

CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPLEX OF N-(1-SILATRANYLMETHYL)-3,5- DIMETHYLPYRAZOLE WITH COBALT DICHLORIDE

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X-ray diffraction is used to determine the crystal and molecular structure of the complex of N-(1-silatranylmethyl)-3,5-dimethylpyrazole with cobalt dichloride (**I**). This is yet another example of the participation of the endocyclic oxygen atom of the silatrane fragment in complexation with a metal atom. Metal dichloride interconnects two heterocyclic systems of dimethylpyrazole (DMP) and silatrane (Sa). The coordination polyhedron of the cobalt atom is a tetrahedron.

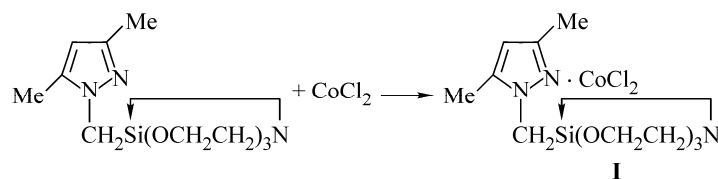
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Many nitrogen-containing heterocycles (pyrrole, indole, carbazole, imidazole, pyrazole, pyrimidine, etc.) are the basis of alkaloids, natural and synthetic antibiotics, and many medicinal products [1, 2]. In particular, 3,5-dimethylpyrazole derivatives have antibacterial properties and are used to treat metabolic syndrome and included in cosmetics and pesticide compositions. They intercept free radicals, preventing aging and skin photodamage [3-6].

In the course of our systematic studies on the creation of new organosilicon compounds [7, 8], which consist of two biologically active components and can be used in medicine, agriculture, cosmetics, and genetic engineering, we set a goal to synthesize the complex of N-(1-silatranylmethyl)-3,5-dimethylpyrazole with cobalt dichloride (**I**). The crystal and molecular structure of **I** was determined by single crystal X-ray diffraction.

Experimental. Complex **I** of the 1:1 composition was synthesized by the interaction of N-(1-silatranylmethyl)-3,5-dimethylpyrazole with anhydrous CoCl₂ in a dry benzene medium with a 83% yield.

Crystals of complex **I** with m.p. = 280-282°C were obtained by recrystallization from acetonitrile. Found: C 34.53, H 5.09, Cl 17.12, and N 9.98. C₁₂H₂₁Cl₂CoN₃O₃Si. Calculated: C 34.88, H 5.12, Cl 17.16, and N 10.17.



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TABLE 1. Experimental Data and Refinement Parameters of the Structure of **I**

Gross formula	C ₁₂ H ₂₁ Cl ₂ CoN ₃ O ₃ Si
Temperature, K	296(2)
Space group, <i>Z</i>	<i>P</i> 2 ₁ / <i>n</i> , 4
2θ _{max} , deg	57
<i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg	6.8594(5), 14.8878(12), 16.8665(13); 101.558(1)
<i>V</i> , Å ³	1687.5(2)
<i>d</i> , g/cm ³	1.627
μ, mm ⁻¹	1.418
Total meas./indep. reflections	15655/4236
Number of reflections with <i>I</i> > 2σ(<i>I</i>)	2642
Limits by <i>h</i> , <i>k</i> , and <i>l</i>	-9 ≤ <i>h</i> ≤ 9, -19 ≤ <i>k</i> ≤ 19, -22 ≤ <i>l</i> ≤ 22
Refinement results	
Weight refinement against <i>F</i> ²	$w = [\sigma^2(F_0^2) + (0.0372P)^2 + 1.5112P]^{-1}$, where
	$P = (F_0^2 + 2F_c^2)/3$
Number of refined parameters	252
<i>R</i> ₁ [<i>F</i> _o > 4σ(<i>F</i> _o)]/over all	0.0438/0.0876
<i>wR</i> ₂	0.0975
<i>GOOF</i>	1.020

TABLE 2. Interatomic Distances* in the Polyhedron of the Silicon Atom of Complexes **I** and **II** and Silatrane **III**

Compound	Bond length, Å							
	Si–N3	Si–C1	Si–O1	Si–O2	Si–O3	O1–C7	O2–C8	O3–C9
I	2.066	1.906	1.639	1.650	1.707	1.423	1.422	1.448
II	2.075	1.911	1.643	1.654	1.702	1.425	1.417	1.444
III	2.118	1.913	1.657	1.677	1.656	1.419	1.413	1.415

*Bond length errors do not exceed 0.004 Å.

