

Crystal Structure of Polymer Hexaaqua-Hexakis(2-Thiobarbiturato)dieuropium(III)

N. N. Golovnev^{a,*} and M. S. Molokeev^b

^a Siberian Federal University, Krasnoyarsk, Russia

^b Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

*e-mail: ngolovnev@sfu-kras.ru

Received February 19, 2014

Abstract—Complex $[\text{Eu}_2(\text{HTBA})_6(\text{H}_2\text{O})_6]_n$ (**I**), where H_2TBA is 2-thiobarbituric acid $\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{S}$, is synthesized. Its structure is determined by X-ray diffraction analysis (CIF file CCDC 987519). The crystals of complex **I** are monoclinic: $a = 14.1033(4)$ Å, $b = 10.0988(4)$ Å, $c = 15.4061(5)$ Å, $\beta = 110.003(1)^\circ$, $V = 2061.9(1)$ Å³, space group $P2_1/n$, $Z = 2$. All three independent ligands HTBA^- are coordinated to Eu^{3+} through oxygen atoms. Six HTBA^- ions (two terminal and four bridging) and two water molecules are coordinated to one of the independent Eu^{3+} ions. The second Eu^{3+} ion is bound to four bridging HTBA^- ions and four water molecules. The coordination polyhedra are square antiprisms. The bridging HTBA^- ions join the antiprisms into layers. The structure is stabilized by numerous hydrogen bonds and the π – π interaction between HTBA^- .

DOI: 10.1134/S1070328414090036

INTRODUCTION

Great interest in metal-organic hybrid materials based on lanthanides has been observed in recent 10–15 years. The advantage of these materials is high monochromaticity of the luminescent radiation [1]. Luminescence of biolabels using lanthanide complexes as labels is one of the high-sensitive methods for biotesting widely used in clinical diagnostics and biotechnology [2]. The complexes can also find use in high-tech devices: organic photodiodes, displays, optical amplifiers, lasers, and luminescent panels [3].

In this work, in the framework of systematic studies of the structures of metal thiobarbiturate complexes [4–10], we obtained single crystals and established by the X-ray diffraction analysis the structure of the new Eu(III) complex with 2-thiobarbituric acid (H_2TBA , $\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{S}$). The latter is widely used in the synthesis of drugs of therapeutic significance, for example, sodium thiopental, thiobarbital, and thiobutabarbital [11, 12]. Some lanthanide (Eu^{3+} , Sm^{3+} , Tb^{3+} , and Dy^{3+}) complexes with β -diketones strongly luminesce [2], and acid H_2TBA contains this β -diketone fragment. Therefore, the synthesis and study of its compounds with lanthanides is practically interesting.

EXPERIMENTAL

Synthesis of $[\text{Eu}_2(\text{HTBA})_6(\text{H}_2\text{O})_6]_n$ (I**).** Salt $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ (reagent grade) (0.177 g, 0.463 mmol) was dissolved in water (10 mL), and solid H_2TBA (reagent grade) (0.200 g, 1.39 mmol) and 1 M NaOH to pH 4 were added. A white finely crystalline precipitate was formed and filtered off in 6–8 h. Single crystals of compound **I** were formed for 2 months at the slow evaporation of the filtrate, separated, and dried in air.

X-ray diffraction analysis. A yellow crystal of compound $0.35 \times 0.1 \times 0.08$ mm in size at 300 K was studied. Reflection intensities were measured on a SMART APEX II single-crystal diffractometer with a CCD detector (Bruker AXS, MoK_α radiation). Experimental absorption corrections were applied using the SADABS program [13] by the multiscan method. The model of the structure was established by direct methods and refined using the SHELXTL program package [14]. The positions of hydrogen atoms were revealed from difference electron density syntheses, idealized, and refined in the form bound to the main atoms. The experimental parameters and results for structure refinement are presented in Table 1.

