

Dedicated to the 115th anniversary of B.A. Arbuzov's birth

Synthesis and Complexing Properties of *p*-Toluenesulfonylamido and Phosphorylamido Derivatives of Second-Generation Hyperbranched Polyester

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Abstract—Hyperbranched polyesters containing terminal *p*-toluenesulfonylamido and diethoxyphosphorylamido groups have been synthesized, and their complexes with copper(II) and cobalt(II) ions have been prepared. The thermal stability of the ligands and their metal complexes has been studied by differential scanning calorimetry.

Keywords: hyperbranched polyester, copper complexes, thermal stability

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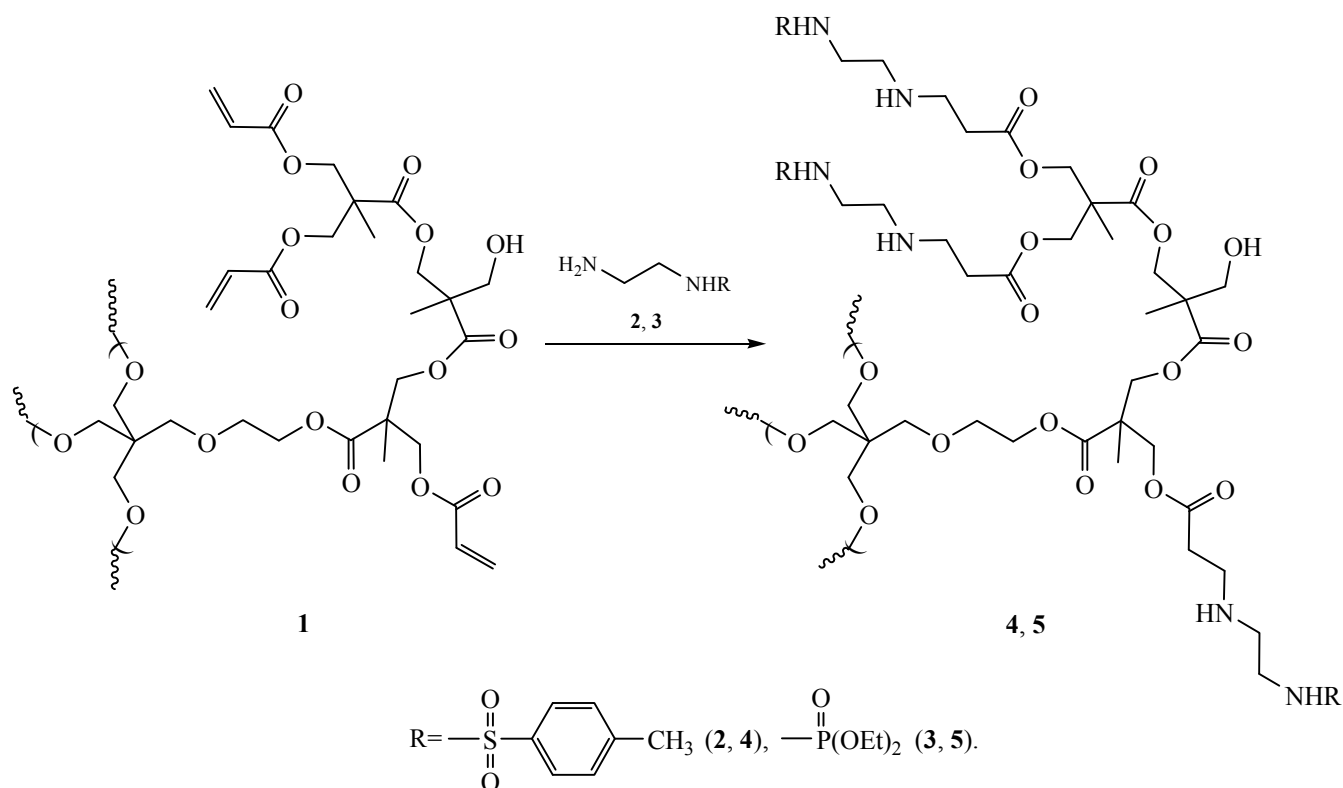
Nontoxic nanosized hyperbranched polyesters possess a broad spectrum of biological properties and are used as drug delivery vehicles and polydentate macro-ligands. Hyperbranched polyesters based on 2,2-bis-(hydroxymethyl)propionic acid and their derivatives have found application in various fields such as modification of polymeric materials (paint-and-lacquer coatings, polymeric nanocomposites), manufacture of electro-optical materials, extraction of metals from aqueous medium, and pharmacology (as nanocontainers) [1–13]. Amino derivatives of hyperbranched polyesters form supramolecular systems with DNA and RNA molecules and exhibit high complexing power toward 3d metal ions [5, 14–17]. Introduction of phosphorus and sulfur atoms into terminal positions of polyesters endows them with thermal stability and enhances their pharmacophoric properties [18–20]. Hyperbranched polyesters with terminal amino, tosylateamido, or phosphorylamido groups have not been reported.

