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Reactions of 1-(3'-Amino)- and 1-(3'-Acetamido)propylsilatranes with Cobalt(II) Chloride and Dicobalt Octacarbonyl

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Abstract—1-(3'-Amino)propylsilatrane (**I**) and 1-(3'-acetamido)propylsilatrane (**II**) react with anhydrous cobalt(II) chloride to give dichlorobis[1-(3'-amino)propylsilatrane]cobalt(II) $\{Co[NH_2CH_2CH_2CH_2Si(OCH_2CH_2)_3N]_2Cl_2\}$ (**III**) and dichlorobis[1-(3'-acetamido)propylsilatrane]cobalt(II) $\{Co[CH_3C(O)NHCH_2CH_2CH_2Si(OCH_2CH_2)_3N]_2Cl_2\}$ (**IV**). Being unstable, compound **IV** transforms into an imidic acid derivative. Reactions of silatranes **I** and **II** with dicobalt octacarbonyl afford hexakis[1-(3'-aminoamido)propylsilatrane]cobalt(II) bis(tetracarbonylcobaltate) $\{Co[NH_2CH_2CH_2CH_2Si(OCH_2CH_2)_3N]_{4.8}[HC(O)NHCH_2CH_2CH_2Si(OCH_2CH_2)_3N]_{1.2}\}[Co(CO)_4]_2$ (**V**) and hexakis[1-(3'-acetamido)propylsilatrane]cobalt(II) bis(tetracarbonylcobaltate) $\{Co[CH_3C(O)NHCH_2CH_2CH_2Si(OCH_2CH_2)_3N]_6\}[Co(CO)_4]_2$ (**VI**), respectively. In acetonitrile, tetracarbonylcobaltate anions of compound **VI** are oxidized with atmospheric oxygen and moisture to cobalt hydroxocarbonate, giving a carbonate gel (**VII**).

Molecules of 1-(3'-amino)propylsilatrane $NH_2CH_2CH_2CH_2Si(OCH_2CH_2)_3N$ (**I**) and 1-(3'-acetamido)propylsilatrane $CH_3C(O)NHCH_2CH_2CH_2Si(OCH_2CH_2)_3N$ (**II**) contain two (**I**) or three (**II**) atoms capable of coordination [1, 2]. It is believed [3–5] that the lone electron pair of the silatranyl N atom is directed toward the interior of the silatrane cage to form a transannular N–Si bond. As a result, the basicity of the N atom decreases substantially, while the electron-donating effect of the $–Si(OCH_2CH_2)_3N$ group increases several times (σ_I = –0.56) as compared to that of $–Si(OEt)_3$ group (σ_I = –0.13) [6–8]. It can be expected that amino or amido silatranes will be coordinated by transition metals only through the $NH_2CH_2–$ or $CH_3C(O)NH–$ fragments.

In this study, we investigated reactions of silatranes **I** and **II** with cobalt(II) chloride and dicobalt octacarbonyl $Co_2(CO)_8$. With amines, $CoCl_2$ usually forms tetracoordinated complexes $[Co(NH_2R)_2Cl_2]$ [9]. Under similar conditions, $Co_2(CO)_8$ undergoes disproportionation [10] (one third of the cobalt atoms is oxidized to Co(II), while the remaining two thirds give a $[Co(CO)_4]^-$ anion):

$$3Co_2(CO)_8 + 12NH_2R \longrightarrow 2[Co(NH_2R)_6][Co(CO)_4]_2 + 8CO.$$

The oxidation is accompanied by replacement of carbon monoxide by RNH_2 groups. In the complex obtained, the Co^{2+} cation is surrounded by six amino ligands and neutralized with two tetracarbonylcobaltate anions. Thus, the reactions of $CoCl_2$ and $Co_2(CO)_8$ with amines afford both tetra- and hexacoordinated Co(II) complexes. Earlier [11, 12], we found that $CoCl_2$ and $Co_2(CO)_8$ react with the functionalized organosilicon amine $NH_2CH_2CH_2CH_2Si(OEt)_3$ to give tetrahedral $[Co(NH_2R)_2Cl_2]$ and octahedral $[Co(NH_2R)_6][Co(CO)_4]_2$ complexes, respectively ($R = CH_2CH_2CH_2Si(OEt)_3$). These complexes are used as the starting substances for preparation of gels and films.

Oxygen absorption and the low- and high-temperature oxidation of Co(II) complexes with 3-aminopropyl(triethoxy)silane have been studied in [11–13]. Silatranes are used as ligands and substituents in several coordination and organometallic compounds [14–20]. The superelectron-donating effect of the silatranyl group was employed in [21] to construct asymmetric structures with nonlinear optical properties.

