

Structure of Tetrakis((1,3-Diethyl-2-Thiobarbiturato)(Butanol-1))dicobalt(II)

N. N. Golovnev^{a, *}, M. S. Molochev^{b, c}, A. I. Smolentsev^{d, e}, and M. K. Lesnikov^a

^aSiberian Federal University, Krasnoyarsk, Russia

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

^cFar East State Transport University, Khabarovsk, 680021 Russia

^dNikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia

^eNovosibirsk National Research State University, Novosibirsk, 630090 Russia

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

Received April 21, 2016

Abstract—The structure of the dimeric complex [Co₂(BuOH)₄(Detba)₄] (**I**), where HDetba is 1,3-diethyl-2-thiobarbituric acid, and BuOH is butanol-1, is determined (CIF file CCDC 1475273), and its IR spectrum is studied. The crystals are monoclinic: $a = 10.7185(5)$, $b = 21.985(1)$, $c = 12.7235(7)$ Å, $\beta = 92.196(2)^\circ$, $V = 2996.1(3)$ Å³, space group $P2_1/c$, $Z = 2$. The Co²⁺ ions in compound **I** are joined in pairs by bridging ligands μ_2 -Detba⁻-O,O'. In addition, each of them is linked through the O atoms to one terminal Detba⁻ ion and two BuOH molecules to form a trigonal bipyramid CoO₅. Hydrogen bonds O—H···O formed by BuOH and Detba⁻ join the binuclear complexes into an infinite chain. The data of IR spectroscopy are consistent with the results of X-ray diffraction analysis.

Keywords: cobalt(II), 1,3-diethyl-2-thiobarbituric acid, butanol-1, dimeric complex, structure, IR spectrum

DOI: 10.1134/S1070328417010031

INTRODUCTION

Cobalt complexes are promising catalysts of the hydrosilylation of alkenes and alkynes [1] and epoxidation [2]. The cage Co(II) compounds containing solvent molecules, for example, aliphatic alcohols, in the pores are of interest [3], since porous materials with useful adsorption and catalytic properties can be obtained by the removal of the solvent molecules [4].

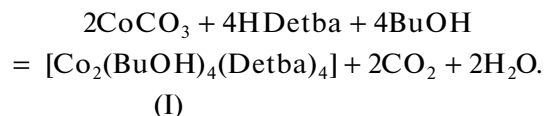
2-Thiobarbituric acid derivatives (H₂Tba) are widely used in medicine [5]. They form coordination compounds with metal ions due to the presence of N, O, and S donor atoms. Some of these coordination compounds can possess useful pharmaceutical properties [6] and find use in technology [7]. Unlike H₂Tba, complexes of its derivatives with *d*-element ions are poorly studied. For example, the structure of only one complex of 1,3-diethyl-2-thiobarbituric acid (HDetba) with Ag(I) was established of all *N,N*-substituted thiobarbituric acids [8]. Some compounds based on HDetba are semiconductors [9] and materials of nonlinear optics [10] and play an important role in medicinal and pharmaceutical chemistry [11].

In this work, complex [Co₂(BuOH)₄(Detba)₄] (**I**), where BuOH is butanol-1, was synthesized and its crystal structure was determined by X-ray diffraction analysis.

EXPERIMENTAL

HDetba (Sigma-Aldrich, 99%), CoCO₃ (reagent grade), and butanol-1 (reagent grade) were used.

Synthesis of I. A mixture of CoCO₃ (0.059 g, 0.50 mmol), HDetba (0.20 g, 1 mmol), and BuOH (2–3 mL) was heated at 70–80°C until the reactants were dissolved completely to form an intensively colored blue-violet solution. The following reaction occurred:



A violet crystalline precipitate was formed due to the evaporation of the solvent at room temperature for 2–3 weeks almost to dryness and then dried between filter paper sheets. A single crystal suitable for X-ray diffraction analysis was chosen directly from the overall mixture of the precipitate. The yield of compound **I** was ~90%.

For C₄₈H₈₄N₈O₁₂S₄Co₂

anal. calcd., %: C, 47.7; H, 6.99; N, 9.45; S, 10.6
Found, %: C, 48.3; H, 7.23; N, 9.55; S, 10.9.

