Phosphorus-containing polymetalloorganosiloxanes

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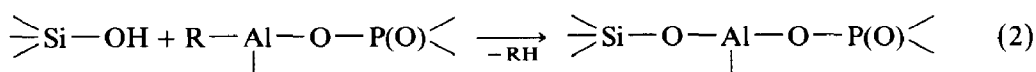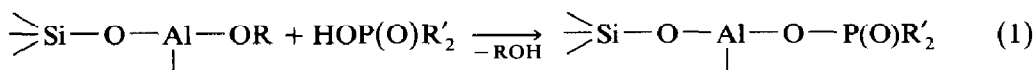
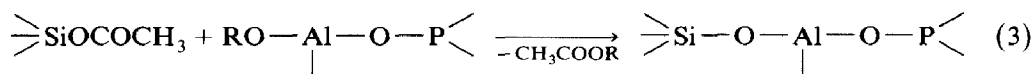(Received September 5th, 1989)

Abstract

Several methods for the synthesis of phosphorus-containing oligo- and polymetalloorganosiloxanes with Al, Cr, Co, Ni and Cu atoms have been developed. In these molecules, the phosphorus atoms can be located in both the main macrochain and in its framework. The structures, the physical and chemical properties of the oligomers and polymers obtained, and the possibility of using these compounds as surfactant modifiers have been studied.

Introduction

Phosphorus-containing polymetalloorganosiloxanes were prepared for the first time over a quarter of a century ago [1]. However, systematic research of this class of hetero-organic oligomers and polymers has been done only in the last decade [2,3]. Interest in compounds of this type stems, first of all, from the fact that the introduction of phosphorus atoms into the main or side chain of polymetallosiloxanes improves their technical characteristics, in particular, it increases their hydrolytic [4] and thermal stability [5]. Phosphorus-containing metallosiloxanes are the most effective silicone rubber stabilizers [6,7] and are promising sorbent surface modifiers [8,9].

There are some synthetic routes to phosphorus-containing metalloorganosiloxanes. One of the earlier and widely accepted methods is that [2] based on the polycondensation of oligo- or poly-diorganosiloxanes with terminal functional groups.

$$\ce{>Si-O-Al-OR + HOP(O)R'_2 ->[-ROH] >Si-O-Al-O-P(O)R'_2} \tag{1}$$

$$\ce{>Si-OH + R-Al-O-P(O)< ->[-RH] >Si-O-Al-O-P(O)<} \tag{2}$$

$$\geqslant SiOCOCH_3 + RO-\underset{|}{Al}-O-P\!\!\diagdown \xrightarrow[-CH_3COOR]{} \geqslant Si-O-\underset{|}{Al}-O-P\!\!\diagdown \quad (3)$$

Use was also made of the reaction of phosphorus-containing siloxane oligomers [10] of general formula $[(CH_3)_3SiO]_{2-m}PO\{[OSi(CH_3)_2]OSi(CH_3)_3\}_n$, where $m = 1$, 2; $n = 1-8$, with zinc acetate. In this case, it was revealed that zinc acetate splits the Si–O–P groups. The copolymers obtained are rubber-like amorphous substances with a vitrification temperature of $108-134°C$. Condensation of tris(trimethylsilyl)-phosphate with copper, iron, and cobalt acetates [11] was carried out according to eq. 4:

$$n\,[(CH_3)_3SiO]\,PO + M(CH_3COO)_n \longrightarrow$$

$$\{[(CH_3)_3SiO]_2P(O)-O\}_n M + n(CH_3)_3COOSi(CH_3)_3 \quad (4)$$
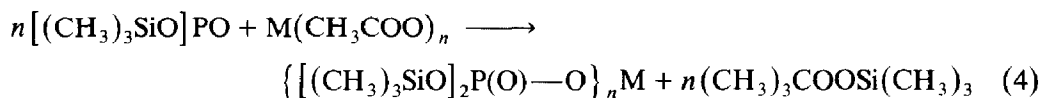
$(M = Cu^{2+}, Co^{2+}, Fe^{3+})$

Reaction 4 is accompanied by the liberation of trimethyl-acetoxysilane, hexa-methylsiloxane being another reaction product. This suggests the cleavage of $\geqslant \underset{\shortparallel}{Si}-O-P\!\!\diagup$ groups by the metal salt with the formation of di- and polyphosphate structures according to eq. 5:

$$[(CH_3)_3SiO]_3PO \xrightarrow[(CH_3COO)_nM]{T°C} [(CH_3)_3Si]_2O + \diagup\!\!P(O)-O-P(O)\!\!\diagdown \quad (5)$$
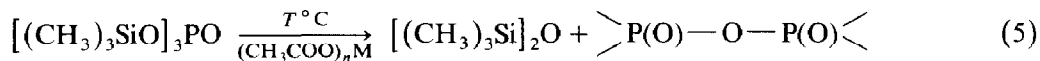
As established for the reaction with copper acetate, the competition between eq. 4 and 5 depends on the temperature. At $90-100°C$ condensation is the predominant process, the yield of $[(CH_3)_3Si]_2O$ not exceeding 10%, while at $115-120°C$ the yield increases to 50%. Above $125°C$, together with the liquid polymer, some crystalline products of partial substitution of acetate groups by bis(trimethylsilyl)phosphate groups were isolated.

Tris(trimethylsilyl)phosphate reacts with finely-dispersed copper, cobalt and iron. Dissolution of the metals is accompanied by their oxidation to Cu^{2+}, Co^{2+} and Fe^{3+}. The mechanism of interaction of the metals is similar to that for mild dissolution of metals in DMF and DMSO solutions [11].

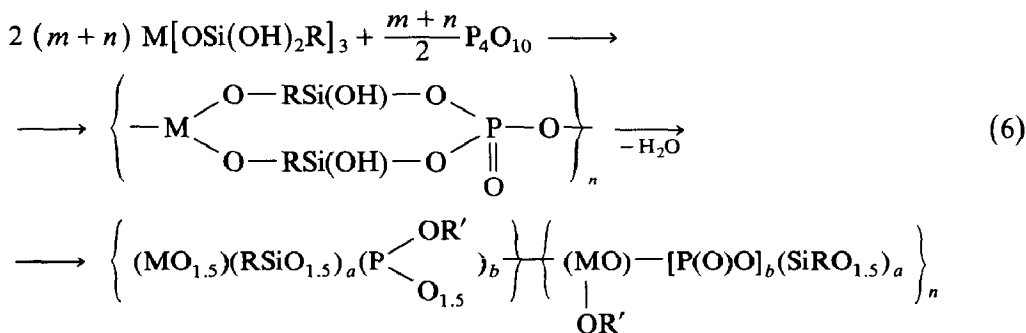In the reaction of permethyloligosiloxanes with metallopolyheterophosphates [12], heteropolymers are formed.

$$\left[\begin{array}{c} \underset{O=P-O}{\overset{O-P=O}{M\diagdown \diagup M}} \end{array} \right]_n$$
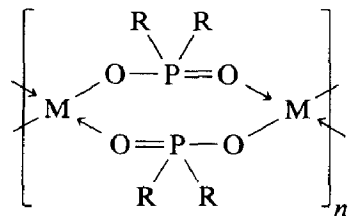
$(R = [OSi(CH_3)_2]_mOSi(CH_3)_3; \ m = 50; \ M = Cu^{2+}, Cr^{3+}, Ni^{2+}, Mn^{2+})$

Methods of synthesis

The results of our research carried out in the field of phosphorus-containing metallosiloxanes, which have been published only in part in Russian as preliminary communication [13–16], patent certificates [4,5,8] and several papers [17–21], are given below. Literature data on the structures of polymers of this type are also critically discussed.
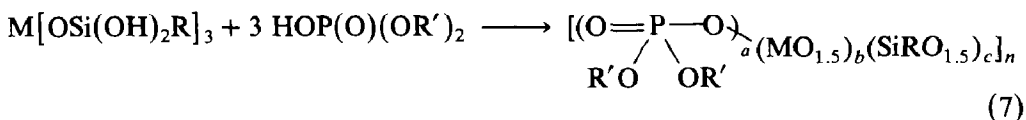
We have developed a convenient and simple method for the synthesis of phosphorus-containing polymetallosiloxanes, based on cleavage of the $\diagdown$M$-$O$-$Si$\diagdown$ groups by tetracoordinated phosphorus compounds such as P_4O_{10}, $R_2P(O)OH$ and

$\text{HO}\diagdown\text{HO}\diagup$C$[P(O)(OH)_2]_2$ in the butanol-benzene system [4,5,17,18].

