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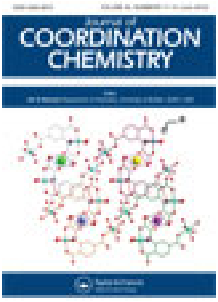

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Stereoelectronic structure of MCl_4-benzoyl chloride (M=Si, Ge, Sn) systems resulting from ab initio calculations and NQR ^{35}Cl

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Stereoelectronic structure of MCl_4-benzoyl chloride (M = Si, Ge, Sn) systems resulting from *ab initio* calculations and NQR ^{35}Cl

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Results of quantum-chemical calculations of MCl_4–C_6H_5COCl (M=Si, Ge, Sn) systems of 1 : 1 composition using RHF/3-21 G* and MP2/3-21 G* levels as well as those of 1 : 2 composition using the RHF/3-21 G* level have been represented. $MCl_4 \leftarrow C_6H_5COCl$ complexes of 1 : 1 composition are energetically more advantageous. They are formed in solid state provided that the M···O distance in individual systems is considerably less than the sum of van der Waals radii of M and O and their total energies are appreciably less than the sum of total energies of components. These conditions are realized only for M=Sn. In systems of 1 : 2 compositions, calculated M···O distances are practically equal to the sum of covalent radii of M and O. Nonetheless, complexes with such composition are not formed in solid state. Total energy of the system which is lower than the sum of its components' energies is not an indispensable condition for complex formation. The ^{35}Cl nuclear quadrupole resonance (NQR) frequencies and asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei have been evaluated using the results of *ab initio* calculations.

Keywords: MCl_4–ligand systems (M=Si, Ge, Sn); Stereo-electronic structure; *Ab initio* calculations at RHF/3-21 G* and MP2/3-21 G* levels; Nuclear quadrupole resonance; Coordination interaction

1. Introduction

The structure of MCl_4–ligand systems (M=Si, Ge, Sn) is dependent on their aggregative state. For example, nuclear quadrupole resonance (NQR) spectra at ^{35}Cl nuclei of $SiCl_4$–$N(CH_3)_3$ and $GeCl_4$–$N(CH_3)_3$ systems unambiguously indicate [1–3] that in crystalline state they represent complexes with coordination polyhedron of electron acceptor's central atom having bipyramidal structure. Such structure of the $GeCl_4 \leftarrow N(CH_3)_3$ complex has also been ascertained using X-ray structural analysis [4]. Quantum-chemical calculations show that these systems are practically comprised of individual components [5–7]. Even being in the same aggregative state, the structure of such system can be varied. For example, on interaction of $SnCl_4$ with ortho-methoxybenzoylchloride, a complex of trigonal-bipyramidal structure of 1 : 1

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composition is formed. In the course of time and being in crystalline state, it transforms into energetically more advantageous *cis*-octahedral complex of same composition [8]. According to non-empirical quantum-chemical calculations, MCl_4 complexes (M=Si, Ge) with organic ligands, in which coordination polyhedron of M has trigonal-bipyramidal structure, are usually energetically not advantageous. Total energy of such complexes usually exceeds the sum of their components' energies. Nonetheless, such complexes can be formed in crystalline state of a substance [5].

