# New polyfunctional silicon-containing amines $C_6[CH_2CH_2SiMe(OCH_2CH_2NR_2)_2]_6$ (R = H, Me) and their reactions with cobalt(11) chloride and dicobalt octacarbonyl

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Hexakis[bis(2-aminoethoxy)methylsilylethyl]benzene and hexakis[bis(N,N-dimethyl-2aminoethoxy)methylsilylethyl]benzene  $C_6[(NR_2CH_2CH_2O)_2SiMeCH_2CH_2]_6$  (4, R = H; R = Me) were prepared from hexakis(methyldichlorosilylethyl)benzene  $C_6(Cl_2MeSiCH_2CH_2)_6$  and 2-aminoethanol or N,N-dimethyl-2-aminoethanol, respectively. Compounds 4 and 5 react with anhydrous cobalt (11) chloride to give poorly soluble dodecachloro{hexakis[bis(2-aminoethoxy)methylsilylethyl]benzene}hexacobalt dodecachloro{hexakis[bis(N,N-dimethyl-2-aminoethoxy)methylsilylethyl]benand zene}hexacobalt { $Co_6[(NR_2CH_2CH_2O)_2SiMeCH_2CH_2]_6C_6$ }Cl<sub>12</sub> (R = H or Me), respectively. Polyfunctional amine 4 reacts with dicobalt octacarbonyl to produce hexakis[bis(2-aminoethoxy)methylsilylethyl]benzenedicobalt(II) tetrakis(tetracarbonylcobaltate) {Co<sub>2</sub>[(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SiMeCH<sub>2</sub>CH<sub>2</sub>]<sub>6</sub>C<sub>6</sub>}[Co(CO)<sub>4</sub>]<sub>4</sub>. N,N-Dimethyl-substituted polyfunctional amine 5 is lowly reactive in the reaction with  $Co_2(CO)_8$ , whereas the simplest model of this compound, viz., bis(N,N-dimethyl-2-aminoethoxy)dimethyl- $(NMe_2CH_2CH_2O)_2SiMe_2,$ slowly reacts with  $Co_2(CO)_8$  to give silane tris[bis(N, N-dimethyl-2-aminoethoxy)dimethylsilane]cobalt(II) bis(tetracarbonylcobaltate){Co[(NMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SiMe<sub>2</sub>]<sub>3</sub>}[Co(CO)<sub>4</sub>]<sub>2</sub>. Thermal decomposition and transformations of the resulting complexes under the action of oxygen and water were studied.

**Key words:** hexakis[bis(2-aminoethoxy)methylsilylethyl]benzene, hexakis[bis(N,N-dimethyl-2-aminoethoxy)methylsilylethyl]benzene, cobalt(II) chloride, dicobalt octacarbonyl, amine complexes, coordination polymers, hydrolysis, xerogel, thermal decomposition.

Transition metal complexes included in organosilicate matrices are prepared by hydrolysis of coordination compounds containing functional organosilicon ligands.<sup>1–5</sup> Organosilsesquioxane structures are formed by hydrolysis of the peripheral triethoxysilyl groups of the complex compounds followed by condensation of the resulting silanols. The relatively high resistance of amino derivatives of cobalt and chromium to hydrolysis enables one to form the siloxane core, the center of the coordination compound remaining virtually unchanged.<sup>6–8</sup> If the ligand contains a large number of functional groups, there is a possibility to synthesize a polymer already in the first step through the formation of coordination bonds. Coordination polymers are of interest as starting compounds for the synthesis of new ceramic materials and heterogeneous catalysts and as porous structures for the ion exchange and adsorption of gases and small molecules.9,10

In the present study, we report a procedure for the preparation of two new hexaalkylated benzenes (Scheme 1), which contain six silicon atoms and 12 amino substituents bound to these silicon atoms. The reactions of these compounds with cobalt(11) chloride and dicobalt octacarbonyl giving rise to coordination polymers were studied.

#### **Results and Discussion**

Synthesis of polyfunctional silicon-containing amines based on hexa(silylalkyl) derivatives of benzene. Hexakis[bis(2-aminoethoxy)methylsilylethyl]benzene (4) and hexakis[bis-(N, N-dimethyl-2-aminoethoxy)methylsilylethyl]benzene (5) were prepared from hexakis(methyldichlorosilylethyl)benzene (1) or hexakis(methyldiethoxysilylethyl)benzene (2) and 2-aminoethanol or N, N-dimethyl-2-aminoethanol, respectively (see Scheme 1).

According to the earlier data,<sup>11</sup> the adjacent substituents in hexa(silylalkyl) benzene derivatives are in *trans* positions with respect to each other. Such an arrangement does not hinder the formation of coordination polymers through the terminal  $-NR_2$  groups but efficiently pro-

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### Scheme 1



X = Cl(1), OMe(2), Me(3); R = H(4), Me(5)

tects the benzene ring from the attack of reagents. Thus, permethylated compound **3** did not give benzene tricarbonyl and bis(arene) derivatives of chromium (Scheme 2).