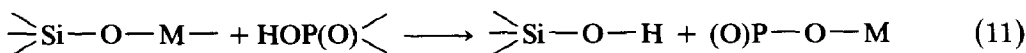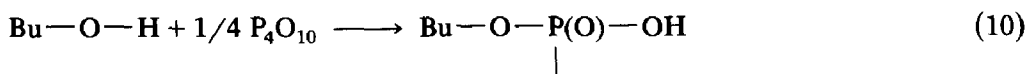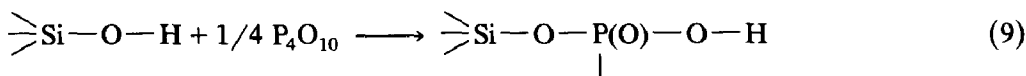The reaction of iron and chromium tris(organodihydroxysiloxy) derivatives with P_4O_{10} is described by eq. 6:

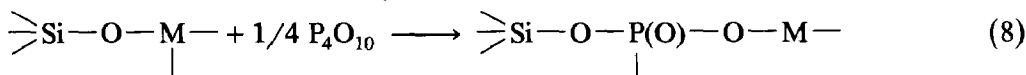$$2\,(m+n)\,M[OSi(OH)_2R]_3 + \frac{m+n}{2}\,P_4O_{10} \longrightarrow$$

$$\longrightarrow \left\{ -M \underset{O-RSi(OH)-O}{\overset{O-RSi(OH)-O}{\diagup\diagdown}} \underset{\overset{\|}{O}}{P-O} \right\}_n \xrightarrow{\;-H_2O\;} \tag{6}$$

$$\longrightarrow \left\{ (MO_{1.5})(RSiO_{1.5})_a(P\underset{O_{1.5}}{\overset{OR'}{\diagup\diagdown}})_b \right\} \left\{ (MO)-[P(O)O]_b(SiRO_{1.5})_a \right\}_n$$

$$\underset{OR'}{}$$

$(a = \text{Si/M};\ b = \text{P/M};\ n = 2, 3;\ m = 3, 4;\ R' = C_4H_9;\ R = C_2H_3,\ C_6H_5)$

Later, the course of this reaction was treated in a different way [22]. The initial step is suggested to be the reaction with silanol groups of metallosiloxane, with the formation of phosphoric acid which further splits the Si$-$O$-$M groups. It has been established, however, that in the reaction of dibutylphosphoric acid with tris(phenyl-dihydroxysiloxy)-iron or -chromium under analogous conditions unsoluble phosphorus-containing polymetallosiloxanes are formed in 80–90% yield according to eq. 7:

$$M[OSi(OH)_2R]_3 + 3\,HOP(O)(OR')_2 \longrightarrow [(O{=}P{-}O)\underset{R'O\quad OR'}{\overset{\diagup\ \diagdown}{}}_a(MO_{1.5})_b(SiRO_{1.5})_c]_n$$

$$\tag{7}$$

$(n = 9\text{--}11;\ a = 2.9\text{--}0.022;\ b = 1;\ c = 0.16\text{--}56;\ R = C_6H_5,\ R' = C_4H_9)$

In the reaction of iron or chromium tris(phenylhydroxysiloxy) derivatives with dibutylphosphoric acid, 85 and 75% of the $\dot{=}$Si$-$O$-$M$\diagdown$ groups, respectively, undergo cleavage, whereas in the reaction of these derivatives with P_4O_{10} only 44% $(M = Fe^{3+})$ and 34% $(M = Cr^{3+})$ of the $\dot{=}$Si$-$O$-$M$\diagdown$ groups are split. Thus, several processes take place simultaneously during the reaction of P_4O_{10} with metallosiloxanes in the butanol-benzene system:

$$\diagup^{\diagdown}_{\diagup}Si-O-\underset{\mid}{M}- + 1/4\,P_4O_{10} \longrightarrow \diagup^{\diagdown}_{\diagup}Si-O-\underset{\mid}{P(O)}-O-M- \tag{8}$$

$$\diagup^{\diagdown}_{\diagup}Si-O-H + 1/4\,P_4O_{10} \longrightarrow \diagup^{\diagdown}_{\diagup}Si-O-\underset{\mid}{P(O)}-O-H \tag{9}$$

$$Bu-O-H + 1/4\,P_4O_{10} \longrightarrow Bu-O-\underset{\mid}{P(O)}-OH \tag{10}$$

$$\diagup^{\diagdown}_{\diagup}Si-O-M- + HOP(O){\diagdown}{\diagup} \longrightarrow \diagup^{\diagdown}_{\diagup}Si-O-H + (O)P-O-M \tag{11}$$

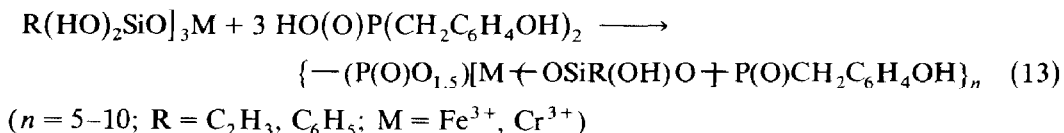$$\diagup^{\diagdown}_{\diagup}Si-O-H + HO(O)P \longrightarrow S \tag{12}$$

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Reaction 8 competes with the processes of hydrolysis (eq. 9) and acid cleavage (eq. 11) of $\geq$Si$-$O$-$M$\langle$ groups.

The reaction of P_4O_{10} with metallosiloxanes seems to start with the formation of a six-membered cyclic activated complex:
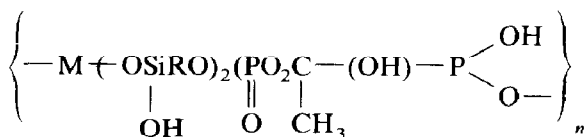
$$\tag{8}$$
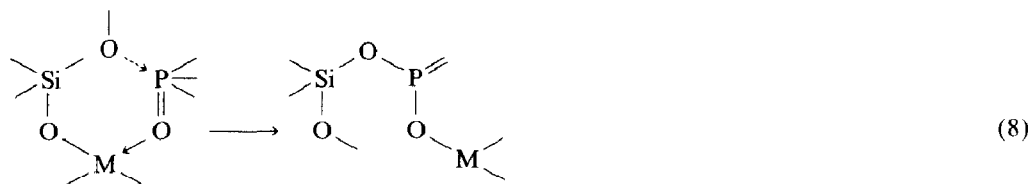
Further decomposition and transformation of this complex are illustrated by reactions 10, 11 and 12.

In the reaction of tris(phenyldihydroxysiloxy)-iron or -chromium with bis(4-hydroxybenzyl)phosphinic acid, the degree of cleavage of the $\geq$Si$-$O$-$M$\langle$ groups amounts to 36 and 20% (M = Fe^{3+} and Cr^{3+}), respectively. The reaction involves loss of the oxybenzyl radical, leading to the formation of cross-linked polymers which are soluble only in aprotic bipolar solvents:

$$R(HO)_2SiO]_3M + 3\ HO(O)P(CH_2C_6H_4OH)_2 \longrightarrow$$

$$\{-(P(O)O_{1.5})[M + OSiR(OH)O + P(O)CH_2C_6H_4OH\}_n \tag{13}$$

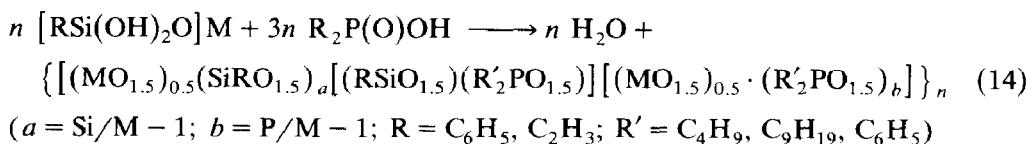$(n = 5\text{–}10;\ R = C_2H_3,\ C_6H_5;\ M = Fe^{3+},\ Cr^{3+})$

The reaction of tris(phenyldihydroxysiloxy)-iron or -chromium with 1-hydroxyethanediphosphonic acid under analogous conditions [17] leads to the lowest deviation from the initial Si/M ratio, the degree of SiOM cleavage amounting to 17.4 and 16.3% for M = Fe^{3+} and Cr^{3+}, respectively.

For high-molecular-weight and less soluble fractions, the unit looks like:

$$\left\{ -M + OSiRO)_2(PO_2C - (OH) - P \begin{matrix} OH \\ \diagdown \\ O- \end{matrix} \right\}_n$$
$$\begin{matrix} & & | & \| & | \\ & & OH & O & CH_3 \end{matrix}$$

The enhanced functionality of this acid does not lead to an increase in the yield of unsoluble polymers. The most soluble low-molecular-weight fraction contains more phosphorus than low-molecular-weight fractions formed by the reaction of metallosiloxanes with other oxygen derivatives of phosphorus [4,5].