$SnCl_4$ complexes with organic ligands, including those with chloranhydrides of benzoic acids, have been produced. NQR spectra at ^{35}Cl nuclei show that at 77 K some of these also have trigonal-bipyramidal structures [9–12]. It has been ascertained using ^{35}Cl NQR method that $SnCl_4$ forms a complex with benzoyl chloride at 77 K, the complex being of 1 : 1 composition and of trigonal-bipyramidal structure [9, 11, 12]; a complex of 1 : 2 composition does not form [9, 12]. The complex of 1 : 1 composition is formed as a result of interaction of carbonyl oxygen with Sn. Oxygen and one chloride are located in axial positions of the trigonal bipyramid. Three other chlorides occupy equatorial positions. Most low-frequency line (21.104 MHz [9, 11, 12]) in the ^{35}Cl NQR spectrum as well as asymmetry parameter (η) of the electric field gradient (EFG) at the ^{35}Cl nucleus (0.9% [11]) which is close to zero correspond to the axial chloride. Two low-frequency close lines (24.220 and 24.382 MHz [9, 11, 12]) with 1 : 2 ratio of intensity are appreciably shifted to high-frequency as compared with most low-frequency line corresponding to axial chloride correspond to equatorial chlorides with comparatively moderate asymmetry of electron distribution ($\eta = 5.5$ and 4.6% [11]). Most high-frequency line in the spectrum (32.047 MHz [9, 11, 12]) and largest asymmetry parameter (24.7% [11]) correspond to the chloride in the COCl group. Its NQR frequency is appreciably higher, whereas its asymmetry parameter is only slightly higher compared with individual benzoyl chloride (29.918 MHz [9, 12–14] and 22% [14]). It has been ascertained using the NQR ^{35}Cl method [12] that $SiCl_4$ and $GeCl_4$ complexes are not formed with benzoyl chloride. ^{35}Cl NQR spectra of $SiCl_4$–C_6H_5COCl and $GeCl_4$–C_6H_5COCl systems consist of spectra of individual components.

Taking into account results of investigation in MCl_4–ligand and, in particular, MCl_4–C_6H_5COCl (M=Si, Ge, Sn) systems using the ^{35}Cl NQR, we can study possibilities of formation of such complexes with various compositions and structures, electron distribution therein using non-empirical methods of quantum chemistry, to compare experimental NQR data of $SnCl_4 \leftarrow C_6H_5COCl$ with computed results.

Earlier [15, 16], we obtained satisfactory correlation between experimental and computed NQR frequencies of chlorine-containing organic and organometallic compounds as well as between asymmetry parameters of EFG at ^{35}Cl nuclei. At that, ^{35}Cl NQR frequencies and asymmetry parameters had been estimated according to equations (1) and (2) as per [17] and according to populations of less diffuse 3*p*-components of valence *p*-orbitals of Cl obtained on calculation by restricted Hartree-Fock method using split and polarized valence basis 6-31G(d). The use of quantum-chemical calculations for estimation of NQR parameters of higher level does not improve correlation with experimental data [15, 16, 18].

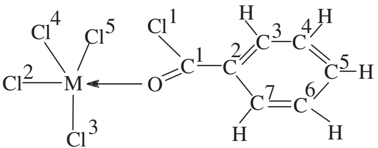
$$\nu = e^2Qq_{\mathrm{aT}}/2h[-N_z + (N_x + N_y)/2](1 + \eta^2/3)^{1/2} \tag{1}$$

$$\eta = |3(N_x - N_y)/(2N_z - N_x - N_y)| \tag{2}$$

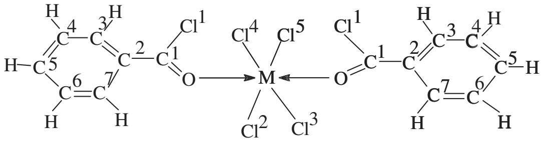
Here: e^2Qq_{aT} – atomic constant of quadrupole interaction; h – Planck constant; N_x, N_y, and N_z – populations of $3p$-components of valence p_x, p_y, p_z-orbitals of indicated atom, respectively. The $e^2Qq_{\mathrm{aT}}/2h$ value has been found using experimental NQR frequency for Cl_2 at 77 K and populations of $3p$-components of valence p-orbitals of Cl of this molecule obtained from its calculation using respective method [15, 16].

2. Results and discussion

We have performed quantum-chemical calculations of MCl_4–C_6H_5COCl (M=Si, Ge, Sn) systems of 1 : 1 composition (I) and of their respective individual components with total geometry optimization using RHF/3-21G* and MP2/3-21G* levels as per the GAUSSIAN 03W program [19]. Chlorine NQR parameters computed according to results of performed calculations were taken as origin of the coordinate system. The z-axis of these systems was directed along Cl–M or Cl–C bonds. Calculation of $MCl_4 \leftarrow 2C_6H_5COCl$ (M=Si, Ge, Sn) systems of *trans*-octahedral structure (II) was also performed using the RHF/3-21G* level. A higher basis set was not used since parameters for Sn were not available in other standard basis sets of the program.


