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Synthesis of the Europium Organic Phosphate and Phosphoramide Complexes

A. V. Zdravkov[a], E. L. Aleksandrova[b], V. A. Aseev[c], and N. N. Khimich[a]

[a] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, nab. Makarova 2, St. Petersburg, 199034 Russia*
e-mail: Khimich@isc.nw.ru

[b] *Ioffe Physico-Technical Institute, Russian Academy of Sciences, St. Petersburg, Russia*

[c] *St. Petersburg State University of Information Technologies, Mechanics, and Optics, St. Petersburg, Russia*

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Abstract—Organic phosphates and phosphoramidates containing alkoxysilyl group were synthesized and used to obtain the corresponding europium complexes. The latter are shown to be applicable for the formation of organic–inorganic hybrids with the components connected with each other through a chemical bond.

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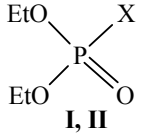
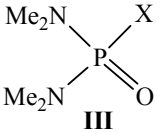
Compounds of rare earth elements are widely used in analytical chemistry, electroplating, photooptics and optoelectronics. A wide range of radiation (200 nm to 5 μm) generated at the interaction of the lanthanide derivatives with light makes them indispensable as a non-linear optical-fiber material to create the laser media [1]. For practical use of the rare earth element derivatives in optics they commonly are included into the chemically and thermally stable and optically transparent coatings and materials. One of the most convenient methods for the synthesis of such matrices is the sol–gel process [2, 3] leading to the formation of silicon oxide matrix, in particular, by the hydrolytic polycondensation of tetraalkoxysilanes [4]. A major shortcoming of the structures obtained by this route is a significant content of hydroxy groups and water molecules, which leads to a strong quenching of the photoluminescence of rare-earth derivatives [5]. Therefore, the introduction of lanthanides in a SiO_2 matrix as the solutions of their salts requires a high temperature processing with the use of special dehydrating agents, e.g., Freons [6]. The easiest way to avoid these labor-intensive operations is to protect the rare earth elements from the photoluminescence quenching by hydroxyl through their complexation with various organic ligands.

Unfortunately, the use for this purpose of usual chelating agents such as 1,3-dicarbonyl compounds is problematic because the necessary stability have only the complexes with strong polar ligands containing aromatic and trifluoromethyl structural fragments simultaneously [7]. However, it is very difficult to obtain such compounds containing, in addition, alkoxysilyl substituents necessary for uniform distribution of the rare earth element in the silica matrix through the formation of an organic–inorganic hybrid whose components are chemically linked. The problem consists in the fact that for the purification of these complexes the common method of column chromatography cannot be used due to the hydrolytic instability of the alkoxysilyl groups. Therefore we turned to well-known tris-trialkylphosphate complexes of rare earth elements and their phosphoric triamide analogs widely used for the separation of these elements by solvent extraction at different pH values [8, 9]. The main task was the synthesis of such complexes containing trialkoxysilyl groups. Their formation was studied by the example of europium compounds.

To obtain the desired complexes **IV–VI** we synthesized the phosphate and phosphoramidate ligands **I–III.**



I, II

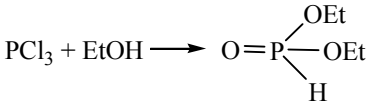


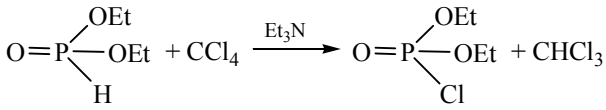
III

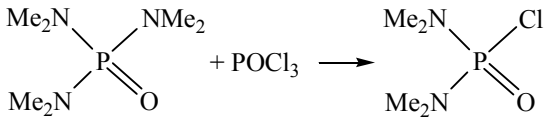
X = $OCH_2CH(CH_2Cl)O(CH_2)_3Si(OEt)_3$ (**I**),
$N(Allyl)(CH_2)_3Si(OEt)_3$ (**II, III**).

In the literature a synthesis was described of an analog of the compound **II** containing hydrogen atom at the phosphoric amide nitrogen atom instead of the allyl group [10]. However, to our knowledge these compounds are unstable and easily decompose in the course of treatment, as evidence the NMR spectra of the distilled product.

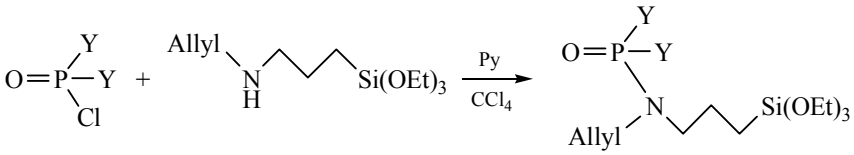
As starting compounds for the synthesis of phosphate ligands $POCl_3$, sodium ethoxide, PCl_3, ethanol, CCl_4, and hexamethylphosphoric triamide [11] were used.