Structure **I** was deposited with the Cambridge Crystallographic Data Centre (CCDC no. 987519;

Table 1. Experimental parameters and refinement results for structure **I**

Parameter	Value
Empirical formula	C ₂₄ H ₃₀ N ₁₂ O ₁₈ S ₆ Eu ₂
<i>M</i>	1270.9
Space group, <i>Z</i>	<i>P</i> 2/ <i>n</i> , 2
<i>a</i> , Å	14.1033(4)
<i>b</i> , Å	10.0988(4)
<i>c</i> , Å	15.4061(5)
β, deg	110.003(1)
<i>V</i> , Å ³	2061.9(1)
ρ _{calcd} , g/cm ³	2.047
μ, mm ^{−1}	3.405
Total number of reflections	24629
2θ _{max} , deg	71.32
Independent reflections (<i>R</i> _{int}), <i>N</i> ₁	9426 (0.0481)
Number of reflections with <i>F</i> > 4σ(<i>F</i>), <i>N</i> ₂	6870
Index range <i>h</i> , <i>k</i> , <i>l</i>	−12 ≤ <i>h</i> ≤ 23, −15 ≤ <i>k</i> ≤ 16, −25 ≤ <i>l</i> ≤ 16
Weighing scheme for <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 1.3193P]$, $P = \max(F_o^2 + 2F_c^2)/3$
Number of refined parameters	299
<i>R</i> (for <i>N</i> ₁ reflections)	0.0609
<i>R</i> (for <i>N</i> ₂ reflections)	0.0373
<i>wR</i> (<i>F</i> ²) (for <i>N</i> ₁ reflections)	0.0880
<i>wR</i> (<i>F</i> ²) (for <i>N</i> ₂ reflections)	0.0775
Goodness-of-fit	1.004
Extinction coefficient	Was not refined
(Δ/σ) _{max}	<0.001
Δρ _{max} /Δρ _{min} , e/Å ³	1.413/−1.902

deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

The independent part of the unit cell of structure **I** contains two Eu³⁺ ions in partial positions 2*e* and 2*f*, three HTBA[−] ions, and three water molecules in general positions. Two independent positions of Eu³⁺ have the same positional symmetry: the 2-fold axis; however, the coordination environments of the ions are different (Fig. 1). One of the Eu³⁺ ions is bound to six HTBA[−] ions (two terminal and four bridging) and two water molecules, and the second ion is bound to four HTBA[−] ions and four water molecules. The HTBA[−] ions are coordinated to Eu³⁺ only through the O atoms. The Eu–O bond lengths (2.330(2)–2.495(2) Å) are typical of the Eu(III) complexes [15]. The structure contains three independent HTBA[−] ions, one of which is terminal (C) and two others are bridging (A and B). Their geometric parameters almost coincide, for example, bond lengths C–H 1.253(3)–1.267(3), C(4)–C(5), C(5)–C(6) 1.383(4)–1.393(4), and C–S 1.676(3)–1.678(3) Å. The values of the parameters indicate the electron density delocalization in the atomic groups O=C–CH–C=O (Fig. 1). Both polyhedra Eu(1)O₈ and Eu(2)O₈ are square antiprisms bound to each other through bridging HTBA[−] ions to form an infinite layer in the plane perpendicular to the direction *x* + *z* (Fig. 2). The layer contains the 24-membered ring *r*(24) including both Eu(1) and Eu(2) atoms. The structure of the complex corresponds to the formula [Eu₂(HTBA–O, O')₄(HTBA–O)₂(H₂O)₆]_{*n*} and a name of catena-[tetrakis(μ₂-thiobarbiturato–O, O')bis(thiobarbiturato–O)-hexaaquadieuro-pium(III)] (Figs. 1 and 2).

An analysis of the structure shows twelve hydrogen bonds (Table 2) N–H...O, N–H...S, O–H...O, and O–H...S involving all HTBA[−] ions and all water molecules. The hydrogen bonds form a 3D framework containing a layer parallel to the *xy* plane and supramolecular motifs R₂²(8), S(6), R₂²(28), and R₄⁴(26) (Fig. 3) [16]. The parameters of the π–π interaction between the HTBA[−] ions (Table 3) of the head-to-tail type (Fig. 4) were determined using the PLATON program [17].