EXPERIMENTAL

3-Aminopropyl(triethoxy)silane (PO “Altaikhimprom”, Slavgorod) was preliminarily fractionated *in vacuo* on a column (1 × 50 cm) packed with Nichrome wire spirals and analyzed on a Tsvet-500 gas chromatograph (stainless steel column 0.3 × 200 cm, XC-2-1 (5%) on Chromaton-N-AWDMCS as a stationary phase, katharometer, helium as a carrier gas). Dicobalt octacarbonyl (GNIIKhTEOS) was of 98% purity (HPLC: Milikhrom-1A, column 2 × 64 mm, Separon-SGX, 5 μm, UV detector, 250 nm, hexane) and was used as purchased. Acetonitrile was desiccated over a 3 Å molecular sieve and distilled over P_4O_{10}. Toluene and diethyl ether were purified by distillation over

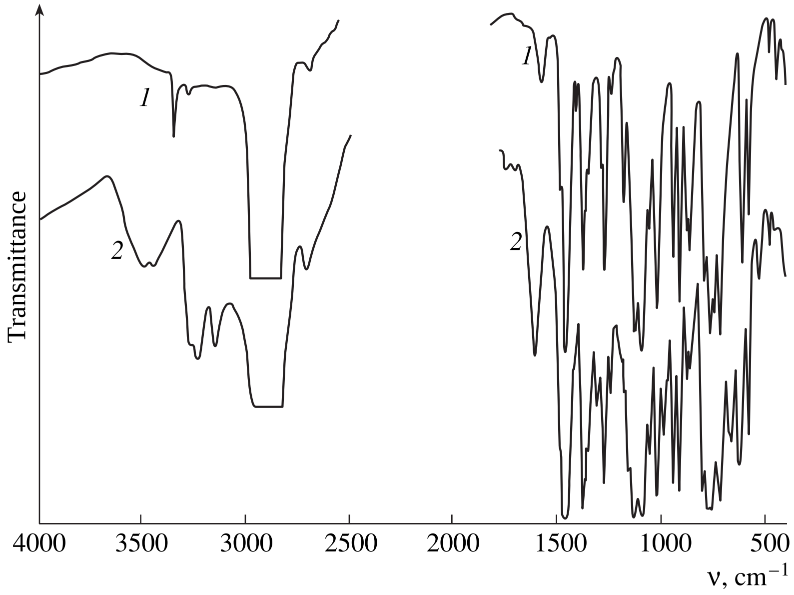

Fig. 1. IR spectra of (*1*) amino silatrane **I** and (*2*) complex **III**.

metallic sodium and P_4O_{10}, respectively. Tetrahydrofuran (THF) was successively refluxed over NaOH and metallic sodium and then distilled. All manipulations with complexes **III**–**VI** and **VIII** were carried out *in vacuo* or under argon in oxygen-free solvents.

1-(3'-Amino)propylsilatrane (I).[1] A mixture of 3-aminopropyl(triethoxy)silane (8.84 g, 0.04 mol) and triethanolamine (5.69 g, 0.04 mol) was heated with simultaneous removal of the alcohol evolved. The product was recrystallized from toluene and then from chloroform. The yield of silatrane **I** was 4.90 g (0.021 mol, 53%). The IR spectrum of **I** is shown in Fig. 1. ^{1}H NMR δ, ppm: 0.360, 0.401, 0.443 (t, 2 H, $–CH_2Si$), 1.245 (s, 2 H, NH_2), 1.521 (m, 2 H, $–CH_2–$), 2.589, 2.623, 2.658 (t, 2 H, $–CH_2N$), 2.782, 2.811, 2.840 (t, 6 H, $–CH_2N$), 3.737, 3.766, 3.795 (t, 6 H, $–CH_2O$).

1-(3'-Acetamido)propylsilatrane (II). A solution of 3-aminopropyl(triethoxy)silane (16.20 g, 0.073 mol) and triethylamine (7.40 g, 0.073 mol) in 50 ml of ether was added dropwise to acetyl chloride (5.75 g, 0.073 mol) in 30 ml of ether while stirring and cooling it with ice water. The reaction mixture was refluxed with stirring for 2 h and then filtered. Triethanolamine (10.90 g, 0.073 mol) was added to the filtrate. The alcohol was removed, and the product was recrystallized from a chloroform–hexane mixture. The yield of silatrane **II** was 9.41 g (0.034 mol, 47%). Its IR spectrum is shown in Fig. 2. ^{1}H NMR δ, ppm: 0.391, 0.429, 0.469 (t, 2 H, $–CH_2Si$), 1.532, 1.565, 1.606, 1.643, 1.676 (m, 2 H, $–CH_2–$), 1.936 (s, CH_3), 2.780, 2.809, 2.839 (t, 6 H, $–CH_2N$), 3.161, 3.194, 3.221, 3.253 (q, 2 H, $–CH_2N$), 3.732, 3.761, 3.790 (t, 6 H, $–CH_2O$), 6.068 (s, 1 H, NH).

