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Formation of Gels and Films from Hexamine- and Hexamidecobalt(II) Carbonylcobalt Complexes

V. V. Semenov, N. F. Cherepennikova, M. A. Lopatin, S. Ya. Khorshev, Zh. Yu. Fominykh, A. I. Kirillov, V. N. Sedel'nikova, and G. A. Domrachev

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhni Novgorod, Russia

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Abstract—When kept in dilute acetonitrile solutions, complexes $[CoB_6][Co(CO)_4]_2$ [B = C_5H_5N, $Me_2NC(O)H$] form gels $CoB_x(MeCN)_y](OH)_2 \cdot 2[CoCO_3 \cdot 2CoO \cdot 2H_2O]$ (x = 2, 3, y = 4, 3), while the polyfunctional complex $[Co\{(EtO)_3SiCH_2CH_2CH_2NH_2)\}][Co(CO)_4]_2$ gives a mixed carbonate–siloxane gel. The gel formation is accompanied by complete decomposition of $[Co(CO)_4]^-$ anions under the action of air oxygen and moisture, to give $CoCO_3 \cdot 2CoO \cdot 2H_2O$. Mechanistically, the gel and film formation involves absorption of molecular oxygen by the hexamine- or hexamidecobalt(II) cation and subsequent decomposition of the unstable oxygenated carbonylcobalt complex.

Metal-containing organosilicon gels are prepared by coprecipitation of tetraalkoxyorganosilanes with alkoxides, halides, or acetates of transition metals [1, 2], as well as by hydrolysis of coordination compounds with functional organosilicon ligands [3, 4]. Dried gels and solid porous materials formed by their thermolysis are employed as heterogeneous catalysts [5]. Thin-film technologies are widely used in electrical, radio, microwave, and laser industry, nonlinear optics, and the production of IC devices, gas sensors, membranes, optical devices, photoelectric cells, radiation detectors, memory elements, and solar energy converters. Ferromagnetic films are very important for the progress of computer and radio engineering [6–9]. Organosilicon film coatings are highly frost-, heat-, ozone-, and moisture-resistant, and have found extensive industrial application [10], in particular, in microelectronics [11]. Earlier we showed [12] that hexa(aminoamide)cobalt(II) carbonylcobalt complex **I** synthesized from (3-aminopropyl)triethoxysilane and octacarbonyldicobalt can serve as a basis for preparing cobalt-containing gels. The latter are colored transparent glasses and porous powders, with the coloring power and strength dependent on the composition of the organosilicate matrix. Of the abundance of transition metal complexes, the strongest tendency to reversible binding of oxygen is characteristic of octahedral cobalt(II) complexes [13, 14]. The polyfunctional organosilicon frame (18 ethoxy groups and 6 silicon atoms) makes complex **I** highly susceptible to gel formation with tetraethoxysilane and organoalkoxysilanes, thus opening the way to a variety of organosilicate matrices. Favorably combining the above properties, the resulting materials hold much promise for heterogeneous catalyst [5, 15, 16], ferromagnetic film [17], and accumulator (oxygen carrier) [13, 14] applications. In the present work we report the results of research on gel and film formation from complex **I** and its pyridine (Py) and dimethylformamide (DMF) analogs.

Complex **I** was prepared by treatment of octacarbonyldicobalt with (3-aminopropyl)triethoxysilane in diethyl ether. The reaction is complicated by CO insertion into the N–H bond, followed by binding of the triethoxy(3-formamidopropyl)silane formed with the cobalt(II) cation. As a result, complex **I** comprises both amine and amide ligands.

$$12RNH_2 + 3Co_2(CO)_8 \longrightarrow 2\underset{\textbf{I}}{\{[RNH_2]_{6-x}[RNHC(O)H]_xCo\}[Co(CO)_4]_2} + (8 - 2x)CO,$$

$$R = (EtO)_3SiCH_2CH_2CH_2.$$

When the reaction is performed under argon at atmospheric pressure, 80–90% of the carbon monoxide evolved is bound by the organosilicon amine. With strictly stoichiometric reactant amonts, x should be 3.2–3.6. Complex **I** was prepared in a vacuum. For complete reaction we used a slight (1.1–1.15) excess of (3-aminopropyl)triethoxysilane which was then washed off with hexane. In the latter case, x in formula **I** should not be higher than 3.2. Complex **I** is an oily crimson-red liquid. It is soluble in many

Gel formation from complexes **I**–**III**

Initial complex	Solvent	c_0, M	Time of gel formation, days	Color		Yield of xerogel, wt%	Specific surface, m^2/g	
				lyogel	xerogel		initial gel	gel heated to 600°C
I	MeCN	0.047	1	Violet	Dark lilac	60	0.4	30
	MeCN	0.016	5	″	″			
	Et_2O	0.053	1	″	Blue		1.1	27
	$(EtO)_3Si(CH_2)_3NH_2$	0.051	3	″	Black			
	Me_2CO	0.049	–[a]					
	THF/H_2O[b]	0.077	23	Brown	Blue	57	33	40
II	MeCN	0.087	6	″	Brown	49	0.6	3
	MeCN	0.040	4	″	″			
	C_5H_5N	0.053	–[a]	Brown[c]				
III	MeCN	0.050	2	Violet	Black			
	DMF	0.055	28	″	″	40	104	17

[a] No gel formed within 30 days. [b] Water was added after gelation of a solution of complex **I** in THF, after which the gel was left to stand for 30 days. [c] Solution color.

organic solvents (diethyl ether, THF, aliphatic alcohols, benzene, toluene, acetone, chloroform), except for alkanes, but decomposes on prolonged storage in chloroform solutions.

