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ORIGINAL RESEARCH

Synthesis and molecular structure of cobalt(II) complex with 1-(1-silatranylmethyl)-1,2,4-triazole

A. D. Vasiliev · E. A. Zel'bst · A. S. Soldatenko · Yu. I. Bolgova · O. M. Trofimova · M. G. Voronkov

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Abstract Reaction of cobalt chloride with 1-(1-silatranylmethyl)-1,2,4-triazole in benzene afforded complex $CoCl_2 \cdot 2L$ (L = 1-(1-silatranylmethyl)-1,2,4-triazole). It was isolated as the solvate $[CoCl_2 \cdot 2L] \cdot CH_2Cl_2$ (**1**) by recrystallization from dichloromethane and structurally characterized by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/m$ with $a = 6.798(2)$ E, $b = 20.326(5)$ E, $c = 11.005(3)$ E, *and* $Z = 4$. The cobalt atom is in slightly distorted square-planar environment, coordinated to two nitrogen atoms from two ligands and two chloride ions.

Keywords Complexes · 1-(1-Silatranylmethyl)-1,2,4-triazole · Cobalt dichloride · X-ray diffraction

Introduction

Silatranes $XSi(OCH_2CH_2)_3N$, pentacoordinate organosilicon compounds with N → Si transannular bond, have attracted much attention owing to the peculiarities of their electronic and molecular structure [1–3]. The intramolecular hypervalent N → Si bonding and the cage skeleton structure are responsible for the characteristics of the chemical behavior of silatranes which has been also investigated extensively [2, 3]. However, their complexation studies involving endo/exo-cyclic heteroatoms (O, N) of silatranyl as well as carbofunctional groups are not widespread. It should be noted that the axial nitrogen atom is inert toward electrophiles because of its lone pair is oriented in silatranyl cage [3].

Based on IR study, it has been speculated that 1-organylsilatranes $RSi(OCH_2CH_2)_3N$ (R = Et, Ph) form adducts with the Lewis acids ($AlBr_3$, $TiCl_4$) in which the metal atom is bound to the equatorial oxygen atom [4]. In the hydrogen bonded complexes and oxonium salts of 1-alkoxysilatranes $AlkOSi(OCH_2CH_2)_3N$ (Alk = Me, Et), the equatorial oxygens are less basic than the axial oxygen so that the latter being a coordinating site [5]. Complexes of 1-isothiocyanatosilatrane $SCNSi(OCH_2CH_2)_3N$ with Lewis acids ($TiCl_4$ and $SnCl_4$) are N-bonded whereas the coordinative bonding of the S-atom is apparent with such Lewis acids, as chromium, molybdenum, and tungsten carbonyls [6]. π-Coordination of transition metals (Cr, Mn and W) to the phenyl group of 1-aryl- and 1-benzylsilatranes has been reported [7–11].

Coordination behavior carbofunctional silatranes with sulfur or nitrogen atoms has been more widely studied with respect to other X-substituted silatranes. Ambiguous results have been reported on the reaction of cobalt chloride with 1-(3′-aminopropyl) silatrane (L) [12, 13]. As follows from IR spectral data, this reaction afforded complex $2L \cdot CoCl_2$, the metal atom of which is connected with the nitrogen atoms of two aminopropyl ligands [12]. As described recently, only triethanolamine hydrochloride $(HOCH_2CH_2)_3N \cdot HCl$ was isolated as the reaction product [13]. These results might be

A. D. Vasiliev
L.V. Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences, Akademgorodok, Krasnoyarsk 660036, Russia

E. A. Zel'bst
East-Siberian State Academician of Education, 6 Niznya Nabereznay, Irkutsk 664011, Russia

A. S. Soldatenko · Yu. I. Bolgova · O. M. Trofimova (✉) · M. G. Voronkov
A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky Str., Irkutsk 664033, Russia
e-mail: omtrof@irioch.irk.ru

because of some differences in experimental conditions. In complexes of 1-(3′-isothiocyanatopropyl)silatrane with Lewis acids ($SnCl_4$, $TiCl_4$), the metal coordination occurs via a hard nitrogen atom of ambidentate NCS ligand [14]. Reaction *N*-(1-silatranylmethyl)- and *N*-(1-silatranylpropyl)ethylenediamine with $CuCl_2$ gave paramagnetic tetrahedral Cu(II) complex with metal-to-ligand stoichiometries of 1:2 [15]. Both nitrogen atoms of ethylenediamine ligands are involved in coordination.