Benzene derivatives 4 and 5 are viscous orange liquids, which undergo hydrolysis by atmospheric moisture. Due to their low volatility, these compounds cannot be subjected to vacuum distillation. Since compound 4 is poorly soluble in saturated hydrocarbons, it can be purified by washing with hexane. The <sup>1</sup>H NMR spectrum showed that the yield of the target product obtained after repeated washing and prolonged heating *in vacuo* was 97%. Compound 5 was purified from impurities with the use of activated carbon and prolonged heating *in vacuo*. The <sup>1</sup>H NMR spectrum of compound 5 (see the Experimental section) has signals for six protons of the Me groups at the Si atom, six SiCH<sub>2</sub> fragments, 24 Me groups at the N atoms, and 12 -CH<sub>2</sub>N methylene groups, which overlap with the signal of six CH<sub>2</sub> groups at the benzene ring and the signal of  $12 \text{ O}-\text{CH}_2$ — groups of the aminoethoxy substituents at the Si atom. The weak triplet of the  $-\text{CH}_2$ -OH methylene group is indicative of the presence of a small impurity of *N*,*N*-dimethyl-2-aminoethanol.

**Reactions with cobalt(II) chloride.** It is known that cobalt chloride can bind two amine molecules to form complexes with composition  $Co(NH_2R)_2Cl_2$ . Previously,<sup>8,12</sup> we have studied the reactions of cobalt(II) and chromium(III) chlorides with primary organosilicon amines. These reactions proceeded rapidly with the evolution of heat, chromium chloride being less reactive. The reactivities of tertiary amines in such transformations were studied using bis(*N*,*N*-dimethyl-2-aminoethoxy)dimethylsilane (**6**) as an example. It appeared that compound **6**, like primary amines, readily reacted with  $CoCl_2$  (Scheme 3) to give complex **7** as a very hygroscopic bright-blue liquid.

## Scheme 3

$$CoCl_{2} + (NMe_{2}CH_{2}CH_{2}O)_{2}SiMe_{2} \longrightarrow$$

$$6$$

$$Co[(NMe_{2}CH_{2}CH_{2}O)_{2}SiMe_{2}]Cl_{2}$$

$$7$$

Polyfunctional hexaalkylated benzene derivatives **4** and **5** rather actively reacted with  $CoCl_2$  (Scheme 4). The reactions proceeded with the heat evolution and were completed in 30 min.

Compounds 8 and 9 are blue solids virtually insoluble in saturated, aromatic, and chlorinated hydrocarbons and



R = H (4, 8), Me (5, 9)

THF and poorly soluble in acetonitrile (8) and DMF (9). Coordination polymers are characterized<sup>9,10</sup> by low solubility in organic solvents. A large number of functional groups in the ligand (two, three, or more) and the remote arrangement of the donor atoms (for example, on opposite sides of the aromatic ring) facilitate the formation of two- and three-dimensional coordination polymers.<sup>9,10</sup> Considering that the starting compounds 4 and 5 satisfy these conditions, the low solubility of complexes 8 and 9 can be taken as indirect evidence in favor of the polymeric structures of the resulting compounds. The use of dilute solutions in these reactions did not prevent the binding of polyfunctional aminobenzenes to form coordination polymers.

The IR spectra of the starting aminobenzene **4** and its complex with cobalt chloride **8** (Fig. 1) showed that the coordination of the primary amino groups in compound **4** to the cobalt(11) cation led to the shifts of the N—H stretching bands to the low-frequency region<sup>13</sup> by 20–70 cm<sup>-1</sup>: **4**, v(N—H) 3350, 3320, 3170 cm<sup>-1</sup>; **8**, v(N—H) 3330, 3200, 3110 cm<sup>-1</sup>. The IR bands of the C—H bonds of the Me groups at the N atom are shifted upon the formation of complex **9** to the low-frequency region by 20–130 cm<sup>-1</sup> compared to the corresponding bands in the IR spectrum of the initial aminobenzene **5** (2810, 2775, 2730 cm<sup>-1</sup>), and their intensities are substantially decreased (Fig. 2). These changes are associ-



Fig. 1. IR spectra of compound 4 (I, liquid film) and its complex with cobalt(II) chloride 8 (2, Nujol mull).



Fig. 2. IR spectra of compound 5 (I, liquid film) and its complex with cobalt(II) chloride 9 (2, Nujol mull).

ated with the fact that the formation of the Co–N bond leads to a decrease in the effective negative charge on the N atom resulting in a change in the charge on the C atom bound to the N atom.<sup>14</sup> The positions of the absorption bands of the alkoxysilyl groups (4: 1250, 1110, 1090, 950,  $800 \text{ cm}^{-1}$ ; 5: 1250, 1110, 1070, 950, 890, 820, 790 cm<sup>-1</sup>), which are not involved in the formation of coordination bonds, remain virtually unchanged. The transformation of the IR spectrum of compound **6** upon the formation of the complex with CoCl<sub>2</sub> is analogous to those described for compounds **4** and **5**.