Silicon-free analogs of complex **I**, hexapyridinecobalt(II) bis(tetracarbonylcobaltate) (**II**) and hexa(dimethylformamide)cobalt(II) bis(tetracarbonylcobaltate) (**III**), were obtained by treatment of ocracarbonyldicobalt with pyridine or dimethyformamide, respectively [18].

$$12B + 3Co_2(CO)_8 \longrightarrow 2\,[CoB_6][Co(CO)_4]_2 + 8CO,$$

$$B = Py\ (\mathbf{II}),\ DMF\ (\mathbf{III}).$$

The complexes are air-sensitive orange (**II**) or light cherry (**III**) powders insoluble in diethyl ether and readily soluble in acetonitrile or ligand-forming solvents.

The gel formation from concentrated solutions of complex **I** under the action of water occurs via hydrolytic condensation of triethoxysilyl groups [12]. Dried gels are colored monolithic nonporous glasses and contain both hexa(aminoamide) and carbonylcobalt groups. We found that complexes **I**–**III** form gels upon prolonged standing in dilute solutions in acetonitrile, diethyl ether, tetrahydrofuran, and ligand-forming solvents (see table). Gelation of a 0.047 M solution of complex **I** is observed after 20 h, while of a 0.016 M solution, after 5 days. We obtained transparent violet gels. The decomposition of complex **II** under the action of oxygen is accompanied by slow gas evolution and gel formation. However, after 30 h, the IR spectrum of a solution of compound **II** in MeCN displayed a strong absorption band at 1870 cm^{-1}, implying preservation of most $[Co(CO)_4]^-$ anions. In a 0.087 M solution of complex **II**, the dark brown gel is formed after 6 days, while in more dilute solutions (c 0.007–0.040 M), after 4 days.

In roughly the same conditions, the bright violet gel from complex **III** is formed double as fast as from complex **II**. The gelation time is strongly dependent on vessel volume and solvent. In large vessels gel formation is faster than in small, on account of the higher rate of oxygen absorption. Ligand-forming solvents much hinder gel formation (see table), while in a pyridine solution of complex **II** no gel formation is observed even after 30 days. In THF complex **I** forms gel very slowly, while in acetone no gel formation occurs at all (see table). Acetonitrile that liberates in the course of gel ripening contains ligand compounds: (3-aminopropyl)triethoxysilane, pyridine, and dimethylformamide. Vacuum drying of gels results is a sharp diminution of volume and formation of lilac, blue, black, or brown coarse powders. Lyogels **II** and **III** rapidly dissolve in acids (HCl, H_2SO_4, AcOH), giving transparent yellow or brown solutions. Xyrogels do not dissolve and do not swell in acetonitrile and ligand-forming solvents. After gelation, lyogels completely lose fluidity but remain transparent, exhibit no opalescence, and form no Tyndall cone. Consequently, they can be classed with cohesive disperse systems [19].

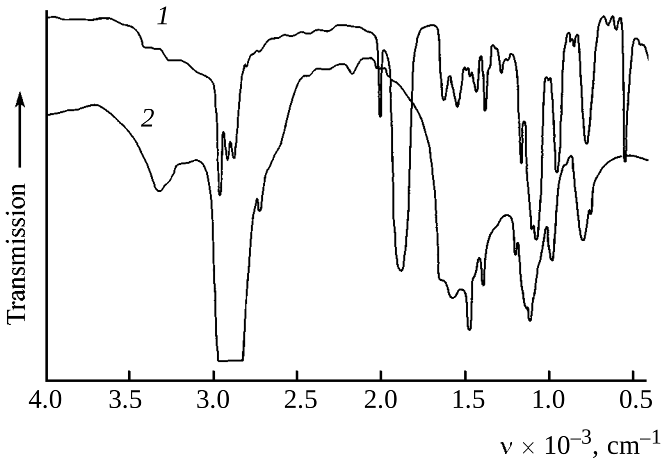

Fig. 1. IR spectra of complex **I** (*1*) before and (*2*) after hardening in air as a film.

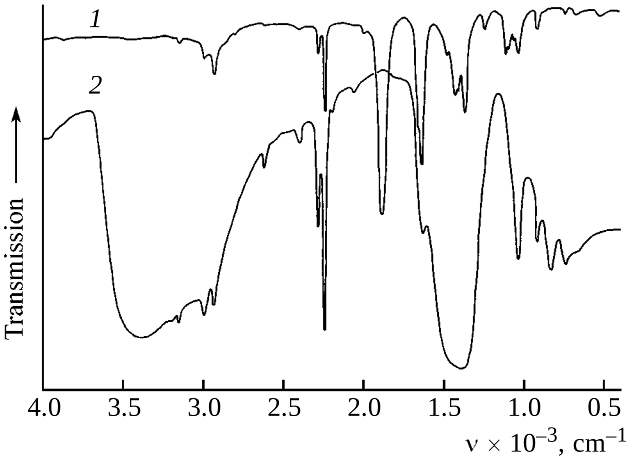

Fig. 2. IR spectra of complex **III** (*1*) before and (*2*) after hardening in air. (*1*) Concentrated solution in MeCN and (*2*) solid film wetted with MeCN.

By IR spectroscopy we studied the behavior of solutions and thin films of complexes **I**–**III** in air. Their stability depends both on ligand B and on conditions of oxygen absorption. In thin films on KBr plates the complexes decompose faster than in acetonitrile. It is known [20] that coordination compounds $[CoB_6][Co(CO)_4]_2$ dissolve in water without decomposition, while tetracarbonyl hydride is more stable in aqueous solutions than in organic solvents, condensed state, or gas phase [21]. Consequently, the decomposition of such complexes is mostly caused by air oxygen rather then moisture. Oxygen absorption by complexes **I**–**III** is readily observed in their dilute organic solutions. When exposed to air, complex **I** in benzene quickly changes from green to reddish-violet, while in acetonitrile it slowly changes from violet to rose-violet. Yellow solutions of complexes **II** and **III** in MeCN quickly get brown in air.