Dichlorobis[1-(3'-amino)propylsilatrane]cobalt(II) (III). Anhydrous Co(II) chloride (0.60 g, 4.6 mmol) was added to a solution of silatrane **I** (2.30 g, 9.9 mmol) in 10 ml of CH_3CN. The reaction mixture was stirred at 25°C for 2 h until $CoCl_2$ was completely dissolved. The resulting bright blue solution was concentrated *in vacuo* to dryness; the solid residue was reprecipitated from a toluene–acetonitrile mixture, washed with ether, and dried *in vacuo* to give complex **III** as a blue powder. The yield of **III** was 2.03 g (3.4 mmol, 74%). Its IR spectrum is shown in Fig. 1. Electronic absorption spectrum (AB) (ν, cm^{-1}): 17400 sh, 16400 sh, 16000 (ε 332 l mol^{-1} cm^{-1}), 15500 sh.

Reaction of silatrane II with cobalt(II) chloride. Anhydrous Co(II) chloride (0.35 g, 2.7 mmol) was added to a solution of silatrane **II** (1.47 g, 5.4 mmol) in 10 ml of CH_3CN. The reaction mixture was homogenized by stirring for 3 h, and the solvent was removed *in vacuo*. Attempts to recrystallize the solid blue residue from mixtures of acetonitrile with toluene, ether, or hexane resulted in the formation of a heavy blue liquid. The solvents were removed by decanting. Drying the liquid *in vacuo* gave complex **IV** as a blue powder. The powder became cohesive when stored at room temperature for one to two days and regained its original friability on washing with hexane. The IR spectrum of **IV** is shown in Fig. 2.

Hexakis[1-(3'-aminoamido)propylsilatrane]cobalt(II) bis(tetracarbonylcobaltate) (V). Dicobalt octacarbonyl (0.71 g, 2.1 mmol) was added to a solution of silatrane **I** (1.93 g, 8.3 mmol) in 20 ml of toluene. After 2 h, a gas (37 ml) evolved, and the brown solution turned crimson-red. The toluene was removed, and the residue was washed with ether to give compound **V** as a pink-lilac powder. The yield of **V** was

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[1] Compounds **I** and **II** were prepared as described in [1, 2].

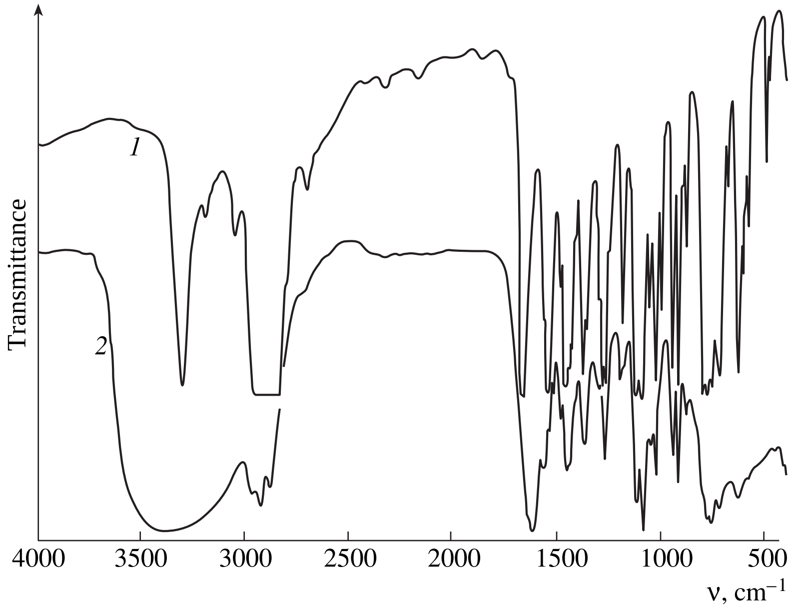


Fig. 2. IR spectra of (*1*) acetamido silatrane **II** and (*2*) the product of its reaction with cobalt(II) chloride.