The reaction of tris(organodihydroxysiloxy) derivatives of iron or chromium with diorganophosphinic acids [19] proceeds [18] according to eq. 14:

$$n\ [RSi(OH)_2O]M + 3n\ R_2P(O)OH \longrightarrow n\ H_2O +$$

$$\{[(MO_{1.5})_{0.5}(SiRO_{1.5})_a[(RSiO_{1.5})(R'_2PO_{1.5})]][(MO_{1.5})_{0.5} \cdot (R'_2PO_{1.5})_b]\}_n \tag{14}$$

$(a = Si/M - 1;\ b = P/M - 1;\ R = C_6H_5,\ C_2H_3;\ R' = C_4H_9,\ C_9H_{19},\ C_6H_5)$

With dinonylphosphinic acid $(C_9H_{19})_2P(O)OH$, regardless of the nature of M, crystalline substances $(RSiO)_2 \cdot [RSi(OH)O] \cdot [(C_9H_{19})_2P(O)O]_2$ (1, 2) were obtained. According to gel chromatographic data, the molecular mass of compound 1

$(R = C_6H_5)$ is 1000; that of compound **2** $(R = C_2H_3)$ is 800. The mass spectra of **1** and **2** show fragment ions of molecular mass m/z 697, 547 and 317, corresponding to $HO[Si(C_6H_5)O]_3P(O)C_9H_{19})_2^+$, $HO[Si(C_2H_3)O]_3P(O)(C_9H_{19})_2^+$ and $P(O)R_2^+$, respectively.

Elemental analysis, IR and mass spectral and gel chromatographic data allow us to assign the following structure to compounds **1** and **2**:
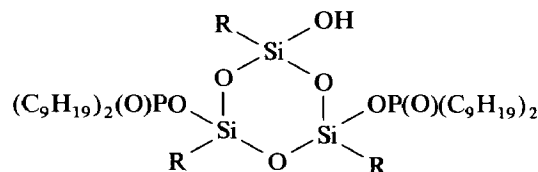
The formation of 1-hydroxy-3,5-dinonylphosphinyl-1,3,5-organocyclotrisiloxanes results from a competing condensation reaction of diorganophosphinic acids with the silanol groups of the trisiloxane rings present in the real structure of $R(HO)_2Si\text{-}ONa \cdot nH_2O$ [23].

Compounds **1** and **2** are formed only when $R' = C_9H_{19}$; with other R' values amorphous oligophospha(λ^5)siloxanes with low metal contents are the reaction products. This indicates that bulky C_9H_{19} radicals hinder further condensation of the trisiloxane ring silanol groups. The yields of compounds **1** and **2** are 40 and 27% with $M = Fe^{3+}$, and 36 and 34% with $M = Cr^{3+}$, respectively.

The degree of cleavage of the $\geq Si\text{-}O\text{-}M\langle$ group in iron and chromium tris(organyldihydroxysiloxy) derivatives in the reaction with $R'_2P(O)OH$ is presented in Table 1.

Bis(phenylhydroxysiloxy)cobalt reacts with dibutylphosphinic acid to form poly-butyloxophospha(λ^5)coba(λ^2)phenylsiloxane. Five fractions with unequal $Si/P/O$ ratios $((15.2-5.5)/(1.4-0.5)/(1.0))$ were isolated by fractional precipitation.

The reaction follows eq. 15:

$$[C_6H_5Si(OH)_2O]_2Co + HOP(O)(C_4H_9)_2 \longrightarrow$$

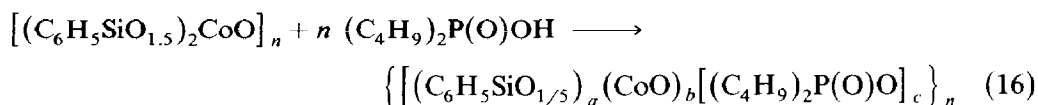$$\{[C_6H_5SiO_{1.5})_a(CoO)_b[(C_4H_9)_2P(O)O]_c\}_n \quad (15)$$
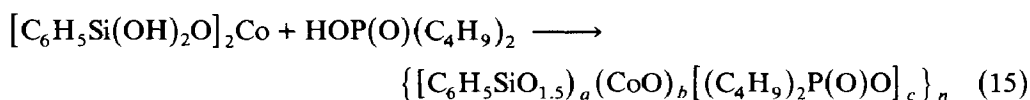
According to elemental analysis and IR and UV spectra, the fifth, most soluble fraction (40% yield) is cobalt polydibutylphosphinate, identified by a specially synthesized standard.

Table 1

Degree of cleavage of the Si–O–M group in $[RSi(OH)_2O]_3M$ in the reaction with $R'_2P(O)OH$

M	R	R'	Cleavage (%)	M	R	R'	Cleavage (%)
Fe	C_6H_5	C_9H_{19}	20.9	Cr	C_6H_5	C_9H_{19}	24.4
Fe	C_6H_5	C_4H_9	22.4	Cr	C_6H_5	C_4H_{19}	27.0
Fe	C_6H_5	C_6H_5	27.6	Cr	C_6H_5	C_6H_5	31.5
Fe	C_6H_5	$HOC_6H_4CH_2$	36.7	Cr	C_6H_5	$HOC_6H_4CH_2$	20.3
Fe	C_6H_5	C_4H_9O	85.0	Cr	C_6H_5	C_4H_9O	75.0
Fe	C_2H_3	C_9H_{19}	14.1	Cr	C_2H_3	C_9H_{19}	17.5
Fe	C_2H_3	C_4H_9	18.3	Cr	C_2H_3	C_4H_9	21.1
Fe	C_2H_3	C_6H_5	28.3	Cr	C_2H_3	C_6H_5	27.3

The reaction of polycobaltphenylsiloxane with dibutylphosphinic acid gives poly-dibutyloxophospha(λ^5)coba(λ^2)phenylsiloxane according to eq. 16:

$$[(C_6H_5SiO_{1.5})_2CoO]_n + n\ (C_4H_9)_2P(O)OH \longrightarrow$$

$$\left\{\left[(C_6H_5SiO_{1/5})_a(CoO)_b[(C_4H_9)_2P(O)O]_c\right\}_n \quad (16)$$

By use of fractional precipitation, three fractions showing a fairly close Si/P/Co ratio = $(2.0–4)/(1.0–1.5)/(1.4–1.0)$ were isolated.

Bis(phenyldihydroxysiloxy)nickel reacts with dibutylphosphonic acid to form insoluble nickel polydibutylphosphinate and polyphenylsiloxane.
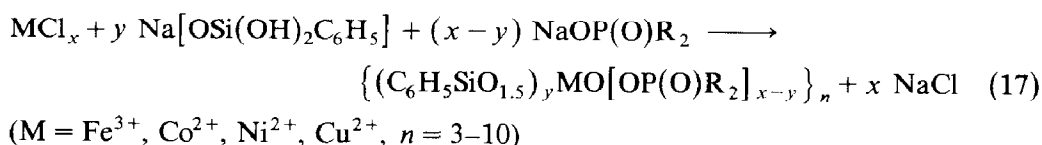
The reaction of tris(phenyldihydroxysiloxy)aluminium with dibutylphosphonic and dibutylthiophosphonic acids proceeds according to eq. 14. The reaction products are polydibutyloxophospha(λ^5)alumo(λ^3)phenylsiloxanes of general formula $\{(AlO_{1.5})_a(C_6H_5SiO_{1.5})_b[(C_4H_9)_2P(Y)O]_c\}_n$ (3).

With $Y = O$, the Si/P/Al ratio is $(4.9–1.6)/(4.0–1.6)/(1.0)$, whereas with $Y = S$ it is $(2.8–2.1)/(3.0–2.7)/(1.0)$. The difference in element distribution in the fractions is negligble in the two cases. The degree of cleavage of the Si–O–M groups in cobalt, nickel and aluminium bis(phenyldihydroxysiloxy) derivatives by dibutylphosphinic acid is 77.4, 74.0 and 25.0, respectively.

In the reaction of dibutylphosphinic acid with polycobaltphenylsiloxane, the degree of cleavage of the $\geqslant$Si–O–Co– group was 44.8%.

As can be seen from Table 1, cleavage of the Si–O–M groups in $[R(OH)_2SiO]_3M$, where $M = Cr^{3+}$, Al^{3+}, Fe^{3+}, by phosphorus acids increases in the cited order of these metals. The aluminium derivative is a Cr^{3+}–Fe^{3+} intermediate. In analogous metal(II) derivatives $[Ph(OH)_2SiO]_2M$ ($M = Co^{2+}$, Ni^{2+}), the $\geqslant$Si–O–M– group is split more readily by phosphorus acids (77.4, 74.0). This seems to be due to the coordination unsaturation of these metals.

Another promising route to phosphorus-containing polymetalloorganosiloxanes is based on the reaction of sodium dibutylphosphinate and phenylsiliconate with metal halide in a toluene-DMSO medium [19,20]. The process follows eq. 17:

$$MCl_x + y\ Na[OSi(OH)_2C_6H_5] + (x - y)\ NaOP(O)R_2 \longrightarrow$$

$$\left\{(C_6H_5SiO_{1.5})_yMO[OP(O)R_2]_{x-y}\right\}_n + x\ NaCl \quad (17)$$

$(M = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, n = 3–10)$

In this case, use was made of sodium siliconate prepared both by a routine technique [24] and by a method [25] noted for minimal use of water, which afforded a condensed oligomer.