Liquid complex **I** hardens in air within 20 h to give thin greenish-gray flakes (thin film) or a swollen dark solid material (thick film). Concentrated solutions of complexes **II** and **III** in acetonitrile give a brown (**II**) or a light lilac (**III**) solid layers. Figures 1 and 2 show the IR spectra of complexes **I** and **III** before and after decomposition. The spectra always change considerably: the absorption bands of carbonylcobaltate anions at 2000 and 1870 cm^{-1} disappear completely; at 3600–3200 cm^{-1} there appear hydroxyl absorption bands, especially strong for complexes **II** and **III**; strong bands are observed at 1300–1500 cm^{-1}; the spectrum of compound **I** shows a weak siloxane band at 1050 cm^{-1}, while the bands at 1080, 950, and 780 cm^{-1}, belonging to SiOEt groups remain strong. The IR spectra of xerogels and the products of their decomposition in films are almost identical to each other.

It is known [22] that $Co_2(CO)_8$ and $Co_4(CO)_{12}$ under the action of oxygen convert to $CoCO_3$, CO, and CO_2. The oxidation of $Co_2(CO)_8$ with oxygen in nonane yields $CoCO_3$, CoO, Co_2O_3, CO, and CO_2 [23]. The observed transformation of the IR spectra led us to suggest that the decomposition of carbonylcobatate anions gives rise to a basic cobalt carbonate $CoCO_3 \cdot xCoO \cdot yH_2O$ [24]. To confirm this suggestion, we synthesized $CoCO_3 \cdot xCoO \cdot yH_2O$ [25] and $Co(OH)_2$ [26], measured their IR spectra, and performed reactions with dimethylformamide and (3-aminopropyl)-triethoxysilane. The IR spectrum of $CoCO_3 \cdot xCoO \cdot yH_2O$ obtained from $CoCl_2 \cdot 6H_2O$ and $Na_2CO_3 \cdot H_2O$ by the procedure in [25] contains two strong absorption bands at 3500–3000 (O–H) and 1550–1300 cm^{-1} (CO_3^{2-}) and is practically identical to the IR spectra of complexes **II** and **III** in air. Unlike this, the IR spectrum of $Co(OH)_2$ consists of a sharp band at 3600 cm^{-1} (OH^-), two broad bands at 500 and 450 cm^{-1} (Co–O), and have nothing in common with the spectra of the products of decomposition of complexes **II** and **III** in films or xerogels obtained from these complexes in MeCN in air.

Cobalt(II) carbonate very slowly reacts with (3-aminopropyl)triethoxysilane, yielding a fine white dispersion. The IR spectrum of the resulting solid phase is almost identical to the spectrum of the xerogel synthesized from complex I. Consequently, the product of this reaction is similar in chemical composition to the xerogel. Treatment of cobalt(II) carbonate with (3-aminopropyl)triethoxysilane appreciably affects the broad and strong OH absorption band in the IR spectrum. This result suggests condensation of hydroxy and triethoxysilyl groups.

Compared with strong OH and CO_3^{2-} bands, the bands of organic fragments in the IR spectra of the xerogels obtained from complexes **II** and **III** are weak. The elemental analyses (see table) show that the most part of the ligand environment of Co(II) ions passes into xerogels and is not removed by heating in a vacuum or by washing with diethyl ether. Consequently, lyogels and xerogels contain $[CoB_6]^{2+}$ ions which impart a strong color to the gels. The presence in the dispersion medium (acetonitrile) of ligand compounds suggests that gel formation is accompanied by partial replacement of the ligands with the solvent. Calculated compositions of xerogels can be brought into agreement with their elemental analysed only one the assumption that part of ligands in $[CoB_6]^{2+}$ are replaced by MeCN or Et_2O. For the xerogels obtained from complexes **I**–**III** we suggest the formula $[CoB_xS_y](OH)_2 \cdot 2[CoCO_3 \cdot 2CoO \cdot 2H_2O]$ {B = $(EtO)_3SiCH_2CH_2CH_2NH_2$, S = MeCN, $x = 3$, $y = 3$; B = $(EtO)_3SiCH_2CH_2CH_2NH_2$, S = Et_2O, $x = 2$, $y = 4$; B = C_5H_5N, $x = 3$, $y = 3$; and B = $HC(O)NMe_2$, S = MeCN, $x = 2$, $y = 4$}.

Ligand exchange in hexamine- or hexamidecobalt(II) cations is the most probable reason for the strong retardation of gel formation in comlex-forming solvents. Taking account of the widely known ability of cobalt(II) to bind oxygen [13, 14], we can suggest the following scheme of formation of carbonate gels. The first stage involves coordination of molecular oxygen by the cationic part and formation of the oxygenated complex $[CoB_5O_2][Co(CO)_4]_2$. After this, oxidation of the anionic part to cobalt carbonate takes place. In the presence of a great excess of B, the equlibrium in reactions (1) and (3) is shifted to the left. This discourage oxygen from replacing ligands in the coordination sphere of Co^{2+} and makes the complex more stable.

$$[CoB_6]^{2+} \rightleftarrows [CoB_5]^{2+} + B, \quad (1)$$

$$[CoB_5]^{2+} + O_2 \rightleftarrows [CoB_5O_2]^{2+}, \quad (2)$$

$$[CoB_6]^{2+} + O_2 \rightleftarrows [CoB_5O_2]^{2+} + B. \quad (3)$$

The absorption of oxygen by complex **I** was proved by GLC (simultaneous determination of H_2, O_2, N_2, and CO). A 70-ml ampule was charged with 0.43 g of compound **I**. The ampule was rotated for 15 min so that the viscous complex formed a uniform thin film on the walls and absorbed air oxygen, and then sealed. After 2 days, the gas phase was subjected to GLC analysis to find hydrogen, nitrogen, and carbon dioxide. Oxygen was not found even in trace amounts, and the $H_2 : CO$ ratio was 2 : 98. The analysis performed after 2 h revealed in the gas phase oxygen and nitrogen (4 : 96 instead of 21 : 78), while hydrogen was lacking. These findings show that complex **I** absorbs oxygen fairly rapidly, whereas hydrogen is evolved slowly as a result of a side reaction. Obviously, this side reaction involves condensation of the tetracarbonylcobalt hydride formed as an admixture in the course of hydrolysis of complex **I** by air moisture [schemes (4) and (5)].

