Investigation of structures of mono- and diorgano-substituted oligosiloxanes containing transition metal atoms

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Oligomeric linear copper-containing diorganosiloxanes with a variable Cu : Si ratio and branched Cu- and Ni-containing organosiloxanes containing the γ-aminopropyl group at the Si atom were investigated. IR spectroscopic studies demonstrated that the distribution of metal atoms throughout the metallosiloxane chain in compounds with a high metal content (M : Si $\geq$ 2) is rather uniform. According to the data from electronic spectroscopy, compounds under study are complexes of metal ions characterized by d—d transitions and an octahedral configuration of the coordination units. The Cu^{II} and Ni^{II} ions are coordinated by the NH_2 groups primarily through interchain interactions. ESR spectroscopic studies demonstrated that the Cu^{II} ions are located predominantly in the main chain to form —O—Cu—O— fragments. The coordination polyhedron changes from a nearly planar square (in the solid phase) to an elongated tetragonal bipyramid (in solution). The spectral parameters of the Cu-containing oligomer containing the γ-aminopropyl group at the Si atom indicate that the N atoms of the amino groups are located in the equatorial plane of the Cu-containing coordination polyhedron.

Key words: organometallosiloxanes; IR, UV, and ESR spectroscopy; structural studies.

Organometallosiloxanes (OMS) are compounds containing RSi—O—M—O fragments. The available procedures for the synthesis of OMS allow one to introduce atoms of different metals into the siloxane chain and to obtain compounds in which the Si : M ratio varies over a wide range. Recently, OMS containing transition metal atoms have been extensively studied as catalytic systems in organic synthesis.[1–5]

The catalytic properties of metal oxide clusters in OMS depend both on the nature of the metal atom and on their structural parameters, which are determined by the degree of rigidity of the siloxane matrix. Studies of the catalytic properties performed so far have been devoted to compounds in which the metal atom is involved either in the framework structure of individual crystal compounds or in the structure of rigid-chain OMS constructed from trifunctional organosilicon fragments $RSiO_{1.5}$. No analogous studies were carried out for compounds in which metal atoms are involved in linear flexible-chain siloxane fragments or for compounds containing a polar organic group at the Si atom. Therefore, one would expect that flexible-chain fragments that link metal atoms and polar groups at the Si atom will lend fresh features to the process of formation of metal oxide clusters. In the case of linear OMS, the presence of two substituents at the Si atom hinders the formation of framework structures typical of monoorgano-substituted OMS containing cyclofused fragments[6]; instead, the resulting compounds should have chain structures containing $-R_2SiO-M-O-$ fragments in which the coordination sphere about the metal atom is supplemented by the O atoms of the adjacent chains. The bonds that formed should be more labile than those in framework structures, thus favoring coordination of the reagents in catalytic processes. In compounds containing the functional group in the organic radical at the Si atom, the metal atom can be coordinated by the heteroatom of the functional group. Structural studies of this type of compounds are of interest because they will aid in revealing correlations between the structural features of OMS and their catalytic activities. In the present work, the structures of a series of OMS of the abovementioned two types were investigated.

Results and Discussion

The metallosiloxane group was constructed according to a general scheme of the exchange reaction of

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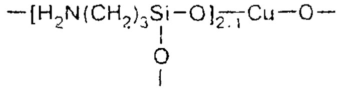
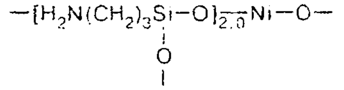
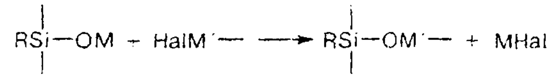
Table 1. Compositions of organometallosiloxanes

