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Synthesis and structural characterization of 1-(3-aminopropyl)silatrane and some new derivatives

Ana–Maria-Corina Dumitriu [a], Maria Cazacu [a,*], Sergiu Shova [a,b], Constantin Turta [a,c], Bogdan C. Simionescu [a,d]

[a] "Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania
[b] Institute of Applied Physics of ASM, Academiei Str. 5, 2028 Chisinau, Republic of Moldova
[c] Institute of Chemistry of ASM, Academiei Str. 3, 2028 Chisinau, Republic of Moldova
[d] "Gh. Asachi" Technical University of Iasi, Department of Natural and Synthetic Polymers, Bd. D. Mangeron 71A, 700050 Iasi, Romania

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ABSTRACT

The research goal was to synthesize and structurally characterize a silatrane intended to be subsequently incorporated into metal complex structures. 3-Aminopropyltrialkoxysilane was reacted with triethanolamine in 1:1 molar ratio, either in bulk, in the presence of metallic sodium, or in a solvent mixture. 1-(3-Aminopropyl)silatrane in carbamate form or having free amine groups was obtained. The latter was reacted with 2-hydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde and $CoCl_2$ or with $CoCl_2$ only. The crystalline reaction products were characterized by elemental and spectral (FTIR and ^1H NMR) analyses and single crystal X-ray diffractometry, which revealed the formation of new, either sought (1-(3-aminopropyl) silatrane, 1-(3-salicyliminopropyl)silatrane) or unexpected (*N*-carboxylated 1-(3-aminopropyl)silatrane and 1-chlorocobaltrane) structures.

1. Introduction

Silatranes, heterotricyclic compounds having an intramolecular transannular dative Si ← N bond, are of high interest both from their structural and applications point of view [1]. The existence of this hypervalent bond in silatranes was clearly established, these compounds being considered as examples of systems where silicon is pentacoordinated [1]. The analysis of the electron density distribution in silatrane led to the conclusion that the interaction between nitrogen and silicon is rather electrostatic and less covalent, involving a negative charge at nitrogen and a positive one at silicon [2].

The decisive influence of the hypervalent Si ← N bond, quite different from a covalent bond, on the physicochemical and spectroscopic characteristics of silatranes has been demonstrated [1,3]. The strength of the dative bond depends not only on the substituent on the silicon, but also on the skeletal structure of the parent ring [1]. On the other hand, the silatranyl group has an important stereoelectronic influence in shaping the reactivity of the exocyclic functional group apical to the transannular bond [4–7]. Although in 2001 a new class of silatranes having six members (Si, O, C, C, C, N) in their tricyclic system and named as six-membered silatranes [8] was reported, silatranes typically consist of five members (Si, O, C, C, N) in their tricyclic system. Such compounds are synthesized directly from inexpensive and widely available starting materials, trialkoxysilane and triethanolamine or substituted triethanolamine in 1:1 molar ratio in the presence or absence of a third reagent. The reaction proceeds smoothly in common solvents such as benzene, toluene or alcohol using a basic catalyst at room temperature or under reflux [1]. A more simple procedure uses the hydrolysis product of organyltrichlorosilanes (polyorganosilsesquioxanes) or polyorganylsiloxanols in the presence of an alkaline metal hydroxide catalyst [9]. The most interesting feature of silatranes consists in the variation of Si–N bond length depending on the axial substituent of Si. Therefore, the optimization of the substituted groups on the silicon atom is important, the properties of the silatranes being correlated with these groups [1]. Therefore, trialkoxy- or trichlorosilanes having different substituents at silicon were used to prepare silatranes: H, CH_3, C_2H_5, $(CH_3)_2CH$, $CH_2{=}CH$, C_6H_5, C_2H_5O, *p*-$CH_3C_6H_4O$ [9], F, Cl, OH, NH_2, SH, PH_2, SiH_3 [10], aminopropyl [11], chloroalkyl [12], allyl, etc. Aminopropylsilatranes are of high interest due to their potential for the preparation of new silatranes by the derivatization of the amino group. Therefore, they act as potential precursor materials for the synthesis of a number of *N*-derivatives of silatranes [1].

Silatranes are relatively stable to moisture being more difficult to hydrolyze as compared to their analogs (trialkoxysilanes) and

* Corresponding author.
E-mail address: mcazacu@icmpp.ro (M. Cazacu).

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can be used in various reactions, e.g. addition, nucleophilic substitution, exchange, complexation, or photochemical reactions [1]. Due to their particularities, silatranes proved useful in many practical areas. In sol–gel processes, they are used as a silica source for the preparation of ultra-fine silica fibers [13] or as ceramic precursor [14], being more stable and controllable hydrolytically. In atomic force microscopy, aminopropylsilatrane is preferred to the easily hydrolysable 3-aminopropyltriethoxysilane to modify the surface of mica in order to obtain reliable imaging of DNA [15]. Silatranes are also used as coupling agents or adhesion promoters for curable silicone compositions or to obtain silatrane-containing polymers, which are useful as molding materials, catalyst supports, adhesion promoters and in non-linear optics (transparent compounds whose hyperpolarizability relies on the existence of donor–acceptor weak bonds) [2]. Due to their demonstrated pilotropic, antiviral, anti-inflammatory, antienzymatic, anticancer and antitumour, antibacterial and antifungal activities, as well as to their antistress and immunostimulant action [1,16], wound cicatrizing and burns healing effects, animal production and seed germination effects, etc., silatranes are widely used in biological systems [1]. Nontoxic or low toxicity silatranes stimulate the biosynthesis of nucleic acids and proteins and the growth of some cells, especially regenerating cells of connective tissue and liver [16]. Silatranes properly derivatized can lead to redox or biological active complexes with transition metals [4].

This paper reports the preparation of 1-(3-aminopropyl)silatrane, **2**, named according to IUPAC rules 1-(3-aminopropyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3.0^{1,5}]undecane, by using two routes, one of them leading to the carbamate complex of the silatrane, **1**, that was characterized as such, the other resulting in the silatrane with a free amine group. The latter was derivatized by reacting with 2-hydroxybenzaldehyde, yielding a new imino-silatrane, **3**. The attempt to prepare in one step the cobalt complex of 2,4-dihydroxybenzimine-silatrane led to the unexpected formation of the new, unreported 1-chlorocobaltrane, **4**. Reaction of the aminopropylsilatrane with $CoCl_2$ caused the decomposition of the silatrane with formation of triethanolamine chlorohydrate, **5**. All crystalline reaction products were investigated by elemental and spectral (FTIR and ^{1}H NMR) analyses and the structures were established by single-crystal X-ray diffraction. It is expected that, among other properties, the resulted compounds to be biologically active.