ACKNOWLEDGMENTS

This work was supported in the framework of the state program of the Ministry of Education and Sci-

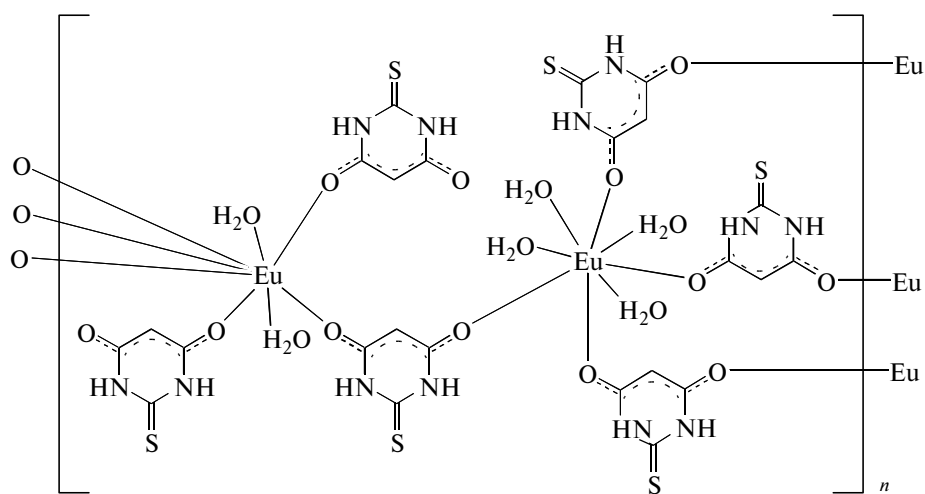


Fig. 1. Structure of complex $[\text{Eu}_2(\text{HTBA-O,O}')_4(\text{HTBA-O})_2(\text{H}_2\text{O})_6]_n$.