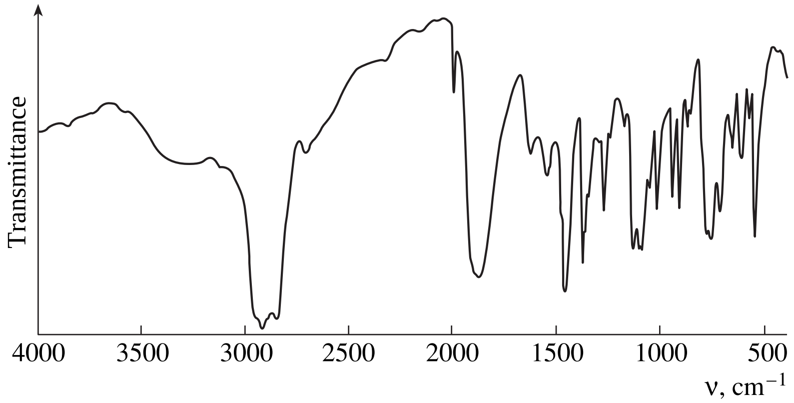


Fig. 3. IR spectrum of complex **V**.

2.08 g (1.1 mmol, 79%). Its IR spectrum is shown in Fig. 3. AB (ν, cm^{-1}): 18000 (ε 60 l mol^{-1} cm^{-1}).

Hexakis[1-(3'-acetamido)propylsilatrane]cobalt(II) bis(tetracarbonylcobaltate) (VI) was obtained in CH_3CN using the same procedure. The yield of **VI** was 74%. Its IR spectrum is shown in Fig. 4. AB (ν, cm^{-1}): 19000 (ε 126 l mol^{-1} cm^{-1}), 17400 (ε 166 l mol^{-1} cm^{-1}), 15800 sh.

Xerogel (VII). Complex **VI** (0.23 g) was dissolved in 1.5 ml of CH_3CN and the solution was kept in an open tube for two days. The resulting transparent violet gel was dried, and the residue was washed with THF and dried *in vacuo* to give xerogel **VII** (0.10 g) as a brown powder. Its IR spectrum is shown in Fig. 4.

Reaction of ethoxysilatrane with cobalt(II) chloride. Ethoxysilatrane (0.49 g, 2.23 mmol) in 5 ml of CH_3CN was added to $CoCl_2$ (0.16 g, 1.23 mmol) in 6 ml of CH_3CN. The reaction mixture was homogenized by stirring at 25°C for 5 h. The solvent was removed. Repeated washing of the solid residue with benzene gave complex **VIII** (0.35 g, 0.616 mmol) as a light blue powder. IR (ν, cm^{-1}): 1480 m, 1365 m, 1350 w, 1260 s, 1170 w, 1130 s, 1090 vs, 1055 vs, 1030 vs, 945 s, 910 vs, 880 m, 830 s, 810 m, 790 vs, 750 w, 690 s, 670 vs, 640 w, 580 w, 460 w. For ethoxysilatrane, IR (ν, cm^{-1}): 1480 m, 1360 m, 1270 s, 1170 w, 1150 m, 1120 vs, 1080 vs, 1060 w, 1030 s, 945 vs, 925 vs, 875 w, 800 vs, 770 vs, 740 s, 725 m, 630 s, 575 m.

Elemental analysis data for complexes **III**–**VIII** are presented in table.

IR spectra were recorded on Perkin-Elmer 57 and Specord 75IR spectrophotometers (Nujol mulls). ^1H NMR spectra were recorded on a Bruker-DPX 200

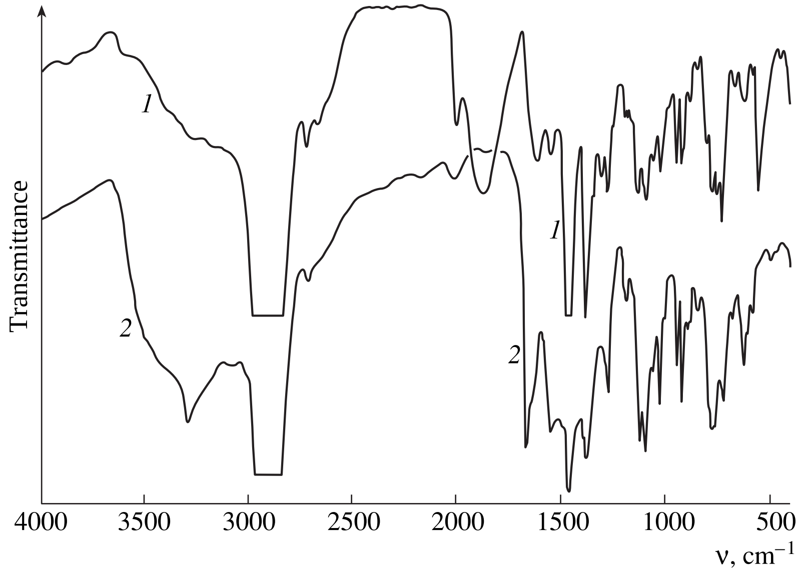
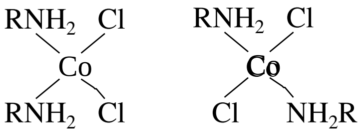


Fig. 4. IR spectra of (*1*) complex **VI** and (*2*) xerogel **VII**.

spectrometer in $CDCl_3$. Electronic absorption spectra were measured on a Specord-M 40 spectrophotometer (10-mm quartz cell) in oxygen-free acetonitrile.