2. Experimental

2.1. Materials

3-Aminopropyltrimethoxysilane, $H_2N(CH_2)_3Si(OCH_3)_3$, (APTMS), (Fluka, M = 179.19, bp = 91–92 °C/15 mm Hg, $d_4^{20} = 1.016$ g/mL).

3-Aminopropyltriethoxysilane, $(C_2H_5O)_3Si(CH_2)_3NH_2$, (APTES), (Fluka, M = 221.37, bp = 213–216, $d_4^{20} = 0.949$).

Triethanolamine, $(HOCH_2CH_2)_3N$, (Sigma–Aldrich), M = 149.19, puriss. p.a. (>99%), 190–193 °C/5 mm Hg, $n_D^{20} = 1.485$, d^{25} = 1.124 g/mL.

2-Hydroxybenzaldehyde (Aldrich), M = 122.12, reagent grade (8%, b.p. 197 °C, m.p. 1–2 °C, density: 1.146 g/mL).

2,4-Dihydroxybenzaldehyde (Aldrich), $(HO)_2C_6H_3CHO$, 98%, M = 138.12, m.p. 135–137.

Cobalt(II) chloride hexahydrate, $CoCl_2{\cdot}6H_2O$, 98% (Sigma–Aldrich).

2.2. Measurements

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer. Analyses were performed in the transmission mode in the 400–4000 cm^{-1} range, at room temperature, with a resolution of 2 cm^{-1} and accumulation of 32 scans. The samples were incorporated in dry KBr and processed as pellets in order to be analyzed.

The proton magnetic resonance (^{1}H NMR) spectra were acquired in $CDCl_3$ or D_2O at 25 °C with a Bruker Avance DRX 400 MHz spectrometer operating at 400.13 MHz for ^{1}H. The spectrometer was equipped with a 5 mm four nuclei, direct detection z-gradient probehead.

The carbon, hydrogen, nitrogen, and silicon contents were determined by standard methods. The molar ratio Co/Cl was estimated by using an Energy-Dispersive X-ray Fluorescence (EDXRF) system EX-2600 X-Calibur SDD.

2.3. X-ray crystallography

Crystallographic measurements for **1**, **2**, **3** and **4** compounds were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer using graphite-monochromated Mo Kα radiation. The crystals were placed 40 mm from the CCD detector. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [17]. All structures were solved by direct methods using SHELXS-97 [18] and refined by full-matrix least-squares on F_o^2 with SHELXL-97 [18] with anisotropic displacement parameters for non-hydrogen atoms. All H atoms attached to carbon were introduced in idealized positions (dCH = 0.96 Å) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. Positional parameters of the H attached to N and O atoms were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. In the structures **3** and **4** the atoms from the silatrane moieties presented large thermal ellipsoids, so that disordered models, in combination with the available tools (PART, DFIX, and SADI) of SHELXL-97 were applied in order to better fit the electron density. In both **3** and **4** structures, the silatrane part was found to be disordered over two resolvable positions with the equal probabilities of 50%. The main crystallographic data together with refinement details are summarized in Table 1.

2.4. Procedures

2.4.1. Synthesis of 1-(3-aminopropyl)silatrane

*2.4.1.1. Procedure I (leading to compound **1**).* A catalytic amount of sodium metal (5 mg) was added to triethanolamine (15.0 mL, 16.8 g, 0.11 mol) in a 250 mL round-bottom flask to form a solution. A glass tube was attached to the flask through a septum to allow the capture of the resulted hydrogen into a rubber balloon. The mixture was heated up to 130 °C for 1 h and then cooled at room temperature. An equivalent amount of (3-aminopropyl)trimethoxysilane (25.0 g, 0.11 mol) was added and the mixture was heated at 60 °C for 1 h. The methanol formed as a result of the reaction occurrence was removed by distillation in rotavap when a white solid remained. White needles crystals, **1**, suitable for single crystal X-ray analysis were separated after 2 days from the extract in THF.

Yield: 8 g (83.9%); *Anal.* Calc. for $C_{19}H_{40}O_8N_4Si_2$ (M = 508 g/mol): C, 44.9; H, 7.9; N, 11.0; Si, 11.0. Found: C, 45.2; H, 7.9; N, 10.54; Si, 10.62%.

FTIR (KBr pellet, cm^{-1}): 3379s, 2936m, 2879s, 2642vw, 2584vw, 2517vw, 2170vw, 1630m, 1562m, 1534m, 1486s, 1476s, 1417vw, 1430vw, 1372m, 1324m, 1279m, 1192w, 1172w, 1124vs, 1098vs, 1088vs, 1053m, 1017m, 940m, 911m, 880w, 862vw, 822w, 806m, 763vs, 719s, 665m, 618m, 584m, 576m, 499vw, 461w.

The poor solubility of the compounds in usual organic solvents did not allow the registration of a qualitative ^{1}H NMR spectrum.

*2.4.1.2. Procedure II (leading to compound **2**).* In one-necked, flat-bottom flask, equipped with reflux condenser were introduced (3-aminopropyl)triethoxysilane (0.24 mol, 4.3 g, 4.4 mL), triethanolamine

Table 1
Crystallographic data, details of data collection and structure refinement parameters for **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{19}H_{40}N_4O_8Si_2$	$C_9H_{20}N_2O_3Si$	$C_{16}H_{24}N_2O_4Si$	$C_6H_{14}CoClNO_3$
Molecular weight (g/mol)	508.73	232.36	336.45	242.56
T (K)	200(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_1/n$	*Pnma*
a (Å)	6.6445(8)	6.638(4)	12.211(5)	16.9041(3)
b (Å)	13.7806(16)	12.9757(11)	14.100(2)	7.8788(2)
c (Å)	27.248(5)	7.1106(17)	19.274(4)	6.78770(10)
α (°)	90	90	90	90
β (°)	90	106.97(4)	92.84(3)	90
γ (°)	90	90	90	90
V (Å^3)	2495.0(6)	585.8(4)	3314.3(15)	904.01(3)
Z	4	2	8	4
D_{calc} (g/cm^3)	1.354	1.317	1.349	1.782
μ (mm^{-1})	0.193	0.192	0.164	2.161
θ_{min}, θ_{max} (°)	2.96–25.99	3.00–26.00	3.00–26.00	3.25–25.97
Crystal size (mm)	0.25 × 0.15 × 0.15	0.20 × 0.10 × 0.10	0.35 × 0.15 × 0.15	0.20 × 0.15 × 0.15
Reflections collected/unique	8559/4508 [R_{int} = 0.0610]	2468/1886 [R_{int} = 0.0151]	17532/6501 [R_{int} = 0.0264]	3778/950 [R_{int} = 0.0224]
Absolute structure parameter	0.45(18)	−0.03(14)		
R_1[a]	0.0676	0.0361	0.0482	0.0338
wR_2[b]	0.0811	0.0911	0.1202	0.0819
Goodness-of-fit (GOF)[c]	1.005	1.080	1.081	1.007
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e/Å^3)	0.307 and −0.269	0.205 and −0.310	0.231and −0.286	0.445 and −0.629

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
[c] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

(6.7 mol, 1.49 g, 1.57 mL), MeOH 14.2 mL, BuOH 1 mL and toluene 50 mL. The mixture was stirred 3 h at 60 °C and then concentrated by rotavap. White crystals, labeled as **2**, were obtained after 24 h.