The present study was aimed at synthesizing new hyperbranched polyesters possessing polyfunctional terminal N,P- and N,S-containing groups, determining their structure, and evaluating their complexing ability. A second-generation hyperbranched polyester polyol containing 16 terminal hydroxy groups was selected as

initial structure for functionalization. Its reaction with acryloyl chloride according to the procedure described in [17] gave polyacrylate **1**. The ¹H NMR data showed that the esterification involved 10 most sterically accessible hydroxy groups. Hyperbranched polyesters with terminal *p*-toluenesulfonylamido and diethoxyphosphorylamido groups were synthesized in two steps (Scheme 1). In the first step, 4-toluenesulfonyl chloride and diethyl chlorophosphate were reacted with ethylenediamine to obtain *N*-(2-aminoethyl)-4-methylbenzenesulfonamide (**2**) and diethyl *N*-(2-aminoethyl)-phosphoramidate (**3**), respectively. The second step was nucleophilic addition of **2** or **3** to the terminal C=C bonds of **1**, which afforded target compounds **4** and **5**.

Unlike the initial second-generation hyperbranched polyester polyol [21], the IR spectrum of **4** showed increased intensity of the broadened O–H stretching band in the region 3600–3150 cm⁻¹ due to a contribution of N–H stretching vibrations. The ester carbonyl band of **4** was observed at 1733 cm⁻¹. The IR spectrum of **4** lacked C=C stretching bands (1635, 1618 cm⁻¹) and bands at 1408, 1296 and 983, 808 cm⁻¹ typical of in-plane and out-of-plane bending vibrations of C–H bonds in the =CH₂ group. These findings

Scheme 1.



suggest complete transformation of the C=C bonds of **1** as a result of addition of amine **2**. The sulfonyl group of **4** gave rise to absorption bands at 1325–1290 and 1155 cm^{-1} , and stretching vibration band of the S–N bond was located at 969 cm^{-1} . The ^1H NMR spectrum of **4** contained signals at δ 0.95–1.25 ppm from protons of methyl groups in the polyester skeleton, signals at δ 2.25–2.45 ppm due to CH_3 groups linked to the benzene rings and $\text{CH}_2\text{C}(\text{O})$ groups, and NH proton signals at δ 2.08–2.09 ppm. The OH proton signals were overlapped by signals of methylene protons of the CH_2NHCH_2 and CH_2NHSO_2 fragments in the region δ 2.46–2.97 ppm. There were no signals assignable to terminal $=\text{CH}_2$ groups (δ 5.84–6.22 ppm), which provided further evidence in favor of complete addition to all terminal C=C bonds of polyacrylate **1**.