$$\mathbf{I} + 2H_2O \longrightarrow [CoB_6](OH)_2 + 2H[Co(CO)_4], \quad (4)$$

$$2H[Co(CO)_4] \longrightarrow H_2 + Co_2(CO)_8. \quad (5)$$

The xerogels formed from complexes **I** and **II** are practically nonporous materials, while the xerogel obtained from complex **III** has a fairly high specific surface. Calcination of xerogels in argon appreciably increases S_{sp} for gel **I** and decreases it for gel **III**. In both cases, the carbonate frame of the gels is destroyed. However, gel **I** after pyrolysis preserves the thermally stable silica frame, while gel **III** lacks such a frame.

The xerogels obtained from complexes **I**–**III** are X-ray amorphous and preserve this state after heating to 250°C in a vacuum. However, those obtained from the pyridine and dimethylformamide complexes form a crystalline cobalt(II) oxide at a higher temperature (600°C, Ar). Such transformation is quite characteristic of cobalt carbonate [24], and this can be considered one more convincing evidence for the carbonate structure of the gels. Along with CoO, small amounts of elemental cobalt in the β form were detected among the pyrolysis products. The X-ray diffraction pattern of xerogel **III** heated to 600°C under argon displays five strong reflexes with interplanar spacings of 2.45, 2.13, 1.50, 1.28, and 1.23 Å (CoO), as well as three weaker reflexes [2.05, 1.77, and 1.25 Å (β-Co)]. Heating of xerogel **I** to 600°C results in no cobalt oxide formation. The X-ray diffraction pattern of the pyrolysis products shows three broadened reflexes with interplanar spacing of 2.03, 1.91, 1.77 Å, belonging to α- (1.91 Å) and β-Co (2.03 and 1.77 Å) (the strongest is the reflex at 2.03 Å). Both α- and β-Co are appreciably amorphized. The X-ray diffraction data suggest that the carbonate gel obtained from polyfunctional organosilicon complex **I** much differs structurally from the gels obtained from organic complexes **II** and **III**. This difference is probably caused by the reaction of SiOEt groups with OH groups of the basic cobalt carbonate, resulting in that the purely carbonate gel becomes mixed carbonate–siloxane. The mixed structure may arise already on the lyogel-formation stage. The concurrent occurrence of two processes, hydrolysis of SiOEt groups and oxidation of $[Co(CO)_4]^-$ anions, should result in such a structure. Analysis of the IR spectra (Fig. 1) gives evidence in favor of a mixed gel with prevailing carbonate component. The spectrum contains a very strong CO_3^{2-} absorption band, a siloxane band of medium intensity, and strong SiOEt bands. The additional silica frame appreciably affects the behavior of the gel in a vacuum. After removal of solvents, the gels obtained from complexes **II** and **III** gradually transform into powders already at room temperature. Unlike this, the gel obtained from complex **I** is more stable and transforms into a powder when heated to 100°C. The lower intensity of the absorption band at 3500–3100 cm^{-1} shows that hydroxy groups of the basic cobalt carbonate react with SiOEt groups, yielding a mixed carbonate–siloxane frame. The specific surface of the mixed carbonate–siloxane xerogel can be increased to 33 m^2/g (see table) if one adds to a gelated dilute solution of complex **I** in THF a calculated amount of water and leaves the mixture to stand for a long time to let SiOEt groups to hydrolyze. The specific surface increases due to increasing contribution of the sesquioxane structure. Therewith, the xerogel acquires an even greater strength, the diminution of volume on drying becomes less considerable, and the product looks like fine granules 2–3 mm in size.

Magnetic studies on the glassy xerogel $\{[O_{1.17}(EtO)_{0.67}SiCH_2CH_2CH_2NH_2]_6Co\}[Co(CO)_4]_2$ obtained by hydrolysis of complex **I** with water in ethanol under argon [12] and on a solid product of decomposition of this gel in air gave the following results. Complex **I** hydrolyzed in anaerobic conditions is a high-spin paramagnetic compound (μ 4.90 BM per Co^{2+}) which does not change magnetic properties on multiple exposure to magetic field {for comparison, the effective magnetic moments of the complexes $[Co(NH_3)_6]Cl_2$ and $[Co(dipy)_3]Cl_2$ are 4.96 and 4.85 BM, respectively [27]}. By contrast, the same weighed sample of the product of decomposition of complex **I** in air is double as strongly drawn into the magnetic field on the first exposure and further on this drawing enhances. Such behavior is associated with the presence in this substance of a ferromagnetic component.

Complex **I** applied on glass from a dropper (neat or in an ethanol solution) hardens under the action of air oxygen or moisture within 20–25 h at room temperature, giving transparent grayish-green flakes which are readily separated from the support. The color change from crimson-red to grayish-green occurs within 1–2 h. Dilution of complex **I** [with (3-aminopropyl)triethoxysilane in 1 : 4, 1 : 12, or 1 : 28 molar ratios] results in formation of a continuous film. Treatment of the glass surface with hexamethyldisilazane vapors fails to increase adhesion of the hardened complex. As shown in [28], the strongest glasses are formed by hydrolysis of complex **I** diluted with trimethoxymethyl- and -phenylsilanes, whereas dilution with tetraethoxysilane gives rise to lilac opaque powders. However, the compositions including complex **I** and $MeSi(OMe)_3$ or $PhSi(OMe)_3$, too, gave no high-quality films on hardening in air. By contrast, ethanol solutions of $(EtO)_3SiCH_2CH_2CH_2 \cdot NH_2$ and $MeSi(OMe)_3$ and of $(EtO)_3SiCH_2CH_2CH_2 \cdot NH_2$ and $PhSi(OMe)_3$, applied on glass give transparent colorless films. The adverse effect of complex **I** on film formation is explained by its polyfunctionality and rigidity. Addition of a mixture of oligodimethylsiloxane-α,ω-diols $HO(SiMe_2O)_nH$ (n = 3–7) as a plasticizer changes the situation dramatically. Molecules of complex **I** linked by flexible siloxane chains form strong transparent layers which undergo no cracking upon hardening. The best films we obtained from the ternary composition complex **I** + $HO(SiMe_2O)_nH$ + $PhSi(OMe)_3$ (weight ratio 1.0 : 1.1 : 0.7, molar ratio 1 : 6 : 6). Comples **I** changes from crimson-red to violet, when it is mixed with silixanediols. The composition is stable for 5–7 days in a vacuum or under argon at low temperatures. The samples were prepared by coating from an ampule filled with argon. The spontaneously formed layers 100–300 μm thick proved suitable for measuring visible absorption spectra. They hardened within 15–20 h and changed from violet to marshgreen. When a composition preliminarily exposed to air was applied, the layer foamed because of vigorous CO liberation.

