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Organosilicon Compounds Containing Carbofunctional Biguanidine Group

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Abstract—The reaction of triethoxysilylpropylamine (AGM-9) with dicyanodiamide was studied. The condensation of AGM-9 with dicyanodiamide occurs in the presence of a catalytic amount of $CuCl_2$ at 125–145°C within 5–24 h; it involves both the amino group of AGM-9 and ethoxy substituents at the Si atoms, with an unusual exchange of a Si–O bond for a Si–N bond. The final reaction product is 1-*N*-(3-triethoxysilylpropyl)-2-*N*-[3-aminopropylsilyl(diethoxy)]biguanidine. Its hydrolytic polycondensation yields an organosilicon polymer, a polycondensate of AGM-9 with 1-*N*-(3-triethoxysilylpropyl)biguanidine, which is a highly efficient sorbent for Ag(I) (static sorption capacity 544 mg g^{-1}).

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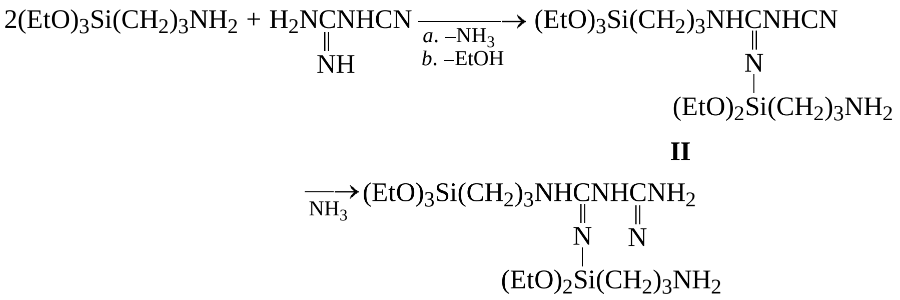
Many organic derivatives of biguanidine are biologically active substances. For example, the biguanidine group is contained in palauamine and styloguanidine alkaloids exhibiting cytotoxic, antibiotic, antifungus, and immunomodulating effect [1], in Glyformin antidiabetic drug [2], in antimicrobial agents and substances for treatment of contact lenses [3], in a patented formulation for hand disinfection [4], etc. Furthermore, organic compounds containing a polydentate biguanidine group are effective complexants [5, 6]. No data are available on organosilicon derivatives of biguanidine. Proceeding with studies of biologically active organosilicon compounds [7] and of organosilicon ion-exchange and complexing resins [8], we prepared in this study organosilicon compounds containing a biguanidine group.

One of the most known routes to organic derivatives of biguanidine is the reaction of amines or their salts with dicyanodiamide, performed in saturated hydrocarbons (C_8–C_{15}) providing the required reaction temperature (120–200°C) [9]. However, heating of an equimolar mixture of dicyanodiamide with (3-triethoxysilylpropyl)amine (AGM-9) in decane for 5 h did not yield the desired organosilicon derivative of biguanidine. The starting AGM-9 was recovered, and dicyanamide under the reaction conditions transformed into melamine.

The first organosilicon compound containing a biguanidine group was prepared only by the reaction of *N*-3-triethoxysilylpropylamine with dicyanodiamide in the presence of a catalytic amount of $CuCl_2$. The reaction was performed in a flask and in a sealed ampule without a solvent at 124–145°C for 5–24 h. We expected that the reaction of AGM-9 with dicyanodiamide, by the analogy with organic diamines [9], would occur in the first step as the condensation followed by the addition of the released ammonia to the triple bond of the intermediate 1-*N*-(3-triethoxysilylpropyl)-4-cyanoguanidine to form the corresponding 1-*N*-(3-triethoxysilylpropyl)biguanidine. However, instead we obtained 1-*N*-(3-triethoxysilylpropyl)-2-*N*-[3-aminopropyl(diethoxy)silyl]biguanidine **I**. The formation of **I** and the observed release of ethanol indicate that one more condensation process involving AGM-9 occurs, with the replacement of a Si–O bond by a Si–N bond. Such an exchange is unusual for the organosilicon chemistry, and its driving force is apparently the acid character of dicyanodiamide and its derivatives [10]. Apparently, both condensation pathways (with the release of ammonia, pathway *a*, and ethanol, pathway *b*) occur simultaneously, and the intermediate reaction product is 1-*N*-(3-triethoxysilylpropyl)-2-*N*-[3-aminopropyl(diethoxy)silyl]-4-cyanoguanidine **II**.

