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Reviews

Magnetic organometallosiloxanes

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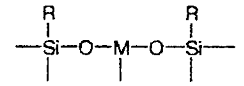
The generalized analysis of a change in magnetic properties of organometallosiloxanes as a function of the number of metal atoms in their molecules (on going from mono- and binuclear to polynuclear crystalline and polymeric compounds) is presented. The relation between the magnetic characteristics and structural parameters of metal-containing fragments is studied. The factors affecting the formation of exchange-coupled ionic pairs and clusters in polymeric systems are analyzed. The ways to the organization of magnetic phases in polymeric systems are considered: the choice of conditions of chemical synthesis, the organization of metal atoms in a common spin system upon incorporation of conducting coordinating additives, and thermocondensation and reduction processes leading to the formation of a metallic phase dispersed in a silicon dioxide matrix.

Key words: organometallosiloxanes, molecular ferromagnetism, magnetic properties, exchange interactions.

At the present time, ferromagnetism stable at temperatures close to 300 K (high-temperature ferromagnetism) has been observed only for inorganic compounds. The development of organic and organoelement ferromagnets is related to fundamental problems of modern chemistry. The solution of this problem requires the initial multispin paramagnetic molecules and methods for organizing these molecules in the condensed phase in such a way that spins would be ferromagnetically arranged. Organometallic compounds are most promising for this purpose, and organometallosiloxanes (OMS) play a special role among them. Organometallosiloxanes are a class of compounds, whose main structural fragment is the group containing a metal atom in the organosiloxane surroundings. At present, organosiloxane derivatives have been obtained for the majority of metals, the fundamentals of the synthesis of OMS have been well developed, and many specific features of their structure and chemical behavior have been studied.[1,2] Thus, there are wide synthetic possibilities for the formation of the magnetic structure by methods of organoelement chemistry using magnetic OMS, in which M is a transition metal atom with unpaired d-electrons. These OMS, their structure,



$$-\underset{|}{\overset{\overset{\textstyle R}{|}}{Si}}-O-\underset{|}{M}-O-\underset{|}{\overset{\overset{\textstyle R}{|}}{Si}}-$$

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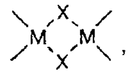
magnetic properties, and the functional relationship between the structure and magnetism are the subject of this work.

Mono- and binuclear organosiloxanes

Ferrosiloxane complexes containing one iron atom in a molecule ($Me_3P{=}O \cdot Fe(OSiMe_3)_3$ (**1**) and $Na[Fe(OSiMe_3)_4]$ (**2**)) have effective magnetic moments μ_{eff} 5.90 and 5.91 μ_B, respectively,[3] which almost coincide with the theoretical value of 5.92 calculated for the d^5-electronic configuration of Fe^{III}.

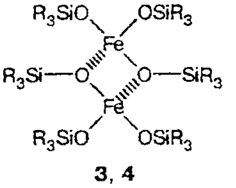
For metallosiloxanes, *e.g.*, alcoxides, carboxylates, *etc.*, a four-membered metallocycle is the typical structural fragment



, X = Hal, O, N, S.

This is a planar tetragon, in which the M—X—M angle (where X = O) can vary in a wide range (88—107°). It is this parameter that most frequently correlates with the magnetic properties of the compound.[4,5] In cyclic systems of this type, the O atom is almost always tricoordinated; these systems allow one to observe a change in magnetic properties as a function of the nature of M or geometric parameters of the metallocycle, which is usually achieved by the variation of the ligand at M.

The four-membered M_2O_2 cycle is the main structural fragment of the bimetallic dimeric ferrosiloxanes $[Fe(OSiR_3)_3]_2$ (**3**, **4**).



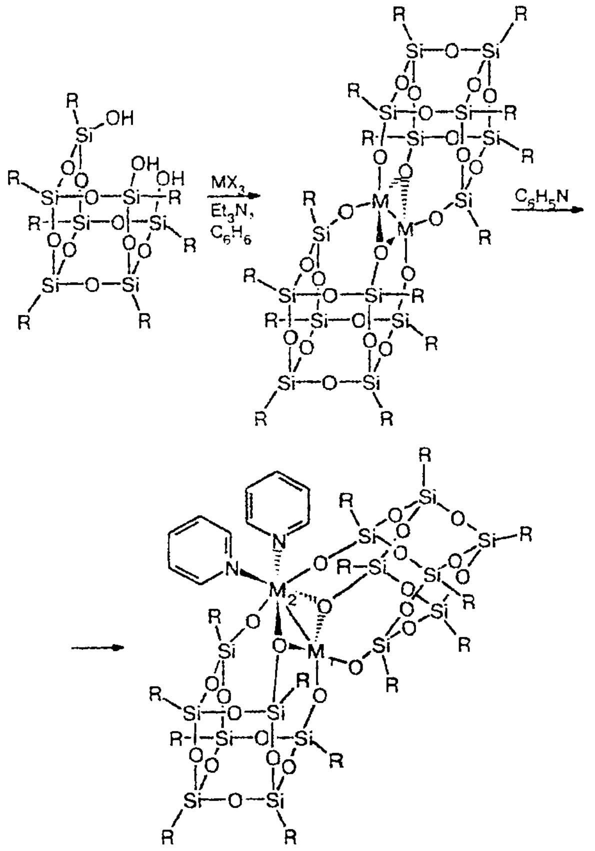
3, 4

3: R = Me
4: R = Et

These compounds are coordination dimers in which Fe atoms are tetracoordinated. They exhibit a decrease in the μ_{eff} value (as compared to the theoretical value)[3] on going from R = Me (**3**) to R = Et (**4**): μ_{eff} = 5.15 and 5.31 μ_B, respectively, which indicates that the antiferromagnetic interaction between the atoms appears in this fragment (the measurements were carried out for solid crystalline samples). In a benzene solution, compound **3** exhibits an insignificant change in the magnetic moment (μ_{eff} = 5.22 μ_B). This suggests that the main contribution to the change in μ_{eff} of the binuclear complexes in comparison with mononuclear complexes is due to the intracomplex interaction of the Fe atoms. When one of the paramagnetic atoms (Fe) is replaced by a diamagnetic atom (Al) in a molecule of the dimer considered,[3] its μ_{eff} increases up to 5.52 μ_B, approaching μ_{eff} of the mononuclear complex (**1**, **2**).

