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Coordination Isomerism of the Complex of *o*-Methoxybenzoyl Chloride with Tetrachlorostannane. The Results of *ab initio* Calculations

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Abstract—Quantum-chemical calculations of three isomers of the *o*-methoxybenzoyl chloride complex with tetrachlorostannane and of their components were performed applying the RHF/3-21G* and MP2/3-21G* methods. It was found that a complex with trigonal–bipyramidal structure is formed, its formation occurred through the interaction of ester (not carbonyl) oxygen atom with tin atom. This complex eventually is transformed into the energetically more favorable *cis*-octahedral complex of the same composition. The tin atom in the latter complex interacts with two oxygen atoms. The reasons for the formation of energetically unfavorable complex of trigonal–bipyramidal structure is the almost equal probability of the existence of various possible forms of *o*-methoxybenzoyl chloride and therefore higher probability of the Sn atom to interact with the ester oxygen atom possessing a much more negative charge than the carbonyl oxygen.

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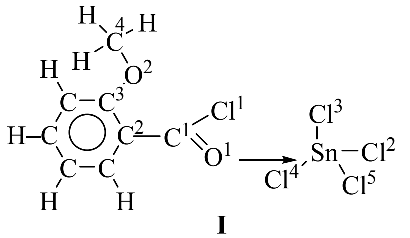
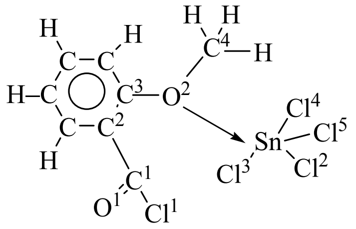
Earlier [1] using nuclear quadrupole resonance (NQR) we revealed the coordination isomerism of the complex *o*-$CH_3OC_6H_4COCl\cdot SnCl_4$. The ^{35}Cl NQR spectrum of the complex recorded immediately after its synthesis and crystallization consists of three lines (32.590, 23.305, and 19.994 MHz) with the intensity ratio 2:6:2 respectively. The high-frequency line in the spectrum belongs to the Cl atom in the COCl group. Its frequency is by 3.646 MHz higher than that of the individual *o*-$CH_3OC_6H_4COCl$ (28.944 MHz [1]). The most intense line of the low-frequency doublet in the spectrum belongs to the three equatorial Cl atoms, while the less intense one, to the axial Cl atom of the electron-acceptor part of complex. However, which of carboxylic oxygen atoms forms the coordination bond with the Sn atom at the complexation, the carbonyl (**I**) or the ester (**Ia**), is unclear. The NQR frequency of the Cl atom in COCl group of the complex of trigonal–bipyramidal structure is close to that in the $C_6H_5COCl\cdot SnCl_4$ (32.047 MHz [2]) and 4-$CH_3OC_6H_4COCl\cdot SnCl_4$ (33.228 MHz [2]) complexes. The carbonyl O atom in these complexes occupies an axial position of the trigonal bipyramid. Therefore, we may assume that the *o*-$CH_3OC_6H_4COCl\cdot SnCl_4$ complex (**I**) of trigonal–bipyramidal structure is formed as a result of interaction of the carbonyl O atom with the Sn atom.

The complex of trigonal–bipyramidal structure stored in the solid state at low temperature transformed into the *cis*-octahedral complex (**II**). In its ^{35}Cl NQR spectrum the two low-frequency lines of the low-frequency quadruplet (21.420, 20.788, 19.893, and 19.662 MHz) belong to two axial Cl atoms, and the two lines at higher frequency, to the equatorial ones. Two other equatorial positions of the octahedron are occupied by O atoms. The NQR frequency of the Cl atom in the COCl group (34.415 MHz) is by 5.471 MHz higher than that in the individual *o*-$CH_3OC_6H_4COCl$ [1].