Indeed, when the reaction is performed in a flask under the conditions of partial removal of the released ammonia from the reaction mixture, the IR spectrum of the reaction product contains a weak doublet at 2190 and 2140 cm^{-1} assigned to $\nu(C\equiv N)$; this band suggests the presence of an impurity of **II** in **I**. On the



$$2(EtO)_3Si(CH_2)_3NH_2 + H_2N\underset{\underset{NH}{\|}}{C}NHCN \xrightarrow[\substack{a.\ -NH_3\\ b.\ -EtOH}]{} (EtO)_3Si(CH_2)_3NH\underset{\underset{\underset{(EtO)_2Si(CH_2)_3NH_2}{|}}{\underset{N}{\|}}}{C}NHCN$$

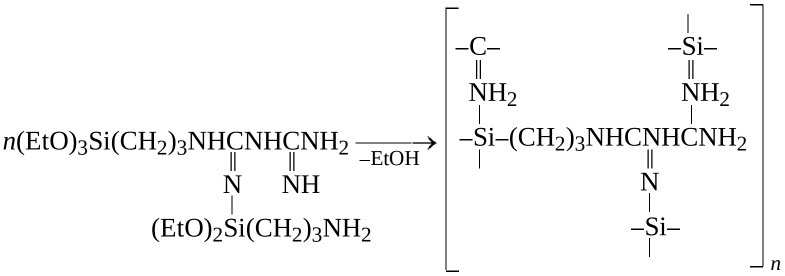
II

$$\xrightarrow[NH_3]{} (EtO)_3Si(CH_2)_3NH\underset{\underset{\underset{(EtO)_2Si(CH_2)_3NH_2}{|}}{\underset{N}{\|}}}{C}NH\underset{\underset{N}{\|}}{C}NH_2$$

I

contrary, compound **I** prepared by the reaction in a sealed ampule does not contain this impurity.

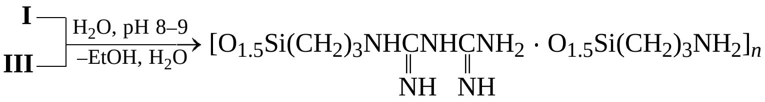
Compound **I** is a viscous undistillable oily liquid. Its composition and structure were proved by elemental analysis and by ^1H, ^{13}C, and ^{29}Si NMR and IR spectroscopy. On attempted distillation, even in a high vacuum, compound **I** transforms into a light brown rubber-like substance insoluble in water and majority of organic solvents; it is apparently a product of further condensation (process *b*), polysilazane **III**.



$$n(EtO)_3Si(CH_2)_3NH\underset{\underset{\underset{(EtO)_2Si(CH_2)_3NH_2}{|}}{\underset{N}{\|}}}{C}NH\underset{\underset{NH}{\|}}{C}NH_2 \xrightarrow[-EtOH]{} \left[\begin{array}{c} \overset{-C-}{\underset{NH_2}{\|}} \qquad\qquad \overset{\overset{|}{-Si-}}{\underset{NH_2}{\|}} \\ -\underset{|}{\overset{|}{Si}}-(CH_2)_3NH\underset{\underset{\underset{\underset{|}{-Si-}}{|}}{\underset{N}{\|}}}{C}NH\overset{|}{C}NH_2 \end{array}\right]_n$$

III

The hydrolytic polycondensation of both polysilazane **III** and compound **I** yields the same polymeric product containing siloxane bonds (Si–O–Si) only, copolycondensate of AGM-9 and 1-*N*-(triethoxysilylpropyl)biguanidine **IV**, apparently because the Si–N and Si–OC bonds are hydrolyzed equally readily.



$$\left.\begin{array}{r}\mathbf{I}\\ \mathbf{III}\end{array}\right] \xrightarrow[-EtOH,\ H_2O]{H_2O,\ pH\ 8–9} [O_{1.5}Si(CH_2)_3NH\underset{\underset{NH}{\|}}{C}NH\underset{\underset{NH}{\|}}{C}NH_2 \cdot O_{1.5}Si(CH_2)_3NH_2]_n$$