Binuclear organometallosiloxane complexes of another type are described.[6] Their molecules (**5**—**9**) contain the same or different metal atoms. The synthesis and structure of these compounds are presented in Scheme 1.

Scheme 1



R = *cyclo*-C_6H_{11}, X = Hal; **5**: $M_1 = M_2$ = Ti;
6: $M_1 = M_2$ = V; **7**: M_1 = Ti, M_2 = V;
8: M_1 = V, M_2 = Cr; **9**: $M_1 = M_2$ = Cr

These compounds are formed of siloxane cubic frameworks. A metal atom is localized in one of the vertices of each cube, and two cubane molecules are coordinationally organized in dimers. In compounds **5**—**9**, the M atoms have different coordination numbers: M_1 is the tetracoordinated atom and M_2 is hexacoordinated due to two additional Py ligands. These framework compounds are antiferromagnetic. The magnetic properties of the compounds obtained and their structural parameters are presented in Table 1.

The variation of M results in the transformation of the M_2O_2 cycle. On going from Ti to V and Cr, the metalloxane M_2O_2 cycle changes from the square to

Table 1. Energies of exchange interaction between M_1 and M_2 (J) and values of the M_1—O—M_2 angles (φ) of framework OMC

Compound	M_1	M_2	d^x, d^y	J/cm^{-1}	φ/deg
5	Ti^{III}	Ti^{III}	d^1, d^1	<−1000	91.2
6	V^{III}	V^{III}	d^2, d^2	−80.5	99.0
7	Ti^{III}	V^{III}	d^1, d^2	−187	
8	V^{III}	Cr^{III}	d^2, d^3	−5.5	98.5

rhombic one (increase in the M_1—O—M_2 angle); the antiferromagnetic interaction (J) decreases in parallel.

Molecules of framework organocoppersiloxanes[7] with the composition $Na_4[(PhSiO_2)_{12}Cu_4]\cdot 8Bu^nOH$ (**10**), $K_4[(CH_2{=}CHSiO_2)_{12}Cu_4]\cdot 6Bu^nOH$ (**11**), and $[K_2((EtSiO_2)_6K_2Cu_4(OSiEt)_6]\cdot 6Bu^nOH$ (**12**) are deformed hexahedra, and Cu atoms enter into the composition of the structural M_2O_2 fragment (Fig. 1). In compound **12**, unlike siloxanes **10** and **11**, the cyclic Cu_2O_2 fragments are arranged in such a way that the lines connecting Cu—Cu inside the cyclic fragments are parallel. Compounds **10**—**12** differ in the nature of the R group connected to Si. Therefore, it is quite natural that μ_{eff} of these compounds are similar: **10**, 0.65 (50 K), 1.65 (300 K); **11**, 0.65 (50 K), 1.60 (300 K); **12**, 0.60 (50 K), 1.55 μ_B (300 K).[8] In all three cases, the μ_{eff} value is lower than the theoretical value of 1.73 μ_B calculated for the d^1-electronic configuration of Cu^{II}. According to this, it is remarkable that μ_{eff} decreases as the temperature decreases. Both these facts indicate the antiferromagnetic interaction in Cu—Cu. A molecule of compound **10** (as in siloxanes **11** and **12**) contains two cyclic Cu_2O_2 fragments linked by the siloxane framework. They are arranged at diametrically opposite sides of a polyhedron. The distance between the planes of the Cu_2O_2 cycles is rather long and equal to 4.05 Å (**10**), 3.89 Å (**11**), and 3.38 Å (**12**), which rules out the exchange interaction between the cyclic fragments. Thus, these compounds should be related to binuclear compounds from the viewpoint of their magnetic properties.

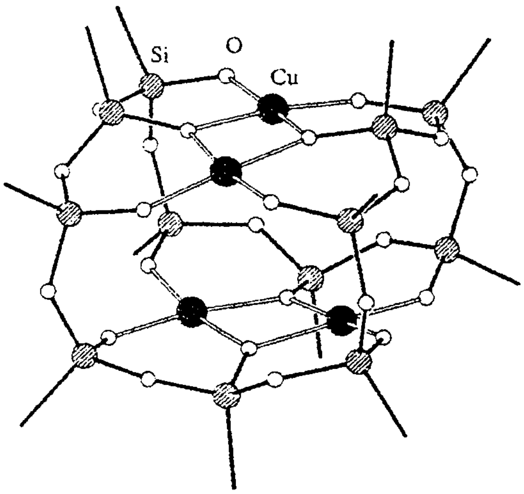


Fig. 1. Structures of compounds **10** and **11** (organic groups at Si are not shown).

The comparison of the structural data and the values of energies of the exchange interaction for compounds containing the cyclic M_2O_2 group in the organosiloxane or organic surroundings is presented in Table 2.

The majority of the ligands listed in Table 2 (except organosiloxanes) are Schiff's bases. The O atoms in the M_2O_2 fragment enter into the alkoxy and phenoxy groups of Schiff's bases. The consideration of the data in Table 2 reveals very high values of the Cu—O—Cu angle regardless of the ligand surroundings and, according to this, the stable antiferromagnetism is observed (negative values of the J constant).

In the case of Fe-containing compounds, a decrease in the bridged M—O—M angle results in a decrease in the antiferromagnetic interaction and appearance of the ferromagnetic interaction (positive J values).

This regularity becomes more distinct when compounds in which the bridged M—O—M angle is noticeably greater than 100° are considered. M_2O_2 metallocycles

Table 2. Geometric parameters and energies of exchange interaction (J) for compounds containing the cyclic M_2O_2 fragment (M = Fe, Cu)

M	Ligand surroundings of metal	M—O—M angle /deg	M···M distance /Å	J/cm^{-1}	Refs.
Fe^{III}	$—OSiR_3$	96.0	3.06	−8.5	3, 9
Fe^{III}	*N*-Salicylidene-5-chloro-2-hydroxybenzylamine	92.6	2.955	1.6	5
Fe^{III}	2-Bis(salicylideneamino)methylphenolate	95.0	3.06	1.2	10
Fe^{III}	2-[Bis(2-benzimidazolylmethyl)amino]ethylate	107.4		−20.5	11
Cu^{II}	EtSi—O—	101.2	3.012	−105	8
Cu^{II}	PhSi—O—	101.7	3.012	−89.3	8
				−255	12
Cu^{II}	$CH_2{=}CHSi—O—$	101.5	3.037	−89.3	8
				−219	12
Cu^{II}	*N*-Salicylidene-5-chloro-2-hydroxybenzylamine	101.6	3.077	−233	5
Cu^{II}	Chloro(*N*-isopropyl-2-hydroxybenzylidene)aminate; Cl	103.5	3.067	−145	13
Cu^{II}	*N*-Isopropyl-2-hydroxybenzylideneaminate	106.0	3.03	<−500	13

