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LETTERS TO THE EDITOR

Aminosilyl Derivatives of Hyperbranched Polyethers and Their Metal Complexes

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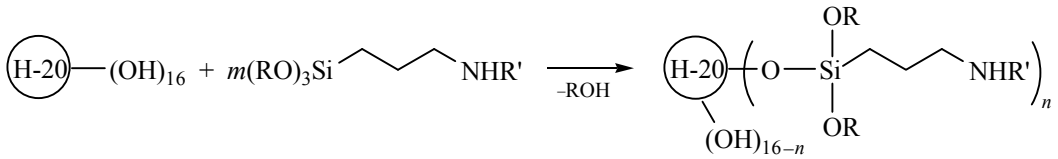
Surface modification of nano-sized hyperbranched polymers with the fragments capable of effective complexation makes it possible to synthesize coordination compounds with practically useful properties. It was demonstrated previously that the modification is possible of non-toxic hyperbranched polyether polyols with acid fragments followed by the synthesis of the appropriate metal complexes possessing biochemical activity [1, 2]. Modification of hyperbranched polyether polyols with aminosilyl groups will provide multifunctional compounds that combine the ability to effective complex formation with the hydrogen bonding with biosubstrates. A similar approach was found very useful in creating next-generation drugs [3] and developing advanced optoelectronic systems [4]. The hyperbranched polyether polyols of the second generation were used by us as precursors of non-toxic, water-soluble polyether polyalkoxysilylamines. Modification of the terminal hydroxy groups of aminosilane was performed as follows:



I, II

I, R = C_2H_5, R' = H, n = 11; **II**, R = CH_3, R' = $CH_2CH_2NH_2$, n = 9.

The content of amino groups in the compounds synthesized was determined by titration [5]. The determination of amine number showed that the functionalization of aminosilane reaches 56–67%. On the basis of polyether polyalkoxysilylamine complex compounds were obtained with Cu(II) soluble in water and DMSO. The electron absorption spectra of compounds $HBP[OH]_5[Si(OEt)_2(CH_2)_3NH_2]_{11}$ (**I**) and $HBP[OH]_7 \cdot [Si(OMe)_2(CH_2)_3NH(CH_2)_2NH_2]_9$ (**II**) have characteristic absorption bands at λ 281 and 270 nm, respectively. Complex compounds $HBP[OH]_5[Si(OEt)_2 \cdot (CH_2)_3NH_2Cu]_n$ (**III**) and $HBP[OH]_7[Si(OMe)_2(CH_2)_3 \cdot NH(CH_2)_2NH_2Cu]_n$ (**IV**) in solution have the absorption bands at λ 788 and 820 nm.

EXPERIMENTAL

Polyether polyalkoxysilylamines **I** and **II** were obtained by the reactions of polyether polyol Boltorn H-20 with 3-aminopropyltriethoxysilane and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane. The reaction was performed in aminosilane excess at a 110–115°C for 5–6 h. The reaction progress was monitored by the amount of the liberated alcohol. The reaction mixture was dissolved in chloroform and precipitated into hexane. The products **I** and **II** are amorphous solids.

Polyether pentahydroxyundeca(3-aminopropyltriethoxysilane) (I). IR spectrum, ν, cm^{-1} (KBr): 3420,

3367 s (N–H, O–H), 2976–2887 s [$\nu_{as,s}(CH_3, CH_2)$], 1738 s (C=O), 1639, 1603 m [δ(N–H)], 1474, 1392 m [$\delta_{as,s}(CH_3)$], 1244 m [δ(Si–CH_2)], 1128 s, 1079 v. s (O–C, Si–O–C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.62 t (SiCH_2CH$_2$, $^3J_{HH}$ 8.4), 1.22 br. m [OC(O)CCH_3, OCH$_2$CH_3], 1.54 two t (SiCH$_2$CH_2CH$_2$, $^3J_{HH}$ 7.3), 2.7 t (CH$_2$CH_2NH$_2$, $^3J_{HH}$ 7.0), 3.18 t (OCH_2CH$_2$O, $^3J_{HH}$ 7.2), 3.7 q (OCH_2CH$_3$, $^3J_{HH}$ 7.2), 3.84 s [C(CH$_2$OC)$_4$]. Found, %: C 48.60; H 8.60; N 4.37; Si 9.23. $C_{157}H_{340}N_{11}O_{58}Si_{11}$. Calculated, %: C 49.04; H 8.63; N 4.19; Si 8.97.

Polyether heptahydroxynona[*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane) (II). IR spectrum, ν, cm^{-1} (KBr): 3433, 3353 s [ν(N–H, O–H)], 2980–2886 s [$\nu_{as,s}(CH_3, CH_2)$], 1731 s (C=O), 1645, 1539 m [δ(N–H)], 1464 m, 1370 w [$\delta_{as,s}(CH_3)$], 1123, 1055 v.s (O–C, Si–O–C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.613 t [SiCH_2CH$_2$, $^3J_{HH}$ 8], 1.12–1.16 m [OC(O)CCH_3], 1.63–1.69 m (SiCH$_2$CH_2CH$_2$), 2.75–2.89 m (NCH_2), 3.3 s (OCH_3), 3.54 t (OCH_2CH$_2$OC, $^3J_{HH}$ 8.6), 3.62 t [COCH$_2$CH_2OC(O), $^3J_{HH}$ 7.7], 3.67 s (CH_2OH), 3.7 s [C(CH$_2$OC)$_4$]. Found, %: C 48.40; H 8.02; N 7.75; Si 7.49. $C_{131}H_{266}N_{18}O_{57}Si_9$. Calculated, %: C 47.80; H 8.44; N 7.74; Si 7.5.

Reaction of polyether polyalkoxysilylamines with copper(II) nitrate. To a solution of 0.5 g of compound **I** or **II** in ethanol–acetone mixture (1:2) was added 1.5 g of copper(II) nitrate hydrate. The reaction mixture was stirred for 7 h at room temperature. The products **III, IV** were washed with acetone and dried in a vacuum.

Compound III. IR spectrum, ν, cm^{-1} (film): 3423, 3250 m (N–H, O–H), 2972–2880 m [$\nu_{as,s}(CH_3, CH_2)$], 1727 m (C=O), 1613, 1513 m [δ(N–H)], 1378 [$\delta_s(CH_3)$], 1128 s, 1045 m (O–C, Si–O–C). Found, %: C 33.98; H 5.97; Cu 14.80; N 6.77; Si 6.51. $C_{135}H_{291}Cu_{11}N_{22}O_{90}Si_{11}$. Calculated, %: C 34.71; H 6.28; Cu 14.97; N 6.60; Si 6.56.

Compound IV. IR spectrum, ν, cm^{-1} (vaseline oil): 3438, 3336 m (N–H, O–H)]; 1725 m (C=O), 1643, 1601 m [δ(N–H)], 1145, 1035 m (O–C, Si–O–C). Found, %: C 31.03; H 6.17; Cu 11.51; N 8.27; Si 4.75. $C_{132}H_{201}Cu_7N_{28}O_{101}$ Si_9. Calculated, %: C 31.30; H 6.80; Cu 11.90; N 7.87; Si 5.26.

The IR spectra were registered on a Bruker Vector 22 Fourier-spectrometer. The ^{1}H NMR spectra were taken on an Avance-600 spectrometer (600 MHz) in $CDCl_3$. the electron absorption spectra were registered on a Lambda 35 spectrophotometer (Perkin Elmer) in the range of 190–900 nm at 25±0.01°C.

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