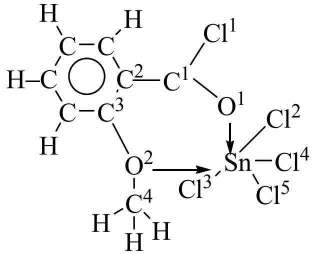
The transformation of the *o*-$CH_3OC_6H_4COCl\cdot SnCl_4$ complex of trigonal–bipyramidal structure into the *cis*-octahedral complex of the same composition at storing in the solid state is still a unique phenomenon, virtually unexplored. Therefore we found it expedient to reveal the coordination centers in the complex of trigonal–bipyramidal structure, to explore stereoelectronic structure of this complex and its energy characteristics by the non-empirical methods of quantum chemistry,



I



Ia



II

and to establish the cause of formation of different isomers of the complex, as well as to estimate the parameters of the ^{35}Cl NQR spectra of the complex from the results of these calculations and compare them with experimental data.

We performed the calculations using the RHF and MP2 methods on the level of the split and polarized valence basis set 3-21G* with the GAUSSIAN 03W program [3] for the possible isomers of the *o*-$CH_3OC_6H_4COCl\cdot SnCl_4$ complex and its individual components, as well as the vibration spectra of these molecules. Unfortunately, the standard basis sets of higher level for the Sn compounds are not available in this program package. However, the use of the basis 3-21G* also yields satisfactory results at the calculation of such compounds (e.g., see [4]). In the calculations, the coordinates origin was placed in the point of location of the Cl atom nucleus for which the NQR parameters we planned to estimate. The *z*-axis of the coordinate system coincided with the respective Cl–C or Cl–Sn bond.

Earlier [5–8] we have obtained satisfactory agreement between experimental and calculated NQR frequencies (ν) for the chlorine-containing organic and organometallic compounds, as well as the asymmetry parameters (η) of the electric field gradient (EFG) at the ^{35}Cl nuclei. In that case we estimated the ^{35}Cl NQR frequencies and asymmetry parameters using the Eqs. (1) and (2) [9], respectively. In the calculation we used not the full occupancy of the valence *p*-orbitals of Cl atoms, but that of their less diffuse 3*p*-components obtained in calculations of the molecules using the restricted Hartree–Fock method with the split and polarized valence basis 6-31G(d). A satisfactory consistence between the experimental and calculated ^{35}Cl NQR parameters of γ-chloropropyltrichlorostannane was also reached using the populations of 3*p*-components of valence *p*-orbitals of chlorine atoms obtained in the calculations by the RHF/3-21G* method [4].

$$\nu = (e^2Qq_{\rm at}/2h[-N_z + (N_x + N_y)/2](1 + \eta^2/3)^{1/2}, \quad (1)$$

$$\eta = |3(N_x - N_y)/(2N_z - N_x - N_y)|. \quad (2)$$

Here $e^2Qq_{\rm at}$ is the nuclear quadrupole coupling constants; *h* is the Planck's constant; N_x, N_y, and N_z are the tracer atom populations of 3*p*-components of valence p_x, p_y, and p_z orbitals, respectively. The value of $e^2Qq_{\rm at}/2h$ is found from the experimental NQR frequency of Cl_2 at 77 K and the population of 3*p*-components of valence *p*-orbitals of Cl atoms of the molecule calculated using an appropriate method [5–8].

Satisfactory fit between experimental and calculated ^{35}Cl NQR parameters can be used for revealing the coordination sites in the *o*-$CH_3OC_6H_4COCl\cdot SnCl_4$ complex of trigonal–bipyramidal structure. According to this method, using the population of 3*p*-components of the Cl valence *p*-orbitals obtained calculating the structures **I** and **Ia** by the RHF/3-21G* and MR2/3-21G* methods, we evaluated the ^{35}Cl NQR frequency and the parameters of electric field gradient (EFG) asymmetry on the ^{35}Cl nuclei of these structures (Table 1). When to estimate the NQR frequency of the Cl atom of the COCl group in the structure **I** we used

