

# The Crystal Structure of Lead(II) 1,3-Diethyl-2-Thiobarbiturate

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**Abstract**—The complex  $[\text{Pb}_2(\text{DETBA})_4]_n$  (**I**), where HDETBA is 1,3-diethyl-2-thiobarbituric acid ( $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ ), was obtained and structurally characterized by X-ray diffraction (CIF file CCDC no. 1031501). The crystals of complex **I** are trigonal:  $a = 12.9503(3)$ ,  $c = 32.077(1)$  Å,  $V = 4658.9(3)$  Å<sup>3</sup>, space group  $R\bar{3}$ ,  $Z = 9$ . One of the crystallographically independent lead ions,  $\text{Pb}(1)^{2+}$ , is coordinated in an octahedral fashion by six  $\text{DETBA}^-$  ions through the O atoms. The other ion,  $\text{Pb}(2)^{2+}$ , is coordinated to six  $\text{DETBA}^-$  ions through three O atoms and three S atoms making up a trigonal prism. The polyhedra  $\text{Pb}(1)\text{O}_6$  and  $\text{Pb}(2)\text{O}_6$  are united through bridging  $\text{DETBA}^-$  ions into infinite layers. The ligands are linked by neither intermolecular hydrogen bonds nor  $\pi$ – $\pi$  interactions.

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## INTRODUCTION

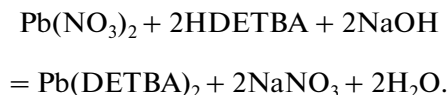
A number of derivatives of 2-thiobarbituric acid (thiobarbiturates [1]) are of therapeutic importance; sodium thiopental [2], thiobarbital (5,5-diethyl-2-thiobarbituric acid), and thiobutabarbital (5-butan-2-yl-5-ethyl-2-thiobarbituric acid) [3] are examples. They contain electron-donating N, O, and S atoms favorably arranged to form functionalized organometallic framework compounds [4]. Earlier, we have obtained and structurally characterized metal complexes with 2-thiobarbituric acid ( $\text{H}_2\text{TBA}$ ) [5–15] and 1,3-diethyl-2-thiobarbituric acid (HDETBA) [16]. Introduction of alkyl substituents into  $\text{H}_2\text{TBA}$  changed both the structures of the coordination polyhedra and supramolecular organization of the resulting complexes. Moreover, we have found that the ethyl substituents in the  $\text{DETBA}^-$  ion are on the same side of the plane of the heterocycle in MDETBA ( $M = \text{Li}$  or  $\text{Na}$ ) (*cis* isomer) [16] and on both sides in KDETBA (*trans* isomer). We assumed that the type of  $\text{DETBA}^-$  conformer in alkali metal complexes depends on the ionic radius of the metal. In the present study, we described the synthesis, structure, and IR spectrum of a new lead(II) complex with 1,3-diethyl-2-thiobarbiturate.

## EXPERIMENTAL

Lead(II) nitrate (reagent grade), HDETBA (99%, Sigma-Aldrich), and NaOH (reagent grade) were used.

**Synthesis of  $[\text{Pb}(\text{DETBA})_2]_n$**  To obtain the crystalline complex  $\text{Pb}(\text{DETBA})_2$  (**I**), a mixture of  $\text{Pb}(\text{NO}_3)_2$

(0.70 mmol), HDETBA (1.40 mmol), and NaOH (1.40 mmol) was stirred in water (5 mL) for 3–4 h and then kept at room temperature for 24 h to completion of the reaction:



The resulting white crystalline precipitate was collected by filtration, washed with ethanol, and dried in air to a constant weight. The yield of the product was 92–95%.

**X-ray diffraction study.** A colorless crystal of complex **I** ( $0.2 \times 0.2 \times 0.1$  mm) was examined at 293 K. Reflection intensities were measured on a SMART APEX II single-crystal diffractometer equipped with a CCD detector (Bruker AXS,  $\text{MoK}_\alpha$  radiation). Experimental absorption corrections were applied using a multiscan technique with the SADABS program [17]. The structure was solved by direct methods and refined with the SHELXTL program package [18]. The hydrogen atoms were located in difference electron-density maps, idealized, and refined together with their parent atoms. Crystallographic parameters and the data collection and refinement statistics for structure **I** are given in Table 1.