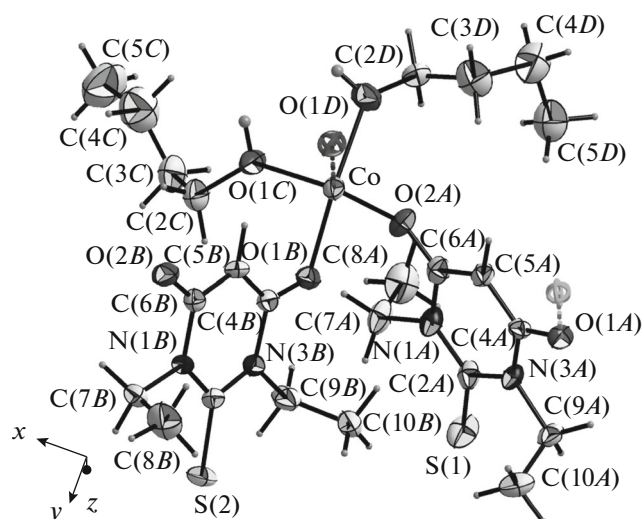


Fig. 1. Independent part of the cell in compound I. Only one of two orientations of the BuOH molecules is shown. The probability of thermal ellipsoids is 50%.

IR of **I** (ν , cm^{-1}): 1161 $\nu(\text{CS})$; 1586 and 1640 $\nu(\text{CO})$; 2961, 2981, and 3094 $\nu(\text{CH})$; and 3367 $\nu(\text{NH})$. Band assignment was made according to [12].

X-ray diffraction analysis. Intensities of X-ray reflections from a violet crystal $0.5 \times 0.2 \times 0.05$ mm in size were measured at 150(2) K on a Bruker-Nonius X8 Apex single-crystal diffractometer with a CCD detector (Bruker AXS) ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å). The cell corresponding to the monoclinic crystal system (space group $P2_1/c$) was determined from the statistic analysis of all reflections. The search for the model was carried out by direct methods using the SHELXS program [13]. As a result, the coordinates of all non-hydrogen atoms were found. The obtained structure was refined by the least-squares method (SHELXL-97). The absence of additional omitted symmetry elements and possible holes was established using the PLATON program [14]. Each BuOH molecule in the independent part of the cell is disordered over two positions. The thermal parameters of all non-hydrogen atoms were refined in the anisotropic approximation. The coordinates of all hydrogen atoms, except for those in the OH groups of the BuOH molecules, were idealized and refined together with heavy atoms by the riding model. The hydrogen atoms of the OH groups were revealed by the difference electron density synthesis, and their coordinates were refined without restraints. Selected crystallographic characteristics and experimental parameters were as follows: $FW = 1211.33$, $a = 10.7185(5)$, $b = 21.985(1)$, $c = 12.7235(7)$ Å, $\beta = 92.196(2)^\circ$, $V = 2996.1(3)$ Å³, space group $P2_1/c$, $Z = 2$, $\rho_{\text{calcd}} = 1.343$ g/cm³, $\mu = 0.754$ mm⁻¹, $2\theta_{\text{max}} = 51.35^\circ$, number of measured reflections 24414, number of independent

reflections 5669, $R_{\text{int}} = 6.27\%$, $R_1 = 9.48\%$, $wR(F^2) = 21.19\%$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.837/-0.834$ e/Å³.

The powder X-ray pattern of the polycrystalline sample of compound **I** at room temperature (a Bruker D8 ADVANCE diffractometer, (Center for Collective Use of the Institute of Physics, Siberian Branch, Russian Academy of Sciences), VANTEC linear detector, $\text{CuK}\alpha$ radiation) coincided with that calculated from the single-crystal data, which confirmed the identity of the polycrystals and the studied single crystal.