The electronic absorption spectra of compounds **7–9** (Fig. 3) are characterized by the presence of a multiplet with three maxima in the region from 18000 to 14000 cm<sup>-1</sup> (**7**, 16700, 15800, 15200 cm<sup>-1</sup>; **8**, 16800, 15900, 15200 cm<sup>-1</sup>; **9**, 16600, 15800, 15200 cm<sup>-1</sup>), which is typical of four-coordinate cobalt complexes, and this



Fig. 3. Electronic absorption spectra of complexes 7-9: *1*, a solution of 7 in MeCN; *2*, a solution of 8 in DMF; *3*, a solution of 7 in MeCN, *4*, a film of compound 7 after storage in air for 20 h.

band belongs to the  ${}^{4}T_{1}(P) - {}^{4}A_{2}$  transition with a vibrational structure.<sup>15</sup> The presence of additional bands is, apparently, attributable to distortions of the tetrahedral structure, which are most clearly manifested in the electronic absorption spectrum of compound **8**. The UV region of the spectra of highly dilute solutions of compounds **8** and **9** shows an absorption band belonging to the hexaalkylated benzene ring (39600 cm<sup>-1</sup> for compound **9**).

Compounds 7–9 are highly sensitive to atmospheric oxygen and moisture. Compound 7 is particularly unstable. It rapidly changed the color to green, which was accompanied by the appearance of an intense IR band at  $3360 \text{ cm}^{-1}$  (Fig. 4) belonging to vibrations of the associated OH groups and a series of bands in the region of 2800-2400 cm<sup>-1</sup> belonging to N-H stretching vibrations of the  $[NMe_2H]^+$  ammonium cation. A shoulder at 1040  $\text{cm}^{-1}$ , which is observed on the low-frequency side of the absorption band at 1070  $\text{cm}^{-1}$  (SiOC), characterizes the SiOSi fragments. These changes indicate that compound 7 underwent hydrolysis to form amino alcohol, silanols (major products), siloxanes, and ammonium salts. The latter were formed through the binding of hydrogen chloride generated in the reaction of the Co-Cl fragment with H<sub>2</sub>O or silanol groups. The electronic absorption spectral data allow one to establish the state of the  $Co^{2+}$  cation characterized by the maximum intensity of absorption bands. The visible region of the spectrum of compound 7 (see Fig. 3, spectrum 1) has a multiplet with maxima at 20500, 18000, 16700, 15800, and 15200 cm<sup>-1</sup>, which is typical of tetrahedral cobalt diamine dichloride complexes. In air, complex 7 underwent chemical transformations, as evidenced by the changes in the electronic absorption spectrum (see Fig. 3, spectrum 4). The changes in the spectrum recorded in solutions in MeCN occurred



**Fig. 4.** Transformation of the IR spectrum of a thin film of complex 7 on exposure to atmospheric oxygen and moisture during 5 min (1), 0.5 h (2), and 20 h (3).

slowly, whereas the spectrum measured in a film changed rapidly. The spectrum of the product (16200, 15800, 14900, and 14300 cm<sup>-1</sup>) is identical with the known spectra<sup>15,16</sup> of salts in which the double-charged tetrahedral  $[CoCl_4]^{2-}$  anion is bound with two  $R_4N^+$  ammonium cations (for example, the spectrum of the compound with  $R = Bu^n$  shows four absorption bands at 16230, 15750, 14900, and 14300 cm<sup>-1</sup>). The observed transformations can be represented by a series of equations (Scheme 5).

### Scheme 5

$$2 7 + 2 H_2O \longrightarrow [Co(NMe_2CH_2CH_2OH)_4]^{2+}[CoCl_4]^{2-} + + 1/n HO(SiMe_2O)_nH$$

2 **7** + 2 H<sub>2</sub>O →

 $\longrightarrow [Me_{2}Si(OCH_{2}CH_{2}NMe_{2}H)_{2}]^{2+}[CoCl_{4}]^{2-} +$  $+ Co[(NMe_{2}CH_{2}CH_{2}O)_{2}SiMe_{2}](OH)_{2}$ 2 7  $\longrightarrow \{[Co[(NMe_{2}CH_{2}CH_{2}O)_{2}SiMe_{2}]_{2}\}^{2+}[CoCl_{4}]^{2-}$ 

According to the last-listed equation in Scheme 5, the spontaneous rearrangement is the least probable process because compound 7 is rather thermally stable in inert atmosphere in the absence of atmospheric moisture.

Compounds 7, 8, and 9 were decomposed by water to form silanol derivatives, which were subsequently converted into polysiloxanes and formed a white gel. The latter were subsequently converted into polysiloxanes and formed a white gel. Complexes 7 and 9 gave hydroxides, whereas complex 8 produced cobalt(II) chloride.

**Reactions with dicobalt octacarbonyl.** Primary amines reacted with  $Co_2(CO)_8$  to give cobalt(11) hexamine bis(tetracarbonylcobaltates)  $[Co(NH_2R)_6][Co(CO)_4]_2$ .<sup>17</sup> Generally, the reactions are accompanied by the insertion of CO, which is liberated in the course of the reaction, at the N—H bond to give formamide derivatives. The latter compounds, like the starting amines, are bound to the Co<sup>2+</sup> cation. As a result, both the amino and amide ligands are involved in the octahedral environment about the Co<sup>2+</sup> cation (Scheme 6).