Table 1. Occupancy (*N*) of 3*p*-components of valence *p*-orbitals of chlorine atoms in the COCl groups in the structures **I**, **Ia,** and **II**, calculated by the RHF/3-21G* and MP2/3-21G* methods, and calculated from these populations the ^{35}Cl NQR frequency (ν) and asymmetry parameters (η) of the electric field gradient on the ^{35}Cl nuclei

Method	Form	N_x, *e*	N_y, *e*	N_z, *e*	ν, MHz	η, %
RHF/3-21G*	**I**	1.159	1.079	0.803	36.236	37.97
	Ia	1.134	1.082	0.821	32.540	27.18
	II	1.142	1.088	0.806	35.005	26.21
MP2/3-21G*	**I**	1.157	1.081	0.790	36.965	34.65
	Ia	1.132	1.079	0.805	33.491	26.46
	II	1.139	1.084	0.799	34.813	26.4

the results of calculations by both methods, the value obtained was significantly higher than the experimental one (Table 1). The calculated asymmetry parameter of EFG at the ^{35}Cl nucleus of this group also proved to be extremely large, not typical of compounds containing this group [2, 7]. At the same time, the NQR frequency of this group in the structure **Ia** estimated from the results of calculations by MR2/3-21G* method matches much better to the experimental one, and that obtained from the results of RHF/3-21G* calculations almost coincides with the experimental one (see Table 1). The asymmetry parameter has a value characteristic of the compounds of HCOCl [2, 7]. Consequently, the calculated electron distribution on the Cl atom of COCl group in the structure **Ia** is almost identical with that determined by ^{35}Cl NQR.

The total energy of the structure **Ia** in view of its value in the zero point calculated by the RHF/3-21G* method is by 4.93 kcal mol^{-1} higher, and calculated by the MR2/3-21G* method is by 6.85 kcal mol^{-1} lower than that of the structure **I**. Apparently, the first method better describes the electronic distribution at the Cl atom of COCl group and the latter is better for the energy characteristics of the molecule. Based on these data we should assume that during crystallization the complex *o*-$CH_3OC_6H_4COCl·SnCl_4$ initially has the structure **Ia** and then transforms into **II**. The calculated NQR frequency of the Cl atom in the COCl group of the latter structure (Table 1) is also close to the experimental one (see above). The EFG asymmetry parameter at the nucleus of the atom has a value characteristic of the carboxylic acid chlorides and their complexes with $SnCl_4$ [7].

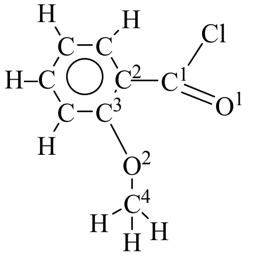
The total energy of the form **II** of the *o*-$CH_3OC_6H_4COCl·SnCl_4$ complex is lower than that of the form **I** by 11.62 kcal mol^{-1} (RHF) or 20.22 kcal mol^{-1} (MP2), and of the form **Ia,** by 16.55 kcal mol^{-1} (RHF) or 13.38 kcal mol^{-1} (MP2). The basic geometric parameters of the forms **Ia** and **II** calculated by the methods RHF/3-21G* and MP2/3-21G* are presented in Table 2. The results of calculations by both methods did not differ in principle. In the **Ia** form the distance Sn←O^2 is significantly shorter than the sum of the van der Waals radii of Sn and O. Judging from the Sn atom bond angles, its coordination polyhedron is a slightly distorted trigonal bipyramid (this follows also from the data of the ^{35}Cl NQR [1]), in which the axial positions are occupied by the atoms O^2 and Cl^2, and the equatorial, by three Cl atoms. The length of the axial Sn–Cl bond is greater than the equatorial, as in the other molecules of trigonal–bipyramidal structure [10, 11]. An exception is the equatorial bond Sn–Cl^5, which is only slightly shorter (RHF) or slightly longer (MP2) than the axial Sn–Cl^2 bond. In the form **II** the Sn←O^1 and Sn←O^2 distances also are significantly shorter than the sum of the van der Waals radii of O and Sn. Judging from the bond angles, the coordination polyhedron of the Sn atom has a *cis*-octahedral structure, as follows from ^{35}Cl NQR data [1]. The O^1–Sn, O^2–Sn, Cl^4–Sn and Cl^5–Sn bonds are located almost in the same equatorial plane of the polyhedron, and the bonds Cl^2–Sn and Cl^3–Sn are perpendicular to it. The last two bonds are slightly longer than the equatorial Cl–Sn bonds (Table 2).