The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Structural Database (CCDC no. 1031501; deposit@ccdc.cam.ac.uk or [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

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

Parameter	Value
Empirical formula	C <sub>16</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> PbS <sub>2</sub>
<i>M</i>	605.68
Space group; <i>Z</i>	$R\bar{3}$ ; 9
<i>a</i> , Å	12.9503(3)
<i>c</i> , Å	32.077(1)
<i>V</i> , Å <sup>3</sup>	4658.9(3)
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	1.943
$\mu$ , mm <sup>-1</sup>	8.378
Number of measured reflections	13104
$2\theta_{\text{max}}$ , deg	25.676
Number of unique reflections ( $R_{\text{int}}$ ), $N_1$	1979 (0.0421)
Number of reflections with $F > 4\sigma(F)$ , $N_2$	1610
Ranges of <i>h</i> , <i>k</i> , and <i>l</i> indices	$-15 \leq h \leq 15, -15 \leq k \leq 12, -38 \leq l \leq 39$
Weighting scheme on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.014P)^2 + 7.151P]$ , $P = \max(F_o^2 + 2F_c^2)/3$
Number of parameters refined	125
<i>R</i> (for $N_1$ )	0.0369
<i>R</i> (for $N_2$ )	0.0226
$wR(F^2)$ (for $N_1$ )	0.0415
$wR(F^2)$ (for $N_2$ )	0.0381
GOOF	1.009
Extinction coefficient	Not refined
$(\Delta/\sigma)_{\text{max}}$	<0.001
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ , e/Å <sup>3</sup>	0.362/−0.450

## RESULTS AND DISCUSSION

The independent part of the unit cell of complex I contains two Pb<sup>2+</sup> ions (in special positions 3*b* and 6*c*) and a DETBA<sup>−</sup> ion with their atoms in general position 18*f* (Fig. 1). Two crystallographically independent positions of the Pb<sup>2+</sup> ions differ in both symmetry and coordination environment. For instance, the Pb(1) ion (on inversion axis  $\bar{3}$ ) is coordinated in an octahedral fashion by six DETBA<sup>−</sup> ions through O(1) atoms. The Pb(2) ion (on axis 3) is coordinated by six DETBA<sup>−</sup> ions through three O(2) atoms and three S atoms making up a trigonal prism. The bonding pattern in complex I is schematically shown in Fig. 2. The Pb–O (2.388(4)–2.490(3) Å) and Pb–S bond lengths (3.129(2) Å) are typical of Pb(II) complexes [19]. In

the DETBA<sup>−</sup> ion, the C(4)–O(1) (1.265(3) Å) and C(6)–O(2) bond lengths (1.312(3) Å) in a known polymorphic monocarbonyl thione modification of HDETBA are different [20]; in contrast, these bonds in complex I are close in length (1.248(7) and 1.265(6) Å, respectively). The same electron density delocalization in the fragments O=C–CH–C=O of the ligand DETBA<sup>−</sup> as in complex I has been noted for complexes MDETBA (M = Li, Na, or K) [16]. The C(2)–S bond in complex I (1.684(3) Å) is somewhat longer than that in HDETBA (1.658(2) Å) [20], in agreement with the coordination of the Pb(2) atom to sulfur atoms. As in MDETBA (M = Li, K, or Na) [16], the N(3)–C(4) and N(1)–C(6) bonds in the DETBA<sup>−</sup> ion of complex I are longer than those in HDETBA [20, 21], which can also be attributed to the coordina-

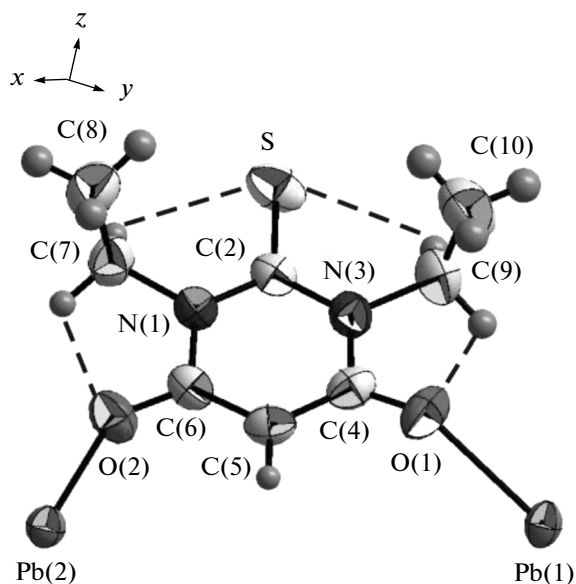


Fig. 1. Crystallographically independent part of the unit cell of  $\text{Pb}(\text{DETBA})_2$ .