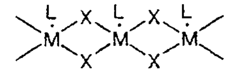
with an angle greater than 110° are most likely impossible. Thus, an increase in this angle results in "open" bimetallic >M—O—M< systems and an exclusively strong antiferromagnetic interaction.[14] When the Fe—O—Fe angle varies within the 142.0—175.0° range, the range of the J value is -87—-100 cm^{-1}. This tendency exists previously in the given case as well: the smallest antiferromagnetic interaction ($J = -87$ cm^{-1}) is observed for the compound with the smallest value of the M—O—M angle equal to 142°.

Evidently, in the general case, a decrease in the M—O—M angle results in a decrease in the M···M distance in the cyclic M_2O_2 fragment. Nevertheless, there are no grounds to assume that the direct transannular exchange interaction appears, because the M···M distances (see Table 2) are still rather large.

It is noteworthy that bimetallic structures can be rather simply synthesized and comprehensively characterized structurally,[15] and they are convenient models for studying the nature of magnetic interactions in transition metals with different variants of d—d-configurations.[16] However, in these binuclear systems, the exchange interaction between metal atoms of adjacent dimer molecules is rather difficult due to steric hindrances, *i.e.*, the formation of a single spin system is improbable. In this respect, polynuclear systems are more promising.

Polynuclear crystalline systems

The binuclear M_2O_2 metallocycles considered above are prone to aggregation, forming polynuclear systems. Spirocyclic structures are the most characteristic example. Magnetic studies of this type of crystalline compounds (M = Co, X = Cl, L = bipy;[17,18] M = Fe, X = Cl, L = py;[17,18] M = Cu, X = O, L = pyrazine, phenazine[19,20]) showed that metal atoms are organized by the exchange interaction along spirocyclic chains, and in some cases, low-temperature ferromagnetism appears. The distinctive feature of organosiloxane metal derivatives (as compared to organic complexes) is their unusually great structural variability[21] due to the high mobility of the Si—O—Si fragment. Spirocyclic (M = Al,[22] Co, Cr, Mn [21]), cubane (M = Ti, Al [21]), prismatic (M = Co, Ni, Mn, Cu [23—25]), and other more complicated polyhedral molecules (M = Co [26]) have been obtained to date. The immobilization of spirocyclic M_2O_2 fragments in the organosiloxane framework results in two structural peculiarities: a noticeable decrease in the M—O—M angle and distortion of the planar character of the M_2O_2 cycle accompanied by the appearance of an inflection along the M···M line. Some geometric parameters of polynuclear OMS are presented in Table 3.



In this case, direct exchange interaction along the M···M line is also hardly possible, since although the M···M distance is somewhat shorter than that in the binary systems, it is still fairly large (see Table 3).

The magnetic properties of polynuclear OMS have been insufficiently studied. The properties of compounds **10**—**12** have been considered above. Compound **17** can be related to polynuclear compounds; its molecule contains six Co atoms entering into the spirocyclic chain closed in a ring (Fig. 2).

The compound has the structure of a hexahedral prism with cyclosiloxane fragments in bases connected by the metallosiloxane —O—Co—O— bridges.[24] As can be seen from Fig. 2, in the compound obtained, the Co atoms are organized in a metallosiloxane system by coordination bonds. The metallosiloxane —Co—O—Co— fragments appearing in this coordination provide an indirect exchange interaction between the Co^{II} ions. The temperature dependence of the magnetic susceptibility of cobaltphenylsiloxane[30] is presented in Fig. 3, and two effects can be distinguished. First, there is a noticeable deviation from the Curie law in the direction

Table 3. Geometric parameters of polynuclear OMS

Compound	Molecular structure	Angle M—O—M /deg	Inflection angle* /deg	Distance M···M /Å	Refs.
10	Hexahedron	101.2	180	3.012	7
11	Hexahedron	101.7	180	3.037	7
12	Hexahedron	101.5	180	3.012	7
$Na^+[(PhSiO_2)_6Cu_6(O_2PhSi)_6]Cl^- \cdot 6\ EtOH$ (**13**)	Prism	91.8—93.1	137		24
$Na_2(PhSiO_2)_6Na_4Ni_4(OH)_2(OSiPh)_6 \cdot 16\ Bu^nOH$ (**14**)	Distorted prism	95.0—100.0	180	3.14—3.18	27
$[(PhSiO)_6(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4Ni_8(\mu_3\text{-}O)_2(PhSiO)_6] \cdot 14\ Bu^nOH$ (**15**)	Distorted prism	93.0—101.0	180	3.07—3.15	23
$Na^+[(PhSiO_2)_6Ni_6(O_2PhSi)_6]Cl^- \cdot 14\ Bu^nOH$ (**16**)	Prism	90.7	132	2.85	28
$Na^+[(PhSiO_2)_6Co_6(O_2PhSi)_6]Cl^- \cdot 7\ Me_2CO \cdot 1.5\ Bu^nOH \cdot$ $\cdot\ 0.5\ EtOH \cdot 10\ Bu^nOH$ (**17**)	Prism	88.1	135— 136	2.87	24
$(py_2Li)\text{-}\mu\text{-}[Co(OSiPh_2O)_2\mu\text{-}Copy]Cl$	Spirocycle	94.3, 97.1	180		29
$Na^+[(PhSiO_2)_6Mn_6(O_2PhSi)_6]Cl^- \cdot 10\ Bu^nOH$	Prism	94.5, 92.5, 92.1	139— 141	3.01—3.06	24

* Dihedral angle between two MOM planes with the common edge along the M···M line.

