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

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**Abstract**—Complex $[Eu_2(HTBA)_6(H_2O)_6]_n$ (**I**), where $H_2TBA$ is 2-thiobarbituric acid $C_4H_4N_2O_2S$, 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, $\beta = 110.003(1)°$, $V = 2061.9(1)$ Å$^3$, space group $P2/n$, $Z = 2$. 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 $HTBA^-$.

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## 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 ($H_2TBA$, $C_4H_4N_2O_2S$). 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 $[Eu_2(HTBA)_6(H_2O)_6]_n$ (I).** Salt $Eu(CH_3COO)_3 \cdot 3H_2O$ (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, Mo$K_\alpha$ 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 | $C_{24}H_{30}N_{12}O_{18}S_6Eu_2$ |
| $M$ | 1270.9 |
| Space group, $Z$ | $P2/n$, 2 |
| $a$, Å | 14.1033(4) |
| $b$, Å | 10.0988(4) |
| $c$, Å | 15.4061(5) |
| β, deg | 110.003(1) |
| $V$, Å$^3$ | 2061.9(1) |
| $\rho_{calcd}$, g/cm$^3$ | 2.047 |
| μ, mm$^{-1}$ | 3.405 |
| Total number of reflections | 24629 |
| $2\theta_{max}$, deg | 71.32 |
| Independent reflections ($R_{int}$), $N_1$ | 9426 (0.0481) |
| Number of reflections with $F > 4\sigma(F)$, $N_2$ | 6870 |
| Index range $h$, $k$, $l$ | $-12 \le h \le 23$, $-15 \le k \le 16$, $-25 \le l \le 16$ |
| Weighing scheme for $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 1.3193P]$, $P = \max(F_o^2 + 2F_c^2)/3$ |
| Number of refined parameters | 299 |
| $R$ (for $N_1$ reflections) | 0.0609 |
| $R$ (for $N_2$ reflections) | 0.0373 |
| $wR(F^2)$ (for $N_1$ reflections) | 0.0880 |
| $wR(F^2)$ (for $N_2$ reflections) | 0.0775 |
| Goodness-of-fit | 1.004 |
| Extinction coefficient | Was not refined |
| $(\Delta/\sigma)_{max}$ | <0.001 |
| $\Delta\rho_{max}/\Delta\rho_{min}$, $e$/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 $Eu^{3+}$ ions in partial positions 2*e* and 2*f*, three $HTBA^-$ ions, and three water molecules in general positions. Two independent positions of $Eu^{3+}$ have the same positional symmetry: the 2-fold axis; however, the coordination environments of the ions are different (Fig. 1). One of the $Eu^{3+}$ 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 $Eu^{3+}$ 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 $Eu(1)O_8$ and $Eu(2)O_8$ 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 $[Eu_2(HTBA{-}O,O')_4(HTBA{-}O)_2(H_2O)_6]_n$ and a name of catena-[tetrakis($\mu_2$-thiobarbiturato-O,O')bis(thiobarbiturato-O)-hexaaquadieuropium(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 $R_2^2(8)$, S(6), $R_2^2(28)$, and $R_4^4(26)$ (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

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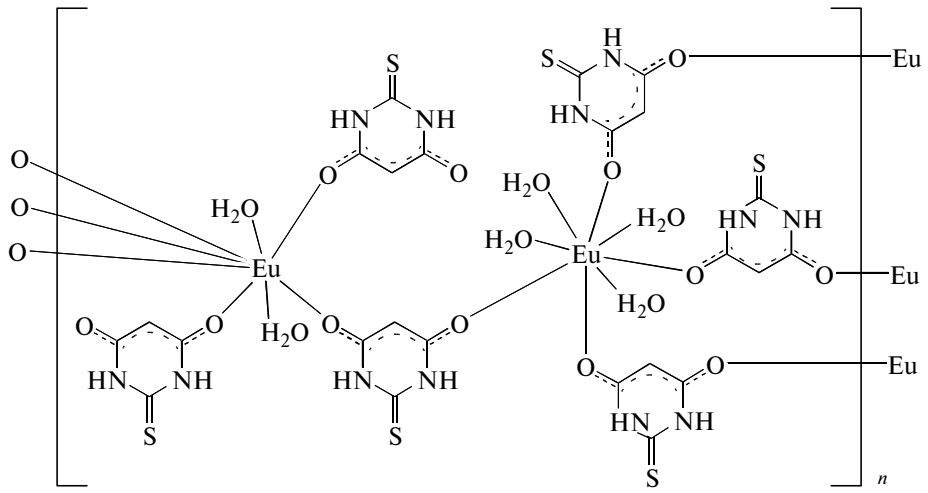