Yield: 0.60 g (77.7%); *Anal.* Calc. for $C_9H_{20}O_3N_2Si$ (M = 232 g/mol): C, 46.5; H, 8.6; N, 12.1; Si, 12.1. Found: C, 46.2; H, 8.7; N, 11.9; Si, 12.3%.

FTIR (KBr pellet, cm^{-1}): 3359s, 3294m, 3192m, 2931s, 2878s, 1631sh, 1580s, 1483s, 1386m, 1329m, 1310m, 1279m, 1192m, 1125vs, 1097vs, 1050s, 1037s, 1020s, 941m, 912m, 880w, 862w, 763s, 718m, 670m, 697m, 620m, 582m, 484w, 455w.

^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm: 0.21–0.25 (2H, –$(CH_3)_2$Si–CH_2–), 1.32–1.40 (2H, –$(CH_3)_2$Si–CH_2–CH_2–CH_2–NH_2); 2.46–2.49 (2H, –$(CH_3)_2$Si–CH_2–CH_2–CH_2–NH_2); 2.83–2.92 (6H, N–CH_2–CH_2–O–); 3.65–3.68 (6H, N–CH_2–CH_2–O–); intensity ratio: 1:1:1:3:3.

2.4.2. Procedure for the synthesis of 1-(3-salicyliminopropyl) silatrane, *3*

In one-necked, flat-bottom flask, equipped with a reflux condenser, were introduced MeOH (15 mL) and **2** (4.64 g, 0.02 mol). 2-Hydroxybenzaldehyde (2.44 g, 0.02 mol) was added, and the reaction mixture was stirred for 3 h at 65 °C and then left for slow evaporation of the solvent. Yellow crystals, **3**, were obtained after 48 h.

Yield: 5 g (74.4%); *Anal.* Calc. for $C_{16}H_{24}N_2O_4Si$ (M = 336 g/mol): C, 57.14; H, 7.14; N, 8.33; Si, 8.33. Found: C, 57.0; H, 7.2; N, 8.28; Si, 8.4%.

FTIR (KBr pellet, cm^{-1}): 3435m, 3260w, 2965m, 2936s, 2919s, 2873s, 2838m, 2807w, 1634vs, 1610s, 1583m, 1505m, 1483m, 1459m, 1441m, 1415m, 1383w, 1371w, 1351w, 1340w, 1278s, 1245w, 1213w, 1197m, 1189m, 1175m, 1127vs, 1101vs, 1053m, 1031m, 1015s, 983w, 960w, 936m, 908s, 876m, 864m, 852m, 810m, 776vs, 718s, 677w, 650m, 614m, 586m, 567w, 484vw, 460w.

^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm: 0.49–0.51 (2H, –Si–CH_2–), 1.80–1.87 (2H, Si–CH_2–CH_2–CH_2–NH_2); 3.58–3.61 (2H, Si–CH_2–CH_2–CH_2–NH_2); 2.83–2.86 (6H, N–CH_2–CH_2–O–); 3.79–3.82 (6H, N–CH_2–CH_2–O–); 6.82–6.87 (1H, aromatic), 6.95–6.97 (1H, aromatic), 7.22–7.25 (1H, aromatic), 7.27–7.32 (1H, aromatic), 8.32, (1H, –CH=N–), 14.03 (1H, –OH) intensity ratio: 2:2:2:6:6:1:1:1:1:1:1.

2.4.3. Procedure leading to 1-chlorocobaltrane, *4*

In one-necked flat-bottom flask equipped with reflux condenser were introduced MeOH (15 mL) and **2** (4.64 g, 0.02 mol). 2,4-Dihydroxybenzaldehyde (2.76 g, 0.02 mol) was added, and the mixture was stirred 3 h at 65 °C when an orange precipitate was formed. The reaction mixture was cooled to room temperature, filtered to give a clear filtrate, to which was further added $CoCl_2{\cdot}6H_2O$ (4.75 g, 0.02 mol) dissolved in 3 mL MeOH. The mixture was left for slow evaporation of the solvent and red crystals, **4**, were obtained after 2 months. These were further investigated.

Anal. Calc. for $C_6H_{12}NO_3SCoCl$ (M = 240.5 g/mol): C, 29.93; H, 4.98; N, 5.82. Found: C, 30.01; H, 4.95; N, 5.79%.

The Co/Cl molar ratio determined by XRF was 1:1 corresponding to %: Co, 24.32; Cl, 14.69 (*Anal.* Calc.: Co, 24.54; Cl, 14.77).

FTIR (KBr pellet, cm^{-1}): 3552s, 3348s3313vs, 3212s, 3158s, 3041s, 2937s, 2724m, 2628w, 1606m, 1549w, 1488s, 1461m, 1442m, 1404s, 1327m, 1227m, 1135vs, 1098vs, 1032s, 1005s, 917m, 900m, 845w, 790w, 748w, 699m, 606m, 545w, 528m, 477w.

^{1}H NMR (400.13 MHz, D_2O), δ, ppm: broad peaks centered at 3.03 (6H, N–CH_2–CH_2–O–Co–); 3.81 (6H, N–CH_2–CH_2–O–Co–).