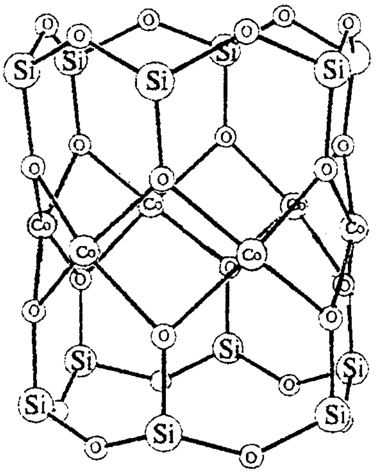


Fig. 2. Structure of cobaltphenylsiloxane (**17**).

of the ferromagnetic interaction. This is also confirmed by the μ_{eff} values presented below, which were calculated from the experimental data. As the temperature decreases, they increase with respect to the value μ_{theor} = 3.87 μ_B calculated for the d^3-electronic configuration.

T/K	297	42.2	19.4	9.5	4.5
μ_{eff}/μ_B	4.05	5.28	5.66	6.91	9.2

Second, the antiferromagnetic component is absent (χ does not increase with an increase in T). Both effects[30] are related to a low value of the bridged Co—O—Co angle[24] in cobaltphenylsiloxane, equal to 88.1°. This value is noticeably lower than that observed for the known cobalt oxo complexes in alkoxy compounds (102—107°)[31] and siloxy derivatives containing the —Si(R_2)—O—Co— fragment (94—97°).[29] Thus, the incorporation of Co atoms into the structure of the polycyclic siloxane framework is accompanied by the disappearance of the antiferromagnetic interaction (the existence of which is characteristic of complexes of this metal with oxo ligands) and the appearance of the ferromagnetic interaction. For the Cu-containing OMS **13** with a framework structure similar to that of compound **17**, the obtained dependence of $\chi \cdot T$ on T (Fig. 4)[12] is similar to that observed for the Co-containing OMS (see Fig. 3): the antiferromagnetic region is absent. As for the Co-containing OMS, in this case, the Cu—O—Cu angle is small (91.5—94.1°) and, according to this, the ferromagnetic interaction (J_f = 42 cm^{-1}), which was not observed previously for Cu ions surrounded by O atoms, is detected.

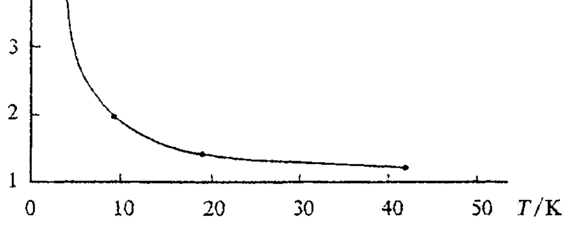


Fig. 3. Dependence of the magnetization on T for compound **17**.

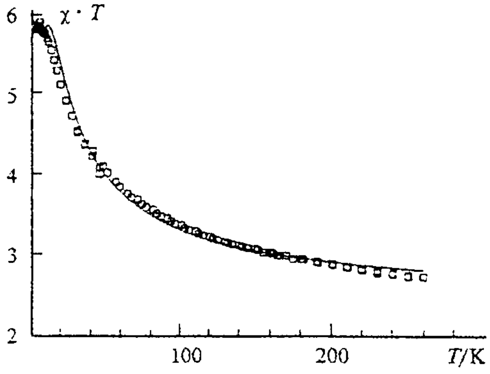


Fig. 4. Dependence of $\chi \cdot T$ on T for compound **13**.

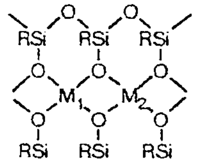


Fig. 5. Structural fragment of metallosiloxane. R = Ph; M_1 = M_2 = Cu (**18**), M_1 = Cu, M_2 = Zn (**19**).

When solvents of crystallization are removed, compounds of **13** and **17** types lose their crystalline structure (become X-ray amorphous); however, the main structural fragments (Fig. 5) are retained.[30]

The study of thus obtained compounds containing Cu atoms (**18**) and alternating Cu and Zn atoms (**19**) shows[32] that the Cu atoms are organized in clusters with the spin-spin exchange (analysis of the shape and width of the singlet ESR line). A partial replacement of paramagnetic Cu ions by diamagnetic Zn atoms in the structure of OMS decreases the fraction of the ESR absorption caused by Cu clusters. In these compounds, the μ_{eff} values increase as the temperature decreases (Table 4) and approach μ_{theor}. This shows a decrease of the contribution of antiferromagnetism, unlike binuclear Cu-containing OMS (see Table 3) for which an opposite tendency is clearly seen.

Thus, the ferromagnetic organization of metal atoms in polynuclear crystalline compounds is mainly determined by the structural parameters of the compound, more exactly, by the value of the M—O—M angle in the framework molecule.

Table 4. Magnetic moments of Cu- (**18**) and Cu,Zn-containing (**19**) phenylsiloxanes

Compound	μ_{eff}/μ_B		μ_{theor}/μ_B*
	297 K	4.2 K	
18	1.56	1.72	1.73
19	1.42	1.62	1.73

* For the d^1-electronic configuration of Cu^{II}.

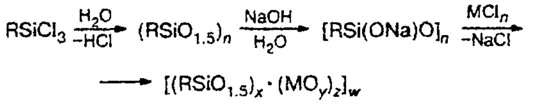
Metal-containing polymeric systems

Metal-containing polymeric systems are attractive due to their wide possibilities for chemical design of ferromagnets.[33,34] For example, their synthesis can be controlled in such a way that paramagnetic M ions would be joined in a single spin system. Another specific feature of polymeric systems is the fact that the distance between M atoms is described by a broad distribution and the exchange interaction appears in coordination clusters, which differ in size and are formed of —M—O—M— fragments in the case of polyorganometallosiloxanes (POMS). The number and configuration of these fragments are determined by the metal content in the polymer and specific conformational features of the polymeric chains.

In POMS, metal atoms are separated by isolating organosiloxane fragments. The exchange interaction between the atoms can be "switched on" by different ways: a) by purely synthetic methods (gradually incorporating metals into the polyorganosiloxane chain and forming structures of a certain type, b) by the creation of "conducting" bridges in the polymer, which can switch on the exchange interaction between metal atoms, and c) by removal of isolating fragments between metal atoms, for example, by thermochemical or reductive processes.[35]

The Fe- and Co-containing POMS were synthesized by the known[36] scheme (Scheme 2).