tion of the  $\text{DETBA}^-$  ion to the metal ions. As with the tetrahedral complexes  $\text{LiDETBA}$  and  $\text{NaDETBA}$ , the  $\text{DETBA}^-$  ion in complex **I** is the *cis* isomer. As already noted, the ligand in  $\text{KDETBA}$  is in the *trans* conformation. Comparison of the radii of the  $\text{Pb}^{2+}$  (1.33 Å) and  $\text{K}^+$  ions (1.52 Å) for the coordination number 6 [22] agrees with the previous hypothesis about the determining influence of the cation size on the conformation of the coordinated  $\text{DETBA}^-$  ion.

The polyhedra  $\text{Pb}(1)\text{O}_6$  and  $\text{Pb}(2)\text{O}_6$  are united through bridging  $\text{HTBA}^-$  ligands into infinite layers in a plane perpendicular to axis  $z$  (Fig. 3). One can distinguish two 12-membered rings  $r(12)$  in every layer; one ring comprises a  $\text{Pb}(1)$  atom and a  $\text{Pb}(2)$  atom, while the other ring contains two  $\text{Pb}(2)$  atoms. Structure **I** can be formulated as  $[\text{Pb}_2(\mu_3\text{-DETBA-O,O',S})_4]_n$  and called *catena-tetrakis*( $\mu_3$ -1,3-diethyl-2-thiobarbiturato-O,O',S)dilead(II).

Analysis of structure **I** with the PLATON program [23] revealed four weak intramolecular hydrogen bonds [24]  $\text{C-H}\cdots\text{O}$  and  $\text{C-H}\cdots\text{S}$  (Table 2) but no  $\pi$ - $\pi$  interactions between the  $\text{DETBA}^-$  ions (the shortest distance between the centers of the rings is 4.941(2) Å).

The IR absorption spectra of  $\text{HDETBA}$  and complex **I** (in KBr pellets) were recorded on a Nicolet 6700 spectrometer. Instead of the band at  $1646\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$  [20]) in the IR spectrum of  $\text{HDETBA}$  (Fig. 4), the spectrum of complex **I** shows a very intense band at  $1587\text{ cm}^{-1}$ . The observed difference in these frequencies suggests the coordination of the ligand through the O atom. Assignment of the other bands in the IR spectrum of crystalline  $\text{HDETBA}$  is lacking [20]. The strong band in the IR spectrum of  $\text{HDETBA}$  at  $1160\text{ cm}^{-1}$  can be assigned, by analogy with 2-thiobarbituric acid [25], to the  $\nu(\text{C}=\text{S})$  vibrations. In the IR spectrum of complex **I**, this band vanishes; in addition, a new band appears at  $1192\text{ cm}^{-1}$ . These results agree with the coordination of the ligand  $\text{DETBA}^-$  through the O and S atoms.