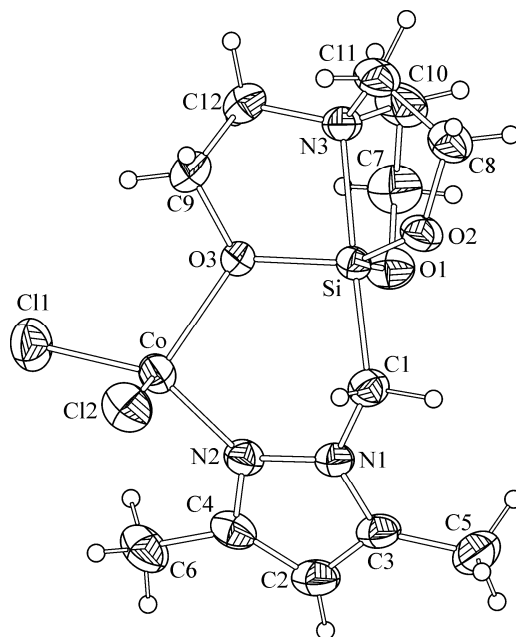
For single crystal XRD of complex **I**, we selected a single crystal with dimensions 0.35×0.27×0.18 mm of blue color with shiny faces. The intensities of the reflections were measured with a SMART APEX II single crystal diffractometer with a CCD detector (Bruker AXS), MoK_α radiation, graphite monochromator. Experimental absorption corrections were introduced using SADABS [10] by the multi-scan method. The structure model was found by direct methods and refined with SHELXL [11]. The C_α carbon atoms are disordered; the main positions of the C_α atoms are 83.0(6)% occupied (Fig. 2). The hydrogen atoms of the CH₂N group in the general position were determined by calculating the electron density differences and refined as bonded to the main carbon atoms. No hydrogen atoms were revealed at C10a, C11a, and C12a, and they were not introduced artificially. All nonhydrogen atoms, except for the latter, were refined in the anisotropic approximation of thermal vibrations. Table 1 shows the experimental conditions and parameters of the structure refinement. The CIF file containing complete information on the structure has been deposited with the CCDC under No. 779195 (www.ccdc.cam.ac.uk/data_request/cif). The bond lengths and angles of complex **I** are given in Tables 2 and 3; atom numbering is shown in Fig. 1.

Results and discussion. Complex **I** represents a new class of polycyclic chelate compounds, i.e., N-(1-heterylmethyl)silatrane, in which the equatorial oxygen atoms of the silatranyl fragment is bonded via the metal atom to the nitrogen atom of the 3,5-dimethylpyrazole heterocycle, as in the complex of N-(1-silatranylmethyl)-3,5-dimethylpyrazole

TABLE 3. Interatomic Distances* in the Pyrazole Ring of Complexes **I** and **II** and Silatrane **III**

Compound	Bond length, Å						
	N1–N2	N2–C4	C2–C4	C2–C3	C3–N1	C3–Me	C4–Me
I	1.372	1.352	1.383	1.384	1.345	1.490	1.499
II	1.361	1.347	1.378	1.383	1.349	1.493	1.493
III	1.365	1.342	1.402	1.386	1.348	1.501	1.498

*See note to Table 2.