Compound	Fragment of the OMS unit	M	N	Si	M : Si	Yield (%)
		%				
1	$-(\mathrm{Me_2Si-O})_{0.5}-\mathrm{Cu-O}-$	55.1	–	12.1	2.0	22.0
2	$-(\mathrm{Me_2Si-O})_{3.1}-\mathrm{Cu-O}-$	20.0	–	27.4	0.31	61.0
3	$-(\mathrm{Ph_2Si-O})_{0.4}-\mathrm{Cu-O}-$	39.8	–	7.0	2.5	14.7
4	$-(\mathrm{Ph_2Si-O})_{2.8}-\mathrm{Cu-O}-$	10.0	–	12.4	0.36	60.9
5	$-(\mathrm{Ph_2Si-O})_{4.7}-\mathrm{Cu-O}-$	6.3	–	13.0	0.21	10.4
6	 $-[\mathrm{H_2N(CH_2)_3}\underset{\substack{\vert\\ \mathrm{O}\\ \vert}}{\mathrm{Si}}\mathrm{-O}]_{2.1}\mathrm{Cu-O}-$	20.2	9.2	18.6	0.48	75.1
7	 $-[\mathrm{H_2N(CH_2)_3}\underset{\substack{\vert\\ \mathrm{O}\\ \vert}}{\mathrm{Si}}\mathrm{-O}]_{2.0}\mathrm{Ni-O}-$	19.8	9.1	18.9	0.5	81.4

alkali metal organosilanolates with transition metal halides:



$$\underset{|}{\overset{|}{\mathrm{RSi}}}\mathrm{-OM} + \mathrm{HalM'}- \longrightarrow \underset{|}{\overset{|}{\mathrm{RSi}}}\mathrm{-OM'}- + \mathrm{MHal}$$

where M is an alkali metal and M′ is a transition metal.

Linear OMS (**1**—**5**) were prepared starting from dipotassium or disodium tetraorganodisiloxanediolates $\mathrm{MO-SiR_2-O-SiR_2-OM}$. The exchange reactions were accompanied by rearrangement[7] giving rise to OMS with a variable M : Si ratio. Branched OMS (**6** and **7**) were prepared from the sodium salt of polysiloxane containing the γ-aminopropyl group at the silicon atom, *viz.*, $[\mathrm{H_2N(CH_2)_3Si(O)ONa}]_n$. The compositions of the resulting compounds are given in Table 1.

The IR spectra of the resulting OMS are shown in Fig. 1. The spectral bands were identified based on the data reported previously.[8] The spectra of compounds **1** and **2** have absorption bands at 810 and 730 cm^{-1}, which confirm the presence of the Si—Me group. The spectra of linear copper-containing diorganosiloxanes **3**—**5** have a narrow intense absorption band at 1130 cm^{-1}, which is indicative of the presence of the Ph—Si group, and absorption bands at 720 and 680 cm^{-1} belonging to vibrations of the monosubstituted benzene ring. The spectra of branched OMS **6** and **7** have absorption bands at 3380 cm^{-1} (symmetric stretching vibrations of the $\mathrm{NH_2}$ group) and 750 cm^{-1} (wagging vibrations of the $\mathrm{NH_2}$ group). Vibrations of the Si—O—Si groups (in the region of 1100—1030 cm^{-1}) are observed for compounds **2** and **4**—**7**, characterized by a low metal content (M : Si ≤ 0.5). The Si—O—M fragment gives a well-resolved signal (at 980—950 cm^{-1}) in the spectra of compounds **1** and **3**, with a high metal content (M : Si ≥ 2). The absence of absorption bands characteristic of Si—O—Si groups in the spectra of these compounds indicates that the distribution of metal atoms throughout the chain is rather uniform; otherwise fragments with a predominant concentration of Si—O—Si and Cu—O—Cu groups should be observed, which should be reflected in the spectral patterns.

The electronic spectra (Table 2) of linear copper-containing oligodiphenylsiloxanes **3**—**5** have only one band in the red region. The position of this band depends only slightly on the composition of the polymer. The λ and ε values are typical of d—d transitions in the Cu$^{\mathrm{II}}$ ion possessing the d^9 electron shell and located in a distorted octahedron.[9,10] The spectral parameters of nickel-containing compound **7** correspond to the six-coordinate Ni$^{\mathrm{II}}$ ion with the d^8 electron shell.[11]

In the spectra of copper- and nickel-containing oligomers **6** and **7**, the band corresponding to the metal ion is regularly shifted as the concentration of these ions in solutions decreases. It is known[9] that the gradual replacement of a nitrogen-containing ligand involved in

