Magnetic properties of metal oxide clusters linked by flexible chain siloxane fragments

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Oligomeric copperdiorganosiloxanes differing in organic environment at the silicon atoms and in the Si/Cu ratio were synthesized. The magnetic properties of all compounds were shown to deviate from the Curie law. Unlike rigid chain oligomers characterized by antiferromagnetic interaction, coordination metal oxide clusters linked by flexible chain siloxane fragments exhibit ferromagnetic properties.

Key words: metal oxide clusters, metalorganosiloxanes, magnetic properties.

Magnetic properties of metalorganosiloxanes[1] have been studied up to the current point of using objects in which the metal atom is localized in the carcass structure of the individual crystalline compound or in the structure of rigid chain polymetalorganosiloxane (PMOS) based on trifunctional organosilicon $RSiO_{1.5}$ fragments. The magnetic properties of metaloxane clusters are determined by both the nature of the metal atom and their structural parameters,[1] which depend, to a considerable extent, on the rigidity of the matrix that contains the metal atoms. Flexible chain fragments linking metal atoms give great freedom to metaloxane fragments during formation of coordination clusters.

Results and Discussion

We studied the magnetic properties of oligo-copperdiorganosiloxanes, in which metal atoms are linked by diorganosiloxane fragments. The compounds were prepared by the exchange of diorganosilanolates of alkali metals with copper(II) halide (Scheme 1).

The exchange reaction is accompanied by rearrangement of the metathesis type,[2] resulting in the formation of products with an elevated and lowered (compared with the stoichiometrically expected) metal content. The compositions of the compounds obtained are presented in Table 1.

IR spectra (Fig. 1) of oligomers 1 and 3 contain a narrow intense band at 800 cm^{-1} (Si—Me), a band at 750 cm^{-1} (Me), and a band at 960 cm^{-1} (Si—O—M), which has (for compound 1) a partial resolution against the background of a broad band in a region of 1100—1000 cm^{-1} (Si—O—Si). The spectra of oligomers 2 and

Scheme 1
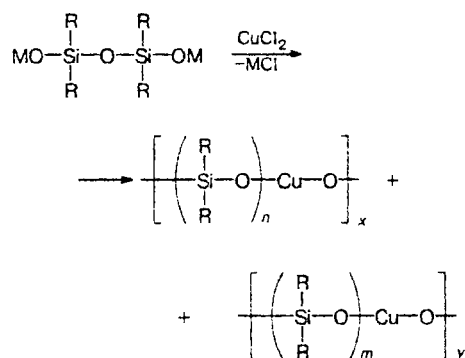
R = Me, M = K; R = Ph, M = Na;
Cu/Si = 1/n to 1/m (see Table 1)

4 exhibit a narrow intense band at 1130 cm^{-1} (Ph—Si) and bands at 730 and 680 cm^{-1} (monosubstituted phenyl ring). Absorption bands at 960 cm^{-1} (Si—O—M) and 1100—1000 cm^{-1} (Si—O—Si) are similar to the corresponding bands in the spectra of oligomers 1 and 3

Table 1. Composition of compounds under study

Oligomer	Fragment of unit	Yield (%)	Cu/Si*
1	—(Me$_2$Si—O)$_{3.1}$—Cu—O—	61.0	0.32
2	—(Ph$_2$Si—O)$_{2.8}$—Cu—O—	60.9	0.36
3	—(Me$_2$Si—O)$_{0.5}$—Cu—O—	22.0	2.0
4	—(Ph$_2$Si—O)$_{0.4}$—Cu—O—	14.7	2.5

* Atomic ratio.

Fig. 1. IR spectra of oligomers 1—4. Numeration of spectra corresponds to numbers of compounds in Table 1.

(the spectral bands were assigned according to data in Refs. 3 and 4). The electronic spectra of oligomeric 1 and 2 exhibit a band in the 690—705 nm region characteristic of d—d transitions in Cu^{II}.[5]

During the structure formation, polymetalorganosiloxanes can form clusters of two types.[6] The first type is represented by intrachain clusters —O—M—O—M—, in which metal oxide fragments are linked by simple valence bonds. They appear due to intermolecular rearrangements.[2] The second type is represented by clusters formed due to interchain coordination. They can be formed both inside one molecule and due to intermolecular coordination. Such PMOS clusters can appear regardless of the presence of absence of intrachain metaloxane fragments.
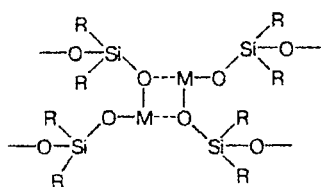
The previous structural studies[7,8] of compounds with the atomic ratio $M/Si \leq 0.5$ indicate that they contain no intrachain clusters, and the metal atoms are united to form exclusively in interchain coordination clusters. Comparison of the spectral parameters of the oligomers obtained shows that the spectra of the compounds with $M/Si \geq 1$ (3, 4) do not contain the absorption band at 1100—1000 cm^{-1} corresponding to vibrations of the Si—O—Si group. Therefore, the major portion of copper atoms are in the composition of intrachain copperoxane clusters —O—M—O—M—O—, whose average size determined by the number of copper atoms can be estimated from $M/Si = 2.0$—2.5.

It has previously been shown[9] that the clusters of both types have different effects on the magnetic properties of PMOS containing metal atoms in the rigid siloxane matrix. Intrachain clusters define the ferromagnetic behavior, and the antiferromagnetic organization is related to interchain clusters.