2.4.4. Procedure leading to triethanolamine hydrochloride, *5*

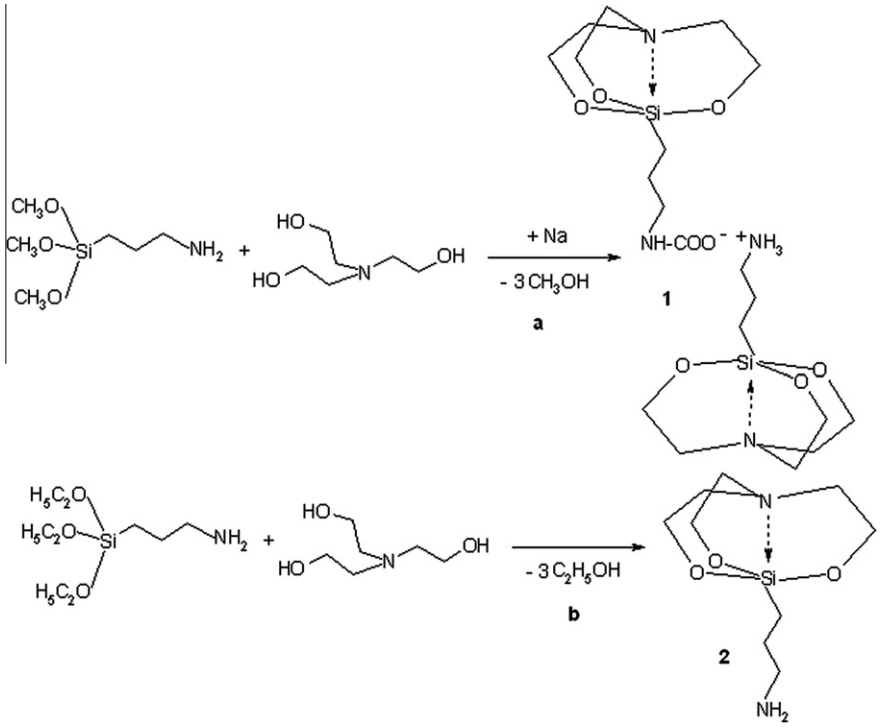
In one-necked, flat-bottom flask were introduced MeOH (15 mL) and **2** (2.32 g, 0.01 mol). $CoCl_2{\cdot}6H_2O$ (4.75 g, 0.02 mol) dissolved in MeOH (3 mL) was added with stirring at room temperature. The mixture was left for slow evaporation and crystals labeled as **5** were obtained after 1 week.

3. Results and discussions

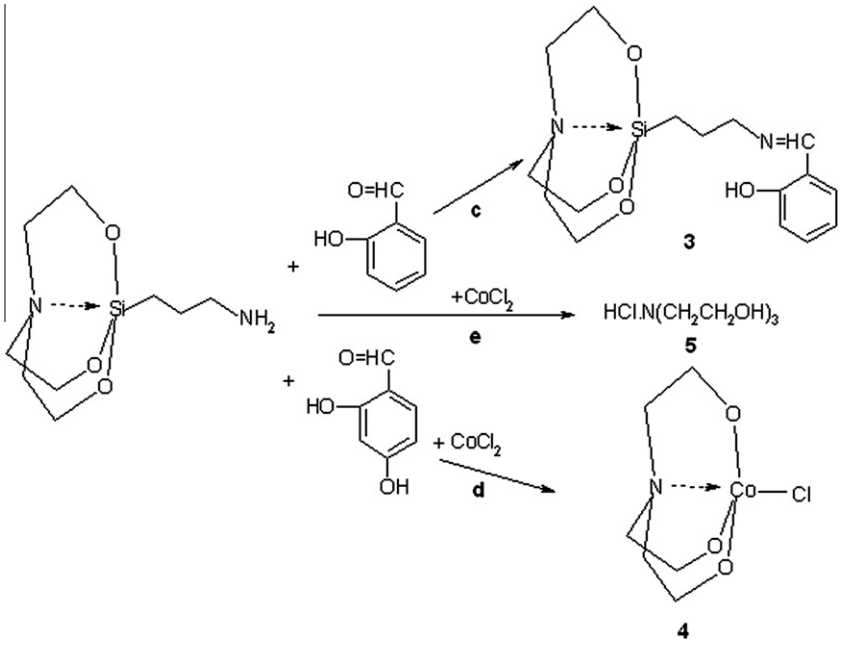
We have approached two procedures to prepare 1-(3-aminopropyl) silatrane, both involving the treatment of a 3-aminopropyltrialkox-

ysilane with triethanolamine in 1:1 molar ratio, in the presence (procedure I, Scheme 1a) [15] or absence (procedure II, Scheme 1b) of a third reagent, metallic sodium. Procedure I used 3-aminopropyltrimethoxysilane and procedure II used 3-aminopropyltriethoxysilane. While procedure I occurred in bulk, without solvent, a mixture of solvents was used as reaction medium in the second approach.

Product formation was verified by FTIR spectroscopy. The most characteristic absorption bands associated with silatrane structure can be found in the spectrum of the compound **2** prepared by procedure II: split band at 1097, 1125, 1020 and 941 cm^{-1} is assigned to Si–O–C–C– structural fragment; the doublet at 718, 763 cm^{-1} is due to a band split in the second frequency ν_{as}(Si–O); 620 and 670 cm^{-1} bands are assigned to ν(Si–C) and ν_s(Si–O), respectively; the band at 582 cm^{-1} is associated to ν(Si ← N); the silatrane cyclic skeleton structure presents specific bands at 1386 and 1483 cm^{-1}, assigned to deformation modes of the CH_2 group [11,19,20], but also at about 1050 cm^{-1}, identified with stretching vibrations of



Scheme 1. Reaction pathway leading to: a – [1-(3-ammoniumpropyl)silatrane]1-(3-carbamatepropyl)silatrane, **1**; b – 1-(3-aminopropyl)silatrane, **2**.



Scheme 2. Reaction pathway leading to: c – 1-(3-salicyliminopropyl)silatrane, **3**; d – 1-chlorocobaltrane, **4**; e – triethanolamine chlorohydrate, **5**.

the C–C bond in the silatrane skeleton, according to literature [9]. The bands at 3294 and 3192 cm^{-1} are assigned to N–H stretching while the medium strong band at 1580 cm^{-1} is assigned to N–H bending [21]. All peaks expected according to literature data are present in ^1H NMR, the intensities ratio corresponding to the presumed structure.

It is assumed [22] that silatrane formation involves a change of hybridization of silicon from sp^3 to sp^2 leading to the formation of the dative Si ← N bond. These neutral pentacoordinated silicon compounds are charge-transfer complexes. The dative bond is weaker than a covalent bond and is very sensitive to the inductive effects of the substituents, and is shortened as the number of electron-withdrawing groups linked to silicon increases. The length of this bond is also influenced by the position, axial or equatorial, occupied by the substituent at the silicon as well as by cage effects [22].