### Scheme 6

$$3 \operatorname{Co}_{2}(\operatorname{CO})_{8} + 12 \operatorname{NH}_{2} \operatorname{R} \longrightarrow$$

$$2 [\operatorname{Co}(\operatorname{NH}_{2} \operatorname{R})_{6-x}(\operatorname{HC}(\operatorname{O})\operatorname{NHR})_{x}][\operatorname{Co}(\operatorname{CO})_{4}]_{2} + (8 - 2x) \operatorname{CO}$$

Bis(N,N-dimethyl-2-aminoethoxy)dimethylsilane (**6**) containing the tertiary amino groups proved to be less active in the reaction with Co<sub>2</sub>(CO)<sub>8</sub> (Scheme 7) compared to 3-aminopropyltriethoxysilane studied earlier. The

reaction proceeded slowly. After precipitation, the yield of tris[bis(N,N-dimethyl-2-aminoethoxy)dimethylsilane]co-balt(II) bis(tetracarbonylcobaltate) (10) was only 17%.

#### Scheme 7

$$3 \operatorname{Co}_2(\operatorname{CO})_8 + 6 \mathbf{6} \longrightarrow$$
  
 $\longrightarrow 2 \{\operatorname{Co}[(\operatorname{NMe}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{O})_2\operatorname{SiMe}_2]_3\}[\operatorname{Co}(\operatorname{CO})_4]_2 + \mathbf{10} + 8 \operatorname{CO}_4$ 

An analogous reaction of compound **5** proceeded even more slowly. We failed to isolate the resulting cobaltate in pure form. By contrast, compound **4** reacted with  $Co_2(CO)_8$  rather readily to give hexakis[bis(2-aminoethoxy)methylsilylethyl]benzenedicobalt(II) tetrakis(tetracarbonylcobaltate) (**11**) (Scheme 8).

#### Scheme 8

$$3 \operatorname{Co}_{2}(\operatorname{CO})_{8} + 4 \longrightarrow$$

$$\longrightarrow \{\operatorname{Co}_{2}[(\operatorname{NH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{O})_{2}\operatorname{SiMeCH}_{2}\operatorname{CH}_{2}]_{6}\operatorname{C}_{6}\}[\operatorname{Co}(\operatorname{CO})_{4}]_{4}$$

$$11$$

$$+ 8 \operatorname{CO}$$

The course of the reaction was monitored by CO liberation. After 1 h, the yield of CO was 50% of the calculated value, and the yield reached 95% after 15 h. Hence, it follows that this reaction afforded the formamide derivative in an insignificant amount. Complexes **10** and **11** were obtained as crimson-colored powders.

The IR spectra of organosilicon amine **6** and the product of its reaction with dicobalt octacarbonyl, *viz.*, complex **10**, are shown in Fig. 5. The IR spectrum of cobaltate



Fig. 5. IR spectra of compounds 6 (1, liquid film) and 10 (2, Nujol mull).



**Fig. 6.** IR spectra of compound **11** (I, Nujol mull) and xerogel **12** (2, 4000–2500 cm<sup>-1</sup>, suspension in fluorohydrocarbon oil; 2200–400 cm<sup>-1</sup>, Nujol mull).

11 is presented in Fig. 6. The complex formation has a substantial effect on the vibrations of the groups bound to the N atom. In the spectrum of compound 11, the stretching bands (3350, 3270, 3170  $\text{cm}^{-1}$ ) and bending bands  $(1590 \text{ cm}^{-1})$  of the N-H bond are shifted to the lowfrequency region by  $20-30 \text{ cm}^{-1}$ . The presence of a small number of amide fragments is evidenced by the low-intensity band at 1650 cm<sup>-1</sup> (amide I). In the spectrum of compound 10, the absorption bands belonging to the Me substituents bound to the N atom are shifted to the highfrequency region and coincide with the C–H stretching vibrations in the spectra of alkanes. This is a consequence of a higher degree of covalence of the Co-N bond in cobalt carbonyl complexes compared to that in the complexes with CoCl<sub>2</sub> (absorption band corresponding to the vibrations  $v(Co-N)^{18}$  is observed at 370 and 350 cm<sup>-1</sup> in the spectra of compounds 8 and 11, respectively). As a result, no substantial decrease in the effective negative charge on the N atom occurs.<sup>14</sup> The spectra of cobaltates 10 and 11 are characterized by the presence of an intense absorption band at 1870 cm<sup>-1</sup> corresponding to the  $[Co(CO)_4]^-$  anion.

The visible region of the electronic absorption spectrum of compound **10** has a broad structureless band (Fig. 7) starting from 15000 cm<sup>-1</sup>. The spectrum of cobaltate **11** shows two bands with maxima at 25400 cm<sup>-1</sup> ( $\varepsilon = 392 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ) and 18700 cm<sup>-1</sup> ( $\varepsilon = 545 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ). The character of the spectra and the extinction coefficients calculated per Co(NH<sub>2</sub>R)<sub>6</sub> group correspond to the octahedral hexaamine cobalt(II) cation.<sup>15</sup>

The structures of compounds 10 and 11 contain the Co atoms, which are in different valence states and have different ligand environment. The carbonyl cobaltate anions are the least thermally stable. Compound 11 withstanded thermal treatment in a sealed evacuated tube up to 150 °C (1 h) without noticeable changes. However,



Fig. 7. Electronic absorption spectra of solutions of compounds 10 (1) and 11 (2) in MeCN.