The oligomers obtained in this work make it possible to consider the same problem for systems with flexible chain siloxane fragments. The results of magnetic measurements are presented in Table 2.

The effective magnetic moment (μ_{eff}) was calculated per unit Cu^{II} ion and compared with the theoretical value (μ_{theor}) for the copper ion with d^9-electron configuration. A linear dependence of the magnetization on the external field strength within the 0—10 kG range is observed for all compounds under study.

Analysis of the results obtained allows one to distinguish two effects. The first effect is a deviation from the Curie law. At 297 K in the oligomers, $\mu_{eff} < \mu_{theor}$ (for 1, $\mu_{eff} = \mu_{theor}$), which indicates a noticeable contribution of the antiferromagnetic interaction between ions. The μ_{eff} values increase with temperature decrease, which indicates the decline of the antiferromagnetic interaction, so that oligomers 3 and 4 become almost pure paramagnetics. In this case, we cannot speak about the influence of flexible chain fragments on the formation of metal oxide clusters, because these compounds, as mentioned above, consist of the Si—O—M and M—O—M fragments. They contain almost no Si—O—Si groups due to the high atomic Cu/Si ratio. A different magnetic behavior is observed for compounds 1 and 2 containing, as mentioned above, Si—O—Si units and

Table 2. Magnetic moments (μ_{eff}) of Cu^{2+} ions in oligocopperdiorganosiloxanes

Oligomer	μ_{eff}/μ_B*		Cu/Si **
	297 K	80 K	
1	1.72	2.63	0.32
2	1.68	2.58	0.36
3	1.45	1.69	2.0
4	1.55	1.71	2.5

* In all cases, $\mu_{theor} = 1.73 \mu_B$.
** Atomic ratio.

interchain clusters. In these oligomers, the μ_{eff} value exceeds (at 80 K) the theoretical value for isolated Cu^{2+}, which indicates the formation of a structure with predominant ferromagnetic interaction. This basically distinguishes the systems under study from those of the rigid chain copperorganosiloxanes studied previously,[1] for which exclusively antiferromagnetic interaction was observed.

The main conclusions can be formulated as follows. Copper atoms in oligomers 1—4 are unified into clusters in which the exchange interaction includes both ferromagnetic and antiferromagnetic components. The predominant ferromagnetic interaction is observed in systems in which the atomic content of copper is comparable with silicon content (or even lower) and coordination interchain clusters are linked by flexible chain siloxane fragments.

Note the found dependence of magnetic ordering on the atomic Cu/Si ratio. At a high value of this ratio, the direct exchange interaction of ions predominates, which results in antiferromagnetism or paramagnetism (at low temperatures); the indirect (through —OSiO— bridges) ferromagnetic interaction of ions and ferromagnetic alignment of spins predominate at a low copper content and low Cu/Si ratios. Thus, the strategy of decreasing antiferromagnetic and increasing ferromagnetic contributions becomes clear: a change in the composition of the main oligomer chain and, perhaps, organic surroundings of silicon, which will be studied in more detail elsewhere.

Experimental

IR spectra were recorded on a Specord M-82 spectrometer in suspensions in Nujol between KBr plates. UV spectra were recorded on a Specord M-40 spectrophotometer within the 180—500 nm range in a 0.1-cm cell.

Magnetic measurements were carried out on a microbalance (Setaram, MTB-8). The μ_{eff} values (in μ_B) were calculated by the Curie formula: $\mu_{\text{eff}} = \sqrt{3kT\chi/(Nm)}$, where χ is the specific magnetic susceptibility of the sample, k is the Boltzmann constant, T/K is temperature, N is Avogadro's number, and m is the number of g-atoms of metal in the weighed sample.

Synthesis of oligomers (1—4). Starting dipotassium salts of oligodimethylsiloxanes and disodium salts of oligodiphenylsiloxanes were prepared by the procedures described previously.[10,11] A solution of $CuCl_2$ (1.35 g, 10 mmol) in Bu^nOH (10 mL) was added with stirring to a solution of dipotassium salt of tetramethyldisiloxanediol in a mixture of Bu^nOH (10 mL) and toluene (15 mL). The pH of the aqueous extract of the reaction medium was monitored during addition. After a neutral reaction was achieved, the reaction mixture was stirred for 1 h, KCl was filtered off, and the remaining solution was

concentrated *in vacuo* on a hot water bath to a half of the initial volume. The precipitate that formed was washed with cool Bu^nOH and dried *in vacuo*. Oligomer 3 was obtained in 22% yield (0.5 g). Found (%): Si, 12.1; Cu, 55.1. A double (v/v) amount of heptane was added to the solution obtained after separation of compound 3. The precipitate that formed was filtered off and dried *in vacuo*. Compound 1 was obtained in 61% yield (1.4 g). Found (%): Si, 27.4; Cu, 20.0. The reaction of disodium salt of tetraphenyldisiloxanediol (4.58 g, 10 mmol) with $CuCl_2$ (1.35 g, 10 mmol) was carried out similarly. Oligomer 4 was obtained in 14.7% yield (0.7 g). Found (%): Si, 7.0; Cu, 39.8. Compound 2 (2.9 g, 60.9%) was obtained by precipitating with hexane. Found (%): Si, 12.4; Cu, 10.0.

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