 cm^{-1}), and two bending vibrational frequencies $\delta(NO_3)$ (810-840 cm^{-1} and 710-730 cm^{-1}). Only three frequencies are usually active in the IR spectrum: ν_e(NO) and two $\delta(NO_3)$ [16]. In the coordination of the nitrate anion, its symmetry can decrease to C_s and C_{2v}. As a result, six intense lines appear in the IR spectrum in the following ranges (cm^{-1}): 970-1040 (totally symmetric vibration); 1550-1410 and 1290-1250 (antisymmetric stretching vibration appearing as two intense lines); 830-800 (non-planar vibration); 780-700 and ~680 (planar bending vibration appearing as two bands) [17, 18]. The IR spectrum of **I** has the lines at 1548 cm^{-1}, 1285 cm^{-1}, 1027 cm^{-1}, 835 cm^{-1}. This evidences that nitrate anions are coordinated with metal in a bidentate-chelate mode.

According to the single crystal XRD data, compound **I** is a centrosymmetric binuclear complex of the europium(III) cation with two molecules of mebicar (related by a symmetry center), bidentate nitrate anions, and two water molecules (Fig. 1). The coordination polyhedron of the metal atom is a 10-vertex polyhedron; the Eu…Eu distance is 9.7433(6) Å.

Almost planar conjugated five-membered heterocycles of mebicar have the form of a "butterfly" or a "partly-open book". Dihedral angles between the planes of the cycles are 58.05(9)°. A significant difference is observed in the MOC bond angles: Eu(1)O(13)C(2) of 166.24(2)° and Eu(1)O(12)C(1) of 143.26(2)°. The OMO angles with carbonyl groups of the ligand have the same value of 70.48(8)°. Apparently, the MOC angle is the most variable in the complex. The carbonyl O(12) and O(13) atoms are coplanar to the cycles and are connected with them. The distances between coordinated water and the europium cation are almost identical: Eu(1)–O(10*w*) of 2.489(2) Å and Eu(1)–O(11*w*) of 2.442(3) Å.

The carbon atoms of CH_3 groups have different arrangement with respect to the bicycle planes; all radicals are outwardly directed. The C(3), C(4), and C(7) atoms deviate rather significantly from the planes of the cycles with respect to the inner part of the bicycles (by 0.231(4) Å, 0.178(4) Å, and 0.321(4) Å respectively), the C(8) atom deviates insignificantly (by 0.065(4) Å). The polyhedra of nitrogen atoms are almost equilateral triangles in the bicycle plane (deviation of ~0.1 Å).

The C(1)–O(12) bond is slightly elongated to 1.245(3) Å as compared to the average value for such urea moieties (1.24 Å) [19] and the C(2)–O(13) bond (1.239 Å) due to coordination of the oxygen atom with the Eu atom. This agrees well with the IR spectroscopy data.

In the cycle containing the N(4) and N(5) atoms, the O–C–N–C moieties are non-planar, the torsion O(13)C(2)N(5)C(5) and O(13)C(2)N(4)C(6) angles are 173.85(3)° and –173.19(3)°. In the cycle containing the N(7) and N(6) atoms, the torsion O(12)C(1)N(7)C(6) and O(12)C(1)N(6)C(5) angles are 172.77(3)° and –172.03(3)° respectively.

TABLE 3. Geometric Parameters of the Hydrogen Bonds in the Structure of **I***

D–H…A	Distance, Å			D–H…A angle, deg
	D–H	H…A	D…A	
O(10*w*)–H(1)…O(7)$^{\mathrm{i}}$	0.850(2)	2.22(2)	2.911(3)	139,(3)
O(10*w*)–H(2)…O(4)$^{\mathrm{i}}$	0.850(2)	2.136(17)	2.899(3)	149,(3)
O(11*w*)–H(3)…O(2)$^{\mathrm{ii}}$	0.850(2)	1.941(12)	2.731(3)	154,(2)

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* Symmetrically equivalent positions: $^{\mathrm{i}}$ 2–*x*, 2–*y*, 1–*z*; $^{\mathrm{ii}}$ 1–*x*, 2–*y*, 1–*z*.

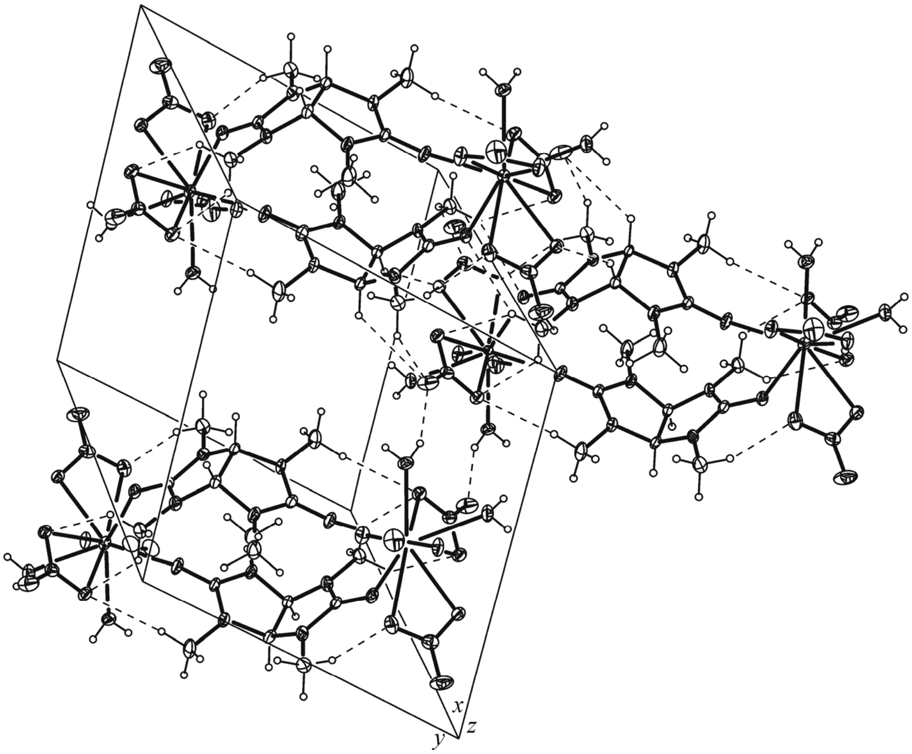

Fig. 2. Fragment of the packing of the crystal of **I**.

The molecules in the crystal of **I** are connected by hydrogen bonds (Table 3, Fig. 2).

For the first time, a binuclear complex of europium(III) nitrate with 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicycle(3.3.0)octane-3,7-dione, or mebicar, was synthesized. By single crystal XRD it was established that the binuclear complex **I** is centrosymmetric. The composition and structure of this complex are confirmed by the elemental analysis data and the results of IR spectroscopy and single crystal XRD. Mebicar is proved to exhibit the bidentate, chelating, and bridging functions due to its structural features and is coordinated via the oxygen atoms of carbamide moieties in acetone medium.

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