heating of compound 11 to 250 °C led to complete decomposition of the  $[Co(CO)_4]^-$  fragments. In the IR spectrum of the solid product, the corresponding absorption band at 1870 cm<sup>-1</sup> disappeared. In the gas phase, H<sub>2</sub> and CO were present in a ratio of 3 : 7. The intensities and shapes of the stretching bands of the MeSi, CH<sub>2</sub>Si, CH<sub>2</sub>OSi, and CH<sub>2</sub>N fragments are changed only slightly. The stretching and bending absorption bands of the N-H bond are changed substantially. The intensities of the bands at 3330, 3180 cm<sup>-1</sup> (v(N-H)), and 1570 cm<sup>-1</sup>  $(\delta(N-H))$  decrease, whereas absorption in the region of 1700-1600 cm<sup>-1</sup> increases. Two bands at 1660 and  $1620 \text{ cm}^{-1}$  should be assigned to the amide group (amide I and amide II, respectively),<sup>19</sup> which is generated due to the insertion of the CO molecule at the N-H bond. Upon heating to 250 °C, the weight loss was 72%. This indicates that not only the  $[Co(CO)_4]^-$  anions decomposed but also some of amine ligands were removed from the environment about the  $Co^{2+}$  cation. This fact was confirmed by a decrease in the intensities of the IR absorption bands of the N-H bond and also by the formation of liquid products upon thermal decomposition. A decrease in the intensities can also be associated with the reaction of the NH<sub>2</sub> groups with cobalt(0) giving rise to H<sub>2</sub>.

Heating of compounds **8**, **9**, and **10** to 600 °C under a slow stream of argon caused the complete destruction of the organic moieties of the molecules and the formation of amorphous black silica-carbon solid phases containing crystalline cobalt compounds. The weight losses were 45, 42, and 30%, respectively. The starting complexes had negligibly small specific surfaces ( $S_{sp}$ ), which is confirmed by the fact that the desorption peak of nitrogen was not found when the specific surface was determined by the BET method. The products of pyrolysis of compounds **8**,

9, and 10 became medium porous materials, and their  $S_{sp}$  were 144, 91, and 65 m<sup>2</sup> g<sup>-1</sup>, respectively. Powder X-ray diffraction analysis revealed the following products: 8,  $\alpha$ -Co (d = 2.16, 1.91 Å),  $\beta$ -Co (d = 2.04, 1.76 Å); 9,  $\alpha$ -Co (d = 2.16, 1.91 Å),  $\beta$ -Co (d = 2.03, 1.76 Å), CoCl<sub>2</sub>·2 H<sub>2</sub>O (d = 5.44, 4.23, 2.77, 2.11, 2.07, 1.76 Å); 10, elemental cobalt in the  $\beta$  form (d = 2.03 and 1.77 Å). The  $\alpha$ -Co :  $\beta$ -Co ratio in the products of thermal decomposition was approximately 1 : 7. The presence of silicon dioxide was confirmed by the presence of the amorphous halo in the reflection angle range  $2\theta = 15-25^{\circ}$ .

It is known<sup>20</sup> that dilute solutions of the cobalt(II) hexamine and hexamide cobalt carbonyl complexes  $[CoAm_6][Co(CO)_4]_2$  produce carbonate (Am = Py, DMF) or carbonate-siloxane (Am =NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OEt)<sub>3</sub>) gels upon prolonged storage in air through the transformation of the carbonyl cobaltate anions into cobalt base carbonate and partial hydrolysis of the Si(OEt)<sub>3</sub> groups. The first step of this process involves adsorption of  $O_2$  by the cobalt(II) hexamine anion, which is then consumed for oxidation of the  $[Co(CO)_4]^-$  anions. The formation of a gel from complex 11 in a solution in 2-aminoethanol (0.03 mol  $L^{-1}$ ) proceeded slowly and was completed in 30 days. After the removal of the solvent in vacuo and washing of the solid phase with ether, xerogel 12 was obtained as a lilac-colored powder. The elemental analysis data agree with the  $\{Co_4C_6[C_2H_4SiMe(OH)(OC_2H_4NH_2)]_6(HOC_2H_4NH_2)_{18}\}$  $\cdot$  (OH)<sub>8</sub>  $\cdot$  2CoCO<sub>3</sub> formula. The IR spectrum of the xerogel (see Fig. 6, spectrum 2) has no absorption band at  $1870 \text{ cm}^{-1}$  belonging to the  $[\text{Co}(\text{CO})_4]^-$  anion. The broad structured band in the region of  $3600-3000 \text{ cm}^{-1}$  is indicative of the presence of the  $CO_3^{2-}$  anions and the alcoholic and silanol groups. Absorption in the region of  $1700-1500 \text{ cm}^{-1}$  is assigned to the carbonate anion and the amino groups ( $\delta(NH_2)$ ). The presence of hexaalkylated silyl-substituted benzene fragments in the xerogel is confirmed by absorption bands at 2925, 2860 cm<sup>-1</sup> (C–H), 1250, and 800 cm<sup>-1</sup> (SiCH<sub>3</sub>, SiCH<sub>2</sub>). The multiplet with the center at 1060 cm<sup>-1</sup> is associated with vibrations of the C–O, C–N, and Si–O bonds of the COH, CNH<sub>2</sub>, SiOC, SiOH, and SiOSi fragments. The above-considered data provide evidence that xerogel 12 has a carbonate structure with the involvement of organic fragments of partially hydrolyzed hexaalkylated silylbenzene and the hexamine cobalt(II) cation, which impart the lilac color to the xerogel.