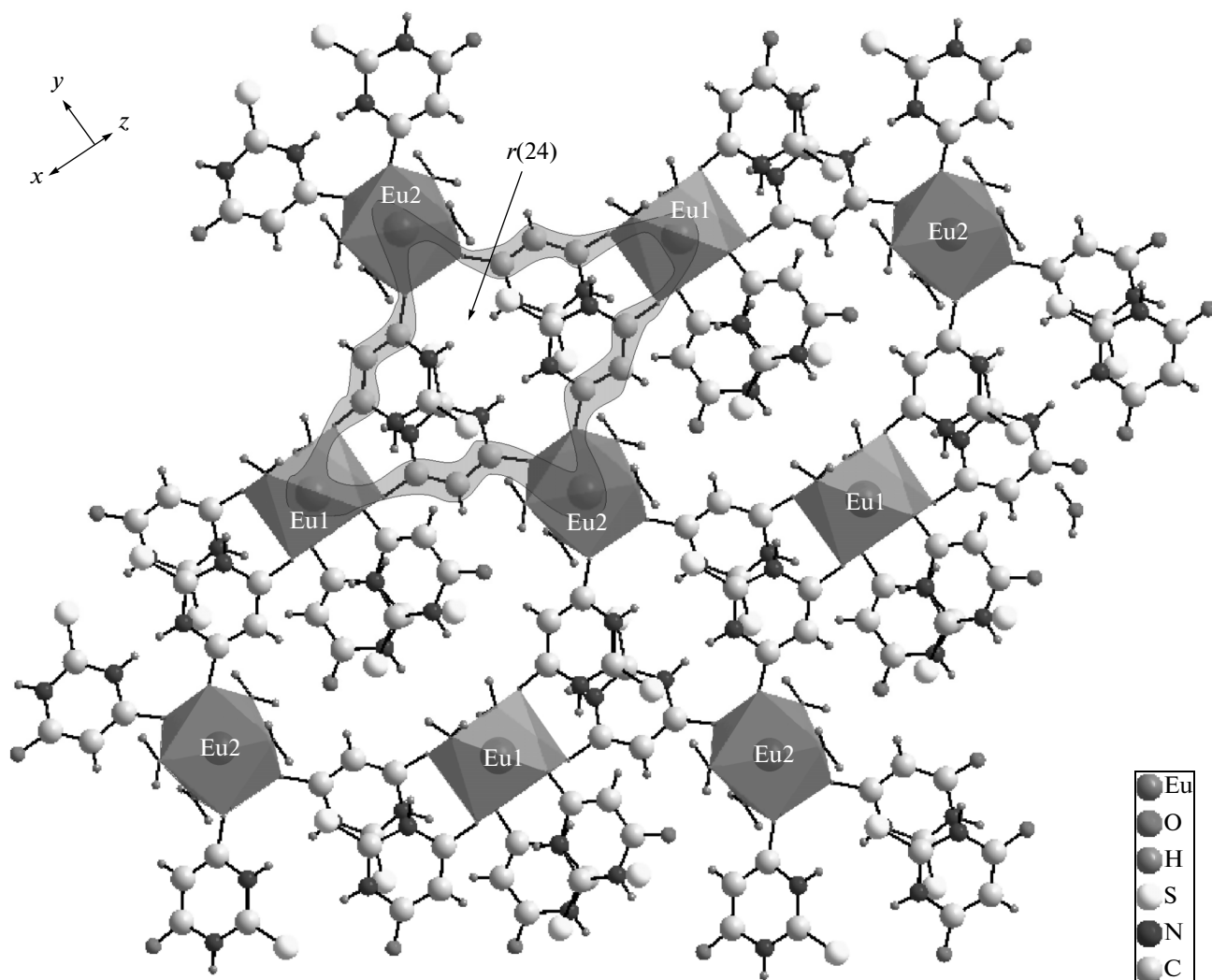


Fig. 2. Structure of the layer perpendicular to the direction $x + z$. The cyclic fragment of the structure is emphasized by lines.

Table 2. Geometric parameters of hydrogen bonds in structure **I**

Contact D—H···A	Distance, Å			Angle DHA, deg	Transform for atom A
	D—H	H···A	D···A		
N(1A)—H(1A)···O(2C)	0.86	2.14	2.932(3)	154	x, y, z
N(1B)—H(1B)···O(1w)	0.86	2.36	3.132(4)	149	x, y, z
N(1C)—H(1C)···O(2B)	0.86	2.05	2.797(3)	145	x, y, z
N(3A)—H(3A)···S(2) ⁱ	0.86	2.53	3.384(3)	176	$x + 1, y, z$
N(3B)—H(3B)···S(1) ⁱⁱ	0.86	2.41	3.261(3)	169	$x - 1, y, z$
N(3C)—H(3C)···O(1C) ⁱⁱⁱ	0.86	2.06	2.901(3)	164	$-x + 2, -y - 1, -z + 1$
O(1w)—H(11w)···S(3) ^{iv}	0.95(3)	2.38(2)	3.282(2)	158(3)	$x, y + 1, z$
O(1w)—H(12w)···O(1C) ^v	0.95(2)	1.85(3)	2.743(3)	157(4)	$-x + 2, -y, -z + 1$
O(2w)—H(21w)···S(2) ^{vi}	0.96(3)	2.31(3)	3.253(3)	170(3)	$-x + 1, -y, -z + 1$
O(2w)—H(22w)···S(2) ^{vii}	0.96(3)	2.36(2)	3.315(3)	176(4)	$x, y - 1, z$
O(3w)—H(31w)···O(1C) ⁱⁱ	0.96(4)	2.09(4)	2.962(4)	152(3)	$x - 1, y, z$
O(3w)—H(32w)···S(1) ⁱⁱ	0.96(2)	2.31(2)	3.238(3)	163(4)	$x - 1, y, z$