(M=Si, Ge, Sn)

I


(M=Si, Ge, Sn)

II

According to calculations performed using both levels, the $SnCl_4$–C_6H_5COCl system represents a complex in which Sn has a trigonal-bipyramidal structure (table 1). Its total energy is appreciably lower as compared with the sum of energies of individual components (table 2). Hence, such complex is energetically advantageous. The $\mathrm{Sn}\cdots\mathrm{O}$ distance in it (table 1) is IG(IG)appreciably less than the sum of van der Waals radii of Sn and O (3.9 Å [20]). Cl^2 and O are located in axial positions of the trigonal bipyramid and three chlorides in equatorial positions. The Cl–Sn axial bond is a bit longer than equatorial Cl–Sn bonds. Values of Sn's valence angles are typical for trigonal-bipyramidal structure: angles between Cl–Sn equatorial bonds are close to 120°, angles between axial and equatorial bonds are close to 90°. The structure of the complex resulting from these calculations agrees, in general, with its experimental ^{35}Cl NQR spectrum (see above). NQR frequencies and asymmetry parameters of EFG at ^{35}Cl nuclei (table 3) calculated using both levels and populations of $3p$-constituents of valence p-orbitals of Cl in the $SnCl_4 \leftarrow C_6H_5COCl$ complex correspond to such structure. NQR frequency of the axial chlorine is appreciably less than that of equatorial ones; axial chlorine atom has axial symmetry of electron distribution, whereas that of equatorial ones considerably differ

Table 1. Bond lengths (d), valence (α), and torsion (β) angles in the (I) molecule with M=Sn calculated at RHF/3-21G* and MP2/3-21G* levels.

	d (Å)			α (°)			β (°)	
Bond	RHF	MP2	Angle	RHF	MP2	Angle	RHF	MP2
C^1–Cl^1	1.731	1.764	$Cl^1C^1C^2$	118.52	117.38	$Cl^1C^1C^2C^3$	0.01	0.00
C^1=O	1.224	1.251	Cl^1C^1O	119.00	120.23	$C^1C^2C^3C^4$	180.0	180.0
C^1–C^2	1.455	1.474	$C^1C^2C^3$	123.16	123.04	$OC^1C^2C^3$	180.0	180.0
Sn–Cl^2	2.367	2.360	C^1OSn	155.63	143.03	Cl^1C^1OSn	0.05	0.05
Sn–Cl^3	2.351	2.343	Cl^3SnO	81.67	79.89	C^1OSnCl^3	179.92	179.98
Sn–Cl^4	2.350	2.345	Cl^4SnO	82.60	81.52	C^1OSnCl^4	60.57	61.23
Sn–Cl^5	2.350	2.345	Cl^5SnO	82.59	81.53	C^1OSnCl^5	−60.70	−61.28
Sn···O	2.228	2.320	Cl^2SnCl^3	97.87	99.62			
			Cl^2SnCl^4	97.64	98.70			
			Cl^2SnCl^5	97.62	98.71			
			Cl^3SnCl^4	117.53	116.26			
			Cl^3SnCl^5	117.57	116.26			
			Cl^4SnCl^5	119.59	120.26			

Table 2. Lengths of axial and equatorial M–Cl bonds and M···O distances (*d*) in MCl_4–C_6H_5COCl systems of 1 : 1 and 1 : 2 compositions calculated at RHF/3-21G* and MP2/3-21G* levels, as well as differences between total energies of these systems and sum of their components (ΔE).