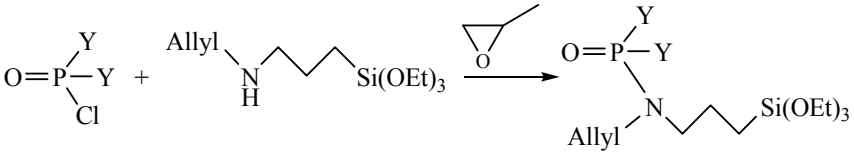






The chlorphosphate formed reacted with allylaminopropyltrietoxysilane and either propylene oxide or pyridine to absorb the liberated hydrogen chloride:

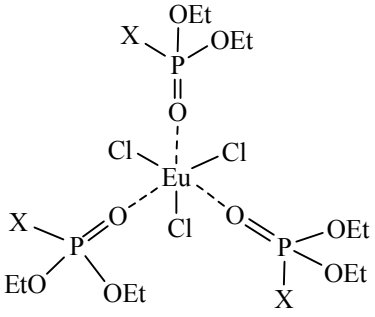




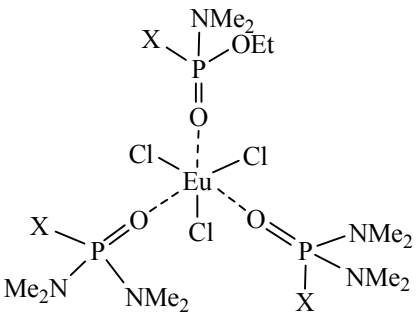
Y = OEt, NMe_2.

Based on these ligands europium complexes with tris(dialkylphosphate) and tris(tetraalkyldiamidophosphate) were synthesized.

Synthesis of the complexes was carried out by mixing solutions of a corresponding phosphate or phosphoramide ligand with the rare earth element



IV, V



VI

X = $OCH_2CH(CH_2Cl)O(CH_2)_3Si(OEt)_3$ (**IV**), $N(Allyl)(CH_2)_3Si(OEt)_3$ (**V, VI**).

chloride in acetonitrile, followed by evaporation of the solvent (by analogy with [12, 13]).

Thus, synthesis methods were developed, and a number of organic phosphates and phosphoramidates effective for the complex formation with the rare earth elements and containing trialkoxysilyl groups in their compositions were obtained. On the basis of these compounds tris-phosphate and tris(amidophosphate) europium complexes were prepared containing triethoxysilyl groups necessary for the formation of organic–inorganic hybrids.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DXP-300 and a Bruker Avance-400 instruments with the operating frequencies of 300 or 400 MHz (^{1}H) and 75 or 100 MHz (^{13}C) respectively, internal reference TMS. The absorption spectra were recorded on an SF-56 spectrophotometer, IR spectra on an SF-2101 Fourier spectrometer. The mass spectra were obtained on an MX-5303 instrument with an electrospray ionization source. Elemental analysis was performed on a Hewlett Packard 185B CHN analyzer. In the synthesis were used HMPA, phosphorus trichloride, phosphorus oxychloride, trietoxysilylpropylamine, and glycidoxypropylethoxysilane from Aldrich. Allyl[(3-(triethoxysilyl)propyl]amine was synthesized by boiling a mixture of allylamine and (3-chloropropyl)triethoxysilane for 4 h. Bis(dimethylamino)chlorophosphate was synthesized by the method described in [11].