To summarize, new polyfunctional hexaalkylated organosilicon 2-aminoethoxybenzenes readily form complexes with  $CoCl_2$ . The reaction with  $Co_2(CO)_8$  is typical only of the derivative containing primary amino groups. The low solubilities of the resulting complexes are indicative of their polymeric structures. Thermal decomposition of these compounds affords porous amorphous structures including crystalline phases of cobalt metal and  $CoCl_2$ .

## **Experimental**

Compounds 1-3 were synthesized with the use of 2-aminoethanol and *N*,*N*-dimethyl-2-aminoethanol (Kaprolaktam Joint-Stock Company, Dzerzhinsk, Russia), methylvinyldichlorosilane (Redkinsky pilot plant, Tver' Region, Russia), and dimethyldichlorosilane (Kremniipolimer, Zaporozh'e, Ukraine). The complexes of compounds 4-6 were prepared with the use of cobalt chloride (Neokhim, St. Petersburg), dicobalt octacarbonyl, and chromium hexacarbonyl (State Scientific-Research Institute of Chemistry and Technology of Organoelement Compounds, Moscow).

Commercial 2-aminoethanol and *N*,*N*-dimethyl-2-aminoethanol were purified by distillation under reduced pressure. According to the HPLC data (Milikhrom-1A,  $2 \times 64$ -mm column; Separon-SGX, 5 µm; UV detector, 250 nm; hexane), dicobalt octacarbonyl contained 98% of the major compound, and this reagent was used without additional purification. Tetrahydrofuran, acetonitrile, dimethylformamide, and *n*-hexane were purified according to known procedures.<sup>21</sup> Hexakis(methyldichlorosilylethyl)benzene (1), hexakis(methyldimethoxysilylethyl)benzene (2), hexakis(trimethylsilylethyl)benzene (3),<sup>11</sup> and triammine(tricarbonyl)chromium<sup>22</sup> were synthesized according to procedures described previously.

The IR spectra were recorded on a Specord IR-75 spectrophotometer in liquid films between KBr plates, Nujol mulls, or mineral oil (fluorohydrocarbon). The UV-Vis spectra of solutions were measured on a Specord M-40 spectophotometer in 5-mm quartz cells. The <sup>1</sup>H NMR spectra were recorded on a Bruker Avance DPX-200 instrument (200 MHz) in solutions in CDCl<sub>3</sub> at 25 °C with Me<sub>4</sub>Si as the internal standard. Powder X-ray diffraction study was carried out on a DRON-3M diffractometer (Cu-Ka radiation, graphite monochromator, diffracted beam). The specific surfaces were determined by nitrogen thermal desorption on a GKh-1 chromatograph. The gases were analyzed on a Tsvet-530 gas chromatograph equipped with a vacuum pump, a mercury pressure gauge, and a three-way cock (0.3×100-cm stainless steel column, NaX molecular sieves, thermal conductivity detector). This apparatus allowed us to measure the pressure in a tube and introduce a gas sample excluding exposure to atmospheric oxygen. The simultaneous determination of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO was performed with the use of argon as the carrier gas. The composition of the gas phase was calculated taking into account the tabular values of thermal conductivities of the gases.<sup>23</sup> Liquid amino alcohols and bis(N.N-dimethyl-2-aminoethoxy)dimethylsilane 6 were analyzed on a 0.3×200-cm stainless steel column with 5% SE-30 on solid Chromaton N-AW-DMCS.

Hexakis[bis(2-aminoethoxy)methylsilylethyl]benzene (4). 2-Aminoethanol (11.91 g, 195 mmol) was added to compound 2 (9.43 g, 10.8 mmol) and the reaction mixture was refluxed at 120 °C for 2 h. Then methanol and excess amino alcohol were distilled off. The residue was washed with hexane and heated *in vacuo* at 70–80 °C for 5 h. Compound 4 was obtained as a viscous orange liquid in a yield of 9.5 g (72%). Found (%): C, 47.00; H, 10.00; Si, 13.09.  $C_{48}H_{114}N_{12}O_{12}Si_6$ . Calculated (%): C, 47.26; H, 9.42; Si, 13.81. <sup>1</sup>H NMR, & 0.16 (s, 18 H, MeSi); 0.79 (br.m, 12 H, CH<sub>2</sub>Si); 2.19 (s, 12 H, NH<sub>2</sub>); 2.51 (br.m, 12 H,  $C_{Ar}CH_2$ ); 2.73 (br.m, 24 H, CH<sub>2</sub>N); 3.64 (br.m, 24 H, CH<sub>2</sub>SiO).