			d (Å)			
Level	M	Composition	M–Cl_a	M–Cl_e	M···O	ΔE (kcal mol^{-1})
RHF	Si	1 : 1	2.030	2.014	3.230	3.55
	Ge	1 : 1	2.141	2.123	3.070	5.01
	Sn	1 : 1	2.367	2.350	2.228	18.47
MP2	Si	1 : 1	2.024	2.010(2.020)	3.167	5.79
	Ge	1 : 1	2.141	2.125(2.127)	2.956	7.61
	Sn	1 : 1	2.360	2.345(2.343)	2.320	18.55
RHF	Si	1 : 2	2.161		1.86	−13.44
	Ge	1 : 2	2.237		2.0	0.86
	Sn	1 : 2	2.406		2.14	1.63

from such symmetry. NQR frequency of chlorine belonging to COCl indicates formation of the complex, this frequency being appreciably higher as compared with individual C_6H_5COCl (see above). However, only calculated asymmetry parameters of EFG at ^{35}Cl nuclei of Cl^1 and Cl^2 agree quantitatively with experimental data. Calculated NQR frequencies of these chlorines as well as NQR frequencies and asymmetry parameters of other chlorines (table 3) appreciably differ from experimental frequencies (see above). This is understandable, in as much as calculation was made for individual molecule of the complex, whereas experimental NQR spectrum was produced for crystalline state of the substance. Judging from calculated NQR frequency of chlorine of COCl of the complex which considerably exceeds experimental frequency, and taking into account that on formation of the complex, experimental NQR frequency of this chlorine appreciably increases as compared with individual benzoyl chloride. One has to suppose that the Sn···O distance in crystalline state of the $SnCl_4 \leftarrow C_6H_5COCl$ complex exceeds to some extent the calculated distance, i.e. exceeds this distance in gaseous state.

Table 3. Populations of 3*p*-components of chlorine valence *p*-orbitals ($N3p$) in (I) (at M=Sn) and PhCOCl molecules calculated at RHF/3-21G* and MP2/3-21G* levels, as well as ^{35}Cl NQR frequencies (ν_c) and asymmetry parameters (η_c) of the EFG at ^{35}Cl nuclei estimated using these populations.

Level	Molecule	Atom	$N3p_x$, *e*	$N3p_y$, *e*	$N3p_z$, *e*	ν_c (MHz)	η_c (%)
RHF	I	Cl^1	1.139	1.086	0.813	33.936	26.54
		Cl^2	1.062	1.061	0.889	19.264	0.0
		Cl^3	1.077	1.054	0.884	20.450	19.01
MP2	I	Cl^1	1.136	1.089	0.799	34.829	22.49
		Cl^2	1.063	1.062	0.889	19.115	0.0
		Cl^3	1.077	1.056	0.882	20.538	17.67
RHF	PhCOCl	Cl	1.118	1.080	0.829	30.464	21.11
MP2	PhCOCl	Cl	1.113	1.079	0.812	31.457	17.96

NQR frequency and asymmetry parameters of the EFG at the ^{35}Cl nucleus in C_6H_5COCl calculated using populations of less diffusive 3*p*-constituents of valence *p*-orbitals of Cl and the RHF/3-21 G* level with total geometry optimization (table 3) are close to experimental values (see above), whereas the same parameters (table 3) resulting from calculation of this molecule using the MP2/3-21G* level appreciably differ from experimental values. This discrepancy between experimental and calculated NQR parameters at halogen nuclei in halogen-containing molecules resulting from calculations thereof using more advanced levels than the RHF was noted above.

Since ^{35}Cl NQR spectra of MCl_4–C_6H_5COCl systems with M=Si and Ge indicate the absence of complex formation [12], it appeared to be expedient to calculate them using RHF/3-21G* and MP2/3-21G* levels with subsequent comparison of results with respective results for $SnCl_4 \leftarrow C_6H_5COCl$. Apart from characteristic valence angles the distance between M and O which is appreciably less than the sum of their van der Waals radii, as well as the difference between lengths of axial and equatorial M–Cl bonds, can serve as signs of trigonal-bipyramidal structure.