Macroscopic examination of the films revealed no inclusions, except for small gas bubbles visible at a high magnification (×400–900). The films remain transparent upon heating to 100°C. Cracking is observed only at 200°C. Transmission electron microscopy and energy-dispersion X-ray fluorescence give evidence for the homogeneous structure of the films.

The IR spectrum of an unhardened composition (complex **I**, oligodimethylsiloxane-α,ω-diols, and trimethoxyphenylsilane) is a superposition of the spectra of its constituents. Hardening in air is accompanied by the following changes: complete disappearance of the bands at 2000 and 1870 cm^{-1}, belonging to carbonyl stretching absorption of the carbonylcobaltate anion; appearance of a broad strong band at 1650–1400 cm^{-1} (CO_3^{2-}), overlapping with amine and formamide bands (1650, 1625, and 1550 cm^{-1}), as well as C–H bending bands (1430, 1380 cm^{-1}); broadening and enhancement of the siloxane bands at 1150–1000 cm^{-1}; and weakening and diffusion of bands in the range 950–750 cm^{-1} (SiOEt and SiOMe).

The above-listed changes are generally identical to those observed on gel formation from complex **I**. They suggest separation of the basic cobalt carbonate and formation of a “cross-linked” carbonate–siloxane structure with preserved hexa(aminoamide)cobalt anions. The function of trimethoxyphenylsilane on hardening is to extend the flexible polysiloxane chain that links two hard cations. Heating to 150°C attenuates the absorption bands (3300–3280 cm^{-1}) of SiOH groups which ensure further progress of thermal condensation. In the IR spectrum of the heated film, NH and NH_2 absorption at 3400–3100 cm^{-1} becomes better and better defined on the background of residual silanol absorption. The appearance at 150°C of a weak band at 2200 cm^{-1} [ν(Si–H)] points to partial reduction of organosilicon to silicon hydride groups. Instead of $[Co(CO)_4]^-$, silanolate or ethylate anions can assume the role of counterions at the (aminoamide)cobalt cation.

By energy dispersive X-ray fluorescence analysis we determined the contents of cobalt and silicon in the film obtained from 0.74 g of complex **I**, 0.81 g of siloxanediols, and 0.51 g of trimethoxyphenylsilane, that was hardened for 20 h in air and then heated for 2 h at 100°C. By the results of three measurements, the cobalt contents were 3.11, 2.94, and 3.23% and the silicon contents, 21.11, 21.00, 21.35%. These values are consistent (nicely for Si and fairly for Co) with theoretical for the unhardened composition (Co 3.67%, Si 21.21%). Hardening in air at room temperature is accompanied by a weight loss of 12– 15% within 20 h, and further heating produces an additional 10–12% weight loss. The processes that occur on film structuring (oxygen absorption, transformation of carbonylcobaltate anions to the basic cobalt carbonate, hydrolysis of the coordination compound and of peripheral triethoxysilyl groups, condensation of ≡Si–OEt and HOSi≡ fragments) are accompanied by oxygen and moisture absorption and liberation of ligand B, carbon oxides, ethanol, and tetracarbonylcobalte hydride [schemes (6–10)].

$$[CoB_6][Co(CO)_4]_2 + O_2 \rightarrow [CoB_5O_2][Co(CO)_4]_2 + B, \quad (6)$$

$$3[Co(CO)_4]^- + (2 + 0.5n)O_2 + 2H_2O \rightarrow [CoCO_3 \cdot 2CoO \cdot 2H_2O] + nCO_2 + (11 - n)CO + 3e^-, \quad (7)$$

$$[CoB_6][Co(CO)_4]_2 + 2H_2O \longrightarrow [CoB_6](OH)_2 + 2H[Co(CO)_4], \quad (8)$$

$$\equiv Si{-}OEt + H_2O \longrightarrow \equiv Si{-}OH + EtOH, \quad (9)$$

$$\equiv Si{-}OEt + HO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + EtOH. \quad (10)$$

Each of these reactions can finally reduce the film weight via evaporation of volatile products whose molecular weights are higher that those of absorbed O_2 and H_2O [reaction (7) also involves weight loss of the solid phase]. The removal from the thin film of CO, CO_2, and EtOH should result in its enrichment with silicon and cobalt. However, the resulting data suggest that structuring involves concurrent processes resulting in loss of cobalt and silicon. The first element is apparently removed as the volatile $H[Co(CO)_4]$, and the second, as low-boiling siloxanes and siloxanediols. Thus, the deeply structured film is similar in elemental composition to the starting material.

The composition obtained from complex **I**, siloxanediols, and trimethoxyphenylsilane was hardened at room temperature in a vacuum. Here we observed no color change from crimson-red to green, as it took place in air. The hardened film was violet, and its IR spectrum contained a strong absorption band (1870 cm^{-1}), implying preservation of the most part of carbonylcobaltate anions. Vacuum hardening was accompanied by gas evolution, which pointed to partial decomposition of complex **I**. We failed to obtain high-quality (of uniform thickness and defectless) films.

