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Ab Initio Calculations of Group IVA Tetrachloride Complexes: VII.[1] Structure and Dynamics of the Formation of $GeCl_4$ Complexes with Hexamethylphosphoric Triamide

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Abstract — Quantum-chemical calculations by the RHF/6-31G(*d*) method were performed for the systems $GeCl_4 \leftarrow [N(CH_3)_2]_3$ and $GeCl_4 \leftarrow {}_2OP[N(CH_3)_2]_3$ with full geometry optimization and varied Ge←O distances. The calculations with full geometry optimization gave trigonal-pyramidal and trans-octahedral structures, respectively, which agrees with experimental NQR data. As the components of a system get closer together, mutual polarization followed by electron density transfer from H atoms of the electron donor onto Cl atoms of the electron acceptor take place. The O and Ge atoms act as conductors in this electron density transfer. Nonempirical quantum-chemical calculations do not reproduce adequately the p_σ density of the axial Cl atom in the trigonal-bipyramidal complex.

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It was shown by ^{35}Cl nuclear quadrupole resonance (NQR) at 77 K [2] that $GeCl_4$ forms with hexamethylphosphoric triamide (HMPA) trigonal-bipyramidal or octahedral complexes, depending on the ratio of the components. At a 1:1 ratio, a quadruplet ^{35}Cl NQR spectrum is observed, in which three high-frequency lines are split only slightly and one low-frequency line is far remote from the others. The spectrum occurs in a lower frequency range compared with that of individual $GeCl_4$. Such NQR spectrum provides unequivocal evidence for the trigonal-bipyramidal structure of the complex, with the triplet of the quadruplet spectrum corresponding to three equatorial Cl atoms. The axial positions of the coordination polyhedron are occupied by the fourth Cl atom which gives the low-frequency line in the NQR spectrum, as well as the ligand O atom. Such structure of the complex is also confirmed by the asymmetry parameters of the electric field gradient on ^{35}Cl nuclei, which point to a significant asymmetry of the electron distribution over its equatorial Cl atoms and to a close-to-axial symmetry of this distribution for the axial Cl atom [3]. At a 1:2 component ratio, a quadruplet NQR spectrum with all bands with the same intensity and close frequencies was initially obtained. After a few days this spectrum transformed into a doublet spectrum with frequencies close to two bands of the quadruplet [2]. These spectra occur at much lower frequencies than that of individual $GeCl_4$. The quadruplet spectrum points to formation of a *trans*-octahedral complex with all the Cl atoms possessing nonequivalent but close electron distributions, and the doublet spectrum, to formation of a complex of the same structure with the Cl atoms equivalent by pairs.

The aim of this work to study in more detail the structure of these complexes and dynamics of their formation by the RHF/6-31G(*d*) method and to compare the results of these quantum-chemical calculations with ^{35}Cl NQR experimental data [2, 3]. To this end, we performed RHF/6-31G(*d*) calculations for the systems $GeCl_4 \leftarrow OP[N(CH_3)_2]_3$ (**I**) and $GeCl_4 \leftarrow 2OP[N(CH_3)_2]_3$ (**II**) with full geometry optimization and varied Ge←O distance. With both systems, the coordinate origin was placed on Cl^1, and the *Z* axis was directed along the Cl^1–Ge bond. The calculations were performed with the Gaussian 03W program [4]. The Ge←O=P fragments were taken linear, and, therefore, imaginary atoms connected with O were introduced in the calculations.

The geometric parameters obtained with full geometry optimization for both 1:1 and 1:2 complexes (Table 1) are consistent with their experimental NQR parameters. For the first complex these parameters correspond to a trigonal-bipyramidal

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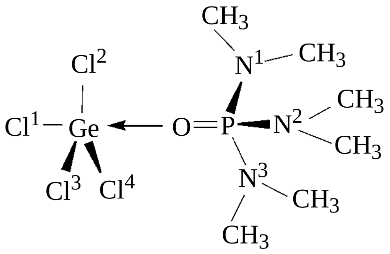
[1] For communication VI, see [1].



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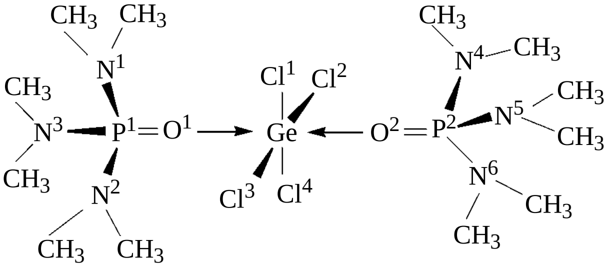

II

and for the second, to a *trans*-octahedral structure. In the first complex, the axial Ge–Cl^1 bond is substantially longer than the three equatorial bonds, the angles between the axial and equatorial Ge←Cl bonds are near 90°, the angles between the three equatorial bonds are close to 120°. In the second complex, all the Ge←Cl bond lengths are close to each other, and the angles between these bonds and angles between Ge←Cl bonds and coordination G←O bond are close to 90°. The distances between the Ge and O coordination centers in both complexes (1.965 and 1.914 Å, respectively) are only slightly longer than the sum of the covalent radii of these atoms (1.88 Å [5]). Note that RHF/6-31G(*d*) calculations with full geometry optimization, too, result in a *trans*-octahedral structure for 1 : 2 complexes of Si and Ge tetrachlorides with pyridine [6, 7], whereas the trigonal-bipyramidal structure established NQR for 1 : 1 complexes of the same tetrachlorides with trimethylamine and tetramethylurea is impossible to reproduce by calculations [1, 8–10]). The latter systems are the most favored by energy at unrealistically large distances between the coordination centers before the complex has formed. The trigonal-bipyramidal structure can be obtained