RESULTS AND DISCUSSION

Reactions of silatranes I, II with cobalt(II) chloride. The reaction of amino silatrane **I** with $CoCl_2$ in acetonitrile yields dichlorobis[1-(3'-amino)propylsilatrane]cobalt(II) $\{Co[NH_2CH_2CH_2CH_2Si(OCH_2CH_2)_3N]_2Cl_2\}$ (**III**). Complex **III** was precipitated with toluene from the solution in CH_3CN and washed with ether to give a bright blue powder. The IR spectra of the starting silatrane **I** and complex **III** are displayed in Fig. 1. It can be seen that the absorption bands of the hydrocarbon radical at the Si atom and those of the silatrane framework [22] remain virtually unchanged (ν 1480, 1360, 1270, 1180, 1130, 1100, 1030, 950, 920, 875, 860, 800, 760, 725, 625, and 575 cm^{-1}). At the same time, the ν(N–H) bands are shifted to the low-frequency range from 3340 and 3270 cm^{-1} to 3240 and 3150 cm^{-1}, while the deformation vibrations occur at higher frequencies (1600 versus 1575 cm^{-1}). In the 3700–3000 cm^{-1} range, the IR spectrum of complex **III** is identical with the spectrum of a previously synthesized [11] complex of $CoCl_2$ with 3-aminopropyl(triethoxy)silane.



(*cis*-**III**) (*trans*-**III**)

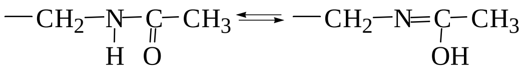
$R = CH_2CH_2CH_2Si(OCH_2CH_2)_3N$

The doublets at 3470 and 3240 cm^{-1} suggest the formation of isomers of complex **III**. The electronic absorption spectrum of complex **III** in acetonitrile (Fig. 5), which consists of a multiple band with a maximum at 16000 cm^{-1}, is characteristic of diaminodichloro complexes of cobalt(II) [23].

Elemental analysis data for complexes **III–VIII**

No.	Empirical formula	Found/calculated, %					Yield, %
		C	H	Cl	Co	Si	
III	$C_{18}H_{40}Cl_2CoN_4O_6Si_2$	37.23/36.36	6.38/6.78	11.15/11.93	9.59/9.91	9.14/9.45	74
IV	$C_{22}H_{44}Cl_2CoN_4O_8Si_2$	39.30/38.94	6.81/6.54	10.82/10.45	8.54/8.68	8.14/8.28	
V	$C_{63.2}H_{120}Co_3N_{12}O_{27.2}Si_6$	41.10/41.51	6.25/6.61		9.53/9.67	9.09/9.22	79
VI	$C_{74}H_{132}Co_3N_{12}O_{32}Si_6$	42.97/43.41	6.67/6.50		8.97/8.63	8.51/8.23	74
VII	$C_{78}H_{160}Co_4N_{14}O_{37}Si_7$	39.06/40.41	6.78/6.96		9.94/10.17	9.08/8.48	
VIII	$C_{16}H_{34}Cl_2CoN_2O_8Si_2$	34.08/33.81	5.88/6.03	12.60/12.47	10.50/10.37	10.01/9.88	55