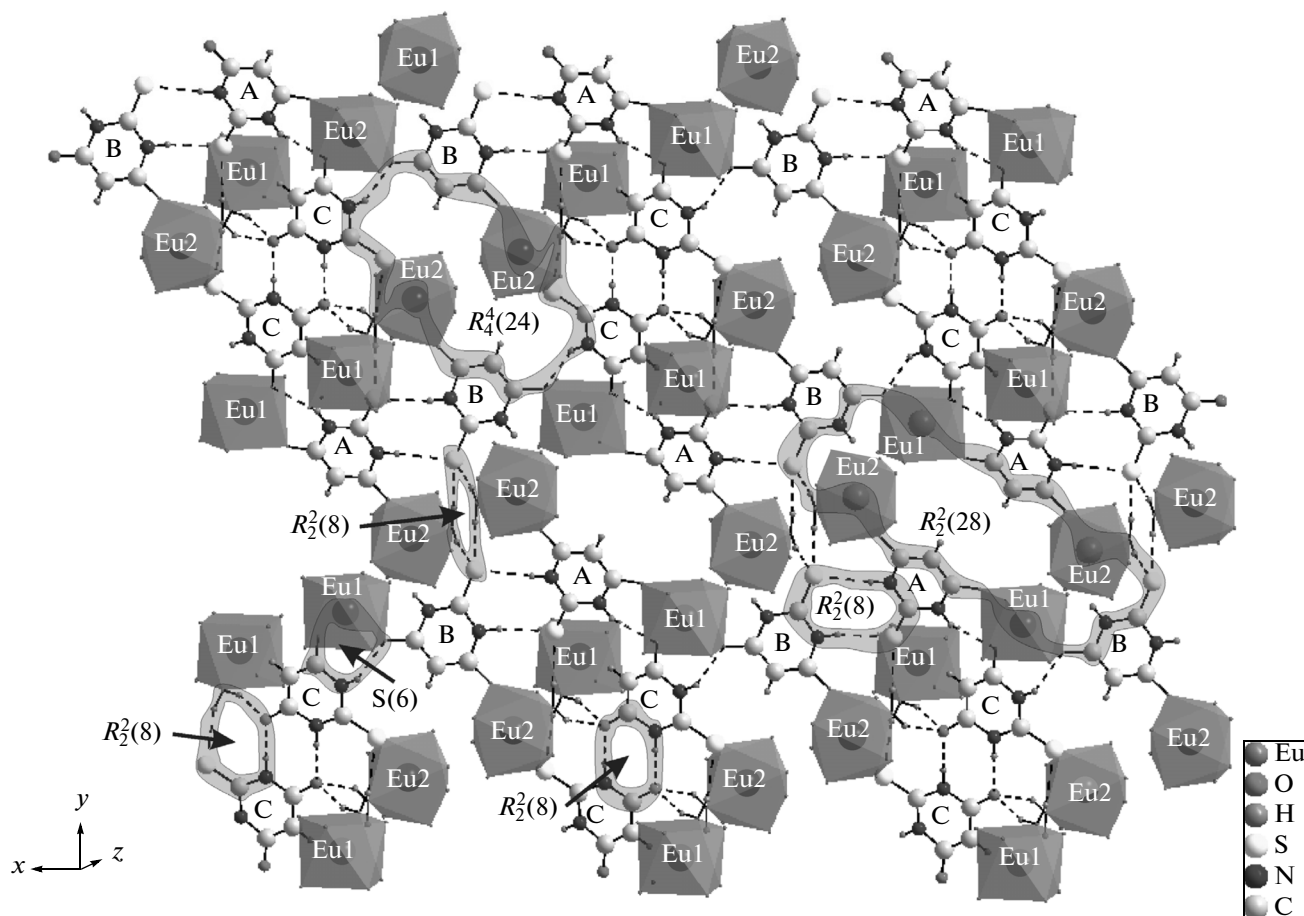
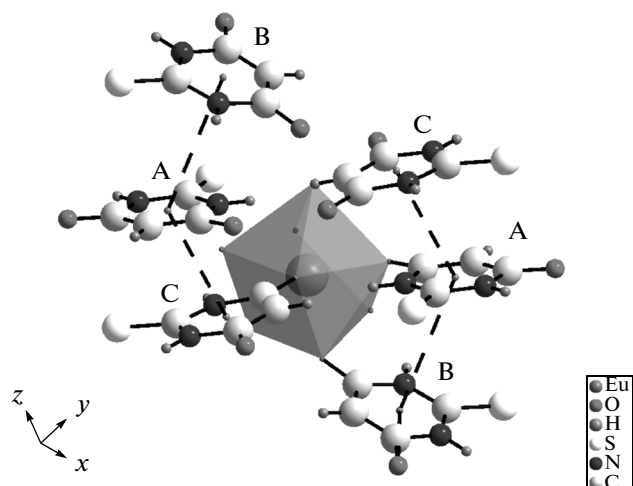
**Fig. 3.** Layer in the plane xy formed by hydrogen bonds. Supramolecular motifs are emphasized and designated. Independent HTBA[−] ions are designated by letters A, B, and C in Figs. 3 and 4.