The Si/P/M distribution in the fractions depends on the composition and structure of sodium phenylsiliconate in solution. The composition of soluble phosphorus-containing polymetallosiloxanes corresponds to the formula $\{(C_6H_5SiO_{1.5})_a$·$(MO_{x/2})_b[MOP(O)R_2]\}_n$ (4), where $a = Si/P$, $b = M/P - 1$, $c = 1.0$ and $x = M$ valence.

The order of introducing sodium phenylsiliconate and dibutylphosphinate affects the number and yield of the end products. Metal polydibutylphosphinate is always formed as a by-product. This shows that the reaction of metal chloride with $R_2P(O)Na$ is a competing and, to some extent, dominating process which is likely to be related to the formation of strong phosphinate rings [26]. Depending on the

nature of the metal, the yield of phosphorus-containing polymetallophenylsiloxanes decreases in the series $FeCl_3$, $CoCl_2$, $CuCl_2$, $NiCl_2$. This order corresponds to an analogous decrease in coordination ability of the above chlorides. The high yield of cobalt-containing polymers is conditioned by the similar geometry of cobalt and sodium ions in the sodium phenylsiliconate structure, as well as by the ready solubility of cobalt polydibutylphosphinate, whose high concentration in solution shifts the competing reaction equilibrium towards the formation of polydibutylphosphoruscobaltphenylsiloxane.

The reaction of sodium phenylsiliconate and dibutylphosphinate with anhydrous zirconium chloride proceeds under analogous conditions according to eq. 17. Three fractions were isolated by fractional precipitation with hexane from the polymer solution in THF. Some time after isolation, the polymer and fractions became less soluble. According to elemental analysis and IR spectral data, the fractions are polydibutylphospha(λ^5)zircono(λ^4)phenylsiloxanes showing a close Si/P/M ratio (1.4–1.5)/(1.1–1.0)/(1.0–0.9). This relatively uniform distribution of elements in the fractions and the absence of polydibutylphosphinatezirconium seems to be due to the absence of crystallization water in the system.

The reaction of sodium phenylsiliconate and dibutylphosphinate with copper dichloride crystallohydrate under analogous conditions proceeds according to eq. 17. In this case, three fractions were isolated on the basis of solubility. The first insoluble fraction was polyphospha(λ^5)cupro(λ^2)phenylsiloxane, with a Si/P/M ratio of 1/1/2. The second fraction isolated by evaporating the aqueous solution was copper polybutoxyphosphate according to elemental analysis and IR spectroscopy. The third fraction, the most soluble in organic solvents, was, according to elemental analysis and IR spectroscopy, polycuprophenylsiloxane with a small amount of phosphate fragments.

In the first two fractions there was only one butoxy group at the phosphorus atom. In the transition from $(C_4H_9)_2P(O)ONa$ to $(C_4H_9O)_2P(O)ONa$, the yield of polyphospha(λ^5)cupra(λ^2)phenylsiloxanes decreases, the Si/P/M ratio in the fractions varying greatly. This is evidently conditioned by competing reactions occurring in the formation of copper polybutoxyphosphate.
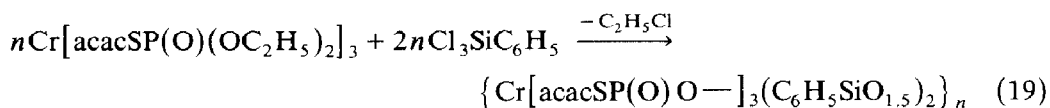
We have also worked out some synthetic routes to phosphorus-containing polymetallosiloxanes containing chelate metallocycles in their macrostructure.

When tris(trimethylsilyl)phosphite reacts with tris(3-chlorosulfenyl-2,4-pentanedionate)chromium in boiling xylene, and insoluble three-dimensional poly(3-thio-2,4-pentanedionato)chromo-P-trimethylsilylphospha(λ^5)oxane is formed in 80% yield (eq. 18).


(18)
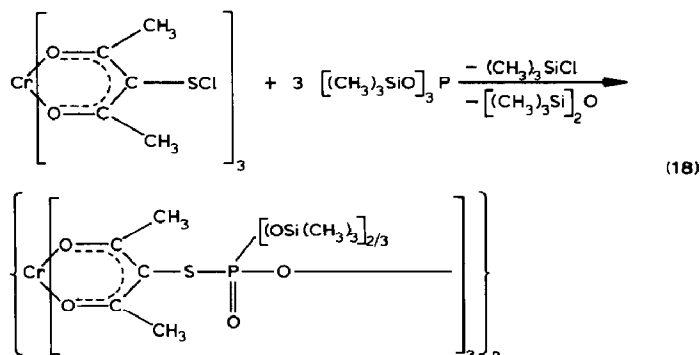
In this case, tri(sulfenylchlorideacetylacetonate)chromium behaves like metal γ-haloacetylacetonates in their reaction with trialkylphosphates [27].

The reaction of tris(3-diethylthiophosphato-2,4-pentadionate) chromium with phenyltrichlorosilane in boiling toluene follows eq. 19:

$$n\text{Cr}[\text{acacSP(O)(OC}_2\text{H}_5)_2]_3 + 2n\text{Cl}_3\text{SiC}_6\text{H}_5 \xrightarrow{-\text{C}_2\text{H}_5\text{Cl}}$$

$$\{\text{Cr}[\text{acacSP(O) O}-]_3(\text{C}_6\text{H}_5\text{SiO}_{1.5})_2\}_n \quad (19)$$

In this case, an insoluble three-dimensional poly(3-thio-2,4-pentadionato-chromo)diethylphospha(λ^5)phenylsiloxane is formed in 86% yield. The formation of polymers in the above two cases proceeds without decomposition of the metal β-diketone ring.

The interaction of the oligomer $\{[\text{OP(O)C}_3\text{H}_7\text{acac}]\text{Ni} \cdot [\text{OP(OC}_3\text{H}_7)_2\text{O}]_2\text{Ni}\}_n$ (5) with phenyltrichlorosilane in boiling toluene also follows eq. 19 and leads to polynickel(3-phosphato-2,4-pentanedionato)nickelphospha(λ^5)phenylsiloxane (6) in 72% yield.

(6)
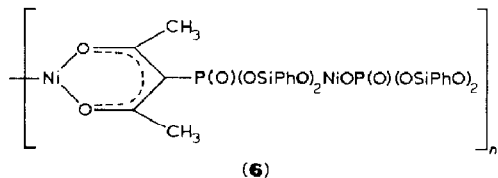
Here, 90% decomposition of the β-diketonate ring occurs.
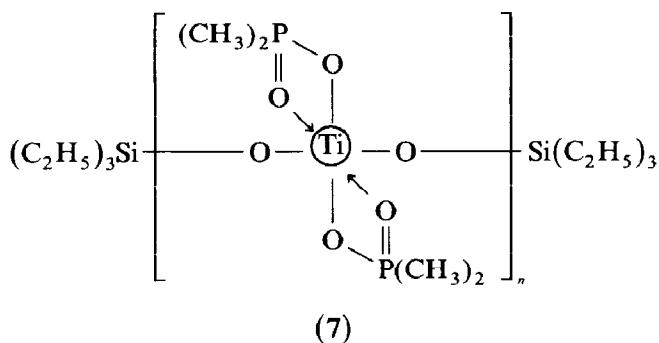
Structure and properties

Depending on the Si/P/M ratio and on the relative arrangement of atoms of these elements, phosphorus-containing polymetallosiloxanes may possess, to a different extent, some properties of either metallophospha(λ^5)oxanes [28,29] or the corresponding metallosiloxanes [30].

During a study of the effect of the number and form of $\overset{\displaystyle}{\underset{\text{II}}{\text{P}}}-\text{O}-\text{M}-\text{O}-\text{Si}$ fragments on the properties of phosphorus-containing metallosiloxanes, the formation of an insoluble fraction having the highest phosphorus and metal contents was always observed [1,31–33]. Analysis of the molecular mass of the phosphorus-containing metallosiloxanes allows us to conclude that there is an interaction between the phosphoryl oxygen and the vacant d-orbitals of the metal atom in these compounds. In this case, either four- or eight-membered rings are formed [28].

The evidence for coordination is displacement of the P–O absorption band towards low frequencies [11,34]. Nevertheless, this kind of displacement [29] was explained by the presence of a phosphorane fragment in the structure of poly-organophosphatotitanoxane.