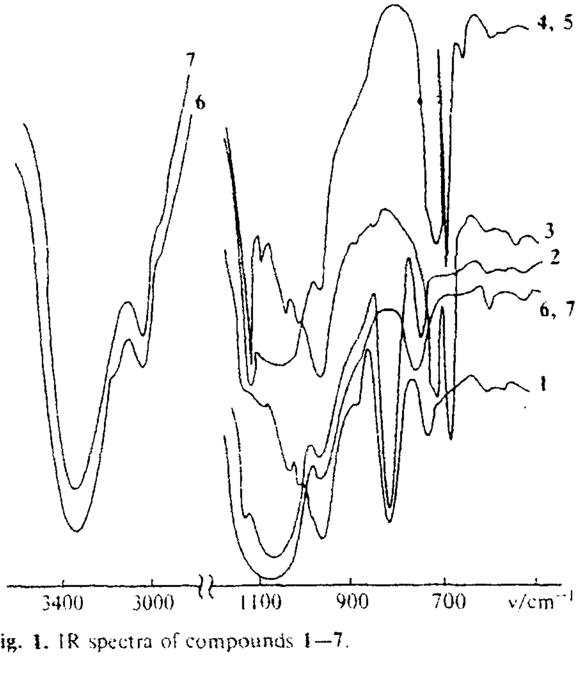


Fig. 1. IR spectra of compounds **1**—**7**.

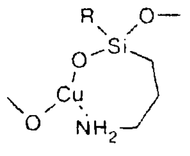
Table 2. Data from UV spectroscopy for compounds **3—7** (in butanol—toluene solutions)

Compound	$C \cdot 10^3$ /mol L^{-1}	λ/nm	ε*
3	4	760	34.5
4	5	740	30.2
5	5	740	32.8
6	5	700	42.5
6	2	720	41.7
6	1	760	39.1
7	5	350, 530	8.1, 6.2
7	3	370, 640	6.2, 4.3
7	1	390, 720	5.1, 2.0

* The ε values were calculated per mole of metal.

the coordination sphere about the metal atom by an oxygen-containing ligand results in a low-frequency shift of the corresponding bands. An analogous effect, *viz.*, shift to the low-frequency region as the concentration of oligomers **6** and **7** in solutions decreases (see Table 2), indicates that the coordination of the Cu^{II} and Ni^{II} ions by the NH_2 groups occurs primarily due to interchain interactions whose contribution depends on the concentration of OMS. Therefore, intramolecular coordination to form a chelate ring (of type **A**), which is seemingly quite probable, is not realized in the case under consideration.

Some characteristic features of the copper-containing oligomers were revealed from analysis of their ESR spectra (Fig. 2). The parameters of the spin-Hamiltonian calculated from these characteristics are given in Table 3.



A

The ESR spectrum of powdered compound **3** is characterized by triaxial anisotropy, which is indicative both of the nonequivalence of the ligand O atoms located along the *x* and *y* axes and of possible substantial distortion of the coordination sphere about Cu^{II}. Dissolution of compound **3** in *n*-butanol led to substantial changes in composition and structure of the coordination polyhedron about the Cu^{II} ion. The ESR spectrum at 77 K (see Fig. 2) is a superposition of signals of two types possessing axial symmetry (*i.e.*, equivalent coordination of the atoms of the ligands in the equatorial plane of the complex occurs). The spectral parameters (see Table 3) correspond to the structure of an elongated tetragonal bipyramid.[12,13] The $A_{\parallel}$ and $g_{\parallel}$ values for the major portion of paramagnetic Cu^{II} centers in a solution of **3** characterize copper complexes which can be represented as —Si—O—Cu—O—Si— fragments. The positions of the ESR lines for the complexes of the second type (these lines in the spectrum shown in Fig. 2 are marked with asterisks), whose portion is no higher than 15—20% of the total amount of the paramagnetic centers in the sample, coincide with the positions of the lines for the $CuCl_2$ complexes in methanolic solutions. We believe that the complexes of the second type are actually —Si—O—Cu(HOR)$_n$ compounds in which the O atoms of the siloxane groups are located in axial positions. It should be noted that the experimental $A_{\parallel}$ and $g_{\parallel}$ values (see Table 3) indicate that the coordination spheres about the Cu^{II} ions contain H_2O molecules,[14,15] which are generally present in small amount in MeOH.