Electronic absorption spectroscopy is very informative of the structure of coordination compounds [29]. It is one of the most powerful tools of investigation of absorption and desorption of molecular oxygen by cobalt complexes. The O_2 absorption gives rise to a metal–ligand charge-transfer band which is stronger than the bands formed by *d*–*d* transitions in the cobalt(II) cation [13, 14]. IR spectral data point to complete decomposition of the $[Co(CO)_4]^-$ anion in the course of film hardening.

The complex $CoCO_3 \cdot xCoO \cdot yH_2O$ is colorless, and, therefore, its visible absorption spectrum should relate to the hexa(aminoamide) cation. Figure 3 shows the spectra of dilute solutions of complexes **I**–**III** in acetonitrile. The spectra contain a multiplet absorption band at 16000–23000 cm^{-1} (ε 10–15 $l\,mol^{-1}\,cm^{-1}$), characteristic of six-coordinate Co(II) compounds [transition $^4T_{1g}(P)$–$^4T_{1g}$] [29].

Figure 4 shows the spectrum of compound **I** in acetonitrile before and after oxygen absorption. As follows from Fig. 4, the complex formation with O_2 sharply enhances absorption at 17000–21000 cm^{-1}, on account of the appearance of a charge-transfer band. The spectrum of the dilute solution shows that the two maxima of this band are shifted red with respect to the maxima of the initial complex (by ~300 cm^{-1}). The oxygen absorption results in an almost complete

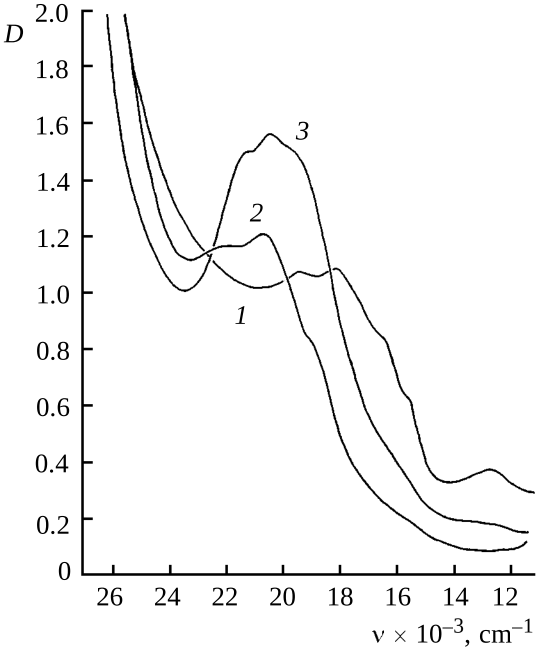

Fig. 3. (*1*–*3*) Electronic absorption spectra of solutions of complexes **I**–**III** in MeCN. Concentration, M: (*1*) 0.047, (*2*) 0.03, and (*3*) 0.04.

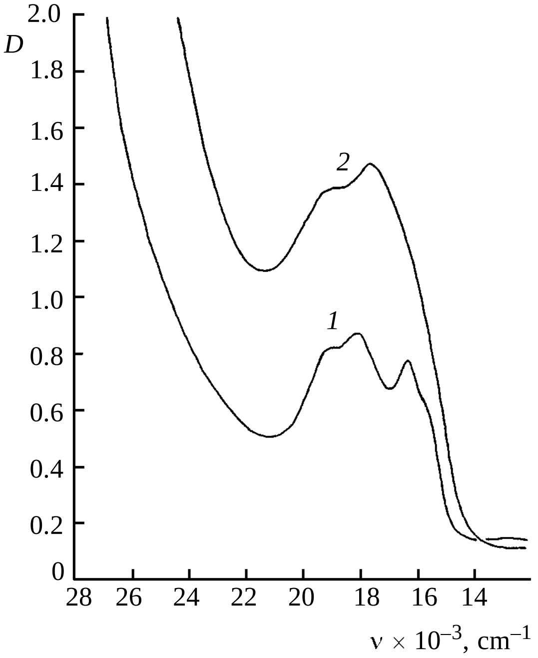

Fig. 5. Electronic absorption spectrum of a vacuum-hardened film. (*1*) Freshly prepared film (195 μm) and (*2*) exposed to air for 20 h.

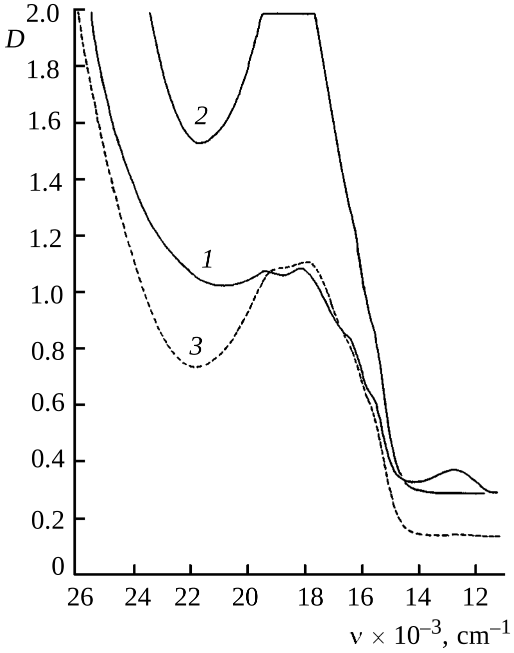

Fig. 4. Electronic absorption spectraum of a solution of complex **I** in acetonitrile. (*1*) Initial solution [0.047 M, ν 19200 cm^{-1}, ε 13 l mol^{-1} cm^{-1}; ν 18100 cm^{-1}, ε 15 l mol^{-1} cm^{-1}; ν 12800 cm^{-1}, ε 1.5 l mol^{-1} cm^{-1}], (*2*) after oxygen absorption for 20 min (0.047 M), and (*3*) after dilution to 0.016 M [ν 18900 cm^{-1}, ε 63 l mol^{-1} cm^{-1}; ν 17800 cm^{-1}, ε 49 l mol^{-1} cm^{-1}].

disappearance of the long-wave shoulders at 16400 and 15600 cm^{-1}, whereas the near UV absorption is enhanced. In view of data in [14], this fact can be explained by the appearance of a Co(d_z^2) ← O$_2$(π_g^*) transition which has a fairly high extinction coefficient.