The reasons for the formation of two isomers of the *o*-$CH_3OC_6H_4COCl·SnCl_4$ complex can be clarified by examining the stereoelectronic structure of possible isomers **III**–**V** of the *ortho*-methoxybenzoyl chloride and their total energies. The energies were determined with accounting for the energy in the zero point.

According to the RHF/3-21G* calculations, the total energy of the structure **III** is by 1.01 and 1.6 kcal mol^{-1} lower than those of the structures **IV**

Table 2. Bond lengths (*d*), bond (ω) and dihedral (β) angles in the molecules **Ia** and **II** calculated by the RHF/3-21G* and MR2/3-21G* methods

Molecule	Bond	*d*, Å		Angle	ω, deg		Angle	β, deg	
		RHF	MP2		RHF	MP2		RHF	MP2
Ia	$\mathrm{Cl^1{-}C^1}$	1.759	1.812	$\mathrm{Cl^1C^1C^2}$	118.72	116.69	$\mathrm{Cl^1C^1C^2C^3}$	–1.67	–8.83
	$\mathrm{C^1{-}O^1}$	1.195	1.229	$\mathrm{Cl^1C^1O^1}$	118.82	119.48	$\mathrm{C^1C^2C^3O^2}$	1.76	2.43
	$\mathrm{C^1{-}C^2}$	1.491	1.502	$\mathrm{C^1C^2C^3}$	129.28	129.39	$\mathrm{C^2C^3O^2C^4}$	94.61	98.82
	$\mathrm{O^2{-}Sn}$	2.283	2.254	$\mathrm{C^3O^2Sn}$	123.76	122.61	$\mathrm{O^1C^1C^2C^3}$	178.96	172.75
	$\mathrm{C^2{-}C^3}$	1.389	1.408	$\mathrm{C^2C^3O^2}$	122.72	122.03	$\mathrm{C^2C^3O^2Sn}$	–105.22	–104.18
	$\mathrm{O^2{-}C^4}$	1.497	1.520	$\mathrm{C^3O^2C^4}$	112.53	111.14	$\mathrm{C^3O^2SnCl^2}$	–62.45	–40.46
	$\mathrm{Sn{-}Cl^2}$	2.370	2.366	$\mathrm{O^2SnCl^2}$	177.17	178.11	$\mathrm{C^3O^2SnCl^3}$	152.06	155.37
	$\mathrm{Sn{-}Cl^3}$	2.349	2.350	$\mathrm{O^2SnCl^3}$	85.68	84.84	$\mathrm{C^3O^2SnCl^4}$	30.47	32.43
	$\mathrm{Sn{-}Cl^4}$	2.341	2.345	$\mathrm{O^2SnCl^4}$	84.04	83.02	$\mathrm{C^3O^2SnCl^5}$	–92.89	–89.94