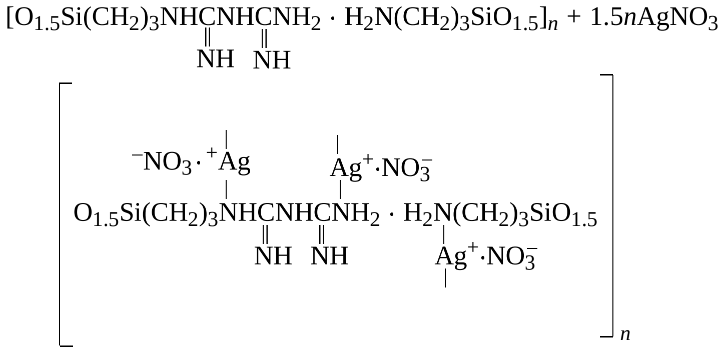
IV

The copolycondensate of (3-triethoxysilylpropyl)-amine and 1-*N*-(3-triethoxysilylpropyl)biguanidine (**IV**) is a colorless or beige amorphous powder; it neither dissolves nor swells in water and organic solvents, which is indicative of its three-dimensionally cross-linked structure. The structure of **IV** is confirmed by the IR data: A strong broad absorption band with a maximum at 1560 cm^{-1} (the similar band is also present in the spectrum of **I**) is due to bending vibrations of the primary amino group $\delta(NH_2)$; a shouder at about 1620 cm^{-1}, also observed in the spectrum of **I**, is due to stretching vibrations of the C=N group in compounds of the guanidine structure; a broad strong band at 1000–1100 cm^{-1} corresponds to the stretching vibrations of the siloxane bond Si–O in the Si–O–Si group; and the band at 900 cm^{-1} is due to bending vibrations $\delta(NH)$ of the primary amino group.

Copolymer **IV** was tested as adsorbent for noble metals Ag(I), Au(III), Pd(II), and Pt(IV). The sorption was performed in the static mode from acid solutions: 0.5–0.6 M HNO_3 for Ag(I) and 3 M HCl for Au(III), Pd(II), and Pt(IV). The static sorption capacities of **IV** for the above elements are given below.

Sorbate	Static sorption capacity, mg g^{-1}
Ag(I)	544
Au(III)	6.6–22
Pt(IV)	30
Pd(I))	30.8

The high sorption activity of **IV** with respect to silver (static sorption capacity 544 mg g^{-1}) is due to its polydentate structure and to the strong tendency of silver to form complexes with nitrogen-containing ligands. The observed drastic decrease in the sorption capacity of **IV** in going from Ag(I) to the other noble metals is associated with the higher stability of amine complexes of Ag(I) compared to those of Au(III), Pt(IV), and Pd(II) [11]. After the interaction of **IV** with $AgNO_3$, the δ(NH) bands of the primary and secondary amino groups in the IR spectrum are shifted toward higher frequencies, from 1560 to 1610 and from 1450 to 1500 cm^{-1}, respectively, and the δ(NH) band of primary amines is shifted toward lower frequencies: from 900 to 870 cm^{-1}. Furthermore, after the sorption of Ag(I), a strong band at 1380 cm^{-1} appears; this band is absent in the spectrum of the starting compound and belongs to stretching vibrations of the nitrate ion. Taking into account these data, the polydentate structure of **IV**, the calculated ratio **IV** : Ag(I) = 1 : 1.5, and the fact that Ag(I) usually forms linear complexes (coordination number 2) with nitrogen-containing ligands [12], we can describe the complexation of Ag(I) with **IV** as follows:



$$[O_{1.5}Si(CH_2)_3NH\underset{\overset{\|}{NH}}{C}NH\underset{\overset{\|}{NH}}{C}NH_2\cdot H_2N(CH_2)_3SiO_{1.5}]_n + 1.5nAgNO_3$$

$$\left[\; O_{1.5}Si(CH_2)_3\overset{{}^{-}NO_3\cdot{}^{+}Ag}{NH}\underset{\overset{\|}{NH}}{C}NH\underset{\overset{\|}{NH}}{C}\overset{Ag^{+}\cdot NO_3^{-}}{NH_2}\cdot H_2\underset{Ag^{+}\cdot NO_3^{-}}{N}(CH_2)_3SiO_{1.5}\;\right]_n$$

Similarly, the shifted δ(NH) bands in the spectrum of **IV** after the sorption of Pd from 3 M HCl should be assigned most probably to the NH bending vibrations in ammonium ions NH_3^+ and NH_2^+ as a result of the reaction of the copolymer with HCl. The sorption capacity of **IV** with respect to Pd is so low that the complexation could hardly affect the IR spectrum. The reactivity of **IV** toward mineral acids is confirmed, along with the shift of the bending frequencies of the amino groups, by the presence of characteristic bands of nitrate (1380 cm^{-1}) and sulfate (600 cm^{-1}) ions in the spectra of the samples treated with nitric and sulfuric acids, respectively.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from thin films. The ^1H, ^{13}C, $^{13}C-\{^1H\}$ (without proton decoupling), and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz for ^1H) in $CDCl_3$. The optical densities of solutions were measured with a KFK-2 photocolorimeter.