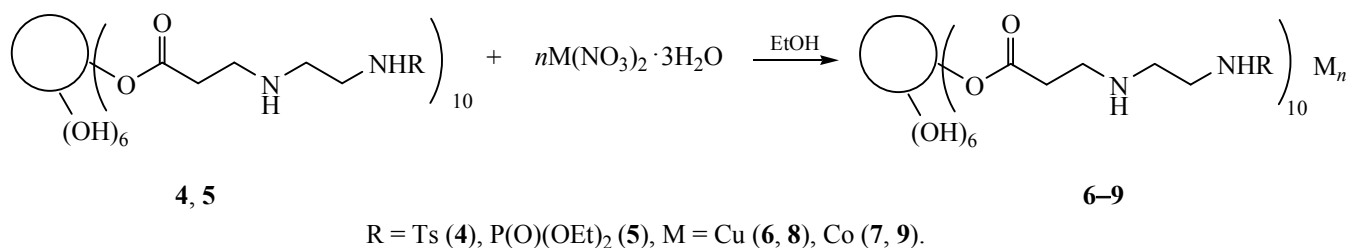
A similar pattern was observed in the IR spectrum of **5**. The band at 3650–3150 cm^{-1} ($\nu\text{O-H}$) was broadened, and its intensity increased, due to superposition of O–H and N–H stretching bands. Neither bands typical of C=C stretching vibrations nor those of in-plane or out-of-plane bending vibrations of $=\text{CH}_2$ groups [22–24] were present, which indicated that diethyl *N*-(2-aminoethyl)phosphorylamide added

to the double bonds of the acrylate fragments of **1**. The band at 1219 cm^{-1} was assigned to stretching vibrations of the P=O groups. In the ^1H NMR spectrum of **5**, protons of the $\text{P}(\text{O})\text{OCH}_2$ and $\text{NHP}(\text{O})$ groups resonated at δ 3.85–3.95 and 4.86–4.89 ppm, respectively, whereas no signals in the region δ 5.84–6.22 ppm were observed.

Hyperbranched polyesters **4** and **5** were brought into reactions with copper(II) and cobalt(II) salts. As a result, complexes **6–9** were obtained (Scheme 2). The IR spectra of complexes **6** and **7** showed increased intensity of the SO_2 stretching band at 1325–1305 cm^{-1} and reduced intensity of the ester carbonyl band at 1734 cm^{-1} in comparison to the spectrum of ligand **4**. Analysis of the IR data led us to presume participation of oxygen atoms of the terminal sulfonamido groups of **4** in the complexation with Cu(II) and Co(II).

In the IR spectra of **8** and **9**, the P=O and C–O–P stretching bands shifted toward lower frequencies by 15 and 5 cm^{-1} , respectively, relative to the positions of the corresponding bands in the spectrum of free ligand **5**; simultaneously, the intensity of the ester carbonyl band decreased. These findings indicated that oxygen atoms of the terminal phosphorylamino fragments of **5** were involved in the complexation.

Scheme 2.



In order to confirm the structure of **4** and **5** and elucidate the role of terminal sulfonamido and phosphorylamino fragments in hyperbranched polyesters, we have synthesized the corresponding dendrons based on ethyl 2,2-bis(hydroxymethyl)propanoate (Scheme 3). Amino and carboxy derivatives of methyl 2,2-bis(hydroxymethyl)propanoate were synthesized by us previously [22] as models of terminal functional fragments of hyperbranched polyester poly(3-diethylaminopropionates) and polyester polycarboxylic acids, and their spectral characteristics were analyzed.