Although the synthesis of 1-(3-aminopropyl)silatrane is reported in literature [1,11], its structure is not known. In the first attempt we chose to work in bulk, without any solvent, in the presence of metallic sodium, according to the procedure described in Ref. [15] when an unexpected structure was obtained, namely silatrane carbamate, **1.** Its IR spectral pattern differs from that of the compound **2** mainly by the absence of the bands corresponding to free NH_2 group. At the same time, a new well-defined band assigned to C=O symmetric stretching of carbamate appears at 1534 cm^{-1} [23], while the N–H bending is shifted to 1562 cm^{-1}. A shifting to higher wavenumbers and splitting of the bands assigned to CH_2 group (1486, 1476 cm^{-1}) also occurred. The other specific bands (C–O–Si and Si ← N) can be found at about the same frequencies as in the uncarbonated silatrane (1017–1124 and 584 cm^{-1}, respectively). The explanation for the formation of this product would be based on well-known tendency of the amines to undergo carbonation in air to form sec-ammonium *N*-carboxylates (carbamates) [24] that is stimulated at high pH values [25] as in the present case when the synthesis occurred in the presence of sodium. Carbamates themselves represent another important class of organic compounds, used in a variety of applications including polyurethanes, pesticides, fungicides, medicinal drugs, and synthetic intermediates [26]. When subjected to heating under vacuum [26] or in presence of moisture [27], the carbamates can decompose to the initial amine.

1-(3-Aminopropyl)silatrane was reacted with 2-hydroxybenzaldehyde to obtain azomethine **3** (Scheme 2c). The reaction product was separated as high quality crystals able to be investigated by single-crystal X-ray diffraction. The structure was first verified by spectral (FTIR and ^1H NMR) analyses. The disappearance of the free amine groups (3294 and 3192 cm^{-1}) and the presence of the band at 1634 cm^{-1} prove the azomethine formation. The other silatrane characteristic bands can also be found in the spectrum at about the same wavelength as in 1-(3-aminopropyl)silatrane.

In the ^1H NMR spectrum one can notice the presence of the peak at 8.32, assigned to the imine proton, besides those belonging to aromatic protons and the displacement of the protons of the propyl group: from 0.21–0.25 (2H, –Si–C*H*$_2$–), 1.32–1.40 (2H, Si–CH$_2$–C*H*$_2$–CH$_2$–NH$_2$); 2.46–2.49 (2H, Si–CH$_2$–CH$_2$–C*H*$_2$–NH$_2$); 2.83–2.92 (6H, N–C*H*$_2$–CH$_2$–O–); 3.65–3.68 (6H, N–CH$_2$–C*H*$_2$–O–) in **2** to 0.49–0.51 (2H, –Si–C*H*$_2$–), 1.80–1.87 (2H, Si–CH$_2$–C*H*$_2$–CH$_2$–NH$_2$); 3.58–3.61 (2H, Si–CH$_2$–CH$_2$–C*H*$_2$–NH$_2$) in **3**.

In a different approach, 1-(3-aminopropyl)silatrane, **2**, was reacted with 2,4-dihydroxybenzaldehyde and subsequently with $CoCl_2$. The aim was to prepare the corresponding azomethine suitable to form a cobalt complex in a one-pot procedure by involving

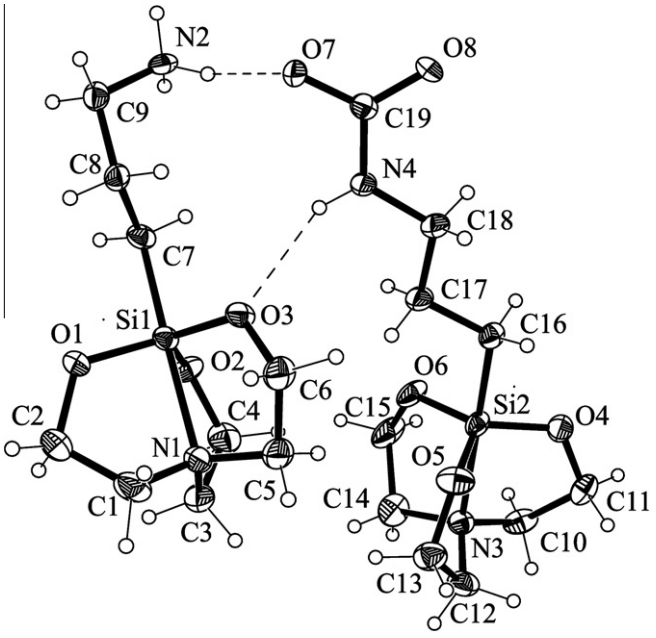


Fig. 1. X-ray structure of compound **1**. Thermal ellipsoids are drawn at 40% probability level. Two intermolecular H-bonds N2–H···O7 [N2–H 0.890 Å, H···O7 1.950 Å, N2···O7 2.810(4) Å, N2–H···O7 162.2°] and N4–H···O3 [N4–H 0.860 Å, H···O3 2.425 Å, N4···O3 3.127(4) Å, N4–H···O3 139.2°] are also shown. Selected bonds (Å) and angles (°): Si2–O6 1.667(3), Si2–O5 1.670(3), Si2–O4 1.674(3), Si2–C16 1.878(4), Si2–N3 2.203(4), Si1–O2 1.657(3), Si1–O1 1.671(3), Si1–O3 1.676(3), Si1–C7 1.878(4), Si1–N1 2.189(4); O6–Si2–O5 118.9(2), O6–Si2–O4 116.57(2), O5–Si2–O4 119.60(2), O6–Si2–C16 97.50(2), O5–Si2–C16 97.04(2), O4–Si2–C16 97.84(2), O6–Si2–N3 82.72(2), O5–Si2–N3 82.29(2), O4–Si2–N3 82.62(2), C16–Si2–N3 179.32(2), O2–Si1–O1 118.39(2), O2–Si1–O3 118.64(2), O1–Si1–O3 118.24(2), O2–Si1–C7 97.40(2), O1–Si1–C7 97.84(2), O3–Si1–C7 96.56(2), O2–Si1–N1 82.24(2), O1–Si1–N1 83.43(2), O3–Si1–N1 82.53(2), C7–Si1–N1 178.69(2).

