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

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Abstract—The complex $[Pb_2(DETBA)_4]_n$ (**I**), where HDETBA is 1,3-diethyl-2-thiobarbituric acid ($C_8H_{12}N_2O_2S$), 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^3, space group $R\bar{3}$, $Z = 9$. One of the crystallographically independent lead ions, $Pb(1)^{2+}$, is coordinated in an octahedral fashion by six $DETBA^-$ ions through the O atoms. The other ion, $Pb(2)^{2+}$, is coordinated to six $DETBA^-$ ions through three O atoms and three S atoms making up a trigonal prism. The polyhedra $Pb(1)O_6$ and $Pb(2)O_6$ are united through bridging $DETBA^-$ ions into infinite layers. The ligands are linked by neither intermolecular hydrogen bonds nor π–π 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 (H_2TBA) [5–15] and 1,3-diethyl-2-thiobarbituric acid (HDETBA) [16]. Introduction of alkyl substituents into H_2TBA 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 $DETBA^-$ ion are on the same side of the plane of the heterocycle in MDETBA (M = Li or Na) (*cis* isomer) [16] and on both sides in KDETBA (*trans* isomer). We assumed that the type of $DETBA^-$ 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 $[Pb(DETBA)_2]_n$. To obtain the crystalline complex $Pb(DETBA)_2$ (**I**), a mixture of $Pb(NO_3)_2$ (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:

$$Pb(NO_3)_2 + 2HDETBA + 2NaOH$$
$$= Pb(DETBA)_2 + 2NaNO_3 + 2H_2O.$$

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 × 0.2 × 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, MoK_α 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).

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

Parameter	Value
Empirical formula	$C_{16}H_{22}N_4O_4PbS_2$
M	605.68
Space group; Z	$R\bar{3}$; 9
a, Å	12.9503(3)
c, Å	32.077(1)
V, Å^3	4658.9(3)
ρ_{calcd}, g/cm^3	1.943
μ, mm^{-1}	8.378
Number of measured reflections	13104
$2\theta_{max}$, deg	25.676
Number of unique reflections (R_{int}), N_1	1979 (0.0421)
Number of reflections with $F > 4\sigma(F)$, N_2	1610
Ranges of h, k, and l indices	$-15 \le h \le 15$, $-15 \le k \le 12$, $-38 \le l \le 39$
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
R (for N_1)	0.0369
R (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
$(\Delta/\sigma)_{max}$	<0.001
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.362/−0.450

RESULTS AND DISCUSSION

The independent part of the unit cell of complex **I** contains two Pb^{2+} ions (in special positions 3*b* and 6*c*) and a $DETBA^-$ ion with their atoms in general position 18*f* (Fig. 1). Two crystallographically independent positions of the Pb^{2+} 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 $DETBA^-$ ions through O(1) atoms. The Pb(2) ion (on axis 3) is coordinated by six $DETBA^-$ 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 $DETBA^-$ 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 $DETBA^-$ 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 $DETBA^-$ ion of complex **I** are longer than those in HDETBA [20, 21], which can also be attributed to the coordina-

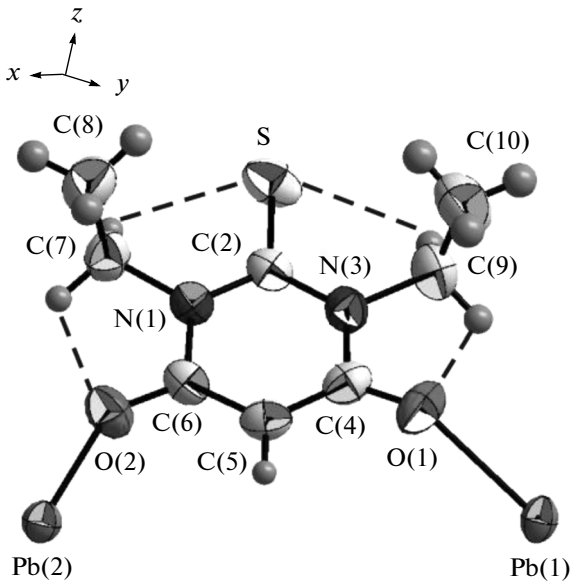

Fig. 1. Crystallographically independent part of the unit cell of $Pb(DETBA)_2$.

tion of the $DETBA^-$ ion to the metal ions. As with the tetrahedral complexes LiDETBA and NaDETBA, the $DETBA^-$ ion in complex **I** is the *cis* isomer. As already noted, the ligand in KDETBA is in the *trans* conformation. Comparison of the radii of the Pb^{2+} (1.33 Å) and 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 $DETBA^-$ ion.

The polyhedra $Pb(1)O_6$ and $Pb(2)O_6$ are united through bridging $HTBA^-$ 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 Pb(1) atom and a Pb(2) atom, while the other ring contains two Pb(2) atoms. Structure **I** can be formulated as $[Pb_2(\mu_3\text{-DETBA–O,O',S})_4]_n$ and called *catena*-tetrakis(μ_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] C–H···O and C–H···S (Table 2) but no π–π interactions between the $DETBA^-$ ions (the shortest distance between the centers of the rings is 4.941(2) Å).