It is evident from IR spectral data that in complexes of 3-formylchromoniminopropylsilatrane with $CuCl_2$, $NiCl_2$, and $CoCl_2$, the metal atom is coordinated with the azomethine nitrogen and carbonyl oxygen [16]. The electronic spectral and magnetic moment data supported square-planar geometry of the Cu(II) and Ni(II) ions and tetrahedral geometry of the Co(II) ion in the complexes. According to IR and UV data as well quantum chemical calculations, 1-(8-quinolylthiomethyl)silatrane as a bidentate ligand (L) reacts with metal chlorides to give two different type of complexes [17]. A strong N → Sn coordination is typical of L·$SnCl_4$ complex. The ligand is coordinated via S,N atoms in L·$ZnCl_2$ complex while complex L·$CuCl_2$ is a mixture of coordination compounds with N → Cu and N → Cu ← S bonds.

Recently, we reported the synthesis and molecular structure of two new metal(II) complexes [$HetCH_2Si(OCH_2CH_2)_3N$]·MCl_2 (Het-3,5-dimethylpyrazolyl, M = Zn, Co) [18, 19]. The structure analysis showed that the metal atom is connected both with pyridinic nitrogen atom of heterocycle and cage oxygen atom to so that a six-membered ring is closed (Fig. 1). Such type a coordination mode was observed at the first time.

As part of our ongoing research, now we describe the synthesis, crystal, and molecular structure of complex arising from the reaction of $CoCl_2$ with 1-(1-silatranylmethyl)-1,2,4-triazole (**2**).

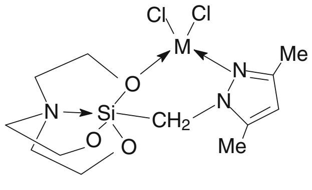


Fig. 1 Chemical representation of complexes of MCl_2 with 1-(1-silatranylmethyl)-3,5-dimethylpyrazole

Experimental

Synthesis

General

All chemical reagents were analytical grade commercial products. Hydrated cobalt chloride $CoCl_2\cdot(H_2O)_6$ was dehydrated upon heating in vacuo (0.002 bar, 260 °C, 2 h). Solvents were purified by standard methods. Initial compound **2** was synthesized as previously described [20]. Melting points were determined using Micro-Hot-Stage PolyTherm A. Infrared spectra were recorded on Varian 3100 FT-IR spectrophotometer in the spectral range of 500–4,000 cm^{-1}, Vertex 70 FIR PE Glass spectrophotometer in the spectral range of 200–400 cm^{-1} with the sample in the form of KBr pellet or oil.

Preparation of complex **1**

*[$CoCl_2\cdot 2L]\cdot CH_2Cl_2$ (L = 1-(1-silatranylmethyl)-1,2,4-triazole) (**1**).* A solution of **2** (280.0 mg, 1.1 mmol) in dry benzene (5 mL) was added dropwise to a stirred solution of dry $CoCl_2$ (140.0 mg, 1.1 mmol) in dry benzene (5 mL) within 2 min at 20 °C. The reaction mixture was magnetically stirred at 60 °C for 2–3 h. The solution slowly assumed the characteristic dark blue color. The resulting precipitate was isolated by filtration and dry under in vacuum desiccator over P_2O_5, and to afford $CoCl_2\cdot 2L$ (730 mg, 91 %): mp 219–220 °C. Anal. Calc. for $C_{18}H_{32}Cl_2CoN_8O_6Si_2$: C 33.65; H 5.02; Cl 11.03; N 17.44. Found: C 33.26; H 5.38; Cl 11.38; N 17.08.

Suitable single crystal of **1** was obtained by recrystallization from dichloromethane to afford **1**: m.p. 222–223 °C. Anal. Calc. for $C_{19}H_{34}Cl_4CoN_8O_6Si_2$: C 31.37; H 4.71; Cl 19.49; N 15.41. Found: C 31.32; H 4.43; Cl 19.18; N 15.05.

Crystal structure determination and refinement

X-ray diffraction analysis for a suitable single crystal were performed on a Bruker AXS SMART APEX II diffractometer with CCD detector using Mo Kα radiation at 100 K. Multi-scan absorption correction was applied using SADABS program [21]. Crystal structure was solved by direct method using SHELXS and full-matrix least-squares refinement was performed using SHELXL [22]. All non-hydrogen atoms were refined anisotropically.