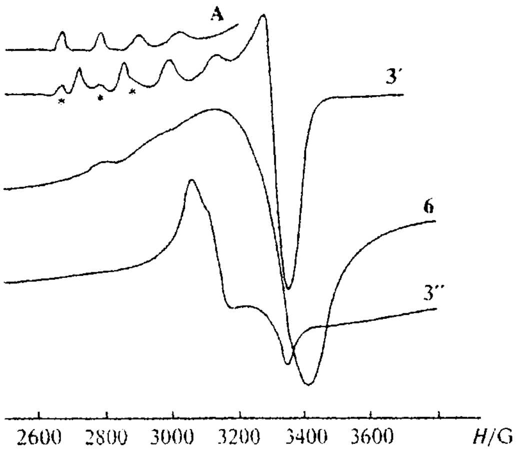


Fig. 2. ESR spectra: A, $CuCl_2$ ([Cu] = $5 \cdot 10^{-3}$ mol L^{-1}) in MeOH; 3′, in Bu^{n}OH; 3″, as a powder; **6**, as a powder (A, 3′, and **6** at 77 K; 3″ at 298 K).

Table 3. Parameters of the ESR spectra of organometallosiloxanes at 77 K (at 298 K, a solution in Bu^{n}OH)

Compound	$A_{\parallel}$±0.3/mT	g_1 ($g_{\parallel}$)*	g_2*	g_3 ($g_{\perp}$)*
3	—	2.247	2.190	2.048
3	—	2.247	2.191	2.053
6	17.1	2.265	—	2.095
3	13.7	2.353	—	2.084
$CuCl_2$ in MeOH	11.6	2.418	—	2.094
$CuCl_2 \cdot 2H_2O$ [10]	—	2.252	2.187	2.037
$CuSO_4 \cdot 5H_2O$ [10]	—	2.264	2.233	2.083

* g±0.005.

It is quite apparent that dissolution of compound **3** in Bu^{n}OH leads to a change in the character of the ESR spectra. The spectra of powdered **3** are analogous to those of many Cu^{2+} salts, for example, of $CuSO_4 \cdot 5H_2O$ and $CuCl_2 \cdot 2H_2O$,[12] and indicate that the solid compounds under study are characterized by a high local concentration of Cu^{II} ions. In solutions with an average concentration [Cu] = $5 \cdot 10^{-3}$ mol L^{-1}, the samples become magnetically dilute and the ESR spectra correspond to isolated mononuclear complexes in which the vacant positions in the coordination sphere of the —O—Cu—O— fragment are occupied by solvent molecules.

The ESR spectrum of oligomer **6** is characteristic of complexes with the octahedral ligand environment about the Cu^{II} ions (see Fig. 2). Large widths of the components of the spectrum are indicative of strong magnetic dipole-dipole interactions between copper ions. Based on an increase in the $A_{\parallel}$ parameter with a simultaneous decrease in the $g_{\parallel}$ value, it can be stated with assurance that the N atoms of the amino groups (see Table 1) are present in the equatorial plane of the coordination polyhedron.[16,17]

Comparison of our results with the data reported previously[3] shows that the uniform distribution of the metal atoms over the siloxane matrix and the UV spectral characteristics corresponding to d—d transitions in the Cu^{II} ion remain unchanged on going from rigid-chain OMS to compounds in which the metal atoms are linked through linear siloxane bridges. Differences are observed in the structural characteristics of the coordination unit. In the former case (rigid-chain OMS), the configuration is a nearly planar square with two additional O atoms remote along the z axis. In the latter case (flexible-chain OMS), the O atoms located along the x and y axes are nonequivalent. In this case, the coordination polyhedron is labile and changes from a distorted octahedron to a tetragonal bipyramid upon dissolution. It was also established that the amino group is coordinated to the metal atom primarily through interchain interactions. The N atom is involved in the coordination sphere about the metal atom and is located in the equatorial plane of the polyhedron. The above-mentioned structural features should be taken into account in studies of catalytic properties of the systems prepared in homogeneous and heterogeneous catalytic reactions.

Experimental

The IR spectra were recorded on a Specord M-82 spectrograph in Nujol mulls between KBr plates. The UV spectra were measured on a Specord M-40 spectrophotometer in the range of 300—900 nm for solutions of compounds in a butanol—toluene mixture (1 : 1, v/v; the concentrations of the solutions are given in Table 2).

The ESR spectra were recorded on a Varian E-3 radiospectrometer (3-cm range) using 4.0 mm-diameter thin-walled quartz tubes at 77 and 298 K.