Hexakis[bis(N,N-dimethyl-2-aminoethoxy)methylsilylethyl]benzene (5). A solution of compound 1 (10 g, 10.82 mmol) in THF (40 mL) was added dropwise with stirring to a solution of N,N-dimethyl-2-aminoethanol (23.2 g, 200 mmol) in THF (30 mL) for 30 min. The reaction was accompanied by a slight warm-up. Then the reaction mixture was stirred at 60 °C for 2 h. The precipitate of HOCH2CH2NMe2 · HCl that formed was filtered off and the filtrate was concentrated. The residue was dissolved in hexane and stirred with AG-3 activated carbon for 5 h. Then the reaction mixture was filtered, the solvent was distilled off, and the residue was heated in vacuo to obtain compound 5 as a viscous orange liquid in a yield of 6.26 g (36%). Found (%): C, 55.75; H, 11.62; Si, 10.78. C<sub>72</sub>H<sub>162</sub>N<sub>12</sub>O<sub>12</sub>Si<sub>6</sub>. Calculated (%): C, 55.55; H, 10.49; Si, 10.83. <sup>1</sup>H NMR, δ: 0.24 (s, 18 H, MeSi); 0.87 (br.m, 12 H, CH<sub>2</sub>Si); 2.26 (s, 72 H, MeN); 2.49 (t, 24 H, CH<sub>2</sub>N, J = 6.2 Hz); 2.6 (br.m, 12 H,  $C_{Ar}CH_2$ ; 3.80 (t, 24 H, CH<sub>2</sub>SiO, J = 6.2 Hz).

**Bis**(*N*,*N*-dimethyl-2-aminoethoxy)dimethylsilane (6). A solution of dimethyldichlorosilane (19.05 g, 150 mmol) in THF (20 mL) was added dropwise with stirring to a solution of *N*,*N*-dimethyl-2-aminoethanol (27.6 g, 310 mmol) and Et<sub>3</sub>N (30.4 g, 290 mmol) in THF (30 mL) for 30 min. The reaction was accompanied by a substantial warm-up. The reaction mixture was stirred at ~20 °C for 1 h and then heptane (40 mL) was added. The mixture was filtered and the precipitate was washed with hexane. The solvent was removed from the filtrate and the residue was distilled *in vacuo*. Compound **6** was obtained as a colorless transparent liquid in a yield of 23.5 g (68%), b.p. 76 °C (1 Torr),  $n_D^{20}$  1.4261 (*cf.* lit. data<sup>24</sup>:  $n_D^{20}$  1.4240). <sup>1</sup>H NMR,  $\delta$ : 0.15 (s, 6 H, MeSi); 2.27 (s, 12 H, MeN); 2.47 (t, 4 H, CH<sub>2</sub>N, J = 6.4 Hz); 3.78 (t, 4 H, CH<sub>2</sub>O, J = 6.4 Hz).

**Dichloro[bis**(*N*,*N*-dimethyl-2-aminoethoxy)dimethylsilane]cobalt(II) (7). Compound 6 (8.33 g, 35.5 mmol) was added to anhydrous CoCl<sub>2</sub> (1.5 g, 11.6 mmol). The reaction was accompanied by a warm-up. The reaction mixture was stirred at 25 °C for 1 h and then at 100 °C for 1 h, washed with hexane, and heated *in vacuo* at 70 °C for 2 h. Compound 7 was obtained in a yield of 3.7 g (88%) as a viscous bright-blue liquid poorly soluble in THF. Found (%): C, 32.12; H, 7.62; Cl, 18.93; Si, 7.41.  $C_{10}H_{26}Cl_2CoN_2O_2Si$ . Calculated (%): C, 32.97; H, 7.19; Cl, 19.47; Si, 7.71. EAS (THF),  $\lambda_{max}$ /nm ( $\epsilon$ ): 553 (22), 602 (78), 629 (91), 654 (91).

**Dodecachloro {hexakis[bis(2-aminoethoxy)methylsilylethyl]benzene}hexacobalt(II) (8).** A solution of compound **4** (2.76 g, 2.26 mmol) in MeCN (100 mL) was added to CoCl<sub>2</sub> (1.76 g, 13.6 mmol). The reaction mixture was stirred at 20 °C for 1 h and then at 80 °C for 1 h. The reaction product precipitated upon cooling. The solvent was decanted from the precipitate and the latter was washed with MeCN. After the removal of the solvent *in vacuo*, complex **8** was obtained in a yield of 4.0 g (89%) as a bright-blue solid, which is insoluble in THF and MeCN and poorly soluble in DMF. Found (%): C, 29.45; H, 6.07; Cl, 20.23; Co, 17.35; Si, 7.93. C<sub>48</sub>H<sub>114</sub>Cl<sub>12</sub>Co<sub>6</sub>N<sub>12</sub>O<sub>12</sub>Si<sub>6</sub>. Calculated (%): C, 28.84; H, 5.75; Cl, 21.28; Co, 17.69; Si, 8.43. EAS (DMF),  $\lambda_{max}$ /nm ( $\epsilon$ ): 532 (200), 595 (438), 625 (563), 654 (463).

