CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPLEX OF 2-(1-SILATRANYLMETHYLTHIO)-4,5-BENZO-1,3-THIAZOLE WITH CoCl₂ AND MeCN

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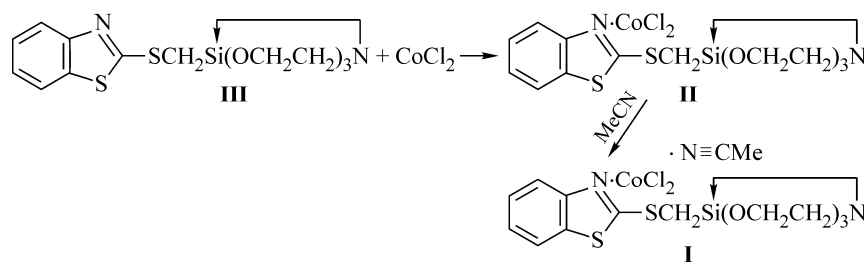
The crystal and molecular structure of the complex of 2-(1-silatranylmethylthio)-4,5-benzo-1,3-thiazole with CoCl₂ and MeCN (**I**) is determined by single crystal X-ray diffraction. The geometry of the silatranylmethyl moiety in complex **I** is compared to the geometry of 1-(2′-benzthiazolylthiomethyl) silatrane. Molecular packing in the crystal is analyzed.

Keywords: 2-(1-silatranylmethylthio)-4,5-benzo-1,3-thiazole, acetonitrile, molecular structure, single crystal X-ray diffraction analysis.

Using single crystal X-ray diffraction, we have previously studied the crystal and molecular structure of the complex of 2-(ethylthio)-4,5-benzo-1,3-thiazole with CoCl₂ of the composition 2:1 at room temperature [1] and 1-(2′-benzthiazo-lylthiomethyl)silatrane at 130 K [2]. In continuation of these studies, we investigated the complex of 2-(1-silatranylmethyl-thio)-4,5-benzo-1,3-thiazole with CoCl₂ and MeCN (**I**).

Complex **I** is remarkable not only by the presence of the silatranylmethyl group, which is characterized by a high electron donating effect and bulkiness, but also by the involvement of N₂ nitrogen belonging to MeCN in the coordination sphere of the cobalt atom.

Experimental. Complex of 2-(1-silatranylmethylthio)-4,5-benzo-1,3-thiazole with CoCl₂ (**II**). 0.45 g (1.3 mmol) of 2-(1-Silatranylmethylthio)-4,5-benzo-1,3-thiazole **III** and 0.17 g (1.3 mmol) of anhydrous CoCl₂ were boiled with a reflux condenser in 10 ml of dry benzole for 4 h under magnetic stirring. The precipitate was filtered off, washed with dry sulphuric ether, and dried in a vacuum dessicator over P₂O₅. The yield of product **II** was 0.55 g (88.71%), T_m = 185-187°C.

Chemical formula	$C_{16}H_{21}Cl_2CoN_3O_3S_2Si$
Temperature, K	296(2)
Space group, Z	$P2_1/n$, 4
$2\theta_{max}$, deg	50,0
a, b, c, Å	7.9529(12), 11.7183(17), 23.864(4)
β, deg	90.219(2)
V, Å^3	2224.0(6)
d, g/cm^3	1.569
μ, mm^{-1}	1.28
Total number of measured reflections	15981
Independent reflections	3914
Number of reflections with $I > 2\sigma(I)$	2093
h, k, l limits	$-9 \le h \le 9, -13 \le k \le 13, -28 \le l \le 28$
Refinement results	
Weight refinement against F^2	$W = [\sigma^2 F_0^2 + (0.0454P)^2 + 1.5112P]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$
Number of refined parameters	254
$R_1 [F_0 > 4\sigma(F_0)]$/over all	0.0543/0.1236
wR_2	0.1045
$GOOF$	1.017

TABLE 2. Main Bond Lengths in the Silatranylmethyl Moiety of **I** and **III** Molecules

Compound	Bond length, Å					
	Si–N	Si–C	(Si–O)$_{av}$	(O–C)$_{av}$	(C–C)$_{av}$	(C–N)$_{av}$
I	2.086(5)	1.901(5)	1.644(2)	1.412(5)	1.490(7)	1.465(6)
III*	2.100(2)	1.912(2)	1.663(2)	1.418(2)	1.516(3)	1.478(2)

*Experiment at 130 K.