	$\mathrm{Sn{-}Cl^5}$	2.364	2.368	$\mathrm{O^2SnCl^5}$	81.71	82.47			
				$\mathrm{Cl^3SnCl^4}$	120.78	121.78			
				$\mathrm{Cl^3SnCl^5}$	114.02	113.62			
II	$\mathrm{Cl^1{-}C^1}$	1.727	1.763	$\mathrm{Cl^1C^1C^2}$	118.24	116.26	$\mathrm{Cl^1C^1C^2C^3}$	–163.93	–159.92
	$\mathrm{C^1{-}O^1}$	1.222	1.252	$\mathrm{Cl^1C^1O^1}$	117.27	117.53	$\mathrm{C^1C^2C^3O^2}$	7.62	6.76
	$\mathrm{C^1{-}C^2}$	1.456	1.475	$\mathrm{C^1C^2C^3}$	119.93	120.15	$\mathrm{C^2C^3O^2C^8}$	139.88	140.82
	$\mathrm{C^2{-}C^3}$	1.399	1.417	$\mathrm{C^1O^1Sn}$	138.08	132.02	$\mathrm{O^1C^1C^2C^3}$	16.88	20.30
	$\mathrm{O^1{-}Sn}$	2.183	2.281	$\mathrm{C^2C^3O^2}$	120.07	118.78	$\mathrm{Cl^1C^1O^1Sn}$	–175.27	–177.68
	$\mathrm{O^2{-}C^3}$	1.394	1.430	$\mathrm{C^3O^2C^8}$	117.09	115.93	$\mathrm{C^2C^3O^2Sn}$	–48.78	–54.18
	$\mathrm{O^2{-}C^8}$	1.497	1.521	$\mathrm{C^3O^2Sn}$	124.55	123.23	$\mathrm{O^1SnO^2C^3}$	47.35	53.63
	$\mathrm{O^2{-}Sn}$	2.293	2.258	$\mathrm{O^1SnO^2}$	72.21	73.14	$\mathrm{C^1O^1SnCl^5}$	–30.41	–32.55
	$\mathrm{Sn{-}Cl^2}$	2.404	2.393	$\mathrm{O^1SnCl^2}$	84.29	83.36	$\mathrm{C^1O^1SnCl^4}$	151.58	150.07
	$\mathrm{Sn{-}Cl^3}$	2.403	2.393	$\mathrm{O^1SnCl^3}$	82.52	81.39	$\mathrm{C^3O^2SnCl^5}$	–133.44	–127.17
	$\mathrm{Sn{-}Cl^4}$	2.385	2.377	$\mathrm{O^1SnCl^5}$	161.43	162.54			
	$\mathrm{Sn{-}Cl^5}$	2.362	2.358	$\mathrm{Cl^2SnCl^3}$	163.29	161.73			
				$\mathrm{Cl^2SnCl^4}$	95.45	95.13			
				$\mathrm{Cl^2SnCl^5}$	94.43	95.63			
				$\mathrm{O^2SnCl^4}$	166.13	164.96			
				$\mathrm{O^2SnCl^5}$	89.23	89.42			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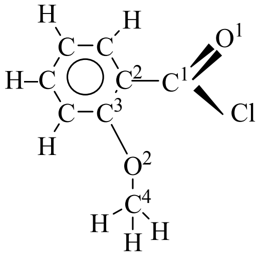
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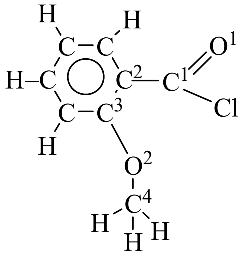
V