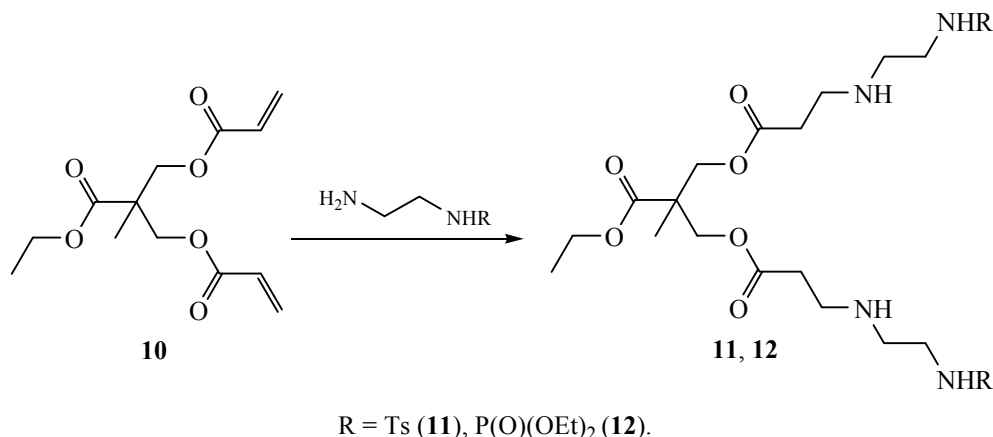
Tosylateamido derivative **11** was synthesized by addition of *N*-(2-aminoethyl)-*p*-toluenesulfonylamide to bis-acrylate **10** (Scheme 3). Phosphorylamino analog **12** was obtained in a similar way. The structure of **11** and **12** was confirmed by IR and NMR spectra. The reactions of dendrons **11** and **12** with copper(II) and cobalt(II) salts afforded complexes **13-16**. According to the IR data, these complexes, like **6-9**, are formed via coordination through the oxygen atoms of the sulfonyl and phosphoryl groups.

The thermal stability of hyperbranched macro-ligands **4** and **5**, 2,2-bis(hydroxymethyl)propanoic acid derivatives **11** and **12**, and their copper(II) and cobalt(II)

complexes **6-9** and **13-16** was estimated by differential scanning calorimetry (Table 1). The DSC curves of both ligands **4** and **5** and metal complexes **6-9** displayed strong exothermic peaks due to thermal decomposition, presumably, via elimination of the terminal *p*-toluenesulfonylamido and diethoxyphosphorylamido groups. It should be noted that complexes **6-9** decompose at lower temperatures than the corresponding ligands **4** and **5**. The difference in the decomposition temperatures of ligands **4** and **5** and complexes **6-9** is related to coordination of the metal ions to oxygen atoms of the terminal fragments, which favors elimination of the latter. This conclusion is supported by comparison of the thermal stabilities of compounds **11** and **12** and their complexes **13-16**. Here, the ligands are also more thermally stable than their metal complexes.

In summary, we have synthesized new second-generation hyperbranched polyesters containing *p*-toluenesulfonylamido and diethoxyphosphorylamido groups in the terminal positions with a degree of functionalization of 62.5% (according to the ¹H NMR data). New polynuclear metal-polymer complexes with copper(II) and cobalt(II) ions have been obtained on the basis of

Scheme 3.



these modified polyesters. According to the differential scanning calorimetry data, the new hyperbranched polyesters are stable up to 220°C, whereas their copper(II) and cobalt(II) complexes decompose at lower temperatures. Polyfunctional *p*-toluenesulfonylamido and diethoxyphosphorylamido derivatives of ethyl 2,2-bis(hydroxymethyl)propanoate have been synthesized for the first time, and their Cu(II) and Co(II) complexes have been prepared. Comparison of the IR spectra and DSC data for the macroligands and their low-molecular-weight analogs with the corresponding data for their complexes suggests participation of the terminal *p*-toluenesulfonylamido and diethoxyphosphorylamido groups in the coordination with Cu(II) and Co(II) ions.

EXPERIMENTAL

The initial second-generation polyester polyol based on ethoxylated pentaerythritol (core) and 2,2-bis(hydroxymethyl)propionic acid (monomer) was commercial product (Sigma-Aldrich; 16 terminal OH groups, *M* 1749, hydroxyl value 480–520); commercially available 2,2-bis(hydroxymethyl)propionic acid, acryloyl chloride (97%), 4-toluenesulfonyl chloride (99%), diethyl chlorophosphate (95%, Acros), ethylenediamine (99%), triethylamine (99%, Fisher Scientific), MgSO₄, NaHCO₃, Cu(NO₃)₂·3H₂O, and Co(NO₃)₂·6H₂O (analytical grade) were used. Organic solvents (acetone, methylene chloride, chloroform, petroleum ether, toluene, ethanol) were preliminarily dried and purified according to standard procedures.