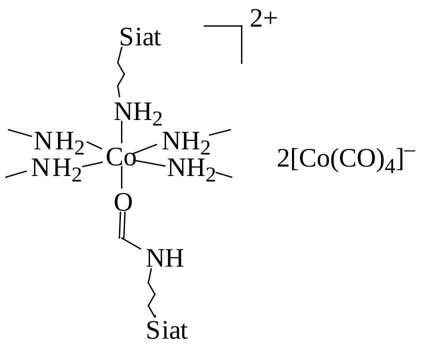
The amido analog of complex **III**, namely, dichlorobis[1-(3'-acetamido)propylsilatrane]cobalt(II) $\{Co[CH_3C(O)NHCH_2CH_2CH_2Si(OCH_2CH_2)_3N]_2Cl_2\}$, is unstable and undergoes further transformations and thus cannot be isolated as individual compound using the reaction of silatrane **II** with $CoCl_2$ in CH_3CN. The reaction product **IV** is a coarse blue powder, which is well soluble in acetonitrile and insoluble in THF. When stored under argon, the powder coheres due to an oily film covering its surface. This film can easily be removed with toluene or hexane, and the powder regains its friability. At 100°C, the powder rapidly changes into a dark blue oil; on cooling to room temperature, the substance remains liquid. The IR spectra of silatrane **II** and the product of its reaction with $CoCl_2$ are shown in Fig. 2. They are nearly identical in the 1500–400 cm^{-1} range, which indicates that the silatrane framework of the ligand is retained in the complex. The changes are most significant in the 3400–3000 cm^{-1} (N–H and O–H stretching vibrations) and 1700–1500 cm^{-1} ranges (absorption bands of amide I and amide II) [24]. The very intense and broad absorption band at 3600–3000 cm^{-1} corresponds to the OH group in the tautomeric form of the secondary amideCH_3–C(OH)=N–CH_2– (of the imidic acid) [25]. This form is stabilized by coordination of the acetamido group of silatrane **II** to the cobalt atom. The bands at 1660 cm^{-1} (amide I) and 1545 cm^{-1} (amide II) coalesce into a broader absorption band at 1630 cm^{-1} of the azomethine group –C=N–.



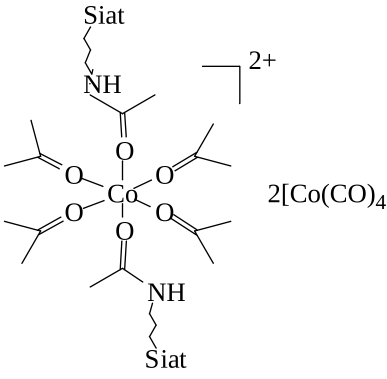
$$-CH_2-\underset{H}{N}-\underset{O}{\overset{}{C}}-CH_3 \rightleftarrows -CH_2-N{=}\underset{OH}{C}-CH_3$$

Hence, compound **IV** is a Co complex with an N-silatranylacetimidic acid $\{Co[RN{=}C(OH)(CH_3)]_2Cl_2\}$, where R = $N(CH_2CH_2O)_3SiCH_2CH_2CH_2$. In a liquid obtained by heating complex **IV**, the silatrane framework is destroyed (IR data). An attempt to synthesize an amido analog of compound **III** in THF failed. The reaction of $CoCl_2$ with silatrane **II** occurred very slowly because of their low solubility in this solvent.

Reactions of silatranes I and II with dicobalt octacarbonyl. Amines and acid amides react with $Co_2(CO)_8$ [10] to give hexakis[amino(amido)]cobalt(II) bis(tetracarbonylcobaltates) $\{Co(NH_2R)_{6-x}[HC(O)NHR]_x\}[Co(CO)_4]_2$. In the case of primary amines, the evolved carbon monoxide is usually inserted in part into the N–H bond to form a formamide derivative, which is also coordinated by a Co^{2+} cation. Thus, the resulting compound contains both amino and amido ligands. The reaction of silatrane **I** with $Co_2(CO)_8$ in toluene is accompanied by vigorous gas evolution and affords hexakis[1-(3'-aminoamido)propylsilatrane]cobalt(II) bis(tetracarbonylcobaltate) $\{Co[NH_2CH_2CH_2CH_2Si(OCH_2CH_2)_3N]_{4.8}[HC(O)NHCH_2CH_2CH_2Si(OCH_2CH_2)_3N]_{1.2}\}[Co(CO)_4]_2$ (**V**) as a pink-lilac powder in 79% yield. The volume of the gas evolved suggests that about 30% of carbon monoxide is combined with the amino groups; as a result, the Co^{2+} coordination sphere includes both amino and formamido silatranyl ligands.



(**V**)



(**VI**)

Siat = $Si(OCH_2CH_2)_3N$

The IR spectrum of compound **V** (Fig. 3) shows a set of absorption bands characteristic of a silatrane framework in the 1300–500 cm^{-1} range. An intense band at 1870 cm^{-1} and a band at 2000 cm^{-1} were assigned to the $[Co(CO)_4]^-$ anion. A set of ill-resolved absorption bands in the 3500–3100 cm^{-1} range (ν(N–H)) corresponds to the $Co(NH_2CH_2–)$ and $Co[HC(O)NH–CH_2–]$ fragments. The formation of formamido ligands is confirmed by the absorption bands at 1625 cm^{-1} (amide I); the doublet at 1555 and 1545 cm^{-1} was assigned to the N–H deformation vibrations in the amido (amide II) and amino silatranes coordinated by the Co^{2+} cation. In the visible AB spectrum (Fig. 5), complex **V** absorbs at 18000 cm^{-1}, which is characteristic of hexacoordinated octahedral amino complexes of cobalt(II) ($^4T_{1g}(P)$–$^4T_{1g}$ transition) [23].