Details of the unit cell, data collection and refinement are summarized in Table 1.

Result and discussion

The reaction of $CoCl_2$ with 1-(1-silatranylmethyl)-1,2,4-triazole (**2**) have been carried out. Mixing the starting cobalt(II) salt with ligand in benzene gave 1-(1-silatranylmethyl)-1,2,4-triazole complex of Co(II) isolated as a

Table 1 Crystal data and structure refinement parameters for $[CoCl_2{\cdot}2L]$ (**1**) complex

Empirical formula	$C_{19}H_{34}Cl_4CoN_8O_6Si_2$
Formula weight	727.46
Crystal system	Monoclinic
Space group	$P2_1/m$
Temperature (k)	100(1)
a (Å)	6.798(2)
b (Å)	20.326(5)
c (Å)	11.005(3)
β (°)	99.033(3)
V (Å^3)	1501.7(6)
Z	4
$2\theta_{max}$ (°)	50
Calculated density (g cm^{-3})	1.604
μ (mm^{-1})	1.056
Crystal size (mm)	0.50 × 0.32 × 0.04
Index ranges	$-8 \leq h \leq 8$
	$-24 \leq k \leq 24$
	$-12 \leq l \leq 13$
Reflection collected	11.065
Independent reflections	2714 [$R_{(int)} = 0.117$]
Reflections observed ($>4\sigma_F$)	1652
Refinement method	Full-matrix least squares on F^2
Refined parameters	196
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.062$
	$wR_2 = 0.137$
R indices (all data)	$R_1 = 0.114$
	$wR_2 = 0.1634$
Largest diff. peak and hole	1.06 and –0.70 e Å^{-3}

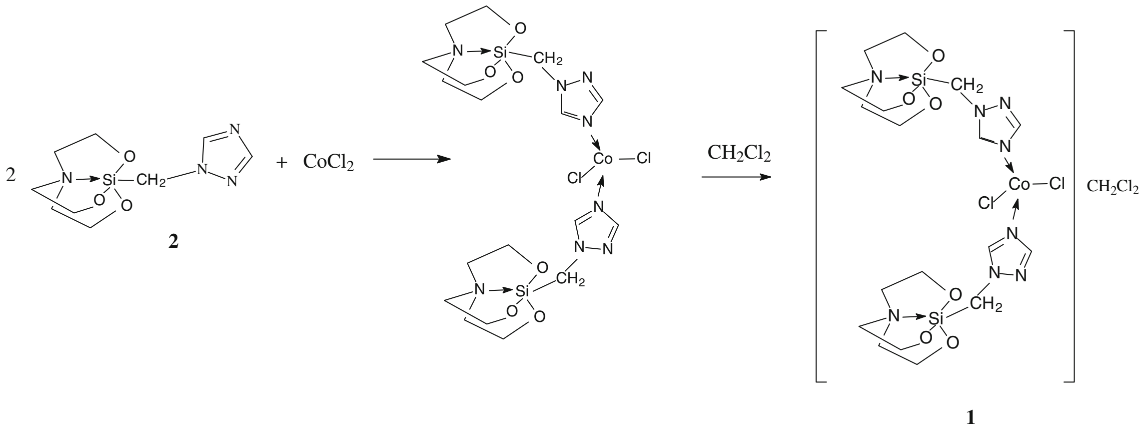
blue powder which was enough stable to air in the solid state. The compound is slightly soluble in dichloromethane, acetonitrile, chloroform, and more soluble in DMF, DMSO. According to the microanalysis data, the resulting product have 1:2 (metal:ligand) stoichiometry. Its recrystallization from dichloromethane and drying the bulk sample under a vacuum afforded the solvate $[CoCl_2{\cdot}2L]{\cdot}CH_2Cl_2$ (**1**) (Scheme 1).