A similar spectral transformation is observed on O$_2$ absorption of the film prepared by vacuum hardening (Fig. 5). Its violet color changes to light brown (within 1 h in air) and then gradually (within 15–20 h) deepens, implying slow absorption of oxygen by the complex Co(II) cation. The observed effects point to fast O$_2$ asorption by oxygen-free solutions and slow oxidation of carbonylcobaltate anions. The same conclusions can be drawn of the IR spectra which show that the latter are present in solutions even after 30-h gel formation in air. In the course of film preparation (in thin layer), $[Co(CO)_4]^-$ faster converst to $CoCO_3 \cdot xCoO \cdot yH_2O$, since the complex is more accessible for oxygen. The film obtained by hardening (Fig. 6) comprises both oxygenated and nonoxygenated cobalt(II) cations. Heating deepens the brown color of the film and enhances not only the two high-frequency (19200 and 17400 cm^{-1}), but also of the two low-

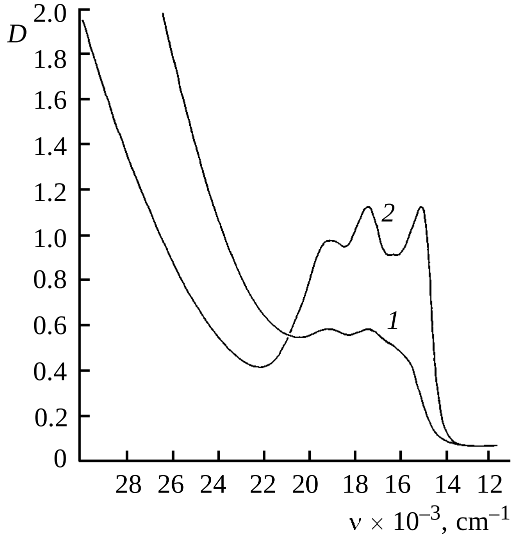

Fig. 6. Electronic absorption spectrum of a film (*1*) hardened in air for 20 h (150 μm) and (*2*) then heated in air for 30 min at 150°C.

frequency (16400 and 15100 cm^{-1}) maxima. These data imply that heating, as well as oxygen absorption and other substitution reactions involving amine ligans cause profound changes in the coordination sphere of the Co(II) cation. The oxygen absorption is an irreversible process both in solutions of **I**–**III** and in the organosilicon film containing the $[\mathrm{CoB}_6]^{2+}$ cation. On attempted desorption of oxygen from solutions of complexes **I**–**III** in acetonitrile either by exposure to a vacuum or by barboting argon, no changes in the absorption spectra or recovery of the initial color of the solution were observed. Evacuation of the film, too, caused no spectral or color changes.

The luminescence spectrum of the film hardened in air consists of a weak emission band at 23260 cm^{-1}. For comparison, we measured the spectrum of a cobalt-free film as close to the cobalt-containing film in the organosilicon content as possible. The composition comprising equimolar amounts of (3-aminopropyl)triethoxysilane, phenyltrimethoxsilane, and oligodimethylsiloxane-α,ω-diols hardened in air within 24 h to give a transparent colorless strong film on a quartz support. The luminescence spectrum of the latter film, too, contained a single emission band at 23260 cm^{-1}. However, this band was 30 times higher in intensity than the similar band of the cobalt-containing film. The latter result can be explained by the luminescence of phenyl groups, while the weakening of the emission band, by the effect of the $[\mathrm{CoB}_6]^{2+}$ cation or the carbonate–siloxane frame.

EXPERIMENTAL

The IR spectra were measured on Specord IR-75 and Perkin–Elmer-577 spectrophotometers for suspensions in Vaseline oil or films of gels on KBr plates. The electronic absorption spectra were measured on a Specord M-40 spectrophotometer for thin films on glass supports or for acetonitrile solutions in 1–10-mm quartz cells. The X-ray phase analysis was performed on a DRON-3M diffractometer ($\mathrm{Cu}K_\alpha$ radiation) with a graphite monochromator. The energy dispersive X-ray fluorescence analysis was performed on a Link AN-1000 energy dispersive X-ray analyzer coupled with a Cambridge Stereoscan-360 scanning electron microscope. The luminescence spectra were measured on a SLM AMINCO MC-200 Monochromator spectrophotometer. Gases were analyzed on a Tsvet-530 gas chromatograph equipped with a vacuum pump, a mercury gage, and a three-way valve, on a 0.3 × 100-cm stainless-steel column packed with NaX molecular sieves. This device allowed the pressure in ampules to be measured and gas samples to be injected in air-proof conditions. Using a thermal conductivity detector and an argon carrier gas allowed simultaneous determination of H_2, N_2, O_2, and CO. The composition of the gas phase was calculated with account for tabulated thermal conductivities of the gases [30].