Diethyl 2-[3-(triethoxysilyl)propoxy]-3-chloropropyl phosphate (I). To a solution of 8.5 g glycidoxypropylethoxysilane in 30 ml of carbon tetrachloride was added 5.6 g of diethylchlorphosphate and 0.5 g of titanium tetrachloride as a catalyst. The reaction was carried out at room temperature. After 7 days the solvent was distilled off in a water-jet pump vacuum, the residue was distilled in a vacuum. Yield 4 g (30%), bp 130°C (0.05 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.60 m (2H, CH_2Si), 1.19 t (9H, SiOCH2CH_3, J = 6.8 Hz), 1.23 t.d (6H, $POCH_2CH_3$, J_1 = 7.2 Hz, J_2 = 2.8 Hz), 1.65 m (2H, OCH_2·$C\underline{H}_2CH_2Si$), 3.43 m (2H, $OC\underline{H}_2CH_2CH_2Si$), 3.63 m (4H, $OC\underline{H}_2CH(CH_2Cl)O$), 3.86 q (6H, $SiOC\underline{H}_2CH_3$, J = 7.0 Hz), 4.11 m (4H, $POC\underline{H}_2CH_3$, J = 7.2 Hz), 4.6 m (1H, $OCH_2C\underline{H}(CH_2Cl)O$). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 6.37 s (CH_2Si), 16.02 d (J_{CP} = 6.6 Hz, $POCH_2\underline{C}H_3$), 18.22 s ($SiOCH_2\underline{C}H_3$), 22.87 s ($OCH_2\underline{C}H_2CH_2Si$), 43.84 d ($J_{CP}$ = 4.6 Hz, $P\underline{C}H_2CH_3$), 58.3 s ($SiO\underline{C}H_2CH_3$), 64.03 t (J_{CP} = 4.6 Hz, $POCH_2CH(\underline{C}H_2Cl)O$), 69.45 d ($J_{CP}$ = 4.4 Hz, $POCH_2$·$\underline{C}H(CH_2Cl)O$), 73.78 s ($O\underline{C}H_2CH_2CH_2Si$), 75.70 d ($J_{CP}$ = 5.3 Hz, $PO\underline{C}H_2CH(CH_2Cl)O$). IR spectrum (KBr), ν, cm^{-1}: 2976 m (ν_{CH}), 2923 m (ν_{CH}), 1447 w, 1260 m (ν_{POC}), 1163 s, 1106 s (ν_{COC}), 1077 s (ν_{SiOC}), 1041s (ν_{POC}), 801 w. The mass spectrum (electrospray ionization): 452.01 ($[M + H]^+$). Found, %: C 43.02; H 8.55. $C_{16}H_{36}ClO_8PSi$. Calculated, %: C 42.61; H 8.05.

Phosphoramidates II and III. Under ice-cooling, to a solution of 8.9 g of (allylaminopropyl)triethoxysilane and 2.7 g of pyridine in 30 ml of hexane was added 5.9 g of diethylchlorphosphate [or bis(dimethylaminophosphate)]. The reaction mixture was stirred with a magnetic stirrer at room temperature. After 6–8 days the solvent was distilled off in a water-jet pump vacuum, the residue was distilled in a vacuum.

Diethyl *N*-allyl-*N*-[3-(triethoxysilyl)propyl phosphoramidate (II). Yield 5 g (40%), bp 125°C (0.05 mm Hg). IR spectrum (KBr), ν, cm^{-1}: 2976 s (ν_{SH}), 2932 s (ν_{SH}), 1639 m [ν(CH=CH_2)], 1447 m, 1387 m, 1257 s, 1165 s, 1106 s (ν_{COC}), 1082 s (ν_{SiOC}), 1032 s (ν_{POC}) 958 s, 793 w. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.45 m (2H, CH_2Si), 1.13 t (9H, $SiOCH_2C\underline{H}_3$, J = 7.2 Hz), 1.19 t (6H, $POCH_2C\underline{H}_3$, J_1 = 7.6 Hz, J_2 = 1.4 Hz), 1.51 m (2H, $NCH_2C\underline{H}_2CH_2Si$), 2.88 m (2H, $NC\underline{H}_2CH_2CH_2Si$), 3.54 m (2H, $NC\underline{H}_2$·CH=CH_2), 3.71 q (6H, $SiOC\underline{H}_2CH_3$, J = 7.2 Hz), 4.19 m (4H, $POC\underline{H}_2CH_3$, J_1 = 7.2 Hz, J_2 = 2.8 Hz), 5.06 m (2H, CH=$C\underline{H}_2$), 5.66 m (1H, CH=CH_2). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm: 7.69 s (CH_2Si), 16.39 d (J_{CP} = 7.2 Hz, $POCH_2\underline{C}H_3$), 18.56 s (SiO·$CH_2\underline{C}H_3$), 21.81 s ($NCH_2\underline{C}H_2CH_2Si$), 48.35 d ($J_{CP}$ = 3.7 Hz, $PO\underline{C}H_2CH_3$), 48.77 d (J_{CP} = 3.6 Hz, $N\underline{C}H_2$·CH_2CH_2Si), 58.62 s ($SiOCH_2CH_3$), 62.22 d (J_{CP} = 5.4 Hz, $PN\underline{C}H_2CH=CH_2$), 117.53 s ($PNCH_2CH=CH_2$), 135.50 s ($PNCH_2CH=\underline{C}H_2$). The mass spectrum (electrospray ionization): 398.21 ($[M + H]^+$). Found, %: C 47.82, H 9.79; N 3.22. $C_{16}H_{36}NO_6PSi$. Calculated, %: C 48.34; H 9.13; N 3.52.