It was attested by elemental analyses and the IR spectrum which showed the absorption band at 3,108 cm^{-1} characteristic for CH_2Cl_2. In addition, the IR spectrum of **1** in oil shows weak stretching bands at 217 and 311 cm^{-1}, which characterize Co–Cl and Co–N stretching vibrations, respectively [23]. The spectra of the complex **1** and free ligand **2** are essentially the same except for ν(C=N) band which is observed at higher frequency in **1** as compared to that in **2** (1,530 and 1,515 cm^{-1}, respectively). Besides, the spectra showed characteristic ν_{as}C–O–Si (1,130–1,080 cm^{-1}), ν_sC–O–Si (650–630 cm^{-1}), and νN–C (1020, 910 cm^{-1}) frequencies of the silatranyl unit. Absorption band is observed at 576 cm^{-1} is assigned to (Si ← N).

Nevertheless, spectroscopic and analytical data obtained for complex **1** were insufficient for determination of a metal coordination mode. Therefore, the molecular structure of **1** was determined by X-ray diffraction studies carried out with single crystal obtained from methylene chloride solution.

Molecular structure

Complex **1** is crystallized in the monoclinic space group $P2_1/m$ being symmetrical in respect to a plane passing through Cl(1), Co, Cl(2) atoms. Selected bond lengths and angles are given in Table 2. The cobalt atom is in a slightly distorted square-planar environment, consisting of two N3-donating atoms from two 1-(1-silatranylmethyl)-1,2,4-triazole ligands and two chloride ions (Fig. 2). The latters have a *cis*-arrangement. The Cl1–Co–N3 and Cl2–Co–N3 angles are, respectively, 106.1(1) and 114.7(1). In complex **1**, the Co–N bond of 2.014(5) Å is almost equal to that in the cobalt complex with 1-(1-silatranylmethyl)pyrazole [19]. The dihedral angle between the nearly planar triazole



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Scheme 1 Synthesis of cobalt(II) complex with 1-(1-silatranylmethyl)-1,2,4-triazole ligands is 108.1(2)°. The Co–Cl1 and Co–Cl2 bond distances differ slightly (2.264(2) and 2.227(2) Å) owing to weak intermolecular contact Cl1...H–C (vide infra).

Table 2 Selected bond lengths (Å) and angles (°) for $[CoCl_2 \cdot 2L] \cdot CH_2Cl_2$ (**1**) complex and L (**2**) determined by single-crystal X-ray diffraction

	1	**2**
Bond lengths (Å)		
Si–N	2.065(5)	2.095(5)
Si–C	1.901(6)	1.906(6)
$(N–C)_{av}$	1.470(8)	1.478(7)
$(C–C)_{av}$	1.476(9)	1.517(6)
$(O–C)_{av}$	1.423(7)	1.423(5)
$(Si–O)_{av}$	1.665(4)	1.661(7)
C2–N2	1.472(7)	1.464(7)
N2–N4	1.366(6)	1.358(6)
N4–C3	1.297(7)	1.315(8)
C3–N3	1.353(7)	1.354(6)
N3–C1	1.343(7)	1.323(8)
C1–N2	1.310(7)	1.329(7)
Co–N3	2.014(5)	–
Co–Cl1	2.264(2)	–
Co–Cl2	2.227(2)	–
Angles (°)		
N1–Si–C2	175.5(2)	–
N2–C2–Si	119.0(4)	117.9(3)
N3–Co–N3	105.3(3)	–
Cl1–Co–Cl2	109.27(9)	–
Cl1–Co–N3	106.1(1)	–
Cl2–Co–N3	114.7(1)	
C1–N3–Co	133.3(4)	

The whole molecule looks like a butterfly (Fig. 2): the Cl–Co–Cl atoms form the body of the butterfly, and the two triazolyl ligands form a pair of wings.

The structure of coordinated ligand in complex **1** differs only slightly from the structure of the free ligand **2** [20]. The bond lengths and angles of triazole ring and silatranyl skeleton in **1** are close to those in **2** (Table 2). Coordination of triazole ring to the cobalt atom results to a small decrease in the N2–C2–Si angle (by 1°) and the N → Si bond (by 0.03 Å) relative to free ligand **2**. The bond lengths and angles of silatranylmethyl group (Table 2) are in the expected range [24] and do not need further discussion.

The donor atom of the 1,2,4-triazole is *N*4, obviously the other coordination site, *N*2, is sterically disfavored by the neighboring substituent. The earliest example is $CuCl_2 \cdot 2$(1-ethyl-1,2,4-triazole), which has copper in a square-planar coordination and the ligands coordinate via *N*4 in *trans* position [25].