According to results of calculations performed using both levels, the structure of coordination polyhedron of M=Si and Ge in MCl_4–C_6H_5COCl systems appreciably differs from the structure of M=Sn. It is close to tetrahedral: angles between the Cl^2–Si and remaining Cl–Si bonds are ≈107.5°, between bonds Cl^3–Si, Cl^4–Si, and Cl^5–Si ≈111.2–111.6°; respective angles at M=Ge are ≈107.5° and 112.2–112.7°. At the same time, the difference between values of long and short bonds of M–Cl practically remain the same at M=Sn and M=Si and Ge (table 2). Hence, this difference is not a sign of trigonal-bipyramidal structure of M's coordination polyhedron in these systems. From M=Si to M=Sn, values of long and short bonds increase (by ≈0.110 Å at Si→Ge and by ≈0.226 Å at Ge → Sn), whereas the M···O distance abruptly decreases (table 2). At all M, it is less than the sum of van der Waals radii of M and O (3.5 Å at M=Si and 3.6 Å at M=Ge [20]). Hence, in gaseous state of these systems there exists interaction between M and O, the value of which is dependent on M. However, in crystalline state the complex is only formed at considerably less M···O distance (at M=Sn) than this sum.

The total energies of the MCl_4–C_6H_5COCl systems is less than the sum of individual components' energies at any M (table 2). However, the complex of 1 : 1 composition in solid state is formed only at M=Sn when the total energy of this system is appreciably less than the sum of initial components' total energies.

According to ^{35}Cl NQR data, the complex of 1 : 2 composition (II) in the MCl_4–$2C_6H_5COCl$ (M=Si, Ge, Sn) system in solid state is not formed even at M=Sn [9, 12]. Variations of M–Cl bond lengths, M···O distances and differences between total energies of these systems and sums of individual components' energies in gaseous state at different M, as well as comparison of these data with data obtained for analogous systems of 1 : 1 composition, were of interest. Therefore, we have performed calculation of these systems with octahedral structure using the RHF/3-21G* level, only for systems of *trans*-octahedral structure. According to these calculations, angles between M–Cl and $M \leftarrow O$ bonds are close to 90°, $O \rightarrow M \leftarrow O$ angles are close to 180° (177.15, 176.90, and 178.03° at M=Si, Ge, and Sn, respectively), and M–Cl and $M \leftarrow O$ bond lengths (table 2) are practically equal to sums of covalent radii of respective atoms (see, for example, [21]). On transition from M=Si to M=Sn, lengths of these bonds increase, $M \leftarrow O$ bond lengths increasing by the same value (0.14 Å). At M···O distances close to the sum of covalent radii of M and O atoms (1.91 at M=Si, 1.96 at M=Ge, and 2.14 at M=Sn [21]), $MCl_4 \leftarrow 2C_6H_5COCl$ complexes in gaseous state can be formed. At the same time, total energy of the system with M=Si exceeds the sum of initial components' energies, whereas with M=Ge and Sn it is slightly less (table 2). It is quite possible therefore that complexes like these do not exist in the crystalline state. On the other hand, calculations of valence vibrational frequencies of MCl_4–$2C_6H_5COCl$ systems with M=Si, Ge and Sn show that imaginary frequencies are absent for them and, hence, the global minimum on the surface of the system's potential energy corresponds to such structures. In accordance to calculations, these structures are stable. For the *trans*-octahedral $SiCl_4$ complex with pyridine the total energy is also appreciably higher than the sum of the components' energies. However this complex exists in the crystalline state [5].

Thus, the $MCl_4 \leftarrow C_6H_5COCl$ complex (M=Si, Ge, Sn) of 1 : 1 composition in solid state can be formed, provided that the M···O distance in an individual system is appreciably less than the sum of van der Waals radii of M and O and total energy of the system is considerably less than the sum of components' total energies. These conditions are realized only for M=Sn. In individual MCl_4–C_6H_5COCl systems of 1 : 2 compositions, M···O distances are close to sums of covalent radii of these atoms. Nonetheless, complexes are not formed in solid state of these systems. Their total energies either exceed the sum of components' total energies (M=Si) or are close to them (M=Ge, Sn). Apparently the total energy of the system, which is lower as compared with the sum of its components' energies, is not an indispensable condition for complex formation.

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