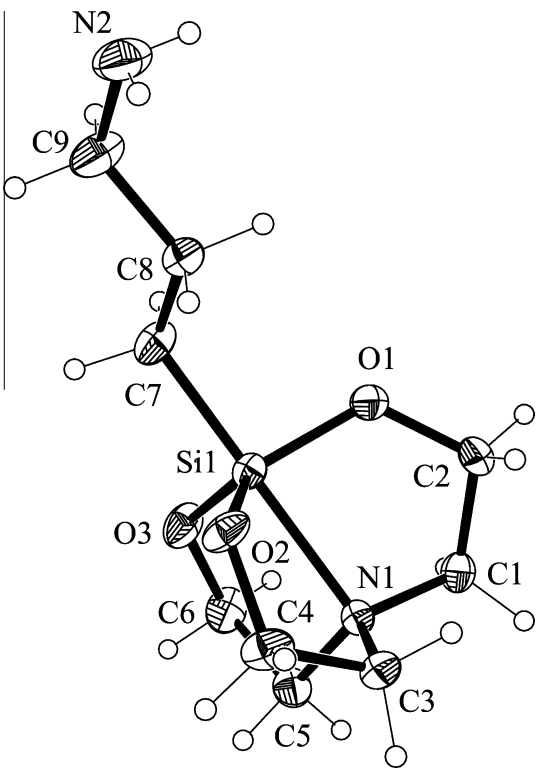


Fig. 2. X-ray structure of compound **2**. Thermal ellipsoids are drawn at 40% probability level. Selected bonds (Å) and angles (°): Si1–O3 1.660(2), Si1–O1 1.664(2), Si1–O2 1.667(2), Si1–C7 1.874(3), Si1–N1 2.171(2); O3–Si1–O1 118.61(1), O3–Si1–O2 117.28(1), O1–Si1–O2 119.38(1), O3–Si1–C7 97.71(1), O1–Si1–C7 97.61(1), O2–Si1–C7 96.47(1), O3–Si1–N1 83.04(9), O1–Si1–N1 82.45(9)°, O2–Si1–N1 82.73(9), C7–Si1–N1 179.10(1).

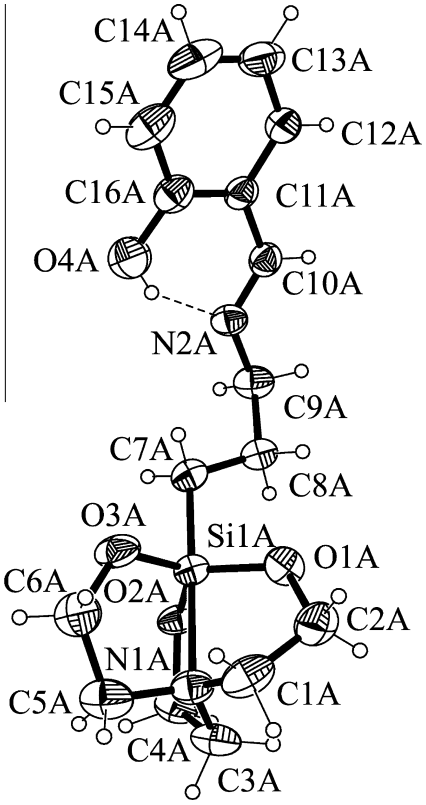


Fig. 3. X-ray structure of compound **3**. Thermal ellipsoids are drawn at 40% probability level. Only one of two disordered positions for silatrane fragment is shown for clarity. H-bond parameters: O4A–H···N2A [O4A–H 0.820 Å, H···N2A 1.795 Å, O4A···N2A 2.528(5) Å, O4A–H···N2A 148.1°]. Selected bonds (Å) and angles (°) (for component A): Si1–O1 1.682(4), Si1–O2 1.638(8), Si1–O3 1.634(8), Si1–C7 1.849(2), Si1–N1 2.185(2); O3–Si1–O2 120.5(6), O3–Si1–O1 120.0(5), O2–Si1–O1 116.5(4), O3–Si1–C7 94.9(4)°, O2–Si1–C7 95.7(4), O1–Si1–C7 96.85(2), O3–Si1–N1 84.3(4), O2–Si1–N1 84.4(4), O1–Si1–N1 83.94(2), C7–Si1–N1 179.07(1).

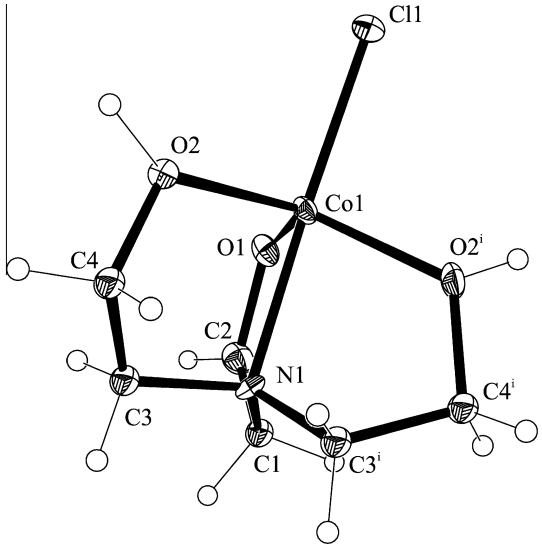


Fig. 4. Molecular structure of compound **4**. Only one of two disordered positions are shown. Thermal ellipsoids are drawn at 40% probability level. Symmetry code: (i) x, 0.5 − y, z. Selected bonds (Å) and angles (°): Co1–O1 1.986(3) Å, Co1–O2 2.043(2) Å, Co1–N1 2.168(4) Å, Co1–Cl1 2.307(1) Å; O1–Co1–O2 117.36(7)°, O2–Co1–O2^{i} 117.16(1)°, O1–Co1–N1 82.09(1)°, O2–Co1–N1 79.60(8)°, O1–Co1–Cl1 99.62(1)°, O2–Co1–Cl1 99.54(6)°, N1–Co1–Cl1 178.29(1)°.

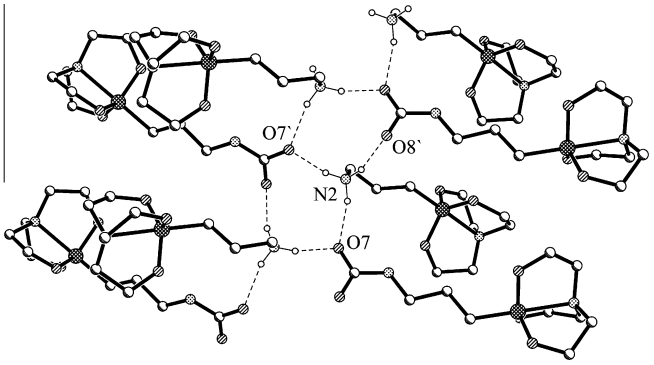


Fig. 5. The association of the RNH_3^+ cations and $RNHCO_2^-$ anions into the bands in the crystal structure **1**. H-bonds parameters: N2–H···O7 [N2–H 0.890 Å, H···O7 1.842 Å, N2···O7(x − ½, −y + $^3/_2$, −z + 1) 2.713(4) Å, N2–H···O7 165.9°]; N2–H···O8 [N2–H 0.890 Å, H···O8 1.978 Å, N2···O8(x − 1, y, z) 2.837(4) Å, N2–H···O8 161.8°].

azomethine group and OH group from 2 position, that from 4 position remaining available for further derivatization. However, the high quality red crystals separated after 2 months proved to be a new, unexpected compound, 1-chlorocobaltrane, **4**, formed by replacement of the aminopropyl substituted silicon in 1-(3-aminopropyl)silatrane with Co having a chlorine atom attached.