For monofunctional monomers containing only one functional group at the silicon and phosphorus atom, the structures of the oligomers and polymers formed are determined by the nature of the metal atom. Thus, the reaction of tetrakis(tri-ethylsiloxy)titanium with dimethylphosphinic acid leads to coordinate oligo-dimethylphosphinatotriethylsiloxytitanoxane (7) with a P/Ti ratio of 2/1 [29].

$$(C_2H_5)_3Si \left[\begin{array}{c} (CH_3)_2P \\ \parallel \\ O \\ \\ -O-\text{(Ti)}-O- \\ \\ O \\ \parallel \\ P(CH_3)_2 \end{array} \right]_n Si(C_2H_5)_3$$
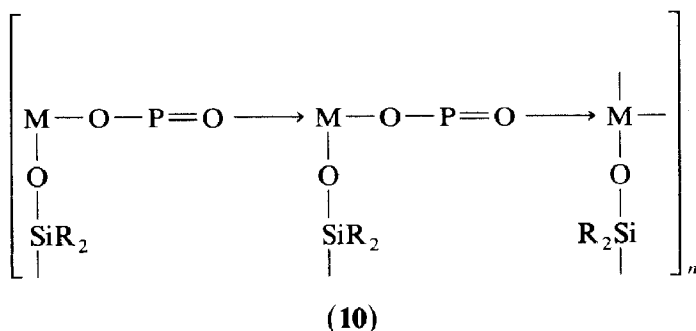
(7)

($n = 3$–6)

In our opinion, this oligomer has structure 7; a similar structure is found for the products of partial hydrolytic condensation of titanium tetraalkoxides [35].

In the reaction of tris(trimethylsilyl)phosphate with Fe^{3+}, Co^{2+} and Cu^{2+} acetates and free metals [11], the structures of the oligomers formed are also determined by the nature of the metal atom. With copper acetate, for example, a crystalline product, a mixture of monomer 8 and dimer 9, is formed.

$$[(CH_3)_3SiO]_2P \underset{O}{\overset{O}{<}} \overset{}{Cu} \underset{O}{\overset{O}{>}} P[OSi(CH_3)_3]_2$$

(8)

(9)
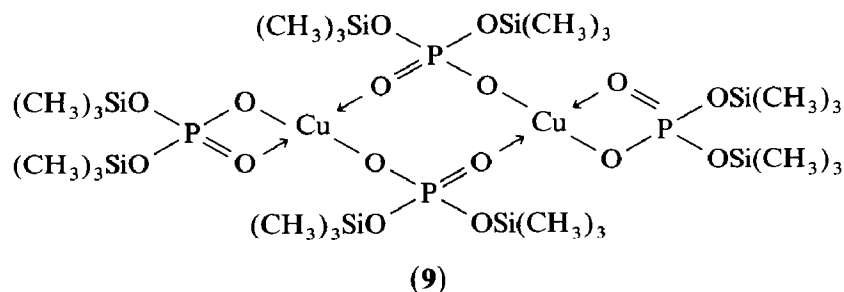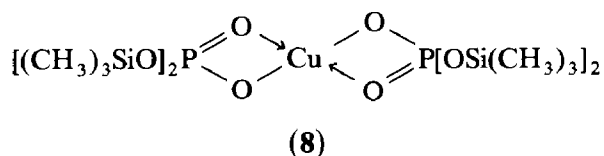
The appearance of three bands in the P–O region in the IR spectra may be assigned, according to Batkina et al. [11], to the presence of two non-equivalent P=O groups. In the reaction of tris(trimethylsilylphosphate) with iron acetate, a coordination polymer composed of eight-membered rings was isolated. We assume the absorption at 300–380 nm [11] to be a charge-transfer band corresponding to the coordination interaction $\geqslant$P=O → M–O–P(O)$\leqslant$. This band is displaced bathochromically in the series Cu > Fe $\geqslant$ Co.

With difunctional silicon- and phosphorus-containing monomers, the structures of the polymers formed are dependent on the steric environment of Si and M. Thus, when dialkyl(diaryl)phosphinate fragments are introduced into linear polyalkoxyalumodiphenylsiloxanes in a 1/1 P/M ratio [33], insoluble polymers are formed in all cases. The formula ascribed to these polymers does not agree with their insolubility and non-melting. These polymers are assumed to have structure 10, owing to the coordination of the phosphoryl oxygen of one chain to the aluminium atoms of the other chain.

$$\left[\begin{array}{ccc} M{-}O{-}P{=}O \longrightarrow & M{-}O{-}P{=}O \longrightarrow & \overset{|}{M}{-} \\ | & | & | \\ O & O & O \\ | & | & | \\ SiR_2 & SiR_2 & R_2Si \\ | & | & | \end{array} \right]_n$$

(10)

If the length of the oligodialkylsiloxane fragment in polyalkoxyalumodimethyl-siloxanes is fairly large, there is no P=O→M coordination. For example, in the reaction of aluminium di(isopropoxy)dimethylphosphinate with polydimethylsilo-xane-α,ω-diols [36] in the Si/M ratio 47/117, soluble polydimethylphos-phinatoalumodimethylsiloxanes were obtained. Their IR spectra showed an absorption band at 1320–1370 cm^{-1} corresponding to non-coordinated P=O group vibrations.

The structures of phosphorus-containing metallosiloxanes obtained from trifunc-tional organosilicon monomers are of special interest [20,37–39]. Polyphospha(λ^5)-metalloorganosiloxanes of this type were prepared by us by treating metalorganyl-siloxy derivatives with phosphorus-containing reactants [17,18]. According to gel chromatography, they have a low molecular mass in the range 4000–5000 and show considerable polydispersity. The polydispersity of phosphorus-containing polymetal-losiloxanes increases in the following order, depending on the character of the substituent at the phosphorus atom:

$$(HO)CH_3CH{\diagdown} < HOC_6H_4CH_2 < C_9H_{19} < C_4H_9 < C_6H_5$$

Maximal dispersity is displayed by heterosiloxanes obtained by the reaction of metal organylsiloxy derivatives with P_4O_{10}. Iron-containing heterosiloxanes show greater polydispersity than analogous chromium compounds.

The yield of insoluble and low-molecular-weight (1000–1500) fractions increases in the same order of changing the substituents at the phosphorus atom as that for polydispersity. Low-molecular-weight fractions appear to be oligomers consisting of six-membered siloxane rings. This is confirmed by the structures of oligomers **I** and **II** obtained from the reaction of tris(phenyldihydroxysiloxy metal derivatives with dinonylphosphinic acid [18].

Phosphorus-containing polymetallosiloxanes obtained by the reaction of sodium phenylsiliconate and dibutylphosphinate with metal chlorides possess a molecular mass above 5000 and a low polydispersity [20].
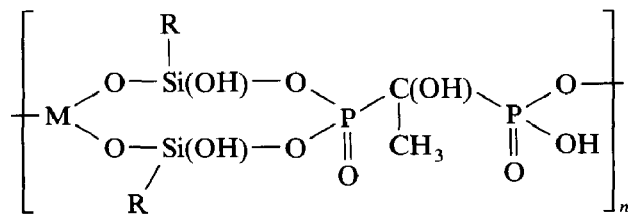
In the IR spectra of phosphorus-containing polymetallosiloxanes, much information concerning the macromolecule structure can be provided from the position, number and shape of the bands in the 1310–1100 and 1100–900 cm^{-1} regions, corresponding to P=O and Si–O, P–O bond vibrations, respectively. In the IR spectra of polymers obtained from P_4O_{10}, oxyethanediphosphonic and bis(4-hy-droxybenzyl)phosphonic acids, regardless of the nature of the metal, there are some adsorption bands corresponding to P=O bond vibrations in the regions 1135–1150, 1240–1140 and 1210 cm^{-1}, respectively, and absorption bands as a flexion in the

region 960–940 cm^{-1}, corresponding to the P–O bond in the P–O–P fragment for polymers obtained from P_4O_{10}.

The IR spectra of polymers synthesized from diorganylphosphinic acids [17,18] also contain two absorption bands at 1260 and 1140 cm^{-1}, indicating the presence of structurally different phosphorus-containing fragments with an intra- and an inter-coordinate phosphoryl oxygen. The displacement of the P=O band towards low frequencies can be explained by the strengthening of the P=O→M coordination interaction, which agrees with the reduced solubility of polymers exhibiting a diorganylphosphinate framework. The presence of these two absorption bands shows that the formation of phosphorus-containing metallosiloxanes is conditioned by two processes: condensation of phosphorus acids with silanol groups and splitting of the Si–O–M group according to:
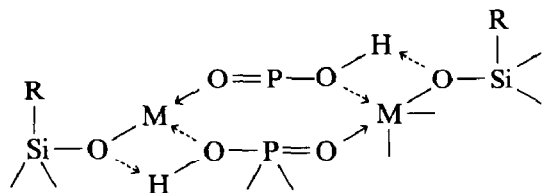
In particular, with oxyethanediphosphinic acid, condensation with the formation of structures of the type **II** seems to be the major process.