In the reaction of silatrane **II** with dicobalt octacarbonyl in CH_3CN, a stoichiometric amount of carbon monoxide was evolved (eight moles per three moles of $Co_2(CO)_8$). Hexakis[1-(3'-acetamido)propylsilatrane]cobalt(II) bis(tetracarbonylcobaltate) $\{Co[CH_3C(O)NHCH_2CH_2CH_2Si(OCH_2CH_2)_3N]_6\}[Co(CO)_4]_2$ (**VI**) was obtained as a brown powder in 74% yield. The powder is soluble in CH_3CN and THF and insoluble in toluene or ether. The IR spectrum of complex **VI** (Fig. 4) contains a set of absorption bands corresponding to the silatrane fragment (1270, 1180, 1135, 1080, 1050, 1030, 950, 925, 880, 800, 760, 725, and 625 cm^{-1}), the tetracarbonylcobaltate anion (2000 and 1870 cm^{-1}), the N–H stretching (3500–3100 cm^{-1}) and deformation (1550 cm^{-1}, amide II) vibrations, and the C=O group (1620 cm^{-1}, amide II). The bands due to the N–H stretching vibrations and the band of amide I are most sensitive to complexation (Fig. 2). In the IR spectrum of complex **VI**, these bands are broadened and shifted to the lower wavenumbers. Their broadening, especially pronounced for the ν(N–H) bands, is probably due to hydrogen bonding. Complexation between acid amides and transition metals is known to primarily involve the acid C=O group [26]. This explains why the band due to amide I is shifted, while the position of the band due to amide II remains virtually unchanged. The electronic absorption spectrum of complex **VI** exhibits an absorption band of complicated structure with a center at 18000 cm^{-1} (Fig. 5). The shape of the band and the positions of its maxima are typical of octahedral hexaamidocobalt(II) cations [23].

When stored in an open tube, a brown 0.075 M solution of complex **VI** in CH_3CN turned violet, becoming significantly thicker after 20 h. Two days later, it changed into a transparent violet gel, which was dried *in vacuo* and washed with THF to give a small amount of xerogel **VII** as a light brown powder. Earlier [13], similar processes were observed for cobaltates $[CoB_6][Co(CO)_4]_2$ (B = Py, DMF, or $NH_2CH_2CH_2CH_2Si(OEt)_3$). Gels were found to have a carbonate structure since the tetracarbonylcobaltate anions oxidize with atmospheric oxygen to cobalt hydroxocarbonate. Most of the hexaamino- or hexaamidocobalt cations $[CoB_6]^{2+}$ are retained in the resulting gels. According to the IR data (Fig. 4), xerogel **VII** is composed of cobalt hydroxocarbonate, hexakis(acetamidosilatranyl)cobalt(II) cations, and free silatrane **II**. Complete oxidation of the tetracarbonylcobaltate anions is evident from the absence of corresponding absorption bands at 1870 and 2000 cm^{-1}. The carbonate fragment gives two intense broad bands at 3600–3100 and 1600–1350 cm^{-1}. A set of peaks in the 1300–600 cm^{-1} range is characteristic of a silatrane framework. Three sharp absorption bands at 3300, 1660, and 1545 cm^{-1} rising above broader carbonate bands indicate the presence of free silatrane **II**. A portion of the acetamidosilatranylcobalt(II) complexes is retained; they absorb at 1620 and 1550 cm^{-1}. The shapes and intensities of absorption bands in the 1100–1000 cm^{-1} range remain unchanged; therefore, gelation is accompanied neither by destruction of the silatrane fragments nor by accumulation of disiloxane ones. Thus, the binder of the gel is cobalt hydroxocarbonate $CoCO_3 \cdot xCoO \cdot yH_2O$ [27]. When a solvent is removed, such an unstable binder is destroyed to give a fine powder. According to the elemental analysis data, the composition of xerogel **VII** can be formulated as $[CoCO_3 \cdot 2CoO \cdot 2H_2O] \cdot [CoB_6](OH)_2 \cdot B$ (B = silatrane **II**).