Scheme 2

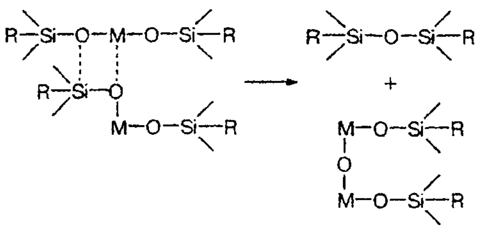


$$RSiCl_3 \xrightarrow[-HCl]{H_2O} (RSiO_{1.5})_n \xrightarrow[H_2O]{NaOH} [RSi(ONa)O]_n \xrightarrow[-NaCl]{MCl_n} [(RSiO_{1.5})_x \cdot (MO_y)_z]_w$$

R = Ph, CH_2=CH; M = Fe, Co; z/x = M/Si; y is metal valence

The polymers obtained were fractionated to yield fractions in which the M/Si ratio varied within 0.4—2.9. The metallosiloxane —RSi—O—M—O—SiR— fragments predominate in POMS with the atomic ratio M/Si ≤ 1. When the M/Si ratio becomes >1, metallosiloxane fragments of the —O—M—O—M—O— type appear in the structure of POMS. The rearrangement of polymeric chains (Scheme 3) is one of the possible ways to form the —O—M—O—M—O— group.

Scheme 3



A procedure for additional incorporation of M atoms into the POMS structure has been developed recently.[36] This allows one to obtain highly metallized systems, in which the M/Si ratio reaches 2.9. Evidently, the magnetic properties are determined by the M—O—M fragments and larger metalloxane clusters, because the strong exchange interaction between metal atoms should appear in these fragments.

The presence of metalloxane and siloxane fragments in polyferrosiloxanes and, as a consequence, the nonequivalence of the Fe atoms were established by the analysis of the Mössbauer (γ-resonance) spectra,[36,37] which exhibit three doublets.

The values of the isomeric shift (0.36 at 300 K and 0.45 at 80 K) are equal for all three doublets and typical of high-spin compounds of Fe^{3+} with coordination number equal to 6.[38] The existence of three doublets with different quadrupole splittings indicates that there are three types of coordination centers of the high-spin Fe^{3+} ions, each of which is the center of an asymmetrical octahedron. The distortion of symmetry of the octahedra is explained by the nonequivalence of the O atoms, which fill the coordination sphere. According to the accepted chemical concepts, the POMS contain O atoms of at least four different types: ≡Si—O—Si≡, ≡Si—O—H, ≡Si—O—M=, and =M—O—M=. One of the variants of filling the coordination sphere is shown Fig. 6. The ratio of different forms of iron, *i.e.*, the ratio of doublets, depends on the Fe/Si ratio. For the compound containing the greatest amount of iron (38.5% Fe; Si/Fe = 2.6), broadening of the doublet signal by 37% is observed at 25 K, which indicates that there is the magnetic organization of clusters of higher order, *i.e.*, clusters containing more than two metal atoms.[37]

The ESR spectra of the Fe-containing POMS (singlet with g = 2.003—2.006)[36] correspond to the spectra

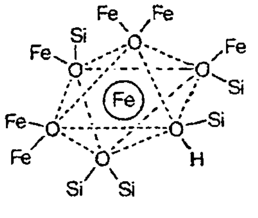
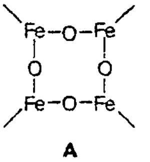


Fig. 6. Example of a possible filling of the coordination sphere of the metal in polyferrosiloxanes.

of Fe^{3+} ions (high-spin d^5-configuration) in a low crystalline field. The Mössbauer spectral studies also showed that the Fe-containing POMS contain no aggregated iron oxides, ferric chloride, which is a starting material for the preparation of Fe-containing POMS, hydrated ferric chloride, and finely dispersed iron oxide.[39] These observations are especially important for analysis of the magnetic properties. The measurements of the magnetic susceptibility and magnetization established[36,40] that for compounds with Fe/Si = 0.4—1.8, the dependences of the magnetization of Fe-containing POMS on the external magnetic field at 77 and 296 K obey the Curie law, and the temperature has no effect on μ_{eff}. For compounds with Fe/Si = 1.8—2.1, the magnetic moment is also constant and temperature-independent (μ_{eff} = 3.6±0.1 μ_B). This observation agrees with the previously mentioned properties of the binuclear ferroxanes with the oxide, hydroxide, and alkoxide bridges.[41,42] The properties of the polymers with Fe/Si ≥ 2.1 are unusual.[43] First, μ_{eff} increases as the Fe/Si ratio increases. Second, μ_{eff} increases as the temperature decreases, and the difference in μ_{eff} values at 77 K and 296 K increases as Fe/Si increases (Fig. 7). Thus, an increase in the content of Fe results in an increase in the contribution of the ferromagnetic component. This interaction is not strong enough to appear as a macroscopic effect, but it is sufficient to cause a change in μ_{eff} in the metalloxide Fe—O—Fe clusters. The fact that the magnetic moment increases as the temperature decreases indicates than the average spin density of unpaired electrons in the cluster increases and the main state of the cluster is a high-spin state. The appearance of the high-spin state at the predominant antiferromagnetic coupling can be explained in terms of spin frustration. This phenomenon appears in molecular systems with two or more possible ways for exchange interaction.

For example, type **A** clusters exhibit only one route of the transfer of the antiferromagnetic interaction when the signs of the spin density are variable, the overall spin is equal to zero, and the main spin state is singlet. In type **B** clusters, the routes of the transfer of the exchange interaction are branched due to the existence of the tricoordinated bridged O atom. The exchange interaction *via* the central and peripheral bridges can differ. If the exchange interaction of the central Fe ion is more strongly transferred *via* the bonds of the central fragment than the same interaction is transferred *via* the peripheral route, the high-spin state of the cluster is stabilized. In the opposite case, the low-spin state is stabilized. A similar behavior was observed[41] for the cyclic hexanuclear ferro complex $(Fe_6(O)_2(OH)_2(OAc)_{10}(C_{10}H_{13}N_4O)_2)\cdot CH_2Cl_2$.