1-*N*-(Triethoxysilylpropyl)-2-*N*-[3-aminopropyl-(diethoxy)silyl]biguanidine I. *a*. An equimolar mixture of 3 g of 1-cyanoguanidine and 8 g of AGM-9 in the presence of a catalytic amount (0.1 g) of $CuCl_2$ was heated in a flask at 125–145°C for 5 h. Then 50 ml of diethyl ether was added, and the precipitate was filtered off. The ether was distilled off, and 6 g (57%) of compound **I** undistillable in a vacuum was obtained; n_D^{20} 1.4720. IR spectrum, cm^{-1}: 3310 [ν_{as}(NH)], 3110 [ν_s(NH)]; weak doublet 2190, 2140 [ν(C≡N)], 1620 [ν(C=N)], 1540 [δ(NH_2)], 1450 [δ(NH)], 1360 [ν(CN)], 1050 [ν(SiOEt)]. Found, %: C 46.68; H 8.99; N15.94; Si 10.64. $C_{18}H_{44}N_6O_5Si_2$. Calculated, %: C 45.00; H 9.16; N 17.50; Si 11.66.

b. A mixture of 4.2 g of 1-cyanoguanidine, 11.0 g of AGM-9, and a catalytic amount (0.1 g) of $CuCl_2$ was heated at 170–180°C for 24 h in a sealed ampule. After the reaction completion, 50 ml of diethyl ether was added. The melamine precipitate was filtered off and washed with ether. The ether extracts were combined with the filtrate. The ether was distilled off, and 8 g (54%) of **I** was obtained, n_D^{20} 1.4661. IR spectrum, cm^{-1}: 3310 [ν_{as}(NH)], 3110 [ν_s(NH)], 1610 [ν(C=N)], 1540 [δ(NH_2)], 1450 [δ(NH)], 1340 [ν(CN)], 1050 [ν(SiOEt)], 900 [δ(NH_2)]. ^{1}H NMR spectrum, δ, ppm: 0.6 q (4H, SiCH2), 1.2 t (15H, CH_3), 1.5 m (2H, CCH_2C), 1.6 t (2H, CCH_2C), 2.6 t (2H, CH_2NH_2), 3.3 t (2H, CH_2NH), 3.8 q (10H, CH_2O). $^{13}C-\{^1H\}$ NMR spectrum, δ_C, ppm: 8.69 s (SiC), 18.4 q (CH_3), 23.12 s (CCH_2C), 27.15 s (CCH_2C), 43.03 s (CH_2NH), 44.85 s (CH_2NH_2), 57.8 t (OCH_2), 166 br.s [HNC(=N)NH], 166.7 br.s [HNC(=NH)NH_2]. ^{29}Si NMR spectrum, δ_{Si}, ppm: 45.00 s (EtO_3Si), 45.52 s (EtO_2Si). Found, %: C 44.93; H 9.42; Si 11.23. $C_{18}H_{44}N_6O_5Si_2$. Calculated, %: C 45.00; H 9.16; Si 11.66.

Copolymer IV. A mixture of 8 g of **I** and 25 ml of aqueous NaOH (pH 8–9) was stirred at room temperature for 1 h and then heated on a water bath for 3 h. The precipitate was washed with water and dried in an oven at 100–110°C. Copolymer **IV** is insoluble in water and organic solvents. Yield 4 g (79%). IR spectrum, cm^{-1}: 3400 [ν(NH)], 1600 [ν(C=N)], 1560 [δ(NH_2)], 1450 [δ(NH)], 1250 [ν(CN)], doublet 1100–1000 [ν(SiOSi)], 900 [δ(NH_2)]. Found, %: C 31.97; H 5.73; N 24.61; Si 17.46. $C_8H_{20}N_6O_3Si_2$. Calculated, %: C 31.58; H 6.57; N 27.63; Si 18.42.

Determination of the sorption activity of IV toward noble metals. A 50-mg portion of **IV** was stirred with 50 ml of a solution of a metal ion in aqueous HCl (for Au, Pt, Pd) or HNO_3 (for Ag). The acid concentration was varied within 0.5–6.0 M, and the metal ion concentration, within 0.05–0.8 mg ml^{-1}. After the experiment completion, the polymer was filtered off and washed on the filter with distilled water. The wash waters were combined with the filtrate, and the residual metal content in the combined filtrate was determined spectrophotometrically [13, 14]. The optical density of the solutions was measured with a KFK-2 photocolorimeter. The sorption capacity of the polymer was calculated as the maximal metal content in unit weight of the polymer at saturation. The working solutions of noble metals were prepared from chemically pure grade $AgNO_3$, $HAuCl_4 \cdot 4H_2O$, $H_2PtCl_6 \cdot 6H_2O$, and $PdCl_2$.

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