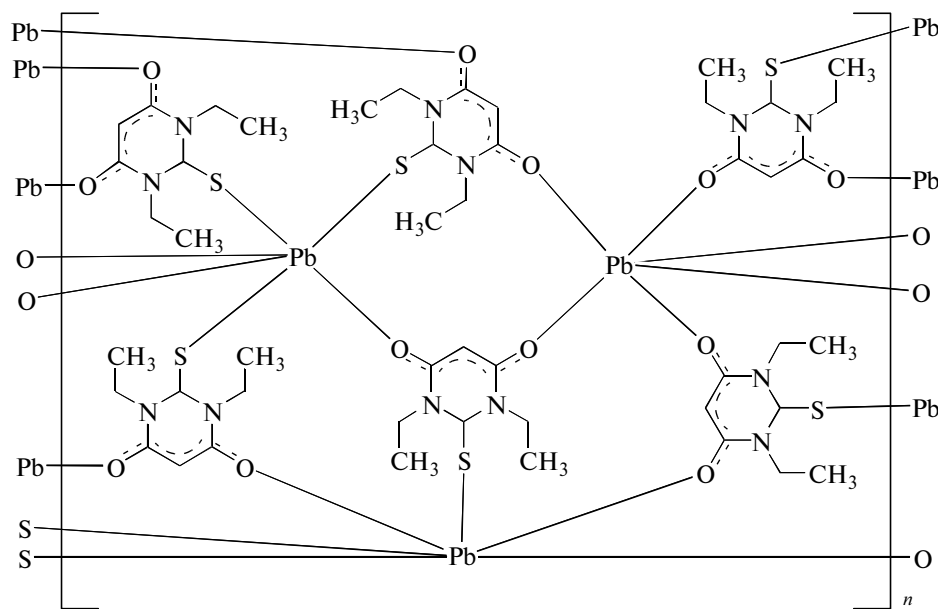
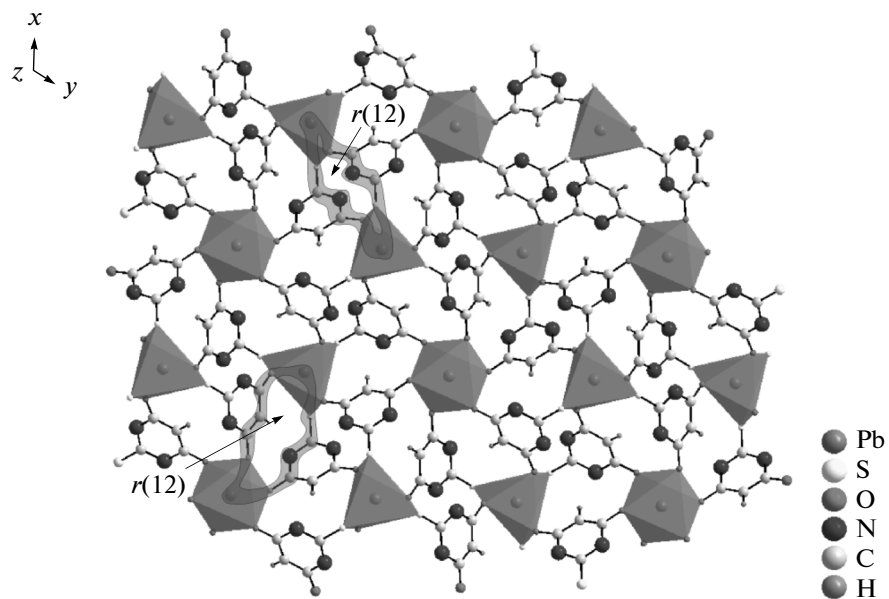
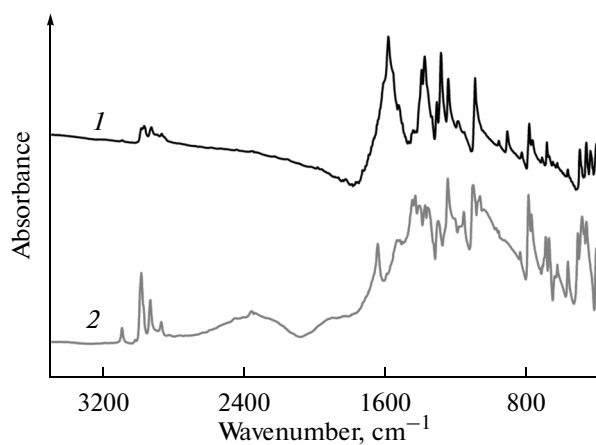


Fig. 2. Structure of the complex  $[\text{Pb}_2(\mu_3\text{-DETBA-O,O',S})_4]_n$ .



**Fig. 3.** Structure of the layer perpendicular to axis  $z$ . The cyclic fragments of the structure are indicated with rings. All  $C_2H_5$  groups are omitted for clarity.



**Fig. 4.** IR spectra of  $Pb(DETBA)_2$  (1) and HDETBA (2).

**Table 2.** Geometrical parameters of the intramolecular hydrogen bonds in structure I

Hydrogen bond	Distance, Å			Angle DHA, deg
	D–H	H...A	D...A	
C(7)–H(71)···O(2)	0.97	2.24	2.657(6)	104
C(9)–H(91)···O(1)	0.97	2.35	2.669(5)	98
C(7)–H(72)···S	0.97	2.56	2.978(6)	106
C(9)–H(92)···S	0.97	2.57	2.998(5)	107

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