The IR spectra were recorded in the range 4000–600 cm⁻¹ on an InfracLYuM FT-08 spectrometer with Fourier transform equipped with an Almaz KRS-5 ATR accessory. The ¹H NMR spectra were recorded from solutions in DMSO-*d*₆ on a Bruker Avance 400 spectrometer (400 MHz). The thermal stability of the synthesized compounds was studied by differential scanning calorimetry using a DSC Q200 V24.9 Build 121 instrument.

***N*-(2-Aminoethyl)-4-methylbenzenesulfonamide (2).** A solution of 15.00 g (78.74 mmol) of 4-toluenesulfonyl chloride in 45 mL of chloroform was added dropwise with stirring at 18°C under dry nitrogen to a solution of 23.62 g (393.70 mmol) of ethylenediamine. The mixture was stirred for 2 h, washed with distilled water to remove ethylenediamine hydrochloride and excess ethylenediamine, dried over MgSO₄, filtered, and evaporated under reduced pressure. Yield 75.2%,

Thermal stability of hyperbranched polyesters, derivatives of 2,2-bis(hydroxymethyl)propanoic acid, and their copper(II) and cobalt(II) complexes

Comp. no.	Decomposition temperature, °C	Comp. no.	Decomposition temperature, °C
4	>250	5	220
6	206	8	179
7	234	9	–
11	>250	12	245
13	195	15	179
14	220	16	200

white powder. IR spectrum, ν , cm⁻¹: 3363 (N–H, amine), 3288 (N–H, amide), 3049 (C–H_{arom}), 2975–2885 (CH₃, CH₂); 1596, 1492, 1440 (C=C_{arom}); 1458–1439, 1404–1364 [δ (CH₃), δ (CH₂)]; 1315–1288, 1146 (SO₂); 1186, 1044, 1018 [δ (C–H_{arom})], 1062 (C–N, amine), 922 (S–N), 814 [δ (C–H_{arom})]. ¹H NMR spectrum, δ , ppm: 2.37 m (3H, CH₃), 2.49–2.53 m (2H, CH₂NH₂), 2.69–2.72 m (2H, SO₂NHCH₂), 3.72 m (3H, NH₂, SO₂NH), 7.36–7.40 m (2H, C₆H₄), 7.61–7.69 m (2H, C₆H₄).

Diethyl *N*-(2-aminoethyl)phosphorylamide (3) was synthesized in a similar way from 3.48 g (57.97 mmol) of ethylenediamine and 2.00 g (11.59 mmol) of diethyl chlorophosphate. Yield 86.8%. IR spectrum, ν , cm⁻¹: 3398–3114 (N–H), 2980–2870 (CH₃, CH₂), 1603 [δ (N–H), amine]; 1482–1443, 1392–1368 [δ (CH₃), δ (CH₂)], 1222 (P=O); 1164, 1021 (C–O–P), 1051 (C–N, amine). ¹H NMR spectrum, δ , ppm: 1.18–1.21 m (6H, CH₃), 2.55–2.58 m (2H, CH₂NH₂), 2.67–2.77 m [4H, NH₂, P(O)NHCH₂], 3.84–3.92 m (4H, OCH₂), 4.93 m [1H, P(O)NH]. ³¹P NMR spectrum: δ_P 9.69 ppm.

Hyperbranched polyesters 4 and 5 (general procedure). A solution of 8.73 mmol of compound 2 or 3 in 15 mL of acetone was added with stirring at 18°C under dry nitrogen to a solution of 0.873 mmol of hyperbranched polyester polyacrylate 1 [17] in 10 mL of acetone. The mixture was stirred for 48 h at 18°C and for 24 h at 40°C, and the solvent was removed under reduced pressure.