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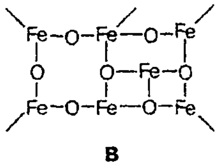


B

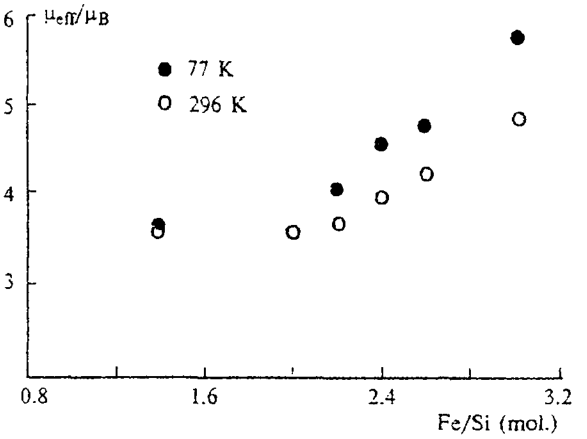
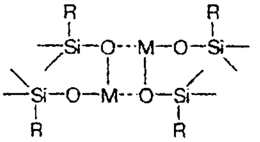


Fig. 7. Dependence of the magnetic moment on the Fe/Si ratio.

A specific feature of the structure of POMS should be noted. In addition to the metalloxane M—O—M clusters formed in the polymer upon rearrangement (see Scheme 3), coordination clusters appear in the polymer structure due to the interchain coordination.



The formation of additional M—O—M groups occurs. The coordination M···O bonds are structurally equivalent to σ-M—O bonds appearing during the synthesis. As in the case of the ferrosiloxane dimer (compounds **3** and **4**), these bond lengths are equal and the M—O—M angles involving bonds of both types are the same. Despite the fact that these bonds are structurally indiscernible, they can be distinguished. When solutions of siloxanes **3** and **4** are diluted, the coordination bonds are cleaved, and the compound becomes monomeric.

The effects on the magnetic properties of intrachain (appeared in the synthesis) and interchain (coordination) clusters can be similarly distinguished by the imitation of dilution of Fe atoms by organosiloxane fragments, *i.e.*, studying the systems in which the content of Fe changes. Polyferrophenylsiloxanes, whose Fe/Si value varies within a wide range from 0.18 to 2.63 (the content of Fe is 7.9—38.5%), were studied.[44] The temperature dependences of the magnetic susceptibility for two compounds of the series indicated[44] are shown in Fig. 8. The qualitative analysis of the magnetic properties leads to the following conclusions. For all compounds, the dependence of χ on T can be divided into two components. The first region is the antiferromagnetic component (a sharp decrease in the region of 50 K). This region of the experimental dependence is the same for all compounds studied. The second region is the ferromagnetic component in the 50—296 K range. The character of this region is distinctly related to the polymer composition: the higher the Fe/Si value, the more pronounced the ferromagnetic component. It has been shown

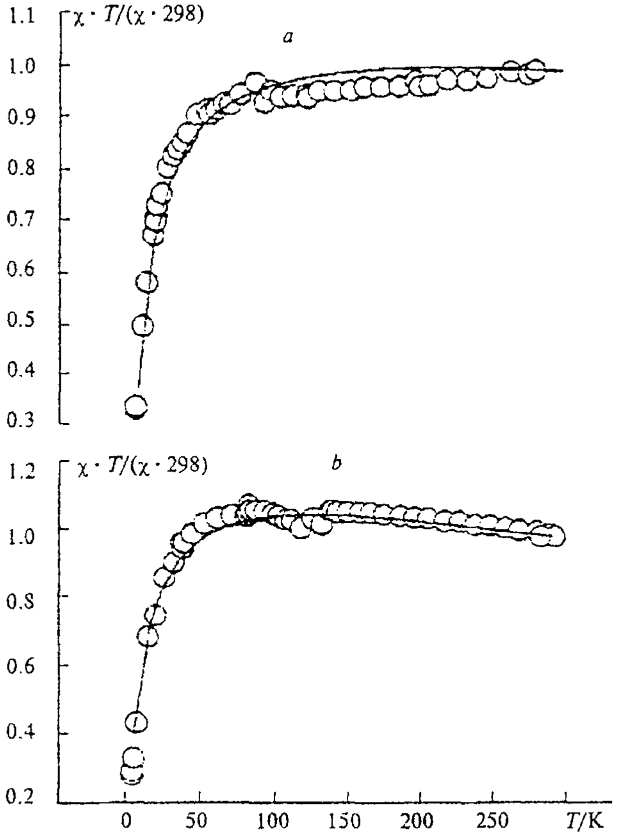


Fig. 8. Dependence of χT on T for two polyferrosiloxanes with the content of iron of 8% (*a*) and 29% (*b*).

previously that the content of intrachain clusters increases as Fe/Si increases. Thus it can be concluded that the ferromagnetic behavior of Fe-containing POMS is mainly determined by intrachain clusters. It should be mentioned, concerning interchain coordination clusters, that their formation is not always possible, and the possibility is independent of the polymer composition. Thus, the constant parameter (antiferromagnetic component) is related to interchain coordination clusters.

Both components were quantitatively characterized,[37] and the experimental data were compared with the theory, which is based on the model of randomly appearing pairs involved in the exchange interaction.[45,46] The pairs of Fe^{3+}—Fe^{3+} ions with spins 5/2 were considered. Taking into account the polymeric nature of the objects (random distribution of Fe^{3+} ions in the system), the probability function of the distribution of pairs over the exchange potential was introduced into the calculation model.[47] For all compounds except those with the maximum content of Fe, a good coincidence of the calculated and experimental data (see Fig. 8) was obtained, which indicates that the chosen "pair" model is adequate. The calculated values of the exchange interaction constant J are presented in Table 5. The ferromagnetic contribution J_f for all compounds studied is almost an order of magnitude higher than the antiferromagnetic contribution (J_{af}). This conclusion is unusual because it demonstrates a decrease in J_f as the content of Fe increases. This is also shown by the change in the parameter $n' = 4\pi n/\lambda^3$ in Fig. 9. Here n is the density of spins (their number per unit volume of the polymer), λ is the parameter of the exchange potential J in the pair model of spins, and $J = J_0 \cdot \exp(-\lambda r)$, where r is the interspin distance. Despite the fact that the density of spins n increases as the content of Fe increases, the parameter n' decreases. This means that the parameter λ increases, *i.e.*, the distribution of ion pairs takes such a form that the fraction of pairs with a small inter-ion distance decreases, and the effective exchange potential becomes shorter-range.