***N*-Allyl-*N*-[3-(triethoxysilyl)propyl]-*N'*,*N'*,*N''*,*N''*-tetramethylphosphoric triamide (III)**. Yield 3.5 g (25%), bp 110–115°C (0.05 mm Hg). IR spectrum (KBr), ν, cm^{-1}: 2929 s (ν_{SH}), 2852 s (ν_{SH}), 2807 m (ν_{SH}), 1641 m [ν(CH=CH_2)], 1434 m, 1304 m, 1192 s, 1100 (ν_{SiOC}), 988 s (ν_{POC}), 929 s, 751 w. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.48 m (2H, CH_2Si), 1.84 t (9H, $SiOCH_2C\underline{H}_3$, J = 7.2 Hz), 1.57 m (2H, $NCH_2C\underline{H}_2CH_2Si$), 2.59 s (6H, $PN(CH_3)_2$), 2.62 s

(6H, $PN(CH_3)_2$), 2.86 m (2H, $NC\underline{H}_2CH_2CH_2Si$), 3.56 m (2H, $NC\underline{H}_2CH{=}CH_2$), 3.78 q (6H, $SiOC\underline{H}_2CH_3$, J = 7.2 Hz), 5.11 m (2H, $CH{=}C\underline{H}_2$), 5.76 m (1H, $C\underline{H}{=}CH_2$). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm: 8.17 s (CH_2Si), 18.85 s ($SiOC\underline{H}_2CH_3$), 22.17 s ($NCH_2\underline{C}H_2CH_2Si$), 37.33 d ($J_{CP}$ = 3.5 Hz, $PN(CH_3)_2$), 48.85 d (J_{CP} = 3.2 Hz, $N\underline{C}H_2CH_2CH_2Si$), 49.34 d ($J_{CP}$ = 3.8 Hz, $N\underline{C}H_2CH{=}CH_2$), 58.4 s ($SiO\underline{C}H_2CH_3$) 117.01 s ($PNCH_2CH{=}\underline{C}H_2$), 136.95 s ($PNCH_2\cdot\underline{C}H{=}CH_2$). The mass spectrum (electrospray ionization): 396.45 ($[M + H]^+$). Found, %: C 48.02; H 10.12; N 10.33. $C_{16}H_{38}N_3O_4PSi$. Calculated, %: C 48.58; H 9.68; N 10.62.

Europium complexes IV–VI. To a solution of anhydrous europium chloride in acetonitrile was added 3 equivalents of compound **I**, or **II**, or **III**. The reaction mixture was stirred for 1 h at room temperature, the solvent was distilled off in a water-jet pump vacuum and dried in a desiccator under argon. Compounds **IV–VI** were isolated quantitatively.

Europium tris{diethyl 2-[3-(triethoxysilyl)propoxy]-3-chloropropyl phosphate} trichloride (IV). IR spectrum (KBr), ν, cm^{-1}: 2974 m (ν_{CH}), 2922 m (ν_{CH}), 1412 m, 1162 s, 1159 s, 1102 s (ν_{COC}), 1076 s (ν_{SiOC}), 1034 s (ν_{POC}), 796 w, 539 w (ν_{EuO}). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 0.66 m (6H, CH_2Si), 1.24–1.29 m (45H, $SiOCH_2C\underline{H}_3$+$POCH_2C\underline{H}_3$), 1.75 m (6H, $OCH_2C\underline{H}_2CH_2Si$), 3.47 m (6H, $OC\underline{H}_2CH_2CH_2Si$), 3.6–3.89 m (12H, $OCH(C\underline{H}_2Cl)C\underline{H}_2O$), 3.96 m (18H, $SiOC\underline{H}_2CH_3$), 4.15 m (12H, $POC\underline{H}_2CH_3$), 4.66 m (3H, $OC\underline{H}(CH_2Cl)CH_2O$). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm: 6.39 s (CH_2Si), 15.99 s ($POCH_2\underline{C}H_3$), 18.25 s ($SiOCH_2\underline{C}H_3$), 22.91 s ($OCH_2\underline{C}H_2CH_2Si$), 43.83 s ($PO\underline{C}H_2CH_3$), 58.6 s ($SiO\underline{C}H_2CH_3$), 64.12 s ($POCH_2CH(\underline{C}H_2Cl)O$), 69.51 s ($POCH_2\underline{C}H(CH_2Cl)O$), 73.85 s ($O\underline{C}H_2CH_2CH_2Si$), 75.98 s ($PO\underline{C}H_2CH$ (CH_2Cl)O). The mass spectrum (electrospray ionization): 1609.3 ($[M + H]^+$), 1573.1 ($[M - Cl]^+$). Found, %: C 35.82, 35.49; H 6.79, 6.83. $C_{48}H_{108}C_{l6}EuO_{24}P_3Si_3$. Calculated, %: C 35.78; H 6.76.