(3-Aminopropyl)triethoxysilane, trimethoxyphenylsilane, and trimethoxymethylsilane were analyzed on a 0.3 × 200-cm stainless-steel column packed with 5% SE-30 on Chromaton N-AW-DMCS. The specific surfaces were determined by the thermal nitrogen desorption technique on a GKh-1 chromatograph, thermal conductivity detector, helium (45 ml/min), and nitrogen (5 ml/min). (3-Aminopropyl)triethoxysilane (Altaikhimprom Production Company, Slavgorod) was distilled in a vacuum on a 1 × 50-cm column packed with nichrome coils. The content of the low-molecular (2-aminoisopropyl)triethoxysilane [31] was 1.8%. The purity of octacarbonyldicobalt (Pilot Plant, State research Institute of Chemical Technology of Organoelement Compounds), according to HPLC data (Milikhrom-1A, 2 × 64-mm column, Separon-SGX, 5 μm, UV detector, 250 nm, hexane), was 98%, and it was used as received. Trimethoxymethylsilaneand trimethoxymethylsilane (Aldrich) were distilled before use. The mixture of α,ω-dichlorooligomethylsiloxanes $\mathrm{ClMe_2Si(OSiMe_2)}_n\mathrm{Cl}$ (n = 2–6) was obtained by partial hydrolysis of dichlorodimethylsilane by the procedure described in [32]. Acetone was dried over molecular sieves (3 Å) and distilled. Acetonitrile and dimethylfomamide were dried over molecular sieves (3 Å) and distilled over P_4O_{10} and CaH_2, respectively. Diethyl ether was distilled over P_4O_{10}. Pyridine was shaken with powdered NaOH, dried over molecular sieves (3 Å), and distilled. Tetrahydrofuran was successively refluxed over NaOH and Na, and distilled. Glass supports for films ($1 \times 25 \times 40$ mm) were treated for 10 h with saturated aqueous NaOH in isopropanol and then for 10 h with sodium dichromate in sulfuric acid, washed with water, and dried at 150–170°C.

Hexapyridinecobalt(II) bis(tetracarbonylcobaltate) (II). A solution of 1.08 g of pyridine in 10 ml of diethyl ether was degassed and mixed in a vacuum with 1.11 g of $Co_2(CO)_8$. The carbon monoxide formed was intermittently removed from the reaction zone. After 2 h, the precipitate that formed was washed with diethyl ether and dried in a vacuum to obtain 1.18 g (62%) of compound **II** as an orange powder. Found, %: C 48.98; H 3.37; Co 22.01. $C_{38}H_{30}Co_3N_6O_8$. Calculated, %: C 52.13; H 3.45; Co 20.20.

Hexadimethylformamidecobalt(II) bis(tetracarbonylcobaltate) (III) was obtained in a similar way from 0.76 g of DMF and 0.83 g of $Co_2(CO)_8$ in 10 ml of diethyl ether. Yield 0.96 g (71%), rose. Found, %: C 36.38; H 4.75; Co 22.45. $C_{26}H_{42}Co_3N_6O_{14}$. Calculated, %: C 37.20; H 5.04; Co 21.06.

Oligodimethylsiloxane-α,ω-diols. A solution of 16.6 g of α,ω-dichlorooligodimethylsiloxanes in 120 ml of diethyl ether was quickly (for 15–20 min) was added dropwise with vigorous stirring and cooling to a solution of 4.30 g of NaOH in 82 ml of H_2O. The organic layer was separated, washed with water, dried over Na_2CO_3, the diethyl ether was removed by distillation, and the residue was distilled in a vacuum to obtain 7.33 g of oligodimethylsiloxanediols as a transparent colorless liquid with a camphor smell, bp 95–105°C (2 mm), n_D^{20} 1.4087.

Preparation of gels. Complex **III**, 0.31 g, was dissolved in 4 ml of acetonitrile (c_0 0.089 M), and the solution was left to stand in an unsealed ampule 16 mm in diameter. After 6 days, a transparent brown gel formed. Volatile products were removed in a vacuum; according to GLC analysis, they contained pyridine. The solid residue was washed with pyridine and dried to obtain 0.15 g of a brown powder-like xerogel. IR spectrum, ν, cm^{-1}: 3320 (OH), 1650, 1585, 1150, 1070, 1030, 685, 580 (C_5H_5N), 1420, 835 (CO_3^{2-}). Found, %: C 24.47; H 3.76; Co 36.71. $C_{23}H_{34}Co_7N_6O_{16}$. Calculated, %: C 25.99; H 3.22; Co 38.81. Xerogels from complexes **I** and **III** were obtained in a similar way. Xerogel from a solution of complex **I** in MeCN. Found, %: C 27.70; H 6.67. $C_{35}H_{88}Co_7N_6O_{25}Si_3$. Calculated, %: C 28.22; H 5.95. Xerogel from a solution of complex **I** in Et_2O. Found, %: C 29.80; H 6.49. $C_{36}H_{96}Co_7N_2O_{26}Si_2$. Calculated, %: C 29.98; H 6.71. Xarogel from a solution of complex **III** in MeCN. Found, %: C 18.52; H 3.62; Co 41.33. $C_{16}H_{36}Co_7N_6O_{18}$. Calculated, %: C 18.97; H 3.58. Co 40.72. The xerogels were slowly (for 2 h) heated under argon to 600°C, heated at that temperature for 15 min, and cooled under argon.

Preparation of films. Complex **I**, 0.74 g, oligodimethylsiloxanediols, 0.81 g, trimethoxyphenylsilane, 0.51 g, and tetrahydrofuran, 1 ml, were mixed in an ampule in a vacuum. The ampule was sealed and cetrifuged. Part of the liquid was withdrawn with a capillary under argon and applied to an object or a KBr plate. After 15–20 h in air, a grayish-green transparent solid film with a good adhesion to the surface formed. For vacuum hardening, the object plate immediately after coating was placed into a wide tube amd evacuated for 8 h. Gradually decaying (for 1 s) gas evolution was observed, and the viscosity of the liquid layer increased. The tube was filled with argon, the support with the film was taken off, and electronic absorption spectrum was immediately measured. The films were dried in air. After 20 h, one more electronic absorption spectrum was measured (Fig. 5). The films were heated in an air thermostat, the temperature was raised for 3–5 min to a specified temperature (100, 150, or 200°C) and maintained for 30 min. The supports with the films were placed between Petri dishes. The resulting spectra are given in Fig. 6.

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