The graphical representation of the crystal structure and molecules was constructed in the DIAMOND program [15]. The structure of compound **I** was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1475273; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The independent part of the cell of compound **I** contains one Co^{2+} ion, two Detba^- ions (A and B), and two BuOH molecules (Fig. 1). The C–O, C–N, and C–C bond lengths and the corresponding bond angles in both Detba^- ligands coincided with those established earlier in other coordination compounds [16–19]. The C(8)–C(7)–C(9)–C(10) torsion angles for A and B Detba^- ions differ considerably: $156.7(6)^\circ$ and $0.5(7)^\circ$, respectively. Therefore, according to the previously proposed classification [16, 17], ion A is a conformer of the type (B) and ion B is a conformer of the type (A). A similar situation where both conformers are present in one compound has been observed previously [18], but this is a rare case. The Co–O bond lengths (1.967(4)–2.148(6) Å (Table 1)) in compound **I** are typical of the Co(II) complexes [20]. Only one structure of the Co(II) complex with the BuOH molecules coordinated through the oxygen atoms was determined [3]. In this structure, the Co–O bond lengths (2.146 Å) are comparable with the values obtained by us: Co–O(1C) 2.010(5) and Co–O(1D) 2.148(6) Å. The Co^{2+} ion is coordinated by two bridging Detba^- ions (A), one terminal Detba^- ion (B), and two terminal BuOH molecules to form a CoO_5 polyhedron in the form of a trigonal bipyramid. Two bridging μ_2 - Detba^- ions are joined by the Co^{2+} ions into a binuclear complex with 12-membered ring closure. A similar ring was observed in other related compounds of H_2Tba [21]. The retention of the $\nu(\text{C}=\text{O})$ frequency of the HDetba molecule at 1640 cm^{-1} [12] in the IR spectrum of compound **I** is consistent with the fact that the O atoms of some carbonyl groups are not involved in the binding of the Detba^- ligand, and the appearance of a new band at 1586 cm^{-1} confirms the O-coordination of Detba^- due to other carbonyl groups. The band at 1161 cm^{-1} $\nu(\text{C}=\text{S})$ in the IR spectra of HDetba and compound **I** indicates that the S

Table 1. Selected bond lengths (Å) and angles (deg) in the structure of compound **I***

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Co–O(2A)	1.967(4)	Co–O(1B)	2.022(5)
Co–O(1A) ^{#1}	2.004(4)	Co–O(1D)	2.148(6)
Co–O(1C)	2.010(5)		
Angle	ω, deg	Angle	ω, deg
O(2A)CoO(1A) ^{#1}	133.2(2)	O(1C)CoO(1B)	96.6(2)
O(2A)CoO(1C)	119.6(2)	O(2A)CoO(1D)	85.2(2)
O(1A) ^{#1} CoO(1C)	103.9(2)	O(1A) ^{#1} CoO(1D)	82.0(2)
O(2A)CoO(1B)	88.7(2)	O(1C)CoO(1D)	84.6(2)
O(1A) ^{#1} CoO(1B)	103.8(2)	O(1B)CoO(1D)	17.5(2)
A		B	
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
S(1)–C(2A)	1.654(7)	S(2)–C(2B)	1.677(6)
O(1A)–C(4A)	1.271(7)	O(1B)–C(4B)	1.266(8)
O(2A)–C(6A)	1.272(8)	O(2B)–C(6B)	1.273(8)
N(1A)–C(2A)	1.382(9)	N(1B)–C(2B)	1.380(9)
N(1A)–C(6A)	1.409(9)	N(1B)–C(6B)	1.408(8)
N(1A)–C(7A)	1.483(8)	N(1B)–C(7B)	1.481(8)
N(3A)–C(2A)	1.386(8)	N(3B)–C(2B)	1.376(9)
N(3A)–C(4A)	1.391(8)	N(3B)–C(4B)	1.413(8)
N(3A)–C(9A)	1.482(8)	N(3B)–C(9B)	1.473(9)
C(4A)–C(5A)	1.386(8)	C(4B)–C(5B)	1.377(9)
C(5A)–C(6A)	1.359(9)	C(5B)–C(6B)	1.385(9)

* Symmetry procedure: ^{#1} $-x + 1, -y, -z + 1$.

atom does not participate in the coordination of the ligand and in hydrogen bonding. Both BuOH molecules and one Detba⁻ ion (B) participate in two inter-

molecular hydrogen bonds O–H···O (Table 2). The hydrogen bonds join the binuclear complexes into an infinite chain along the *x* axis (Fig. 2). Supramolecular

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

D–H···A	Distance, Å			Angle D–H···A
	D–H	H···A	D···A	
O(1C)–H(1C)···O(2B) ^{#1}	0.92(9)	1.68(9)	2.565(6)	163(9)
O(1D)–H(1D)···O(2B) ^{#2}	0.85(9)	1.9(1)	2.724(7)	155(8)

* Symmetry procedure: ^{#1} $2 - x, -y, 1 - z$; ^{#2} $x, 1/2 - y, -1/2 + z$.