(11)

In the IR spectrum of phosphorus-containing polycoba(λ^2)phenylsiloxane obtained by the reaction of polycobaltphenylsiloxane with dibutylphosphinic acid in a P/O ratio of 1/1, only one absorption band of the P=O bond was found in the 1130 cm^{-1} region. In the IR spectrum of phosphorus-containing polycoba(λ^2)phenylsiloxane synthesized by the reaction of sodium phenylsiliconate and sodium dibutylphosphinate with cobalt chloride, an absorption band corresponding to the P=O→Co group is observed at 1125 cm^{-1}. The spectrum contains two bands at 930 and 960 cm^{-1} corresponding to vibrations of the P–O and Si–O bonds, respectively, in the $\geq\!\!P\!-\!O\!-\!Co\!-\!O\!-\!Si\!\leq$ group. In the spectra of polycoba(λ^2)-phenylsiloxane and cobalt polydibutylphosphinate these bands were absent.

In the electron spectra of absorption in the visible region of polyphospha(λ^5)-coba(λ^2)phenylsiloxanes [20] obtained according to eq. 14 and 17, absorption maxima at 520–530 ($\epsilon = 8$–10) and 730–620 nm ($\epsilon = 500$) are observed. They correspond to $^4T_{1g}(F)$–$^4T_{1g}(P)$ and $^4A_{2g}$–$^4T_{1g}(P)$ transitions in the octahedral and tetrahedral surrounding, respectively [40]. The fine structure of the second band is caused by a spin-orbital interaction, which causes splitting of the $^4T_{1g}(P)$ level, and transitions on the neighbouring doublet levels of the same intensity become allowed [40].

The lower extinction of the $^4A_{2g}$–$^4T_{1g}(P)$ band in the UV spectra of poly-oxophospha(λ^5)coba(λ^2)phenylsiloxane at 620–730 cm^{-1} compared with that of cobalt dibutylphosphinate shows a reduced contribution of tetrahedral configuration [20].

From X-ray structural analysis, polyoxaphospha(λ^5)coba(λ^2)phenylsiloxane possesses a more ordered structure than the initial polycobaltphenylsiloxane and cobalt polydibutylphosphinate. There are two reflections at 11 and 7.5° in the diffractogram of polyoxophospha(λ^5)coba(λ^2)phenylsiloxane, and only one reflection (7°) in the diffractogram of cobalt polydibutylphosphinate. The reflection at 11° indicates the presence of another layer, whereas the increase in reflection angle to 7.5° provides evidence for a shortened distance between the phosphorus and metal atoms.

On the basis of elemental analysis and IR spectroscopy, it has been suggested [37] that the structures of polymetalloorganosiloxanes with Si/M ratio = 6 contain a sandwich complex of two trisiloxane rings, in which the coordination capacity fo the metal is always constant and equal to 6. An interesting suggestion has been made [41] about monomeric siloxanes being the intra-complex compounds, with due account being taken of the nature of the metal. However, the possibility of a monomer–polymer transition with retention of the structure of the monomer and the initial sodium phenylsilanolate [23] has not been considered [41].

Some general considerations on the structures of polymetallosiloxanes [38] obtained from trifunctional organosilicon compounds have led to a cyclic network structure with the network density being inversely proportional to the number of silanol groups in a unit. Our ideas concerning the structure of polyoxophospha-(λ^5)metallophenylsiloxanes were based on the X-ray diffraction pattern of sodium phenylsiliconate [23], as well as on some notions about the structures of metal polyphosphinates [26], monomer [41] and polymer [30] metallosiloxanes.

The polyoxophospha(λ^5)metalloorganosiloxane structure presented in Fig. 1 is proposed on the basis of IR, UV-gamma-resonance spectroscopic, gel chromatographic and X-ray structural analysis data.

This structure displays two clearly-defined sets of planes, one of which has a larger interplanar distance and belongs to the dibutylphosphinate fragment (according to the reflection angle); the other set has a smaller interplanar distance and a correspondingly larger reflection angle. This set of planes is absent in the structure
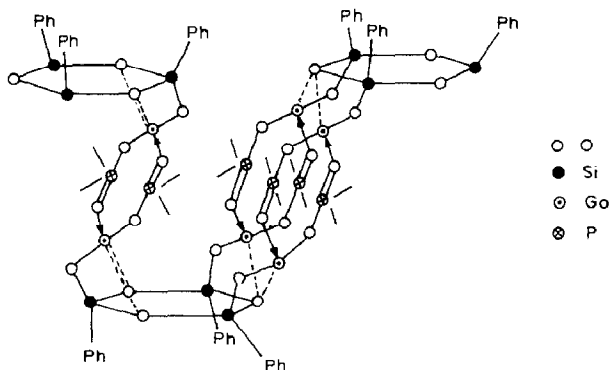

Fig. 1. The proposed structure for polyoxophospha(λ^5)metalloorganosiloxanes.

of both cobalt polydibutylphosphinate and polycoba(λ^2)phenylsiloxane. In the reaction of polycoba(λ^2)phenylsiloxane with dibutylphosphinic acid, the $-Co-O-Si\lessgtr$ groups containing a tetrahedral cobalt atom are split to a greater extent, which is confirmed by UV spectroscopy [20].

The above concepts concerning the structure of polydibutyloxophospha-(λ^5)coba(λ^2)phenylsiloxane, the absence of the 940 cm^{-1} band, the low intensity of the 970 cm^{-1} band and the presence of an intense diffuse band at 3200–3400 cm^{-1} in copper- and nickel-containing polyoxaphospha(λ^5)metallosiloxanes as well as the loss of solubility of the polymer after isolation provide evidence for the fact that that these metals considerably change the macro-chain geometry.

Polyoxophospha(λ^5)metallophenylsiloxanes containing Fe^{3+} instead of Cu^{2+} or Ni^{2+} do not lose their solubility with time, analogously to polyferro(λ^3)phenylsiloxane [42].

Using Mössbauer spectroscopy, we studied the surrounding symmetry of the iron atom in polydibutylphospha(λ^5)ferro(λ^3)phenylsiloxane [19] and in model compounds such as iron polybutylphosphinate and polyferrosiloxane (Table 2).

Table 2 shows that in polyoxophospha(λ^5)ferro(λ^3)phenylsiloxanes quadrupole splitting decreases, which means that the surrounding symmetry of the iron atom increases. The isomer shift in the spectrum of polyoxophospha(λ^5)ferro(λ^3)phenyl-siloxanes has an intermediate value between the shifts in the spectra of iron polydibutylphosphinate and polyferro(λ^3)phenylsiloxane.

This indicates the presence of $\gtrless P-O-Fe-O-Si\lessgtr$ fragments. The higher δ value of the isomer shift of polyoxophospha(λ^5)ferro(λ^3)phenylsiloxanes compared with that of polyferro(λ^3)phenylsiloxane is due to π-donation of the phosphoryl oxygen lone pair on the d-orbital of the iron atom, i.e. due to an intra- and inter-molecular $\gtrless P=O \rightarrow Fe\lessgtr$ interaction.

The high E values are indicative of a distortion of the iron atom's octahedral configuration. This may result from the presence of water molecules or differently bound oxygen atoms of phenylsiliconate in the coordination sphere. The IR spectrum of polyphospha(λ^5)ferro(λ^3)phenylsiloxanes displays a band at 3200–3400 cm^{-1} due to the presence of associated hydroxyl.

The Mössbauer spectral data and solubility data, as well as the present ideas of a well-ordered cyclo-network structure of these polymers [38], involving an intra-complex metal ion [39,41], impose certain limitations on the selection of the structure (Fig. 2).

Fig. 2 shows the suggested structure of polybutyloxophospha(λ^5)ferro(λ^3)phenyl-siloxane. Here, the presence of phosphinate bridges is possible not only between the phenylsiliconate layers, but inside the layer as well, which should diminish the

Table 2

Degree of cleavage of the Si–O–M group in $[C_6H_5(OH)_2SiO]_nM$ in the reaction with $(C_4H_9)_2P(O)OH$

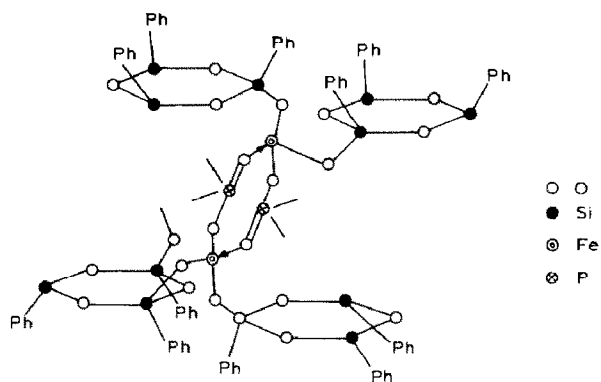| M	Cleavage (%)
Ni	74.0
Co	77.4
Al	25.0

Fig. 2. The proposed structure for polyphospha(λ^5)ferro(λ^3)phenylsiloxanes.

structure ordering. This is supported by the absence of bands at 940 cm^{-1} in the IR spectrum [19]. The presence of phosphinate bridges is a characteristic of the structural features of polyoxophospha(λ^5)metalloorganosiloxanes.