Compound 4. Yield 75.2%, dark brown resin decomposing above 250°C. IR spectrum, ν , cm⁻¹: 3600–3150 (O–H, N–H), 3043 (C–H_{arom}), 2963–2868 (CH₃, CH₂), 1733 (C=O); 1598, 1495, 1440 (C=C_{arom}); 1458–1439, 1398–1364 [δ (CH₃), δ (CH₂)]; 1325–1290, 1155

(SO₂); 1220, 1122 [O–C(O)]; 1182, 1044, 1018 [δ (C–H_{arom})], 1091 [CH₂–O, δ (O–H)], 969 (S–N), 815 [δ (C–H_{arom})]. ¹H NMR spectrum, δ , ppm: 0.95–1.25 m [36H, OC(O)CCH₃], 2.08–2.09 m (10H, CH₂NHCH₂), 2.25–2.44 m [50H, C₆H₄CH₃, C(O)CH₂], 2.46–2.97 m (66H, OH, CH₂NHCH₂, CH₂NHSO₂), 3.22–3.67 m (29H, CH₂OH, OCH₂), 3.84–4.36 m [45H, CH₂OC(O)], 7.36–7.41 m (20H, C₆H₄), 7.60–7.69 (20H, C₆H₄). Found, %: C 49.53; H 12.32; N 5.89; S 6.77. C₁₉₅H₂₈₈N₂₀O₇₅S₁₀. Calculated, %: C 49.62; H 12.21; N 5.94; S 6.79.

Compound 5. Yield 77.9%, dark brown resin, decomposition point 220°C. IR spectrum, ν , cm⁻¹: 3650–3150 (O–H, N–H), 2981–2877 (CH₃, CH₂), 1735 (C=O); 1481–1440, 1393–1365 [δ (CH₃), δ (CH₂)], 1219 (P=O); 1165, 1122 (C–O), 1051 (C–N, amine), 1025 [C–O, δ (OH)]. ¹H NMR spectrum, δ , ppm: 1.13–1.33 m [96H, OC(O)CCH₃, CH₂CH₃], 1.84 m (10H, CH₂NHCH₂), 2.34–2.94 m [87H, OH, CH₂NHCH₂, CH₂NHP(O), C(O)CH₂], 3.36–3.64 m (29H, CH₂OH, CH₂OCH₂), 3.85–3.95 m [40H, P(O)OCH₂], 3.98–4.34 m [45H, CH₂OC(O)], 4.86–4.89 m [10H, NHP(O)]. ³¹P NMR spectrum: δ_P 9.69 ppm. Found, %: C 43.42; H 13.88; N 6.14; P 6.80. C₁₆₅H₃₁₈N₂₀O₈₅P₁₀. Calculated, %: C 43.36; H 13.93; N 6.13; P 6.79.

Complexes 6–9 (general procedure). A solution of 0.16 g (0.645 mmol) of Cu(NO₃)₂·3H₂O or Co(NO₃)₂·6H₂O in 2 mL of ethanol was added with stirring at ~18°C under dry nitrogen to a solution of 0.129 mmol of compound 4 or 5 in 3 mL of chloroform. The mixture was kept for 24 h at 18°C and for 8 h at 45°C, the solvent was removed under reduced pressure, and the product was isolated by precipitation with petroleum ether and dried under reduced pressure (1 mm, 50°C) for 19 h.

Complex 6. Yield 43.8%, dark green powder, decomposition point 206°C. IR spectrum, ν , cm⁻¹: 3624–3132 (O–H, N–H), 3062 (CH_{arom}), 2973–2878 (CH₃, CH₂), 1734 (C=O); 1598, 1495 (C=C_{arom}), 1458–1380 [δ (CH₃), δ (CH₂), NO₃]; 1325–1306, 1155 (SO₂), 1217 (C–O); 1185, 1045, 1018 [δ (CH_{arom})], 1089 [O–C, δ (OH)], 997 (S–N), 815 [δ (CH_{arom})].

Complex 7. Yield 60.3%, dark brown resin, decomposition point 234°C. IR spectrum, ν , cm⁻¹: 3600–3131 (O–H, N–H), 3063 (CH_{arom}), 2975–2870 (CH₃, CH₂), 1732 (C=O); 1598, 1496 (C=C_{arom}), 1463–1379 [δ (CH₃), δ (CH₂), NO₃]; 1325–1305, 1155 (SO₂), 1215 (C–O); 1186, 1041, 1019 [δ (CH_{arom})], 1091 [O–C, δ (OH)], 966 (S–N), 815 [δ (CH_{arom})].