After recrystallization of complex **II** (0.40 g, 0.83 mmol) from acetonitrile we obtained 0.39 g (90%) of complex **I** in the form of blue crystals with T_m = 213-215°C. Found, %: C 36.70, H 3.62, Cl 13.45, Co 11.21, N 7.87, S 12.18, Si 5.29. $C_{16}H_{21}Cl_2CoN_3O_3S_2Si$. Calculated, %: C 36.56, H 3.99, Cl 13.50, Co 11.22, N 8.00, S 12.21, Si 5.35.

For a single crystal X-ray analysis of complex **I** we selected a single crystal with the dimensions of 0.22×0.20×0.06 mm. reflection intensities were measured on a single crystal X-ray SMART APEX II diffractometer with a CCD detector (Bruker AXS), MoK_α radiation. Experimental absorption corrections were introduced using the SADABS program [3] by the multi-scan method. The structural model was solved by direct methods and refined using the SHELXL program package [4].

The positions of hydrogen atoms were found from electron density difference syntheses; then they were idealized and refined as riding. Table 1 lists the experiment parameters and structure refinement results. The CIF-file containing full information on the studied structure has been deposited in CCDC with number 775842. Bond lengths and bond angles of complex **I** are given in Tables 2 and 3; atom numbering is shown in Fig. 1.

Results and discussion. The coordination polyhedron of the cobalt atom in complex **I** is a tetrahedron formed by two chlorine and two nitrogen atoms. The Co–N1 and Co–N2 bonds, which differ only by 0.01 Å, bind completely different organic ligands. The first of them is (1-silatranylmethyl)benzothiazole and the second is acetonitrile.
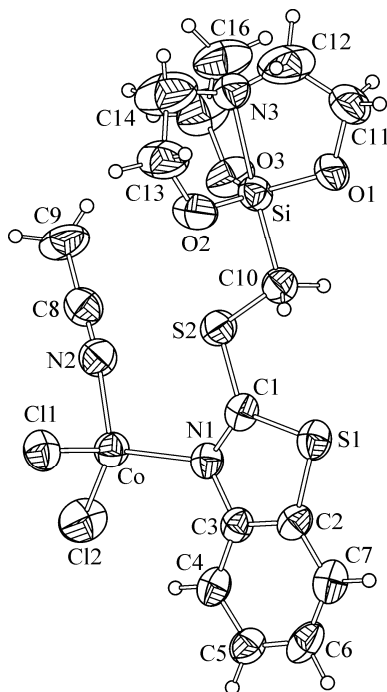
Fig. 1. Complex of 2-(1-silatranyl-methylthio)-4,5-benzo-1,3-thiazole with CoCl$_2$ and MeCN (**I**).

TABLE 3. Bond Lengths d, Å in the Benzthiazole Moiety of **I** and **III** Molecules

Compound	Bond						
	S1–C1	S1–C2	S2–C1	S2–C10	N1–C1	N1–C3	C2–C3
I	1.739(5)	1.737(6)	1.725(5)	1.790(5)	1.323(6)	1.414(6)	1.382(7)
III*	1.761(2)	1.742(2)	1.745(2)	1.799(2)	1.301(2)	1.393(2)	1.402(2)

*Experiment at 130 K.

The coordination polyhedron of the silicon atom in complex **I** is a trigonal bipyramid that is common for silatranes [5]. The length of the N3→Si coordination bond of 2.089(5) Å is close to that observed in the 1-hydrosilatrane (2.071 Å) [6], N-(1-silatranylmethyl)imidazole (2.088 Å) [7], and -benzimidazole (2.088 Å) [8] molecules and coincides with this bond length in N-(1-silatranylmethyl) pyrrole (2.089 Å) [9], 2-(1-silatranylmethyl)-1,2,3-benzotriazole (2.089 Å) [10], differing from 1-(2′-benzothiazolylthiomethyl)silatrane (2.100 Å) [2] by only 0.011 Å.

Compared to 1-(2'-benzothiazolylthiomethyl)silatrane (**III**) [2] that we have previously studied, the bond lengths and bond angles in the 2-(1-silatranylmethylthio)benzothiazole ligand of complex **I** differ insignificantly: by 0.01-0.03 Å (Tables 2 and 3). In the thiazole heterocycle, the lengths of both N1–C1 and N1–C3 bonds of the nitrogen atom that is also bonded to the cobalt atom in complex **I**, is longer by 0.02 Å than those in the molecule of **III**, where additional coordination is absent (Table 2). It is this coordination that explains the elongation of both endocyclic C–N bonds.

The lengths of coordination N1–Co and N2–Co bonds are 2.031(4) Å and 2.017(5) Å respectively and are close to those in the complex of 2-(ethylthio)-4,5-benzo-1,3-thiazole with CoCl$_2$ [1]. The same correlation is also observed for Co–Cl bond lengths in these complexes.