The FTIR spectrum of compound **4** presents the main bands characteristic for triethanolamine-derived atrane but slightly shifted from those of silatrane: 1135, 1098, 1032 and 1005 cm^{-1} assigned to sequence Co–O–C–C– and 528 for ν(Co ← N).

The ^1H NMR peaks in compound **4** (3.81 for –O–CH_2– and 3.03 ppm for –CH_2–N<) are downfield shifted as compared with corresponding ones from free triethanolamine (3.68–3.71 and 2.73–2.76 ppm, respectively), both spectra being registered in D_2O solution. The largest shift (0.27 ppm) was recorded for the peak corresponding to the protons from –CH_2–N< group, which reflects the presence of the partial positive charge on the tertiary nitrogen in this compound [9,28]. The peak broadening is due to the presence of paramagnetic cobalt ion.

When mixed only with $CoCl_2$, 1-(3-aminopropyl)silatrane decomposed forming triethanolamine chlorohydrate, **5**, as proved by the X-ray structural analysis of the formed crystals (Scheme 2e).

The X-ray single-crystal investigation revealed that in all synthesized compounds, the silicon, as well as the cobalt atom, exhibits a pentacoordinated environment with slightly distorted trigonal-bipyramidal geometry. The perspective view of **1**–**4** structures, along with atom-labeling schemes is given in Figs. 1–4, respectively.

Crystal **1** has an ionic structure build of RNH_3^+ cations and $RNHCO_2^-$ anions in 1:1 ratio, where R is the propylsilatrane moiety (Fig. 1). The ionic components of the structure are linked into the bands along [011] (Fig. 5), due to the multiple N–H···O H-bonds, the formation of which being completely realized in the crystal. The father extension of the crystal structure occurs via the weak C–H···O intermolecular contacts with distances: C6–H 0.97 Å, C6–H···O2′ (1 + x, y, z) 3.544(5) Å, H···O2 2.62 Å, C6–H···O2 160.1°; C11–H 0.97 Å, C11–H···O8′ (1 − x, y − ½, ½ − z) 3.280(5) Å, H···O8 2.45 Å, C11–H···O8 143.9°; C15–H 0.97 Å, C15–H···O4′(x − 1, y, z) 3.273(5) Å, H···O4 2.61 Å, C15–H···O4 125.9°. The others intermolecular contacts are equal or exceed the sum of van-der-Waals radii.

The crystal structure **2** is built from the parallel packing along [001] of the infinite ribbons, the view of which is depicted in Fig. 6. Within the ribbon the molecules are consolidated through N–H···O and C–H···N and C–H···O intermolecular contacts (Fig. 6).

The asymmetric part of the unit cell in crystal structure **3** contains two discrete molecules (denoted as A and B) as crystallographically independent units, which exhibit quite similar

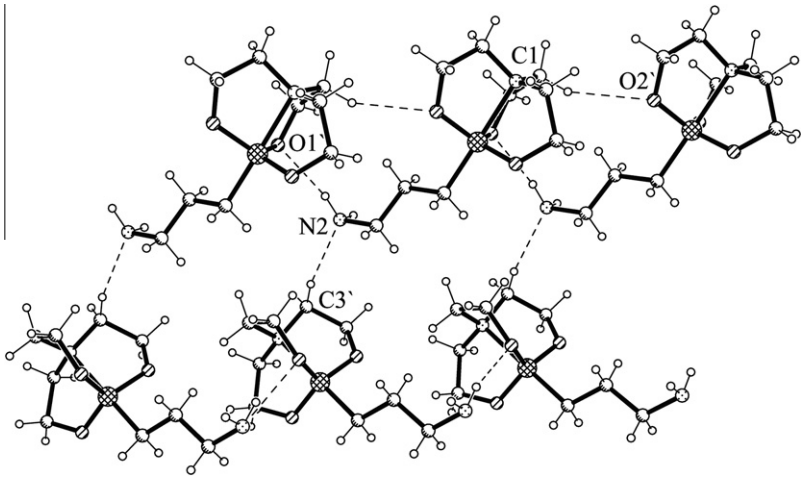


Fig. 6. View of crystal structure **2**. Three intermolecular H-bonds: N2–H···O1 [N2–H 0.898 Å, H···O1 2.472 Å, N2···O1($x-1, y, z$) 3.327(4) Å, N2–H···O1 159.1°]; C3–H···N2 [C3–H 0.99 Å, H···N2 2.50 Å, C3···N2($-x, y-½, 2-z$) 3.454(4) Å, C3–H···N2 161.4°] and C1–H···O2 [C1–H 0.99 Å, H···O2 2.65 Å, C1···O2($1+x, y, z$) 3.566(3) Å, C1–H···O2 154.4°] are also shown.

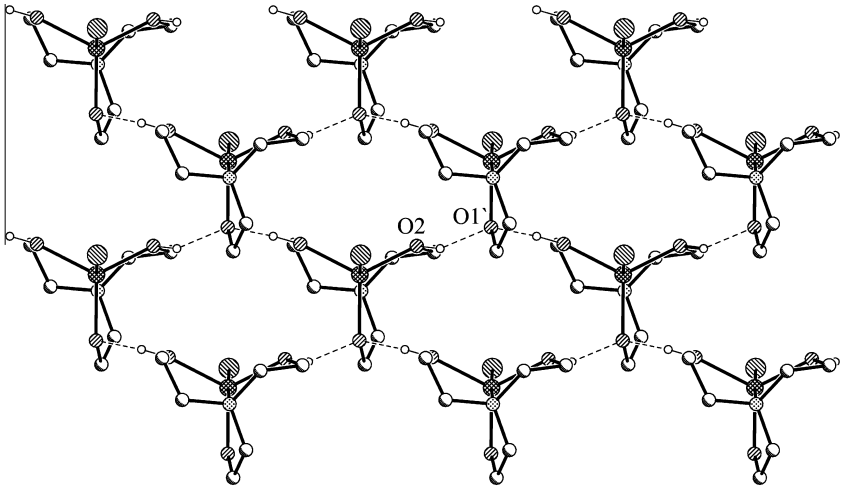


Fig. 7. 2D supramolecular layer in crystal structure **4**. H-bond: O2–H···O1 [O2–H 0.965 Å, H···O1 1.616 Å, O2···O1($-x+{}^{3}/_{2}, 1-y, ½+z$) 2.580(3) Å, O2–H···O1 179.3°].

geometric parameters. In both molecules all the carbon and oxygen atoms of silatrane fragments are disordered over two resolvable positions with the equal probabilities of s.o.f. As an example, the structure of molecule A is presented in Fig. 3.