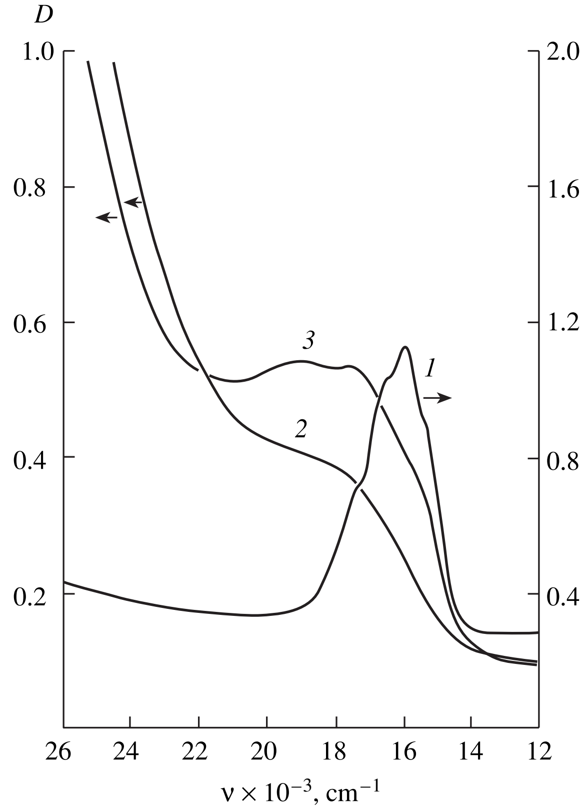


Fig. 5. Electronic absorption spectra of complexes **III**, **V**, and **VI** in acetonitrile (*c* = (*1*) 2.47×10^{-3}, (*2*) 2.15×10^{-3}, and (*3*) 1.6×10^{-3} mol/l, respectively).

A highly diluted (0.0016 mol/l) solution of complex **VI** in acetonitrile formed no gel in air because of a too low concentration of the binder. When aerated, the initial light brown solution turned violet and then (within 10 to 15 min) became turbid. The suspension was allowed to settle; the electronic absorption spectrum of the resulting solution, recorded one hour after the aeration, shows a more intense and differently shaped band in the 21000–15000 cm^{-1} range. Such effects are usually attributed to oxygen absorption and to the presence of a metal–ligand charge transfer band, which is more intense than *d–d* transitions in a Co^{2+} cation [28]. Under similar conditions, complex **V** forms no gel even on prolonged storage in air. Oxygen absorption turns the solution deep brown and intensifies the band at 18000 cm^{-1}. Apparently, the differences in the behavior of compounds **V** and **VI** can be explained by the stability of their complexes with molecular oxygen and by its ready transfer from a Co^{2+} cation to a tetracarbonylcobaltate anion.

Silatranes **I** and **II** form complexes with $CoCl_2$ and $Co_2(CO)_8$ only through the $–NH_2$ and $–NHC(O)CH_3$ groups, whereas *n*-donor centers of the silatranyl fragment (oxygen and nitrogen atoms) take no part in coordination (IR data). In the 1300–500 cm^{-1} range corresponding to the vibrations of the silatrane cage, the starting organosilicon compound and the resulting complex have the same set of bands. At the same time, it is known [3] that complexation between silatranes $X–Si(OCH_2CH_2)_3N$ ($X = C_2H_5$, C_2H_5O, or C_6H_5) and $AlBr_3$ (1 : 1 complexes) or $TiCl_4$ (1 : 1 and 1 : 2 complexes) involves O–M bonding. In connection with this, it was interesting to study a $CoCl_2$–silatrane system for amino- and amido-free silatranes. The reaction of Co(II) chloride with ethoxysilatrane ($X = C_2H_5O$) in acetonitrile gave a solid sky-blue precipitate (**VIII**). The precipitate was not divided into the starting components by washing it repeatedly with toluene, (unlike $CoCl_2$, ethoxysilatrane is soluble in toluene). The IR spectra of complex **VIII** and ethoxysilatrane significantly differ in the range of the silatrane Si–O–C vibrations (1150–1080 and 800–630 cm^{-1}), which can be due to Co–O coordination bonding. According to the elemental analysis data, compound **VIII** is $\{Co[C_2H_5OSi(OCH_2CH_2)_3N]_2Cl_2\}$. Thus, $CoCl_2$ can form complexes with nonfunctionalized silatrane; however, if the Si atom bears an amino- or amido-containing substituent, only these functions are involved in coordination. Compound **VIII** is very sensitive to atmospheric moisture. The IR spectrum of partially air-hydrolyzed product contains a set of absorption bands corresponding to –SiOH (broad band at 3400–3100 cm^{-1}), N–H (3320 and 3160 cm^{-1}), and $\equiv NH^+Cl^-$ (2750–2500 cm^{-1}).

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