Fig. 2 shows molecular packing in the crystal. Parallel arrangement of the planar moieties of **A** and **B** molecules is due to the supramolecular interaction between the π-conjugated orbitals of the rings. Apart from such a pair interaction, there
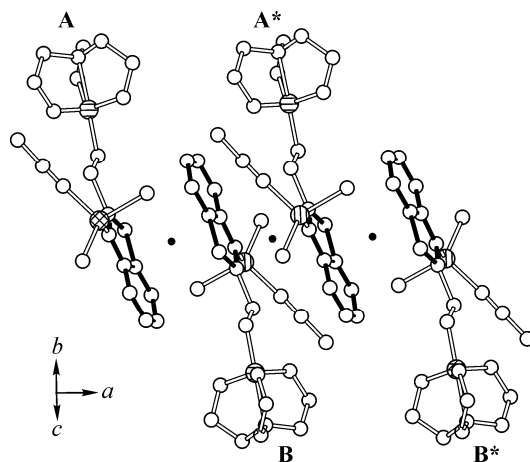
Fig. 2. Mutual position of molecular pairs with the π–π interaction of rings in the crystal of **I**. Black dots are the centers of inversion. Si atoms are vertically dashed; Co atoms are dashed horizontally. The **A** and **A*** (B and **B***) molecules are bound by the translation *a*.

TABLE 4. Parameters of the π–π Interaction of Molecules in the Crystal of **I**

Cg_i–Cg_j	d(Cg–Cg), Å	α, deg	β, deg	γ, deg	Cg_i_p	Cg_j_p	Shift, Å
Cg_1–Cg_2	3.974(3)	1.6(2)	27.61	28.62	−3.489(2)	−3.521(2)	
Cg_2–Cg_1	3.974(3)	1.6(2)	28.62	27.61	−3.522(2)	−3.489(2)	
Cg_1–Cg_1	3.871(3)	0	22.38	22.38	3.579(2)	3.579(2)	1.474

Note. Cg_1 is the S(1)–C(1)–N(1)–C(3)–C(2) ring plane; Cg_2 is the C(2)–C(3)–C(4)–C(5)–C(6)–C(7) ring plane; d(Cg–Cg) is the distance between ring centroids; α is the angle between ring planes; β is the angle between the vector connecting ring centers and the normal to the first ring plane; γ is the angle between the vector connecting ring centers and the normal to the second ring plane; Cg_i_p is length of the perpendicular from the center of the first ring to the plane of the second; Cg_j_p is the length of the perpendicular from the center of the second ring to the plane of the first; shift is the distance between the center of the first ring and the center of the perpendicular projection of the second ring on the plane of the first.

is a similar bond between the pairs, but only five-membered rings are involved in this binding (**B** and **A*** molecules) (Fig. 2). The geometric parameters of this interaction, which were calculated using PLATON [11], are listed in Table 4.

REFERENCES

1. M. G. Voronkov, É. A. Zel'bst, A. D. Vasiliev, et al., *J. Struct. Chem.*, **52**, No. 5, 985-988 (2011).
2. Yu. É. Ovchinnikov, Yu. T. Struchkov, N. F. Chernov, et al., Dokl. Akad. Nauk, **328**, No. 3, 330/331 (1993).
3. G. M. Sheldrick, *SADABS, Version 2.01*, Bruker AXS Inc. Madison, Wisconsin, USA (2004).
4. G. M. Sheldrick, *Acta Cryst. Sect. A*, **64**, No. 1, 112-122 (2008).
5. V. Pestunovich, S. Kirpichenko, and M. Voronkov, in: *The Chemistry of Organic Silicon Compounds*, Z. Rappoport and Y. Apeloig (eds.), Chichester: Wiley (1998), Vol. 2. Ch. 24, 1447.
6. A. A. Korlyukov, M. Yu. Antipin, Yu. I. Bolgova, et al., *Izv. Akad. Nauk, Ser. Khim.*, No. 1, 25-30 (2009).
7. M. G. Voronkov, V. S. Fundamenskii, É. A. Zel'bst, et al., *Dokl. Akad. Nauk*, **401**, No. 1, 41-43 (2005).
8. M. G. Voronkov, É. A. Zel'bst, V. S. Fundamenskii, et al., *J. Struct. Chem.*, **46**, No. 6, 1122 (2005).
9. M. G. Voronkov, É. A. Zel'bst, A. A. Kashaev, et al., *Dokl. Akad. Nauk*, **386**, No. 1, 56-60 (2002).
10. M. G. Voronkov, É. A. Zel'bst, V. S. Fundamenskii, et al., *Dokl. Akad. Nauk*, **381**, No. 3, 348-350 (2001).
11. A. L. Spek, *J. Appl. Cryst.*, **36**, No. 1, 7-13 (2003).