To the best of our knowledge, compound **4** is the first reported example of cobalt containing metallatranes (Fig. 4). The Co^{2+} ion has a slightly distorted trigonal-bipyramidal coordination provided by tridentate thriethanolamine ligand and chloride anion in apical position at 2.307(1) Å. The central atom is displaced from the average equatorial 3O plane at 0.335(2) Å towards chlorine atom. The X-ray study demonstrated that triethanolamine ligand in compound **4** is coordinated to Co atom in monodeprotonated form, so that the charge balance is in agreement with the formation of species **4**. Two negative charges provided by Co^{2+} ion are balanced by the one negative charge of monodeprotonated tridentate ligand and one negative charge of chloride anion. The view of crystal packing for compound **4** is depicted in Fig. 7. It consists of alternate two-dimensional layers oriented along a *bc* crystallographic plane. The layers are built from neutral molecules **4** connected via a system of intermolecular O–H···O hydrogen bonds. Each molecule acts ones as proton acceptor and twice as proton donor, thus fulfilling all H-bonds opportunities in the crystal.

H-bond: O2–H···O1 [O2–H 0.965 Å, H···O1 1.616 Å, O2···O1($-x+{}^{3}/_{2}, 1-y, ½+z$) 2.580(3) Å, O2–H···O1 179.3°.

4. Conclusion

3-Aminopropyltrialkoxysilane was reacted with triethanolamine to obtain 1-(3-aminopropyl)silatrane. Either silatrane having a free amine group or an ammonium carbamate pair were obtained depending on the reaction conditions. A new azomethine structure was obtained by reacting 1-(3-aminopropyl)silatrane with 2-hydroxybenzaldehyde. The attempt to prepare the azomethine derived from aminopropylsilatrane with 2,4-dihydroxybenzaldehyde and its cobalt complex resulted in formation of a new, unexpected crystalline atrane. The treatment of 1-(3-aminopropyl)silatrane with $CoCl_2$ led to the complete decomposition of the silatrane with separation of triethanolamine chlorohydrate. The biological activity of the obtained compounds will be further studied.

Acknowledgements

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Appendix A. Supplementary data

CCDC 832513, 832514, 832515 and 832516 contain the supplementary crystallographic data for complex **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] J.K. Puri, R. Singh, V.K. Chahal, Chem. Soc. Rev. 40 (2011) 1791.
[2] B. Pedersen, G. Wagner, R. Herrmann, Echet '98, Electronic Conference on Heterocyclic Chemistry, 29 June–24 July, 1998, Available from: <http://www.ch.ic.ac.uk/ectoc/echet98/pub/048/index.htm>.
[3] V.F. Sidorkin, V.A. Pestunovich, M.G. Voronkov, Russ. Chem. Rev. 49 (1980) 414.
[4] P. Tharmaraj, D. Kodimunthiri, C.D. Sheela, C.S. Shanmuga Priya, J. Coord. Chem. 62 (2009) 2220.
[5] C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371.
[6] J.H. Iwamiyat, G.E. Maciel, J. Am. Chem. Soc. 115 (1993) 6835.
[7] M.W. Kim, D.S. Uh, S. Kim, Y. Do, Inorg. Chem. 3 (1993) 5883.
[8] N.V. Timosheva, A. Chandrasekaran, R.O. Day, R.R. Holmes, Phosphorus, Sulfur, Silicon Relat. Elem. 59 (2001) 168.
[9] M.G. Voronkov, Pure Appl. Chem. 13 (1966) 35.
[10] A. Yoshikawa, M.S. Gordon, V.F. Sidorkin, V.A. Pestunovich, Organomet. Chem. 20 (2001) 927.
[11] Y. Lin, Bo Song, A. Han, S. Hu, F. Ye, Z. Xie, Phosphorus, Sulfur, Silicon Relat. Elem. 186 (2011) 298. and references therein.
[12] V.B. Kazimirovskaya, V.M. D'yakov, M.G. Voronkov, Pharm. Chem. J. 35 (9) (2001) 465.
[13] M. Krissanasaeranee, T. Vongsetskul, R. Rangkupan, P. Supaphol, S. Wongkasemjit, J. Am. Ceram. Soc. 91 (2008) 2830.
[14] W. Charoenpinijkarn, M. Suwankruhasn, B. Kesapabutr, S. Wongkasemjit, A.M. Jamieson, Eur. Polym. J. 37 (2001) 1441.
[15] Y.L. Lyubchenko, L.S. Shlyakhtenko, Methods 47 (2009) 206.
[16] M.G. Voronkov, V.P. Baryshok, Pharm. Chem. J. 38 (2004) 3.
[17] CrysAlis RED, Oxford Diffraction Ltd.,Version 1.171.34.76, 2003.
[18] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1990.
[19] P. Hencsei, L. Párkányi, I. Kovács, Chem. Heterocycl. Compd. 32 (1996) 1376.
[20] L. Chen, Q. Xie, L. Sun, H. Wang, J. Organomet. Chem. 678 (2003) 90.
[21] T. Yu, K. Wakuda, D.L. Blair, R.G. Weiss, J. Phys. Chem. 113 (2009) 11546.
[22] J.M. Anglada, C. Bo, J.M. Bofill, R. Crehuet, J.M. Poblet, Organomet. Chem. 18 (1999) 5584.
[23] H.S. Park, Y.M. Jung, J.K. You, W.H. Hong, J.N. Kim, J. Phys. Chem. A 112 (2008) 6558.
[24] F. Meijide, A. Antelo, M. Alvarez, V.H. Soto, J.V. Trillo, A. Jover, J.V. Tato, Cryst. Growth Des. 11 (2011) 356. and references therein.
[25] R. Srivastava, D. Srinivas, P. Ratnasamy, J. Catal. 233 (2005) 1.
[26] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 926.
[27] B.R. Ramachandran, A.M. Halpernand, E.D. Glendening, J. Phys. Chem. A 102 (1998) 3934.
[28] A.A. Naiini, J. Pinkas, W. Plass, V.G. Young Jr., J.G. Verkade, Inorg. Chem. 33 (1994) 2137.