Complex 8. Yield 77.9%, dark brown powder, decomposition point 179°C. IR spectrum, ν , cm⁻¹: 3659–3134 (O–H, N–H), 2987–2872 (CH₃, CH₂), 1732 (C=O), 1471–1369 [δ (CH₃), δ (CH₂), NO₃], 1207 (P=O); 1164, 1124, 1101 (C–O), 1019 (C–O–P, δ (OH)).

Complex 9. Yield 57.5%, black–purple resin. IR spectrum, ν , cm⁻¹: 3650–3150 (O–H, N–H), 2988–2870 (CH₃, CH₂), 1734 (C=O), 1477–1370 [δ (CH₃), δ (CH₂), NO₃], 1204 (P=O); 1165, 1120, 1110 (C–O), 1019 (C–O–P, δ (OH)).

2-(Ethoxycarbonyl)-2-methylpropane-1,3-diyl diacrylate (10). A solution of 9.60 g (106.11 mmol) of acryloyl chloride in 50 mL of chloroform was added with stirring to a solution of 5.73 g (35.40 mmol) of ethyl 2,2-bis(hydroxymethyl)propionic acid [25] and 11.54 g (106.11 mmol) of triethylamine in 30 mL of chloroform on cooling to 0°C. The mixture was stirred for 16 h at 25°C under dry nitrogen and washed with 2 M aqueous HCl, 5% aqueous NaHCO₃, and distilled water. The organic phase was dried over MgSO₄ and evaporated under reduced pressure, and the residue was kept for 12 h at 30°C in a vacuum drying box. Yield 87.4%, light yellow resin. IR spectrum, ν , cm⁻¹: 3084 (=CH), 2982–2876 (CH₃, CH₂), 1725 (C=O); 1635, 1618 (C=C); 1470–1448, 1400–1367 [δ (CH₃), δ (CH₂)]; 1407, 1296 [δ (=CH)]; 1259, 1172, 1137 (C–O); 1058, 1016 (CH₂–O); 983, 807 [δ (=CH)]. ¹H NMR spectrum, δ , ppm: 1.54–1.58 m (3H, CH₃CH₂), 1.64 s (3H, CCH₃), 4.49–4.55 m (2H, CH₃CH₂O), 4.69 s [4H, CCH₂OC(O)], 6.37–6.40 m (2H, CH=CH₂), 6.54–6.60 m (2H, CH=CH₂), 6.72–6.76 m (2H, CH=CH₂).

Compounds 11 and 12 (general procedure). Compound 10, 1.2 g (4.44 mmol), was dissolved in 5 mL of acetone, and a solution of 9.33 mmol of compound 2 or 3 in 10 mL of acetone was added with stirring at 18°C under dry nitrogen. The mixture was kept for 24 h at 40°C, and the solvent was removed under reduced pressure.

Compound 11. Yield 88.9%, light yellow resin decomposing above 250°C. IR spectrum, ν , cm⁻¹: 3395–3201 (N–H), 3064 (C–H_{arom}), 2988–2834 (CH₃, CH₂), 1732 (C=O); 1598, 1495, 1440 (C=C_{arom}); 1455–1430, 1398–1364 [δ (CH₃), δ (CH₂)]; 1325–1290, 1155 (SO₂), 1219 (C–O); 1182, 1046, 1019 [δ (C–H_{arom})], 1091 (CH₂–O), 951 (S–N), 815 [δ (C–H_{arom})]. ¹H NMR spectrum, δ , ppm: 1.12–1.22 m [6H, CH₃CH₂O, CCH₃], 2.07–2.08 m (2H, CH₂NHCH₂), 2.29–2.37 m [10H, C₆H₄CH₃, CH₂C(O)], 2.47–2.91 m (12H, CH₂NHCH₂, CH₂NHSO₂), 4.01–4.21 m [6H; CH₂OC(O)], 7.35–

7.42 m (4H, H_{arom}), 7.59–7.69 m (4H, H_{arom}). Found, %: C 49.97; H 12.41; N 7.55; S 8.54. C₃₁H₄₆N₂O₁₀S₂. Calculated, %: C 50.01; H 12.37; N 7.53; S 8.59.