**Fig. 1.** Structure of complex $[Eu_2(HTBA–O,O')_4(HTBA–O)_2(H_2O)_6]_n$.

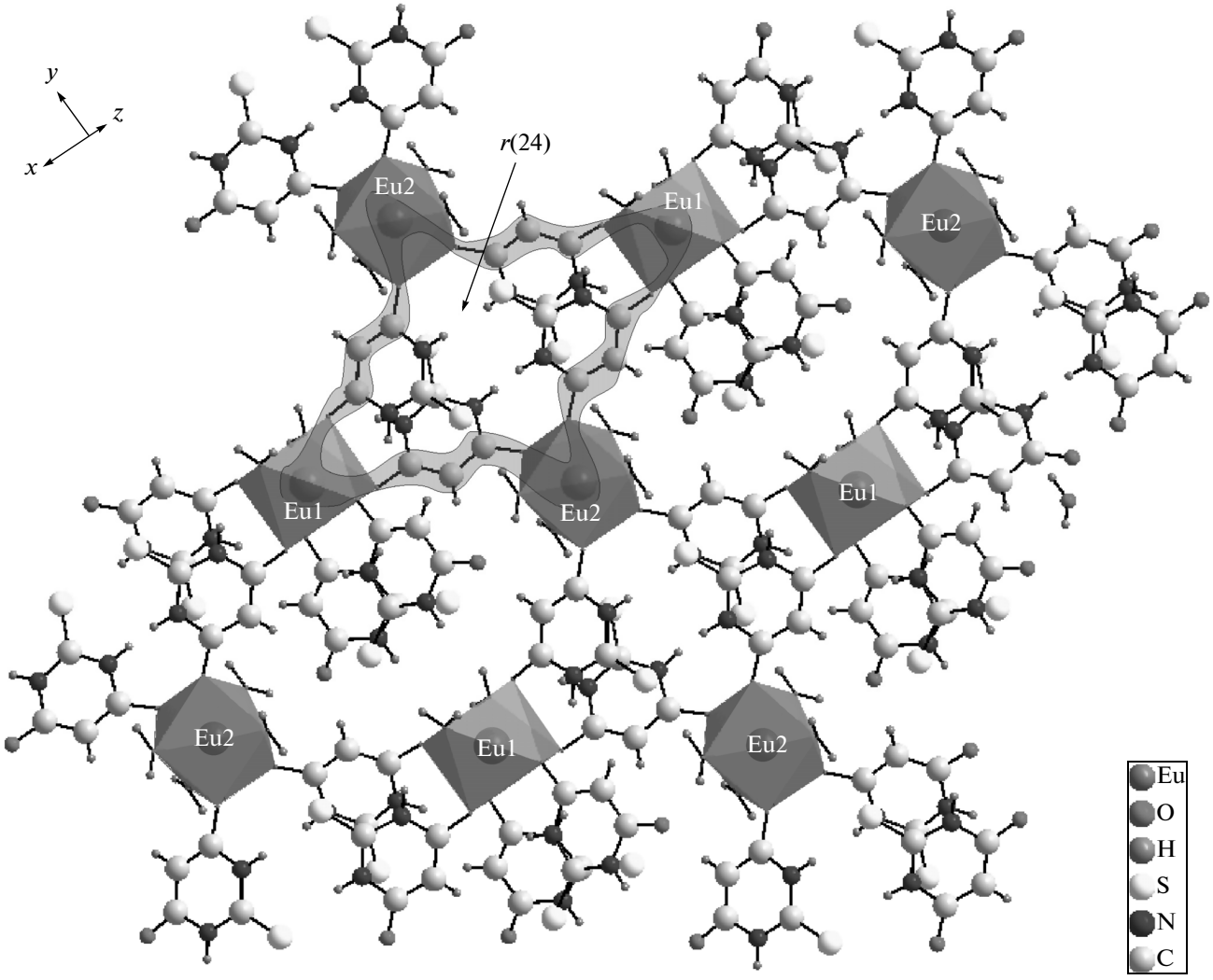


**Fig. 2.** Structure of the layer perpendicular to the direction $x + z$. The cyclic fragment of the structure is emphasized by lines.