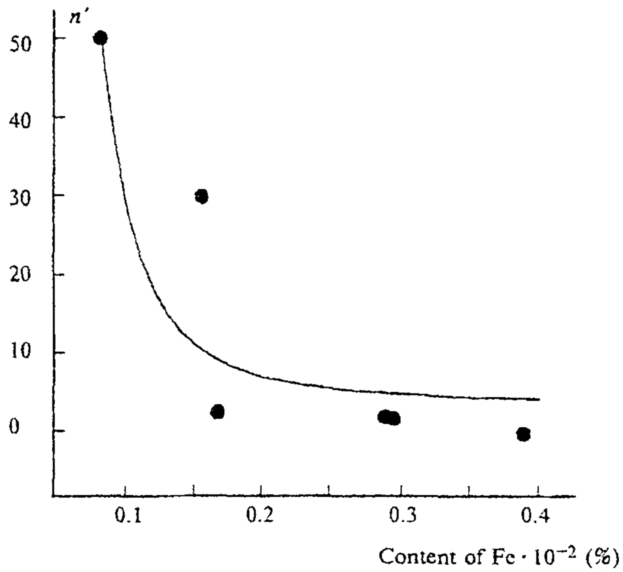


Fig. 9. Dependence of the parameter n' on the content of Fe in polyferrosiloxanes.

The results obtained indicate the direction of further research in the area of synthesis. Undoubtedly, a substantial increase in the metal content in the siloxane chain is not reasonable. The fractions with a low metal content (8—16% Fe) are of the greatest interest. It is likely that these are precisely the systems in which the optimum magnetic properties are formed for the struc-

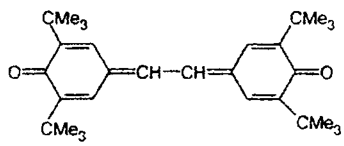
Table 5. J values for Fe-containing POMS

Content of Fe (%)	Fe/Si	J/K
7.9	0.18	70
15.4	0.49	65
16.7	1.11	33
29.4	1.56	31
28.8	1.61	28
38.5	2.63	4

ture with the long-range exchange potential, which organizes many Fe^{3+} ions in a single spin system (in any event, more ions than in polymeric fractions with a high iron content). Of course, it is of interest to study partial fractions of this group of compounds. It can be assumed that the formation of intrachain pairs of Fe^{3+} ions depends on the concentration of the metal in the system. Thus, the gradual incorporation of M into the siloxane chain will make it possible to develop favorable conditions for the formation of ferromagnetic structures. Another way is by blocking the interchain coordination by the introduction of organic ligands to the metal, *i.e.*, decreasing the antiferromagnetic contribution.

The dependence of χ on T was also studied for six Co-containing compounds[37,44] (content of cobalt 5.1—24.6%). For Co compounds, unlike Fe compounds, the magnetic susceptibility is independent of the content of Co, and all experimental points are described by a single temperature dependence, which is similar to that established for structurally organized cobaltphenylsiloxane (see Fig. 3). For the Co-containing POMS studied, the averaged value $J_f = 1.5$ K. The magnetic behavior of the Fe-, Co-containing POMS is also characterized by the fact that the ferromagnetic interaction is predominant in these compounds.

Another way of developing ferromagnets based on POMS is the organization of M atoms in a single exchange-coupled system with the ferromagnetic arrangement of spins,[48] which can be achieved by the introduction of conjugated organic compounds in POMS. These conjugated compounds coordinate M atoms and allow a high electronic "conductivity" between them. Stilbenediquinone **20**, *p*-nitrobenzene, *p*-benzoquinone, and nitroxyl radical **21** were studied as such additives.



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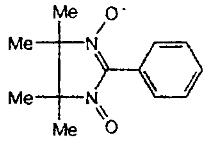

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Each of these molecules, being a bidentate ligand, can coordinate two M atoms. This results in the formation of a network of metalloatoms connected by bridges of conjugated bonds including the exchange interaction between the M atoms. The quantity of the additive was 5—11 moles of organic compound per Fe atom. The experiment showed that when the additives are introduced into the Fe-containing POMS (content of Fe 15.4%), for which the dependence of the magnetization on the external field is rigorously linear, an additional magnetization appears as a deviation from the linear dependence in low fields (1—4 kG). The additional magnetization is small, because the coordinating compounds organize the M atoms with a fixed distance determined by the size of the organic molecule. Since in polymers the set of M···M distances is rather wide, the organization of M atoms requires a series of coordinating molecules with different lengths. This direction is promising for the development of organometallic ferromagnets.

In all cases considered, we discussed the ferromagnetism at the microlevel when the exchange interaction constant J has a positive value. However, POMS make it possible to achieve a ferromagnetic macroeffect. The simplest approaches based on the principle of partial removal of isolating Si—O—Si fragments between M atoms were studied. The high-temperature condensation of POMS in an inert atmosphere in the 400—800 °C temperature range results in its partial thermal decomposition. The thermal condensation at 400 °C results in the rearrangement of the structure of the coordination Fe^{3+} centers and partial reduction of Fe^{3+} to Fe^{2+} without formation of ferromagnetic products. As the temperature increases from 550 to 800 °C, the depth and rate of the reduction of Fe increase sharply.[49] At the final stages, magnetically ordered structures of α-Fe dispersed in the SiO_2 matrix and iron carbides are formed. Only organic groups at the Si atom are involved in these processes, and the M/Si ratio in the products obtained remains the same as in the initial polymers.[50] The scheme of the formation of the ferromagnetic phase upon pyrolysis includes several stages of radical reactions. The first stage is the thermal homolysis of the Si—C bond with the generation of free radicals:

$$\equiv Si{-}Ph \longrightarrow \equiv Si^{\cdot} + {}^{\cdot}Ph.$$

Then the chain process of the β-scission of the free radicals occurs (Scheme 4) resulting[50] in the formation of the reduced Fe and SiO_2 phase.