Polyoxophospha(λ^5)metalloorganylsiloxanes as surface modifiers

As known [9], modification of the silica gel surface with polymetalloorganylsiloxanes improves its sorption characteristics. We have worked out some methods for modifying silica gels using polyoxophospha(λ^5)metalloorganylsiloxanes [8,21]. It is shown, by physical and chemical methods, that these polymers are fixed on the silica gel surface by means of the metallosiloxane skeleton without participation of the phosphorus-containing groups. An increase in the specific surface, micropore volume and limiting sorption volume is indicative of the formation of a tracery surface structure. Chemical testing consisted in treating the modified silica gel surface with acid and alkali. Acid treatment leads to a sorbent displaying ion-exchange properties. The modification of silicon dioxide with polyoxophospha(λ^5) zircono(λ^4)phenylsiloxane gives a sorbent possessing anion-exchange properties. The adsorption of water, alcohol, benzene and hexane vapours by silica gels modified with polyphosphametalloorganylsiloxanes decreases in the following order: $H_2O > C_2H_5OH > C_6H_6 > C_6H_{14}$. The adsorption of water vapour depends on the nature of the metals in the modifiers - polyphosphametallosiloxanes - and decreases in the order Cu > Co > Fe. This series is in agreement with coordination unsaturation of the metal ion in the polymer.

Calcination of modified silica gels at 300–320 °C does not change the adsorption value. However, the adsorption equilibrium is achieved considerably faster after calcination.

A sorbent for gas-liquid chromatography of hydrocarbons and alcohols was prepared by modifying bentonite with polydibutyloxophospha(λ^5)coba(λ^2)phenylsiloxane [8]. The separation coefficient of a mixture of heptane, octane and nonane on this sorbent is 1.8; that of a mixture of hexane with benzene is equal to 2. The sorbent is noted for its higher thermal stability, which allows high-boiling hydrocarbons to be separated. It also proved to be very effective for the separation of n-alkanols.

We have also studied on the possibility of using polyoxophospha(λ^5)metalloorganosiloxanes as silicon rubber stabilizers. The maximum stabilizing effect is

observed when 5% of polybutyloxophospha(λ^5)ferro(λ^3)phenylsiloxane is added.

Modifying a titanium electrode with the above-mentioned oligomer (6) containing nickel, phosphorus and silicon makes the electrode sensitive to nickel ions. For such an electrode the dependence of the potential on the pH in a universal buffer solution is almost linear and is expressed by the equation $E = a - bx$, where $a = 262$ and $b = 41$ mV. It should be noted that the potential-pH dependence does not change for several months. The electrode responds to a change in the nickel ion concentration within the range $10^{-5} - 10^{-1}$ mol/l.

Annealing the modified electrode at $200-250\,^\circ$C for 30 min increases the stability of the electroanalytical parameters with time.

Experimental

IR spectra ($4000-400$ cm^{-1} region) were recorded on a Specord IR-75 spectrometer in chloroform and vaseline oil. UV spectra were recorded on a Hitachi-220A spectrophotometer in chloroform (cuvette length 1 cm; concentration 10^{-2} M). Mössbauer spectra were recorded on a YaGRS-4 spectrometer with an AI-4096 multi-channel analyser. The γ-radiation source was ^{57}Co in chromium. Gel chromatography was performed as described in [19]. Mass spectra were recorded on an MX-1320 spectrometer (70 eV).

Al^{3+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Cu^{2+} tris and bis(organylhydroxysiloxy) derivatives were obtained by the procedure described in [41]; polymetalloorganosiloxanes were prepared by the method reported in [20]. Phosphoric acids were obtained as described in [43,44].

Polydibutylphospha(λ^5)coba(λ^2)phenylsiloxane. Synthesis and isolation were performed as in [18]. Method A. To [C$_6$H$_5$(HO)$_2$SiO]$_2$Co (16 g, 0.04 M), (C$_4$H$_9$)$_2$P(O)OH (7.65 g, 0.04 M) was added. By fractional precipitation of the polymer from toluene with petroleum ether in ratios of 1/1, 1/3, 1/5 and 1/7 and removal of the solvents, 5 fractions were isolated. Fraction 1 (yield 18.1%). Found: Si 17.3; P 2.4; Co 3.0. {(CoO)(C$_6$H$_5$SiO$_{1.5}$)$_{12.2}$[(C$_4$H$_9$)$_2$P(O)O]$_{1.4}$}$_n$ calcd.: Si 18.0; P 2.3; Co 3.1%. Fraction 2 (yield 6.5%). Found: Si 17.1; P 3.0; Co 2.5. {(CoO)(C$_6$H$_5$SiO$_{1.5}$)$_{14.4}$[(C$_4$H$_9$)$_2$P(O)O]$_{2.2}$}$_n$ calcd.: Si 17.0; P 2.8; Co 2.4%. Fraction 3 (yield 2.6%). Found: Si 17.3; P 1.7; Co 6.4. {(CoO)(C$_6$H$_5$SiO$_{1.5}$)$_{5.5}$-[(C$_4$H$_9$)$_2$P(O)O]$_{0.54}$}$_n$ calcd.: Si 17.8; P 1.6; Co 6.8%. Fraction 4 (yield 16.1%). Found: Si 16.6; P 3.0; Co 10.4. {(CoO)(C$_6$H$_5$SiO$_{1.5}$)$_{3.4}$[(C$_4$H$_9$)$_2$P(O)O]$_{0.5}$}$_n$ calcd.: Si 16.0; P 2.6; Co 9.9%. Fraction 5 (yield 40.6%). Found: Si 0.6; P 15.4; Co 11.1%.

Method B. To polycoba(λ^2)phenylsiloxane, [(C$_6$H$_5$SiO$_{1.5}$)$_2$CoO]$_n$ obtained as described in [25] (3.25 g, 0.0045 M) in 130 ml of toluene, (C$_4$H$_9$)$_2$P(O)OH (1.65 g, 0.009 M) in 50 ml of toluene was added. The mixture was boiled for 6 h with separation of water in a Dean-Stark trap; the solvent was distilled off and the polymer was dried in vacuum at $80\,^\circ$C. By fractional precipitation from toluene with petroleum ether in ratios of 1/1 and 1/2 and removal of the solvents, three fractions were isolated. Fraction 1 (yield 39.0%). Found: Si 10.4; P 5.7; Co 15.2. {(CoO)$_{0.4}$(C$_6$H$_5$SiO$_{1.5}$)$_2$[(C$_4$H$_9$)$_2$P(O)O]}$_n$ calcd.: Si 10.4; P 5.9; Co 15.7%. Fraction 2 (yield 26.8%). Found: Si 6.9; P 9.5; Co 11.9. {(CoO)(C$_6$H$_5$SiO$_{1.5}$)$_{1.2}$-[(C$_4$H$_9$)$_2$P(O)O]$_{1.5}$]$_n$ calcd.: Si 7.0; P 9.7; Co 12.4%. Fraction 3 (yield 26.0%). Found: Si 14.4; P 5.9; Co 7.5. {(CoO)(C$_6$H$_5$SiO$_{1.5}$)$_{4.2}$[(C$_4$H$_9$)$_2$P(O)O]$_{1.5}$}$_n$ calcd.: Si 13.7; P 5.4; Co 6.9%.

The synthesis of polyphospha(λ^5)nickel(λ^2)phenylsiloxane was carried out in a similar manner [18]. To [C$_6$H$_5$(HO)$_2$SiO]$_2$Ni (9.59 g, 0.026 M), (C$_4$H$_9$)$_2$P(O)OH (4.6 g, 0.026 M) was added. The product yield was 12 g (86%). The product was extracted with toluene in a Sohxlet apparatus. Fraction 1, colourless viscous substance soluble in toluene (yield 7.8 g). Found: C 54.6, Si 20.8. [C$_6$H$_5$SiO$_{1.5}$]$_n$ calcd.: C 55.1, Si 12.0%. Fraction 2, insoluble, light-green substance (yield 5.6 g). Found: Si 1.6, P 10.2, Ni 19.4%.