Compound 12. Yield 86.1%, light brown resin, decomposition point 245°C. IR spectrum, ν , cm⁻¹: 3450–3123 (N–H), 2983–2826 (CH₃, CH₂), 1732 (C=O); 1460–1444, 1393–1366 [δ (CH₃), δ (CH₂)], 1234 (P=O); 1203, 1168, 1138, 1122 (C–O), 1051 (C–N, amine), 1024 (C–O–P, δ OH). ¹H NMR spectrum, δ , ppm: 1.13–1.22 m (18H, CH₃CH₂O, CCH₃), 2.04–2.11 m (2H, CH₂NHCH₂), 2.31–2.83 m [16H, CH₂NHCH₂, CH₂NHP(O), CH₂C(O)], 3.85–3.92 m [8H, P(O)OCH₂], 4.03–4.21 m [6H, CH₂OC(O)], 4.84–4.87 m [2H, NHP(O)]. ³¹P NMR spectrum: δ_p 9.69 ppm. Found, %: C 42.07; H 14.53; N 7.83; P 8.71. C₁₆₅H₃₁₈N₂₀O₈₅P₁₀. Calculated, %: C 42.02; H 14.57; N 7.84; P 8.68.

Complexes 13–16 (general procedure). A solution of 0.18 g (0.731 mmol) of Cu(NO₃)₂·3H₂O or Co(NO₃)₂·6H₂O in 2 mL of ethanol was added to a solution of 0.731 mmol of compound **11** or **12** in 3 mL of chloroform. The mixture was stirred for 24 h at 18°C, heated to 45°C, and stirred for 8 h at that temperature. The product was isolated by precipitation with petroleum ether and dried under reduced pressure (1 mm, 50°C) for 19 h.

Complex 13. Yield 88.4%, light brown powder, decomposition point 195°C. IR spectrum, ν , cm⁻¹: 3662–3129 (O–H, N–H), 3064 (C–H_{arom}), 2980–2828 (CH₃, CH₂), 1730 (C=O); 1598, 1498 (C=C_{arom}), 1452–1359 [δ (CH₃), δ (CH₂), NO₃]; 1319–1304, 1155 (SO₂), 1253 (C–O); 1184, 1044, 1018 [δ (C–H_{arom})], 1091 [CH₂–O, δ (O–H)], 941 (S–N), 814 [δ (C–H_{arom})].

Complex 14. Yield 70.6%, dark brown resin, decomposition point 220°C. IR spectrum, ν , cm⁻¹: 3651–3121 (O–H, N–H), 3067 (C–H_{arom}), 2978–2878 (CH₃, CH₂), 1727 (C=O); 1596, 1498 (C=C_{arom}), 1455–1375 [δ (CH₃), δ (CH₂), NO₃]; 1321–1303, 1155 (SO₂), 1255 [O–C(O)]; 1185, 1044, 1019 [δ (C–H_{arom})], 1091 [CH₂–O, δ (OH)], 947 (S–N), 815 [δ (C–H_{arom})].

Complex 15. Yield 73.2%, dark green resin, decomposition point 179°C. IR spectrum, ν , cm⁻¹: 3629–3124 (O–H, N–H), 2982–2872 (CH₃, CH₂), 1733 (C=O), 1474–1369 [δ (CH₃), δ (CH₂), NO₃], 1194 (P=O); 1137, 1018 [C–O, δ (OH)].

Complex 16. Yield 78.7%, dark purple resin, decomposition point 200°C. IR spectrum, ν , cm⁻¹: 3634–3129 (O–H, N–H), 2983–2873 (CH₃, CH₂), 1731

(C=O), 1478–1371 [δ (CH₃), δ (CH₂), NO₃], 1198 (P=O); 1167, 1135, 1018 [C–O, δ (O–H)].

CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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