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

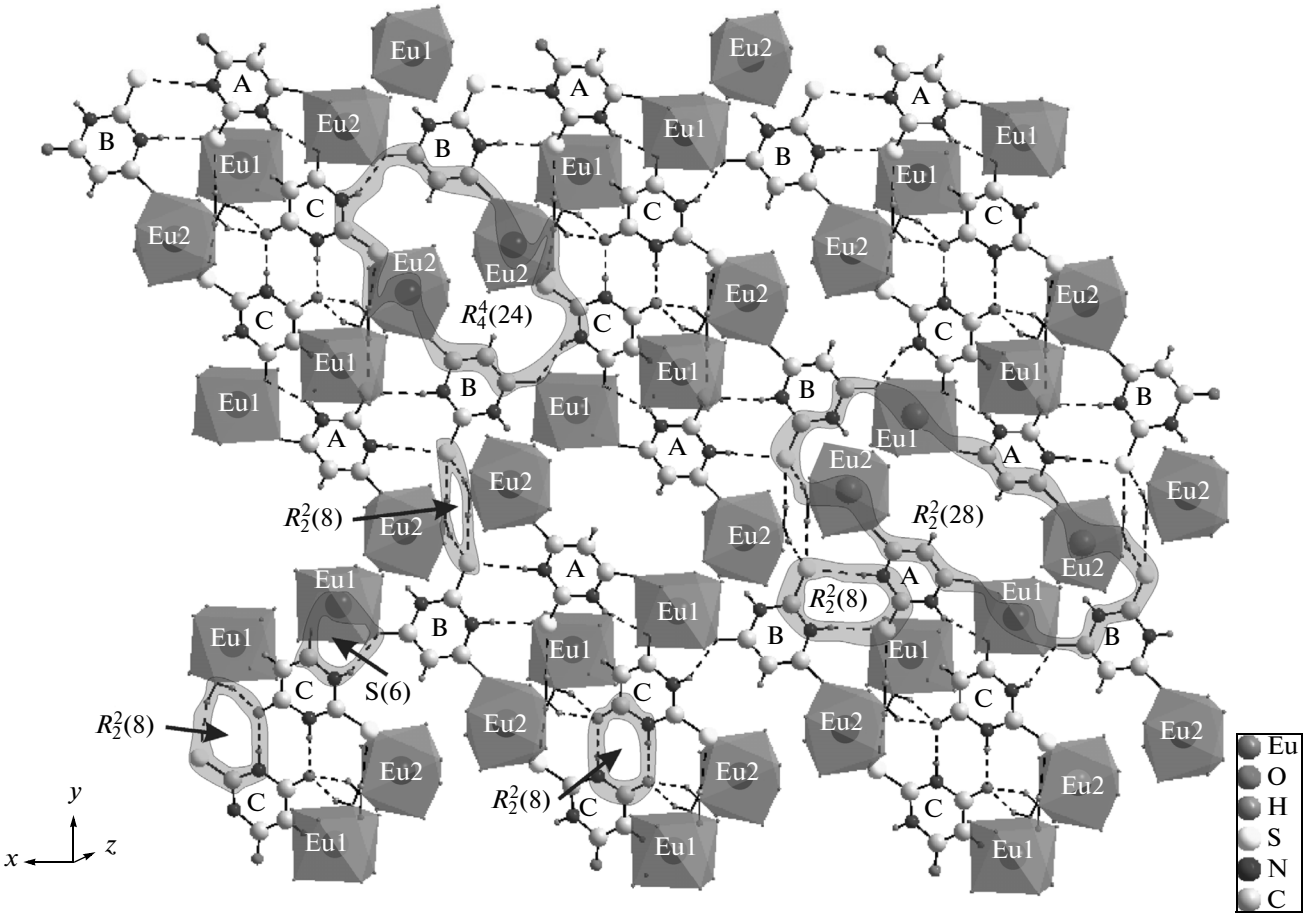


**Fig. 3.** Layer in the plane *xy* formed by hydrogen bonds. Supramolecular motifs are emphasized and designated. Independent $HTBA^-$ ions are designated by letters A, B, and C in Figs. 3 and 4.

**Table 3.** Parameters of the π–π interaction of $HTBA^-$ in crystal **I***

| $Cg_i$–$Cg_j$ | *d*(Cg–Cg), Å | α, deg | β, deg | γ, deg | $Cg_i$_p, Å | Shift, Å |
|---|---|---|---|---|---|---|
| $Cg_1$–$Cg_2'$ | 3.916(2) | 26.0(1) | 26.5 | 18.8 | 3.506(1) | 1.744(2) |
| $Cg_1$–$Cg_3''$ | 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(1*A*), C(2*A*), N(3*A*), C(4*A*), C(5*A*), and C(6*A*); $Cg_2$ is the center of the ring N(1*B*), C(2*B*), N(3*B*), C(4*B*), C(5*B*), and C(6*B*); $Cg_3$ is the center of the ring N(1*C*), C(2*C*), N(3*C*), C(4*C*), C(5*C*), and C(6*C*); $Cg_2'$ 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 $(2 - x, -y, 1 - z)$; $Cg_i$_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.

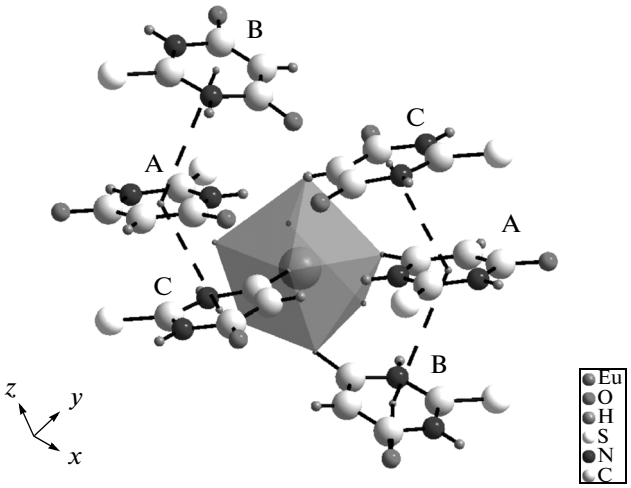


**Fig. 4.** π–π interaction between the centers of the rings of the $HTBA^-$ ions.

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