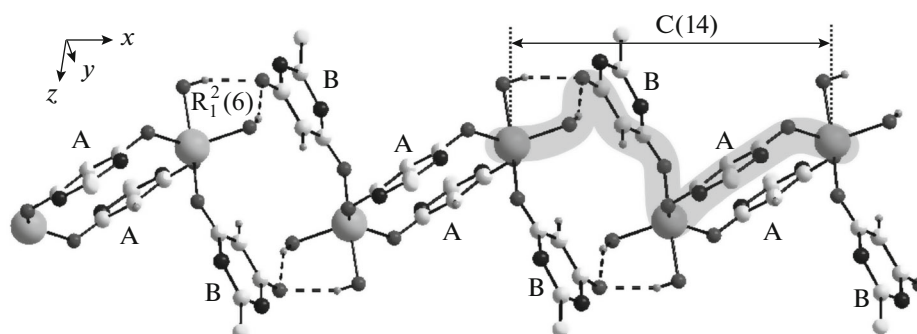


Fig. 2. Hydrogen bonding in compound I. The $\text{CH}_3\text{--CH}_2$ fragments of the Detba^- ions and $\text{CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$ of the BuOH molecules are omitted.

motifs $\text{R}_1^2(6)$ and $\text{C}(14)$ can be distinguished in the chain. The minimum distance between the centers of the Detba^- rings ($5.774(4)$ Å) indicates the absence of the $\pi\text{--}\pi$ interaction.

ACKNOWLEDGMENTS

This work was carried out at the Siberian Federal University in terms of the state task of the Ministry of Education and Science of the Russian Federation for 2014–2016 (project no. 3049).

REFERENCES

- Sun, J. and Deng, L., *ACS Catalysis*, 2016, vol. 6, no. 1, p. 290.
- Sha, S., Yang, H., Li, J., et al., *Catal. Commun.*, 2014, vol. 43, p. 146.
- Chen, Q., Lin, J.-B., Xue, W., et al., *Inorg. Chem.*, 2011, vol. 50, no. 6, p. 2321.
- Butova, V.V., Soldatov, M.A., Guda, A.A., et al., *Russ. Chem. Rev.*, 2016, vol. 85, no. 3, p. 280.
- Dawon, R.M.C., Elliot, D.C., Elliot, W.H, and Jones, K.M., *Data for Biochemical Research*, Oxford: Clarendon, 1986.
- Masoud, M.S., Khalil, E.A., Hindawy, A.M., et al., *Spectrochim. Acta, Part A*, 2004, vol. 60, no. 12, p. 2807.
- Mahmudov, K.T., Kopylovich, M.N., Maharramov, A.M., et al., *Coord. Chem. Rev.*, 2014, vol. 265, p. 1.
- Golovnev, N.N., Molokeyev, M.S., and Lutoshkin, M.A., *Russ. J. Inorg. Chem.*, 2015, vol. 60, no. 5, p. 572.
- Shu, Y., Mikosch, A., and Winzenberg, K.N., *J. Mater. Chem.*, 2014, vol. 2, p. 3895.
- Razvi, M.A.N., Bakry, A.H., Afzal, S.M., et al., *Mater. Lett.*, 2015, vol. 144, p. 131.
- Ahluwalia, V.K. and Aggarwal, R., *Proc. Nat. Acad. Sci. India. A*, 1996, vol. 62, no. 5, p. 369.
- Bideau, J.P., Huong, P.V., and Toure, S., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1976, vol. 32, p. 481.
- Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, no. 1, p. 112.
- PLATON. *A Multipurpose Crystallographic Tool*, Utrecht (Netherlands): Univ. of Utrecht, 2008.
- Brandenburg, K. and Berndt, M., *Diamond, Visual Crystal Structure Information System CRYSTAL IMPACT*, Postfach, p. 1251.
- Golovnev, N.N., Molokeyev, M.S., Vereshchagin, S.N., et al., *Polyhedron*, 2015, vol. 85, p. 493.
- Molokeyev, M.S., Golovnev, N.N., Vereshchagin, S.N., and Atuchin, V.V., *Polyhedron*, 2015, vol. 98, p. 113.
- Golovnev, N.N., Molokeyev, M.S., and Vereshchagin, S.N., *J. Struct. Chem.*, 2016, vol. 57, no. 1, p. 167.
- Golovnev, N.N., Molokeyev, M.S., and Golovneva, I.I., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 5, p. 300.
- Cambridge Structural Database. Version 5.36*, Cambridge: Univ. of Cambridge, 2014.
- Golovnev, N.N., Molokeyev, M.S., Vereshchagin, S.N., and Atuchin, V.V., *J. Coord. Chem.*, 2013, vol. 66, no. 23, p. 4119.

Translated by E. Yablonskaya