and **V**, respectively. Moreover, for each structure **III** and **V** one imaginary frequency of stretching vibrations was obtained and, consequently, according to these calculations, they correspond to the transition states of the molecule. However, these data are apparently within the error of their determination. For a more reliable determination of the *o*-$CH_3OC_6H_4COCl$ structure, the calculation of structures **III–V** was carried out also by the MR2/3-21G* method. The ratio of their total energies remains the same as in the previous case: the structure **III** is energetically more favorable than **IV** and **V** by 3.28 and 3.51 kcal mol^{-1}, respectively. The imaginary frequency of stretching vibrations has only the structure **V**. At the calculation of structures **III–V** by the RHF/6-31G(d)* method the structure **IV** was found to be energetically most favorable. Its total energy is by 0.13 and 1.35 kcal mol^{-1} lower than those of the structures **III** and **V**, respectively. Each of two latter has one imaginary frequency of stretching vibrations. The structure **IV** has no imaginary frequencies. The calculation by MP2/6-31G(d) method shows that the total energy of the structure **III** is by 0.34 kcal mol^{-1} lower than that of the structure **IV**. Calculating by this method the structure **V** with full optimization of its geometry, we obtain the structure **IV**.

The calculations by all the above methods gave the dihedral angles $ClC^1C^2C^3$ in the structure **III** almost equal to 180°, in the structure **V** 0°, and in the structure **IV** –22.94° (RHF/3-21G*), 36.53° (MP2/3-21G*), 47.77° (RHF/6-31G*), and 52.07° (MP2/6-31G*).

Thus, according to the above calculations, the three structures of *o*-$CH_3OC_6H_4COCl$ differ insignificantly by the energy. The difference is within the calculation error. Therefore, the results of the calculation of structures **III–V** by different quantum-chemical methods do not coincide. Apparently, the existence of these structures in the gaseous state of the substance is almost equally probable. When *o*-$CH_3OC_6H_4COCl$ is mixed with $SnCl_4$, the probability of interaction with the Sn atoms of the ester oxygen atom is higher compared to the carbonyl, since the negative charge of the former is substantially higher than on the latter. For example, charges on the ester oxygen atom in the structures **III–V** calculated by the RHF/6-31G(d) method are –0.691, –0.648, and –0.641 *e*, and on the carbonyl oxygen, –0.434, –0.445, and –0.478 *e*, respectively. Calculations by the MP2/6-31G(d) method gave the charges on the ester oxygen atom of –0.630, –0.659, and –0.653 *e*, on the carbonyl oxygen, –0.458, –0.468, and –0.506 *e,* respectively. Hence, initially the 1:1 complex **Ia** of the trigonal–bipyramidal structure is formed. The existence of *o*-$CH_3O\cdot C_6H_4COCl$ and $SnCl_4$ is energetically more favorable in the complex than in the mixture of the individual components, since the total energy of the complex is by 16.24 kcal mol^{-1} (RHF) or 25.32 kcal mol^{-1} (MP2) lower than the sum of total energies of the individual components. In time, this complex is transformed into the more complicated and more energetically favorable form **II**, with the Sn atom linked with two O atoms.

ACKNOWLEDGMENTS

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REFERENCES

1. Dolgushin, G.V., Lazarev, I.M., Feshin,V.P., and Voronkov, M.G., *Zh. Obshch. Khim.*, vol. 54, no. 6, p. 1430.
2. Feshin, V.P., Dolgushin, G.V., Lazarev, I.M., Sapozhnikov, Yu.E., Yasman, Ya.B., and Voronkov, M.G., *Dokl. Akad. Nauk SSSR*, 1988, vol. 300, no. 5, p.1181.

3. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Shallacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *Gaussian 03*, Revision D.1. Gaussian, Inc. Wallingford, CT, 2005.
4. Feshin, V.P. and Feshina, E.V., *Zh. Obshch. Khim.*, 2010, vol. 80, no. 8, p. 1298.
5. Feshin, V.P. and Konshin, M.Y., *Z. Naturforsch., A*, 1996, vol. 51, p. 549.
6. Feshin, V.P. and Feshina, E.V., *Z. Naturforsch., A,* 2000, vol. 55, p. 555.
7. Feshin, V.P., *Elektronnye effekty v organicheskikh i elementoorganicheskikh molekulakh* (Electronic Effects in Organic and Organoelement Molecules), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 1997.
8. Feshin, V.P., *Geminal'noe vzaimodeistvie v organicheskoi i elementoorganicheskoi khimii* (Geminal Interaction in Organic and Organoelement Chemistry), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 2009.
9. Das, T.P. and Hahn, E.L., *Nuclear Quadrupole Resonance Spectroscopy*, New York: Acad. Press, 1958.
10. Bilton, M.S. and Webster, M., *J. Chem. Soc., Dalton Trans.*, 1972, no. 6, p. 722.
11. Feshin, V.P., Nikitin, P.A., Voronkov, M.G., Gar, T.K., Viktorov, N.A., Gurkova, S.N., and Gusev, A.I., *Dokl. Akad. Nauk SSSR,* 1984, vol. 274, no. 3, p. 665.