The crystal structure is affected by weak intermolecular hydrogen bonding Cl...H–C (Cl...H 2.66, C...Cl 3.580(6) Å, and Cl...H–C 162°), which are connected of the Cl1 atom with and the H_C atom of the neighboring molecules so that polymeric chains of molecules are arranged along crystallographic *a* axis. Eight-membered metallacycle with eight atoms (Cl1H1C1N3CoN3C1H) is formed owing these intermolecular interactions (Fig. 3).

In spite of drying the bulk sample under a vacuum, the single-crystal X-ray structure determination revealed inclusion of one disordered solvent molecule (CH_2Cl_2) in the asymmetric unit (Fig. 3). This molecule is located so that one Cl atom is in a symmetry plane while second Cl and C atoms are displaced from this plane.

The X-ray data also revealed inclusion of one solvent molecule (CH_2Cl_2) in the crystal unit (vide infra).

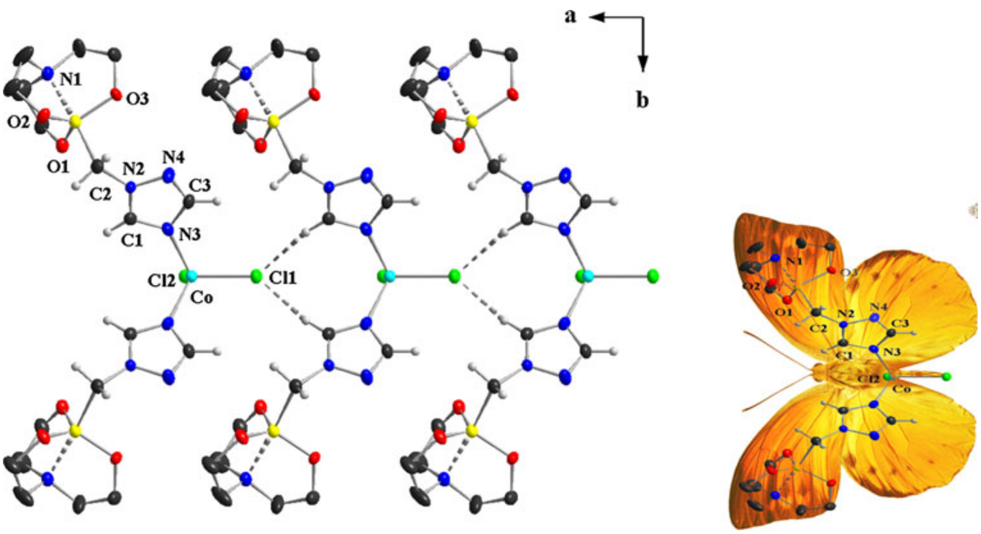

Fig. 2 Molecular structure scheme of complex **1** showing the atom-numbering. Intermolecular hydrogen bond Cl···H–C is shown as a *dashed line*. The hydrogen atoms of the silatranyl cage, and the uncoordinated solvent molecules, are omitted for the clarity

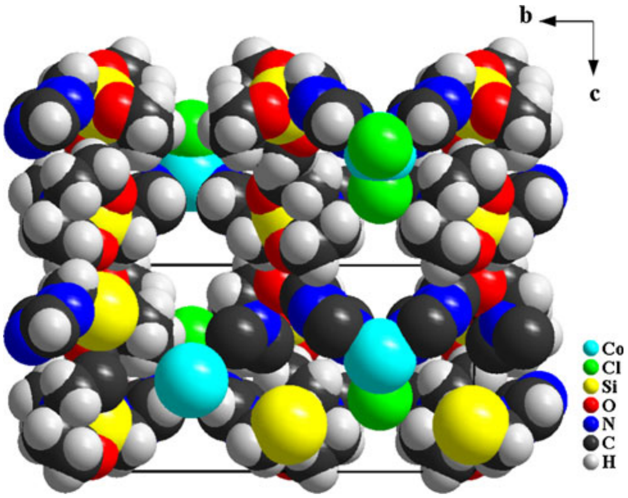

Fig. 3 Crystal packing of complex **1** (plane projection on *bc* sell). The CH_2Cl_2 molecules (not depicted in figure) occupy the free positions within *hollow crystals*

Supplementary data

CCDC 864366 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre (CCDC), 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033, e-mail: deposit@ccdc.cam.ac.uk.

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