**Fig. 1.** Complex of N-(1-silatranylmethyl)-3,5-dimethylpyrazole with CoCl_2 (**I**).

with zinc dichloride (**II**) [9]. Owing to Co-O3 and Co-N2 interactions, the pyrazole and atrane moieties are linked by a six-membered SiO3CoN2N1C1 ring. Therefore, in complex **I**, the interatomic N1-N2 and Si-O3 distances are somewhat larger than in initial N-(1-silatranylmethyl)-3,5-dimethylpyrazole (**III**) [12]. This difference is more pronounced for the Si-O3 bond (Tables 2 and 3).

The coordination polyhedron of the cobalt atom is a tetrahedron formed by two chlorine atoms (Cl1 and Cl2), the nitrogen atom N2 of the pyrazole heterocycle, and the equatorial oxygen atom O3 of the silatranyl group.

In the complexes of organic compounds with CoCl_2 , the interatomic distances in the cobalt atom polyhedron tend to the lengths of the same bonds in complex **I** (Co-Cl (2.230(1) Å), Co-N (2.007(2) Å), and Co-O (2.055(2) Å) [13, 14]). The bond angles in the cobalt atom tetrahedron of complex **I** are in the range $98.63(9)^\circ$ (N2CoO3 angle) — $117.32(8)^\circ$ (N2CoCl2 angle), which is typical of complexes containing this type of metal polyhedra [13, 14]. A similar distortion of bond angles was observed previously (refcode MAMYAB [13]). The other angles in the cobalt atom polyhedron in complex **I** are close to tetrahedral.

The coordination polyhedron of the silicon atom in complex **I** is a trigonal bipyramid (usual for silatranes) whose axial angle C1SiN3 is close to 180° (174.6°) and equatorial angles OSiO are close to 120° . The lengths of the $\text{N} \rightarrow \text{Si}$ bond in complexes **I** and **II** are almost equal (2.066(4) Å and 2.075(4) Å) and shorter than that in the molecule of **III** by 0.05 Å and 0.04 Å respectively. This suggests that the coordination interaction of the equatorial oxygen atom O3 with the metal atom in

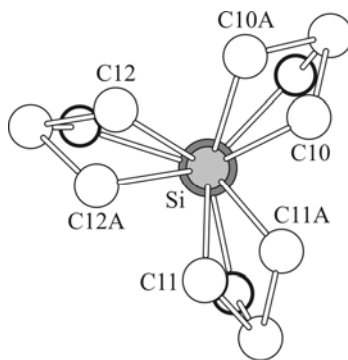


Fig. 2. Fragment of the molecule of **I** with two positions of disordered carbon atoms.

silatranes shortens the N → Si bond. It should be noted that the participation of the equatorial oxygen atom O3 of the silatrane fragment in the formation of the bond with the metal atom (O–M) in complexes **I** and **II** extends the Si–O3 bond by 0.05 Å, while the Si–O1 and Si–O2 bonds are shorter by 0.02 Å compared to those in the molecule of **III**. For equivalent SiOCCN heterocycles in the molecules of **I** and **II**, the Si–O3 bond length is larger by 0.06–0.07 Å than the length of Si–O1 and Si–O2 contacts (Table 2). This is caused by that the oxygen atom O3 is involved in two coordination spheres simultaneously, those of the silicon and cobalt atoms. The other valence interatomic distances in the silicon atom polyhedron in the molecules of **I**, **II**, and **III** are close to the standard values for silatranes within the error limits.

The data in Table 3 show that the lengths of the endocyclic bonds in the pyrazole heterocycle in complexes **I** and **II** are almost the same as in the molecule of **III**, except for the C2–C4 bond that is shorter by 0.02 Å.

The nitrogen atom is displaced from the plane of three carbon atoms C10, C11, and C12 towards the inside of the silatrane cell by 0.42 Å (Fig. 2), which is somewhat larger than the standard value for silatranes (0.38 Å). Neither hydrogen bonds nor reduced van der Waals contacts were found in the packing of the molecules of complex **I**.

Thus, complex **I** is yet another representative in which the equatorial oxygen atom O3 of the silatranyl group is bonded via the metal atom to the nitrogen atom N2 of the azole heterocycle, forming the six-membered SiOC_oNNC heterocycle with a strained conformation.

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