Europium tris{diethyl *N*-allyl-*N*-[3-(triethoxysilyl)propyl]phoshoricamidato} trichloride (V). IR spectrum (KBr), ν, cm^{-1}: 2986 m (ν_{CH}), m 2932 (ν_{CH}), 1628 m [ν($CH{=}CH_2$)], 1417 m 1352 m 1241 s, 1185 s , 1114 s (ν_{SiO}), 1032 s (ν_{SiO}), s 993 (ν_{PO}), 948 m, 792 w, 529 w (ν_{EuO}). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 0.46 m (6H, CH_2Si), 1.15 m (27H, $SiOCH_2C\underline{H}_3$), 1.22 m (18H, $POCH_2C\underline{H}_3$), 1.54 m (6H, $NCH_2\cdot C\underline{H}_2CH_2Si$), 2.91 m (6H, $NC\underline{H}_2CH_2CH_2Si$), 3.59 m (6H, $C\underline{H}_2CH{=}CH_2$), 3.71 m (18H, $SiOC\underline{H}_2CH_3$), 4.19 m (12H, $POC\underline{H}_2CH_3$), 9.5 m (6H, $CH{=}C\underline{H}_2$), 5.71 m (3H, $C\underline{H}{=}CH_2$). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm: 7.73 s (CH_2Si), 16.44 s ($POCH_2\underline{C}H_3$), 18.62 s ($SiOCH_2\underline{C}H_3$), 21.92 s ($NCH_2\underline{C}H_2CH_2Si$), 48.39 s ($PO\underline{C}H_2CH_3$), 48.8 s ($N\underline{C}H_2CH_2CH_2Si$), 58.87 s ($SiO\underline{C}H_2CH_3$), 62.43 s ($PN\underline{C}H_2CH = CH_2$), 118.3 s ($PNCH_2CH{=}\underline{C}H_2$), 136.1 s ($PNCH_2\underline{C}H = CH_2$). The mass spectrum (electrospray ionization): 1450.64 ($[M + H]^+$). Found, %: C 39.82; H 7.73; N 2.79. $C_{48}H_{108}Cl_3EuN_3O_{18}P_3Si_3$. Calculated, %: C 39.74; H 7.50; N 2.90.

Europium tris{phosphoric tris[*N*-allyl-*N*-[3-(triethoxysilyl)propyl-*N*',*N*',*N*'',*N*''-tetramethylamido]}-trichloride (VI). IR spectrum (KBr), ν, cm^{-1}: 2919 m (ν_{CH}), m 2852 (ν_{CH}), 2807 m (ν_{CH}), 1634 m [ν($CH{=}CH_2$)], 1394 m, 1273 s, 1182 s, 1150 (ν_{SiOC}), s 983 (ν_{POC}), 921 s, 751 w, 542 w (ν_{EuO}). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.51 m (6H, CH_2Si), 1.89 m (27H, $SiOCH_2C\underline{H}_3$), 1.58 m (6H, $NCH_2C\underline{H}_2CH_2Si$), 2.64 m (36H, $PN(CH_3)_2$), 2.86 m (6H, $NC\underline{H}_2CH_2CH_2Si$), 3.59 m (6H, $C\underline{H}_2CH{=}CH_2$), 3.88 m (18H, $SiOC\underline{H}_2CH_3$), 5.16 m (6H, $CH{=}C\underline{H}_2$), 5.76 m (3H, $C\underline{H}{=}CH_2$). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm: 8.24 s (CH_2Si), 19.2 s ($SiOCH_2\underline{C}H_3$), 22.46 s ($NCH_2\underline{C}H_2CH_2Si$), 37.7 s ($PN(CH_3)_2$), 49.2 s ($N\underline{C}H_2CH_2CH_2Si$), 49.65 s ($N\underline{C}H_2CH{=}CH_2$), 58.92 s ($SiO\underline{C}H_2CH_3$), 117.37 s ($PNCH_2CH{=}\underline{C}H_2$), 137.8 s ($PNCH_2\underline{C}H{=}CH_2$). The mass spectrum (electrospray ionization): 1445.3 ($[M + H]^+$). Found, %: C 39.45; H 8.29; N 8.41. $C_{48}H_{114}Cl_3N_9O_{12}P_3Si_3Eu$. Calculated, %: C 39.9; H 7.95; N 8.72.

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