Table 3. Parameters of the π – π interaction of HTBA[−] in crystal **I***

$\text{Cg}_i\text{--Cg}_j$	$d(\text{Cg--Cg}), \text{\AA}$	α, deg	β, deg	γ, deg	$\text{Cg}_i\text{--p}, \text{\AA}$	Shift, $\text{\AA}$
$\text{Cg}_1\text{--Cg}_2'$	3.916(2)	26.0(1)	26.5	18.8	3.506(1)	1.744(2)
$\text{Cg}_1\text{--Cg}_3''$	3.790(2)	9.6(1)	27.1	19.4	3.575(1)	1.258(2)

* Cg_1 is the center of the ring N(1A), C(2A), N(3A), C(4A), C(5A), and C(6A); Cg_2 is the center of the ring N(1B), C(2B), N(3B), C(4B), C(5B), and C(6B); Cg_3 is the center of the ring N(1C), C(2C), N(3C), C(4C), C(5C), and C(6C); Cg_2' was obtained from Cg_2 by the transform $(3/2 - x, y, 1/2 - z)$; Cg_3'' was obtained from Cg_3 by the transform $(2 - x, -y, 1 - z)$; $\text{Cg}_i\text{--p}$ is the distance between the center of the ring Cg_i and the plane of the ring Cg_i involved in the π – π interaction.

**Fig. 4.** π – π interaction between the centers of the rings of the HTBA[−] ions.

ence of the Russian Federation for research works of the Siberian Federal University in 2014.

REFERENCES

1. Binnemans, K., *Chem. Rev.*, 2009, vol. 109, p. 4283.
2. Zhang, L., Wang, Y., Ye, Z., et al., *Bioconjugate Chem.*, 2012, vol. 23, p. 1244.
3. Dzhabarov, V.I., Knyazev, A.A., Strelkov, M.V., et al., *Liq. Cryst.*, 2010, vol. 37, no. 3, p. 285.
4. Golovnev, N.N. and Molokeev, M.S., *Russ. J. Inorg. Chem.*, 2013, vol. 58, no. 10, p. 1193.
5. Golovnev, N.N. and Molokeev, M.S., *J. Struct. Chem.*, 2013, vol. 54, no. 5, p. 968.
6. Golovnev, N.N., Molokeev, M.S., and Belash, M.Yu., *J. Struct. Chem.*, 2013, vol. 54, no. 3, p. 566.
7. Golovnev, N.N., Molokeev, M.S., Vereshchagin, S.N., and Atuchin, V.V., *J. Coord. Chem.*, 2013, vol. 66, no. 23, p. 4119.
8. Golovnev, N.N. and Molokeev, M.S., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2013, vol. 69, no. 7, p. 704.
9. Golovnev, N.N., Molokeev, M.S., Vereshchagin, S.N., et al., *Polyhedron*, 2014, vol. 70, p. 71.
10. Golovnev, N.N. and Molokeev, M.S., *J. Struct. Chem.*, 2014, vol. 55, no. 1, p. 125.
11. Mashkovskii, M.D., *Lekarstvennye sredstva: posobie dlya vrachei* (Medicinal Drugs: Guide for Physicians), Moscow: Novaya volna.
12. Bamanie, F.H., Shehata, A.S., Moustafa, M.A., and Mashaly, M.M., *J. Am. Sci.*, 2012, vol. 8, no. 1, p. 481.
13. Sheldrick, G.M., *SADABS. Version 2.01*, Madison (WI, USA): Bruker AXS Inc., 2004.
14. Sheldrick, G.M., *SHELXTL. Version 6.10*, Madison (WI, USA): Bruker AXS Inc., 2004.
15. *Cambridge Structural Database. Version 5.34*, Cambridge (UK): Univ. of Cambridge, 2012.
16. Steed, J.W. and Atwood, J.L., *Supramolecular Chemistry*, New York: Wiley, Ch. 1–2, 2009.
17. *PLATON. A Multipurpose Crystallographic Tool*, Utrecht (The Netherlands): Utrecht Univ., 2008.

Translated by E. Yablonskaya