In polyferrophenylsiloxanes,[49] the degree of reduction of Fe reaches 20—46%. Some organic groups (13—17%) remain in the pyrolyzed residue in the form of condensed polyaromatic structures. The process occurs similarly for Co-containing POMS and mixed Fe-, Co-containing POMS. The compounds formed are ferromagnetic, and they exhibit the saturation of the magnetization already in low fields, lower than 10 kG

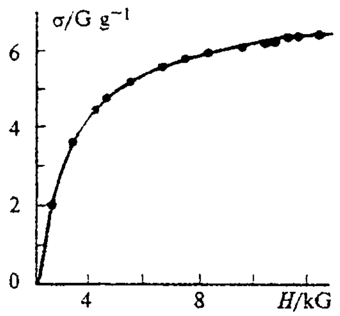
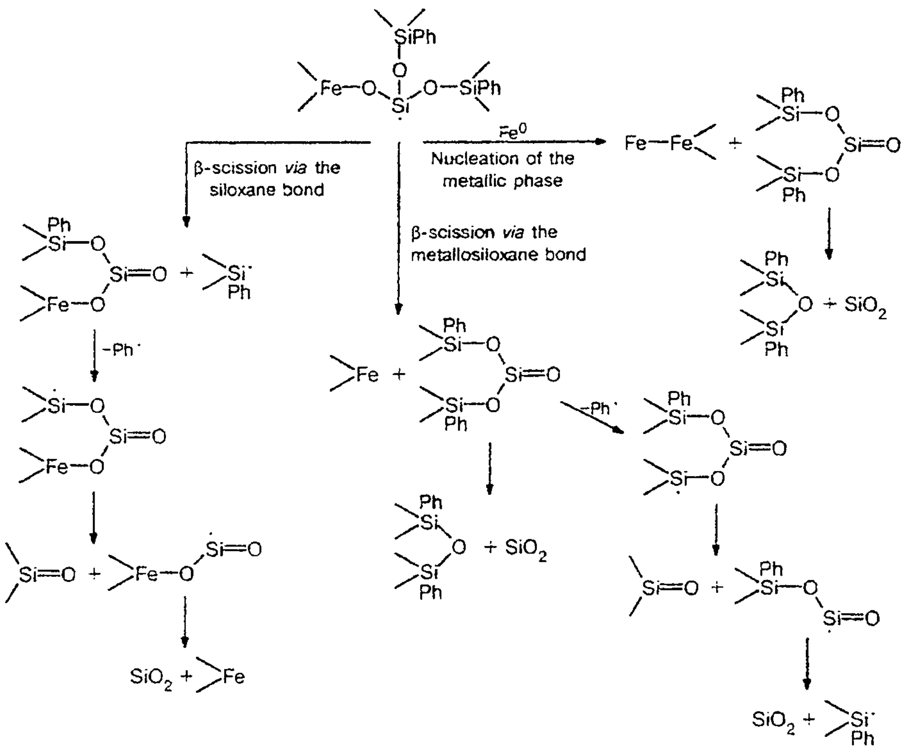


Fig. 10. Dependence of the magnetization on H for Fe-containing POMS.

Scheme 4



(Fig. 10). The specific magnetization σ varies[51] within 6—35 G g^{-1} depending on the composition of the initial compound. However, this value does not have high information content, since it does not take into account the metal content in the initial compound. On going to the molar magnetization σ′, it is established that this parameter depends regularly on the atomic Si/M ratio in the initial compound (Fig. 11).

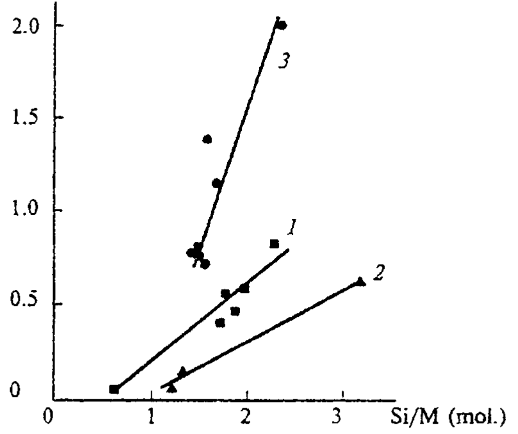
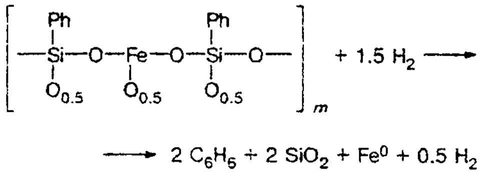


Fig. 11. Dependence of the magnetization of saturation on the Si/M ratio for Fe- (*1*), Co- (*2*), and Fe-, Co-containing (*3*) POMS.

The experimental points are arranged in three groups. In all cases, the dependence of σ′ on Si/M is close to linear, which indicates that the depth of reduction of M increases as Si/M in the polymer increases. For the compound with Si/Fe = 2.4, the magnetization is equal to 8000 G mol^{-1}, which is close to the magnetization of pure iron (~12000 G mol^{-1}). In the reduction of the mixed Co-, Fe-containing POMS, Co catalyzes the reduction of Fe. For the compound with Fe/Co = 0.4, the quantity of Fe^{3+} is equal[51] to 11.1%, and that of Fe^0 is 88.9%. The magnetization of this compound is much higher than that of pure iron and equal to 13900 G mol^{-1}. The formation of the metallic Fe—Co phase also makes a contribution to the magnetization.

The ferromagnetic phase can be obtained under milder conditions, for example, by the reduction of metals in the siloxane chain by hydrogen (p = 30—50 atm, T = 230—350 °C)[52] (Scheme 5). The degree of reduction of

Scheme 5



$$\left[-\underset{O_{0.5}}{\overset{Ph}{Si}}-O-\underset{O_{0.5}}{Fe}-O-\underset{O_{0.5}}{\overset{Ph}{Si}}-O-\right]_m + 1.5\,H_2 \longrightarrow 2\,C_6H_6 + 2\,SiO_2 + Fe^0 + 0.5\,H_2$$

iron is 31—50%, and the resulting products contain no polyaromatic compounds, which appear in pyrolytic processes. When metal atoms of different natures are present in the siloxane chain, the degrees of their reduction are different according to the reduction potential. This provides an additional possibility for controlling the composition of the reduction products and their magnetic properties.

It can be concluded that there is no single universal method for the achievement of the ferromagnetic organization of metal atoms in organometallosiloxanes. In the case of polynuclear framework systems, the best results can be expected when the structural rigidity of the framework increases, which is accompanied by a decrease in the M—O—M angle. For polymeric systems, there are a wider range of possibilities, including purely synthetic approaches, which make it possible to form metalloxane clusters with the ferromagnetic interaction. The method of organization of metal atoms in a single exchange system by the incorporation of conjugated organic compounds into polyorganometallosiloxanes is undoubtedly promising as well.

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