The precise calibration of the magnetic field was performed using diphenylpicrylhydrazyl ($g = 2.0036$) and Mn^{2+} ions in an MgO matrix as the standards. The principal values of the g tensor ($g_{\parallel}$ and $g_{\perp}$), the constants of hyperfine interaction ($A_{\parallel}$) of the unpaired electron with the nucleus of the copper ion, and the g_1, g_2, and g_3 values for the complexes possessing triaxial anisotropy were determined from the ESR spectra according to a procedure reported previously.[18] The number of paramagnetic centers in the samples was determined using double integration of the ESR spectra relative to the auxiliary standard, *viz.*, a single crystal of $CuSO_4 \cdot 5H_2O$ with the known spin content.

Disodium and dipotassium tetraorganodisiloxanediolates, which were used as the starting compounds for the preparation of linear copper-containing OMS, were synthesized according to procedures reported previously.[19,20] The exchange reactions of alkali metal organosilanolates with copper halides were performed as described previously.[21] A solution of $CuCl_2$ (1.35 g) in BuOH (10 mL) was added with stirring to a solution of dipotassium tetramethyldisiloxanediolate (2.43 g, 10 mmol) in a mixture of BuOH (10 mL) and toluene (15 mL). In the course of addition, the pH of aqueous extracts of aliquots withdrawn from the reaction mixture was monitored. After the reaction mixture became neutral, it was stirred for 1 h, filtered from KCl, and concentrated to one-half of the initial volume *in vacuo*. The precipitate that formed was washed with cold butanol and dried *in vacuo*. Compound **1** was obtained in a yield of 0.5 g (22%). Found (%): Cu, 55.1; Si, 12.1. Heptane (twofold volume) was added to the solution obtained after separation of compound **1**. The precipitate that formed was filtered off and dried *in vacuo*. Compound **2** was obtained in a yield of 1.4 g (61%). Found (%): Cu, 20.0; Si, 27.4.

The reaction of disodium tetraphenyldisiloxanediolate (4.58 g, 10 mmol) with $CuCl_2$ (1.35 g, 10 mmol) was carried out analogously. The reaction solution was concentrated *in vacuo* and the precipitate that formed was filtered off. Compound **3** was obtained in a yield of 0.7 g (14.7%). Found (%): Cu, 39.8; Si, 7.0. Heptane (equal volume) was added to the solution remained after separation of compound **3**. The precipitate that formed was filtered off and dried *in vacuo*. Compound **4** was obtained in a yield of 2.9 g (60.9%). Found (%): Cu, 10.0; Si, 12.4. Heptane (twofold volume) was added to the solution obtained after separation of compound **4**. The precipitate that formed was filtered off and dried *in vacuo*. Compound **5** was obtained in a yield of 0.5 g (10.4%). Found (%): Cu, 6.3; Si, 13.0.

Branched copper- and nickel-containing OMS bearing the γ-aminopropyl group at the Si atom were prepared according to a known procedure.[22] Water (0.54 g, 30 mmol) and NaOH (0.4 g, 10 mmol) were added to a solution of $H_2N(CH_2)_3Si(OEt)_3$ (2.2 g, 10 mmol) in a mixture of butanol (10 mL) and toluene (10 mL). The reaction mixture was stirred for 0.5 h, after which the alkali completely dissolved and the solution became homogeneous. A solution of $CuCl_2$ (0.67 g, 5 mmol) in butanol (10 mL) was added with stirring to the reaction mixture. In the course of addition, the pH of aqueous extracts of aliquots withdrawn from the reaction mixture was monitored. After the reaction mixture became neutral, it was stirred for 1 h, filtered from NaCl, and concentrated to one-half of the initial volume *in vacuo* on a hot water bath. The precipitate that formed was washed with cold butanol and dried *in vacuo*. Compound **6** was obtained in a yield of 1.13 g (75.1%). Found (%): Cu, 20.2; N, 9.2; Si, 18.6. Compound **7** was obtained analogously from $H_2N(CH_2)_3Si(OEt)_3$ (2.2 g, 10 mmol), water (0.54 g, 30 mmol), NaOH (0.4 g, 10 mmol), and $CuCl_2$ (0.67 g, 5 mmol) in a yield of 1.77 g (81.4%). Found (%): N, 9.1; Ni, 19.8; Si, 18.9.