Polyphospha(λ^5)alumo(λ^3)phenylsiloxane. The synthesis and isolation of poly-phospha(λ^5)alumo(λ^3)phenylsiloxane were performed as described in [18]. To [C$_6$H$_5$(HO)$_2$SiO]$_3$Al (25 g, 0.025 M), (C$_4$H$_9$)$_2$P(O)OH (4.45 g, 0.025 M) was added. The mixture was fractionated by solubility. Fraction 1, precipitate formed in the course of synthesis (yield 7 g (25%)). Found: C 51.8; Si 4.5; P 12.2; Al 2.3. {(AlO$_{1.5}$)(C$_6$H$_5$SiO$_{1.5}$)$_{1.6}$[(C$_4$H$_9$)$_2$P(O)O]$_4$}$_n$ calcd.: C 52.3; Si 4.7; P 12.9; Al 2.6%. Fraction 2, precipitate formed upon partial removal of the solvent (yield 5 g (20%)). Found: C 52.8; Si 14.4; P 5.6; Al 3.1. {(AlO$_{1.5}$)(C$_6$H$_5$SiO$_{1.5}$)$_{4.8}$[(C$_4$H$_9$)$_2$P(O)O]$_{1.6}$}$_n$ calcd.: C 52.3; Si 15.1; P 5.3; Al 2.8%. Fraction 3 was obtained after complete removal of the solvent (yield 9.5 g (36%)). Found: C 53.6; Si 18.6; P 2.4; Al 4.5%.

The synthesis and isolation of polyphospha(λ^5)thio(λ^2)alumo(λ^3)phenylsiloxane were carried out analogously. To [C$_6$H$_5$(HO)$_2$SiO]$_3$Al (25 g, 0.025 M), (C$_4$H$_9$)$_2$PSOH (4.85 g, 0.025 M) was added. Fraction 1 (yield 7.2 g (26%)). Found: C 48.4; Si 6.3; P 10.2; Al 2.9. {(AlO$_{1.5}$)(C$_6$H$_5$SiO$_{1.5}$)$_{2.1}$[(C$_4$H$_9$)$_2$P(O)O]$_3$}$_n$ calcd.: C 49.2; Si 6.6; P 10.4; Al 3.0%. Fraction 2 (yield 2.9 g (10%)). Found: C 48.7; Si 8.6; P 8.8; Al 3.0. {(AlO$_{1.5}$)(C$_6$H$_5$SiO$_{1.5}$)$_{2.8}$[(C$_4$H$_9$)$_2$P(O)O]$_{2.7}$}$_n$ calcd.: C 49.2; Si 8.4; P 8.9; Al 2.9%. Fraction 3 (yield 14.2 g (50%)). Found: C 48.8; Si 15.8; P 4.05; Al 4.5%.

Polydibutylphospha(λ^5)zircono(λ^4)phenylsiloxane. To zirconium chloride (anhydrous) (10.2 g, 0.043 M) in 100 ml of dry toluene, a solution of sodium phenylsiliconate C$_6$H$_5$(HO)$_2$SiONa · 1.5H$_2$O (20.7 g, 0.086 M) obtained as de-scribed in [24] in 250 ml of toluene-DMSO (10/1) was added. The mixture was stirred for 6 h at room temperature. To this mixture sodium dibutylphosphinate, (C$_4$H$_9$)$_2$P(O)ONa (17.2 g, 0.086 M), in 10 ml of DMSO was added. The mixture was stirred for 19–20 h. The sodium chloride precipitate was separated in a centrifuge. The solution was boiled with separation of water in a Dean-Stark trap for 6 h. When liberation of water was stopped, toluene was distilled off under a reduced pressure. The cooled solution was poured into distilled water (1 l). The polymer was filtered off, washed with water from DMSO and dried in vacuum at 80°C. Yield 6.4 g (68%). Three fractions were isolated by use of fractional precipitation of the polymer from toluene with hexane in ratios of 1/1 and 1/2 and removal of solvents. Fraction 1 (yield 48.8%). Found: C 43.5; Si 8.4; P 7.0; Zr 18.5. (C$_6$H$_5$SiO$_{1.5}$)$_{1.5}$(ZrO$_2$) · [(C$_4$H$_9$)$_2$P(O)O]$_n$ calcd.: C 42.7; Si 8.4; P 6.9; Zr 18.9%. Fraction 2 (yield 23.8%). Found: C 43.6; Si 8.4; P 6.8; Zr 18.8%. Calcd. see fraction 1. Fraction 3 (yield 21.2%). Found: Si 8.9; P 12.4; Zr 16.6%. Calcd. see fraction 1.

Polyphospha(λ^5)cupro(λ^2)phenylsiloxane. To a solution of CuCl$_2$ · 2H$_2$O (34.1 g, 0.2 M) in 80 ml of DMSO and 200 ml of toluene, a solution of {[C$_6$H$_5$(HO)$_2$SiO]Na}$_n$ (34.8 g, 0.4 M) in 50 ml of DMSO and 260 ml of toluene was added. The solutions of CuCl$_2$ · 2H$_2$O and [C$_6$H$_5$Si(HO)$_2$ONa]$_n$ were prepared as described in [25]. The mixture was stirred for 6 h at room temperature. To this mixture a solution of sodium dibutylphosphate, (C$_4$H$_9$O)$_2$P(O)ONa (48.0 g, 0.2 M),

in 40 ml of DMSO and 100 ml of toluene was added and mixed for 20 h at $20\,^\circ$C. The mixture was boiled for 4 h using a Dean-Stark trap without separating NaCl. Toluene was distilled off under a reduced pressure and the cooled residue was poured into distilled water (1 l), after which the aqueous solution turned green. The polymer was filtered off, washed with water from DMSO and dried in vacuum at $80\,^\circ$C. Three fractions were isolated based on solubility. Fraction 1 was a blue substance, insoluble in organic solvents (yield 21.6%). Found: C 26.0; Si 5.8; P 7.0; Cu 28.5. $\{(CuO)_{2.1}(C_6H_5SiO_{1.5})[(C_4H_9)P(O)O_{1.5}]\}_n$ calcd.: C 26.7; Si 6.2; P 6.9; Cu 28.5%. Soluble fraction 3 was a green viscous substance (yield 24.5%). Found: C 47.8; Si 18.2; P 0.5; Cu 9.5. $\{(CuO)(C_6H_5SiO_{1.5})_{4.5}[(C_4H_9)P(O)O_{1.5}]_{0.1}\}_n$ calcd.: C 48.7; Si 18.6; P 0.5; Cu 9.4%. After evaporation of the aqueous solution a blue substance, insoluble in organic solvents, was isolated (Fraction 2 (yield 17.5%)). Found: C 26.9; P 17.0; Cu 24.7. $\{(CuO)(C_6H_5SiO_{1.5})_{0.01}[(C_4H_9)P(O)O_{1.5}]_{1.5}\}_n$ calcd.: C 24.7; P 17.8; Cu 24.6%.

Poly(3-thio-2,4-pentanedionato)chromotrimethylsilylphosphoroxane. To $(ClS-acac)_3Cr$ (5.48 g, 0.01 M) in 100 ml of dry xylene, $[(CH_3)_3SiO]_3P$ (8.94 g, 0.03 M) was added. The mixture was heated for 6 h, with the removal of trimethylchlorosilane. The solution was evaporated and the precipitate, an insoluble polymer, was washed with benzene and dried in vacuum. Yield 9 g. Found: C 26.4; Si 1.0; P 14.0; Cr 8.1. $\{Cr[(PO_3)_3]_{0.1}[(acacSP(O)O_{1.5})_3]_{0.8}[acacSP(O)OSi(CH_3)O_{1.5}]_{0.1}\}_n$ calcd.: C 26.8; Si 1.3; P 14.4; Cr 8.08%.

Poly(3-thio-2,4-pentanedionato)chromodiethylphosphatophenylsiloxane. To $[(C_2-H_5O)_2P(O)Sacac]_3Cr$ (4.27 g, 0.01 M) in 150 ml of dry xylene, $C_6H_5SiCl_3$ (2.11 g, 0.01 M) was added. The mixture was heated for 5 h. The solution was evaporated to half its volume; the precipitate was filtered off, washed with benzene and dried in vacuum. Yield 4.9 g (86%). Found: C 37.8; H 4.6; Si 5.4; P 9.5; Cr 5.3. $\{Cr[acacSP-(O)(OC_2H_5)_{0.6}O]_3[C_6H_5SiO_{1.5}]_2\}_n$ calcd.: C 37.6; H 4.1; Si 5.7; P 9.4; Cr 5.2%.

Poly(3-propylphosphonoyl-2,4-pentanedionato)nickelphosphonatophenylsiloxane. To the previously described [46] oligomer of composition $\{[OP(O)(OC_3H_7)acac]Ni[OP(OC_3H_7)_2O]_2NiO\}_n$ (6.56 g, 0.01 M), C_6H_5SiCl (6.3 g, 0.03 M) in 100 ml of dry toluene was added. The mixture was boiled for 7 h, evaporated, and the precipitate was filtered off, washed on a filter with dry benzene, and dried in vacuum. Found: C 23.3, H 5.0, Si 4.2, P 5.5, Ni 16.6. $\{[NiO(H_2O)_2][PO_{2.5}]-(C_6H_5SiO_{1.5})_{1.1}[acacP(O)\cdot(OC_3H_7)O]_{0.1}\}_n$ calcd.: C 22.6, Si 4.4, P 15.9, Ni 16.8%.

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