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

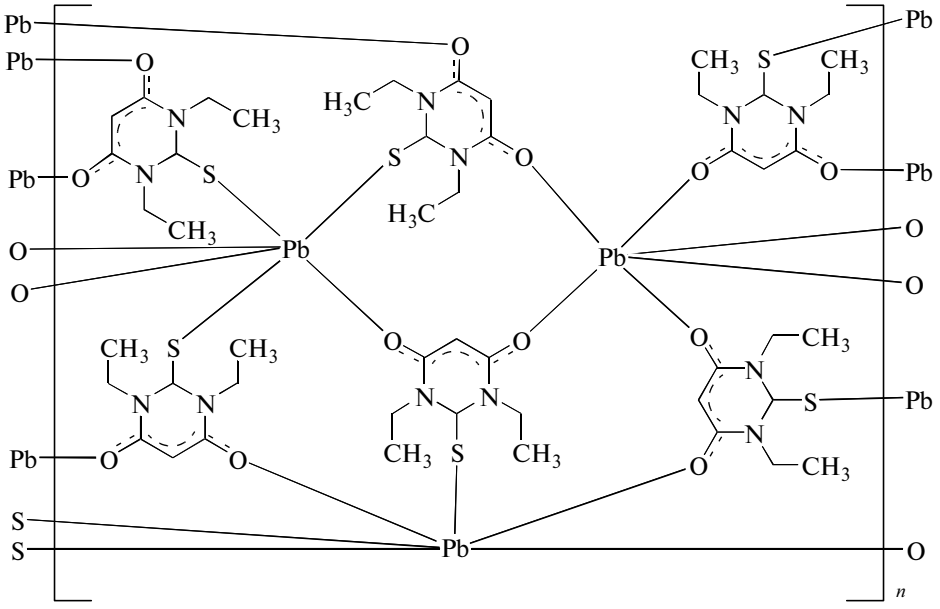

Fig. 2. Structure of the complex $[Pb_2(\mu_3\text{-DETBA–O,O',S})_4]_n$.

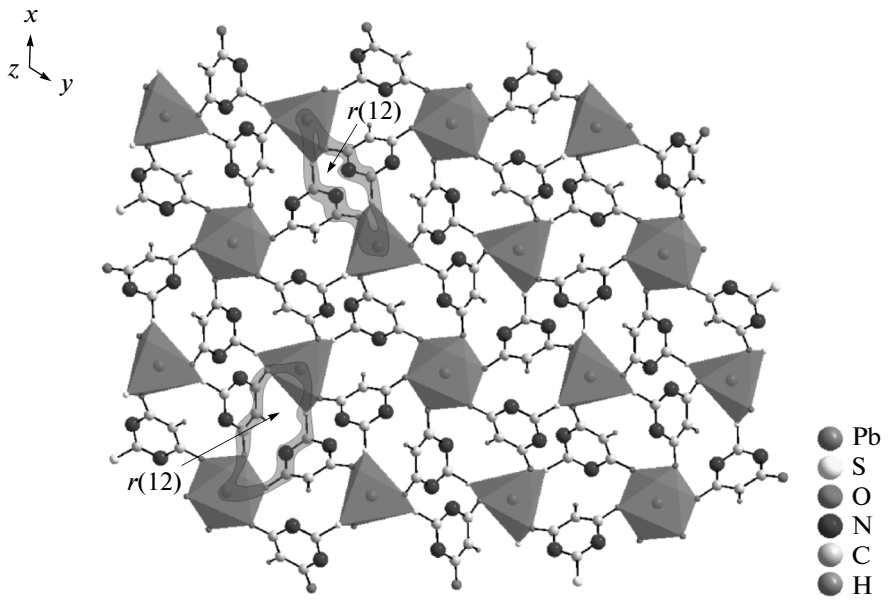

Fig. 3. Structure of the layer perpendicular to axis *z*. The cyclic fragments of the structure are indicated with rings. All C_2H_5 groups are omitted for clarity.

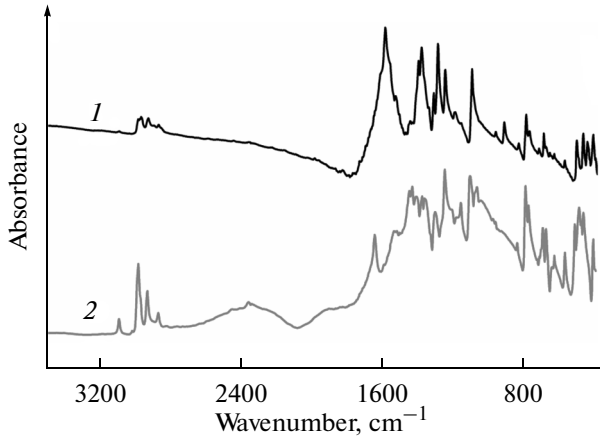

Fig. 4. IR spectra of $Pb(DETBA)_2$ (*1*) and HDETBA (*2*).

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

Hydrogen bond	Distance, Å			Angle DHA, deg
D–H···A	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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