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References

1. V. S. Kulikova, M. M. Levitsky, and A. L. Buchachenko, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 3019 [*Russ. Chem. Bull.*, 1996, **45**, 2870 (Engl. Transl.)].
2. V. V. Smirnov, M. M. Levitsky, S. M. Nevskaya, and A. L. Buchachenko, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 209 [*Russ. Chem. Bull.*, 1997, **46**, 204 (Engl. Transl.)].
3. M. M. Levitsky, A. I. Kokorin, V. V. Smirnov, N. V. Karpilovskaya, A. V. Kudryashov, S. M. Nevskaya, and E. N. Golubeva, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1946 [*Russ. Chem. Bull.*, 1998, **47**, 52 (Engl. Transl.)].
4. V. S. Kulikova, M. M. Levitsky, A. F. Shestakov, and A. E. Shilov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 450 [*Russ. Chem. Bull.*, 1998, **47**, 435 (Engl. Transl.)].

5. V. V. Smirnov, M. M. Levitsky, S. M. Nevskaya, and E. N. Golubeva, *Kinet. Katal.*, 1999, **40**, 86 [*Kinet. Catal.*, 1999, **40** (Engl. Transl.)].
6. V. A. Igonin, O. I. Shchegolikhina, S. V. Lindeman, M. M. Levitsky, Yu. T. Struchkov, and A. A. Zhdanov, *J. Organomet. Chem.*, 1992, **423**, 351.
7. A. A. Zhdanov, M. M. Levitsky, A. Yu. D´yakonov, O. I. Shchegolikhina, A. D. Kolbanovskii, R. A. Stukan, A. G. Knizhnik, and A. L. Buchachenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2512 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2271 (Engl. Transl.)].
8. *Spektry i khromatogrammy elementoorganicheskikh soedinenii. Vyp. 2. IK- i UF-spektry siloksanov i silazanov* [*Spectra and Chromatograms of Heteroorganic Compounds. 2. IR and UV Spectra of Siloxanes and Silazanes*], Khimiya, Moscow, 1976, 46 pp. (in Russian).
9. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam—Oxford, 1982, 408 pp.
10. M. Koto, H. Jonnassen, and J. Fanniny, *Chem. Rev.*, 1964, **64**, 99.
11. J. Miller, *Adv. Inorg. Chem. Radiochem.*, 1962, B, 133.
12. S. A. Al´tshuller and B. M. Kozyrev, *EPR soedinenii elementov promezhutochnykh grupp* [*ESR Studies of Compounds Containing Elements of Intermediate Groups*], Khimiya, Moscow, 1972, 198 pp. (in Russian).
13. V. V. Saraev and F. K. Shmidt, *EPR metallokompleksnykh katalizatorov* [*ESR Studies of Metal-Complex Catalysts*], Izd-vo IGU, Irkutsk, 1985, 85 pp. (in Russian).
14. G. M. Larin, V. V. Minin, B. V. Levin, and Yu. A. Buslaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2725 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2470 (Engl. Transl.)].
15. A. I. Kokorin, E. N. Golubeva, N. A. Zubareva, V. I. Pergushov, S. N. Lanin, and A. A. Kuznetsova, *Zh. Fiz. Khim.*, 2000, **74**, 237 [*Russ. J. Phys. Chem.*, 2000, **74** (Engl. Transl.)].
16. J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys.*, 1974, **165**, 691.
17. A. I. Kokorin, K. I. Zamaraev, V. Y. Kovner, Yu. E. Kirsh, and V. A. Kabanov, *Europ. Polymer J.*, 1975, **11**, 719.
18. G. M. Zhidomirov, Ya. S. Lebedev, S. N. Dobryakov, N. Ya. Shteinshneider, A. K. Chirkov, and V. A. Gubanov, *Interpretatsiya slozhnykh spektrov EPR* [*Interpretation of Complex ESR Spectra*], Nauka, Moscow, 1975, 216 pp. (in Russian).
19. K. A. Andrianov and M. A. Sipyagina, *Izv. Akad. Nauk, Ser. Neorg. Mater.* [*Bull. Acad. Sci. USSR, Div. Inorg. Mater.*], 1968, **4**, 2016 (in Russian).
20. Pat. USA 3453304, 1969; *Chem. Abstrs.*, 1969, **71**, 50205g.
21. M. M. Levitsky, A. R. Arutyunyan, B. G. Zavin, V. V. Erokhin, and A. L. Buchachenko, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1691 [*Russ. Chem. Bull.*, 1999, **48**, 1670 (Engl. Transl.)].
22. A. A. Zhdanov, N. V. Sergienko, and E. S. Trankina, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2530 [*Russ. Chem. Bull.*, 1998, **47**, 2448 (Engl. Transl.)].

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