**Dodecachloro {hexakis [bis (**N,N-dimethyl-2-aminoethoxy)methylsilylethyl]benzene}hexacobalt(II) (9). A solution of compound 5 (5.76 g, 3.7 mmol) in MeCN (15 mL) was added to CoCl<sub>2</sub> (2.8 g, 21.6 mmol). The reaction was accompanied by a slight warm-up. Then the reaction mixture was stirred at ~20 °C for 2 h, the solvent was distilled off *in vacuo*, and the residue was washed with hexane. Bright-blue solid product **9** was obtained in a yield of 7.5 g (88%). Found (%): C, 37.33; H, 6.55; Cl, 16.30; Co, 14.67; Si, 6.89. C<sub>72</sub>H<sub>162</sub>Cl<sub>12</sub>Co<sub>6</sub>N<sub>12</sub>O<sub>12</sub>Si<sub>6</sub>. Calculated (%): C, 37.03; H, 6.99; Cl, 18.21; Co, 15.14; Si, 7.21. EAS (MeCN),  $\lambda_{max}$ /nm: 602, 633, 658, 694.

**Tris[bis(***N*,*N***-dimethyl-2-aminoethoxy)dimethylsilane]cobalt(II) bis(tetracarbonylcobaltate) (10).** Dicobalt octacarbonyl  $Co_2(CO)_8$  (1.21 g, 3.54 mmol) was added to a solution of compound **6** (1.67 g, 7.12 mmol) in ether (10 mL) in a Chugaev—Zerewitinoff apparatus equipped with a gas burette. After 15 h, CO was liberated in a yield of 76% of the calculated value. The reaction mixture was filtered off, the solvent was distilled off *in vacuo*, and the residue was washed with hexane. Compound **10** was obtained in a yield of 0.68 g (17%) as a crimson-colored powder. Found (%): C, 42.69; H, 7.07; Co, 16.42; Si, 8.06.  $C_{41}H_{78}Co_3N_6O_{14}Si_3$ . Calculated (%): C, 43.19; H, 6.90; Co, 15.51; Si, 7.39. EAS (MeCN),  $\lambda_{max}/nm: 532, 602$ .

Hexakis[bis(2-aminoethoxy)methylsilylethyl]benzenedicobalt(II) tetrakis(tetracarbonylcobaltate) (11). Dicobalt octacarbonyl Co<sub>2</sub>(CO)<sub>8</sub> (2.94 g, 8.61 mmol) was added to a solution of compound 4 (3.5 g, 2.87 mmol) in ether (10 mL). After 15 h, CO was liberated in a yield of 95% of the calculated value. The reaction mixture was washed with ether and reprecipitated with ether from a solution in MeCN. Compound 11 was obtained in a yield of 2.1 g (36%) as a crimson-red powder. Found (%): C, 38.46; H, 5.72; Co, 17.79; Si, 8.48. C<sub>64</sub>H<sub>114</sub>Co<sub>6</sub>N<sub>12</sub>O<sub>28</sub>Si<sub>6</sub>. Calculated (%): C, 38.02; H, 5.68; Co, 17.49; Si, 8.33. EAS (MeCN),  $\lambda_{max}/nm$  ( $\epsilon$ ): 400 (392), 532 (545).

Hydrolysis of complexes 7–9. Distilled water (10 mL) was added to a weighed sample of the corresponding compound (1.0-1.5 g). After one day, an aqueous solution (or a suspension of siloxanes in water) was decanted. The precipitate was washed with water on a filter and dried upon heating. The suspension was filtered off, washed with water, and dried. Hydrolysis of compounds 7 and 9 afforded a dark-green precipitate (cobalt(II) hydroxide) and a suspension of white flakes (polysiloxanes). The IR spectrum of Co(OH)<sub>2</sub> (Nujol mulls),  $v/cm^{-1}$ : 3450 v.s (associated OH groups); 1600 v.w (H<sub>2</sub>O); 660 s and 560 s (Co-O). The IR spectrum of polysiloxanes (Nujol mulls),  $v/cm^{-1}$ : 3380 (OH); 1620 (H<sub>2</sub>O); 1250, 800 (Si-CH<sub>2</sub>, Si-Me); 1050 (Si-O-H, Si-O-Si). Hydrolysis of complex 8 afforded only polysiloxanes and an aqueous solution of CoCl<sub>2</sub> and ethanolamine. The IR spectrum of polysiloxanes is identical with that of siloxanes prepared by hydrolysis of complexes 7 and 9. The presence of CoCl<sub>2</sub> in water was confirmed by electonic absorption spectroscopy.

**Preparation of xerogel 12.** A solution of complex **11** (0.3 g) in 2-aminoethanol (5 mL) was kept in an open tube. After 4 days, an increase in the viscosity of the lilac-colored solution was observed. After 30 days, a gel formed. The solvent was removed *in vacuo* upon heating and the residue was washed with ether. Xerogel **12** was obtained as a lilac-colored powder in a yield of 0.5 g. Found (%): C, 33.36; H, 8.74; Co, 14.88; Si, 7.07.  $C_{74}H_{218}Co_6N_{24}O_{44}Si_6$ . Calculated (%): C, 33.28; H, 8.23; Co, 13.24; Si, 6.31. IR (Nujol mull), v/cm<sup>-1</sup>: 3220, 1550 (NH<sub>2</sub>); 2650 (H<sub>3</sub>N<sup>+</sup>); 1870 (C=O); 1620 (H<sub>2</sub>O); 1250, 800 (Si–CH<sub>2</sub>, Si–Me); 1060, 880, 720, 590 (Si–O–C).

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