Table 1. Bond lengths (*d*) and bond angles (ω) in systems **I** and **II** and in the individual components [*d*(Ge←O) = ∞], calculated by the RHF/6-31G(*d*) method with full geometry optimization[a]

I						II			
Ge←O	1.965	∞	Ge←O	1.965	∞	1.914			
Bond	*d*, Å		Angle	ω, deg		Bond	*d*, Å	Angle	ω, deg
Ge–Cl^1	2.234	2.116	Cl^{1}GeCl^2	93.57	109.49	Ge–Cl^1	2.278	Cl^{1}GeCl^2	89.81
Ge–Cl^2	2.179	2.116	Cl^{1}GeCl^3	93.92	109.46	Ge–Cl^2	2.293	Cl^{1}GeCl^3	91.41
Ge–Cl^3	2.173	2.116	Cl^{1}GeCl^4	93.77	109.46	Ge–Cl^3	2.278	Cl^{2}GeCl^4	88.98
Ge–Cl^4	2.174	2.116	Cl^{1}GeO	179.43	–	Ge–Cl^4	2.293	Cl^{3}GeCl^4	89.81
P=O	1.496	1.465	Cl^{2}GeCl^3	119.70	109.46	P^1=O^1	1.492	Cl^{1}GeO^1	89.56
P–N^1	1.642	1.670	Cl^{2}GeCl^4	119.67	109.46	P^1–N^1	1.649	Cl^{2}GeO^1	88.55
P–N^2	1.652	1.672	N^{1}PO	108.61	110.23	P^1–N^2	1.648	Cl^{3}GeO^1	91.22
P–N^3	1.638	1.669	N^{2}PO	112.35	118.38	P^1–N^3	1.648	Cl^{4}GeO^1	90.65
			N^{3}PO	109.99	110.24			Cl^{1}GeO^2	91.21
			N^{1}PN^2	109.83	102.51			Cl^{2}GeO^2	90.67
			N^{1}PN^3	111.15	112.66			Cl^{3}GeO^2	89.55
			N^{2}PN^3	104.91	102.53			Cl^{4}GeO^2	88.56
								N^{1}P^{1}O^1	108.95
								N^{2}P^{1}O^1	109.44
								N^{3}P^{1}O^1	113.71
								N^{4}P^{2}O^2	109.45
								N^{5}P^{2}O^2	108.94
								N^{6}P^{2}O^2	113.70

[a] Dihedral angles in complex **I**, deg: Cl^{2}GeOPN^1 79.29, Cl^{2}GeOPN^2 –42.40, and Cl^{2}GeOPN^3 –158.87. Dihedral angles in complex **II**, deg: Cl^{1}GeO^{1}P^{1}N^1 30.71, Cl^{1}GeO^{1}P^{1}N^2 156.72, Cl^{1}GeO^{1}P^{1}N^3 –86.03, Cl^{1}GeO^{2}P^{2}N^4 65.24, Cl^{1}GeO^{2}P^{2}N^5 –60.79, and Cl^{1}GeO^{2}P^{2}N^6 182.51.

Table 2. Populations of Cl valence *p* orbitals (ΣNp) and 3*p* components of these orbitals ($N3p$) in system **I**, calculated by the RHF/6-31G(*d*) method with varied Ge←O distance, and the ^{35}Cl NQR frequencies (ν) and asymmetry parameters of the electric field gradient on ^{35}Cl nuclei (η), calculated from the latter populations

Ge←O	Orbital	Cl^1			Cl^2				
		Np_x, e	Np_z, e	ν, MHz	Np_x, e	Np_y, e	Np_z, e	ν, MHz	η, %
8.0	$N3p$	1.282	1.015	24.836	1.283	1.282	1.013	25.064	0.38
	ΣNp	1.919	1.376		1.917	1.917	1.371		
5.0	$N3p$	1.281	1.017	24.594	1.285	1.281	1.012	25.236	2.08
	ΣNp	1.920	1.383		1.919	1.917	1.371		
3.0	$N3p$	1.278	1.023	23.707	1.298	1.274	1.006	26.111	12.77
	ΣNp	1.926	1.396		1.929	1.920	1.376		
2.5	$N3p$	1.275	1.028	22.923	1.304	1.268	1.005	26.283	18.82
	ΣNp	1.931	1.413		1.937	1.923	1.384		
1.965	$N3p$	1.269	1.028	22.396	1.297	1.255	1.024	23.75	25.22
	ΣNp	1.944	1.424		1.953	1.930	1.432		

only if the distance between the distance between the coordination centers is fixed at about 2.0 Å. Therewith, the total energy is much higher than that for the energetically most favorable structure [1, 8–10]. In our case, 1 : 1 complex **I** has the most favorable structure.

Correctness of the quantum-chemical calculations of the electronic and steric structure for the earlier studied Si and Ge tetrachloride complexes was assessed by consideration of their NQR ^{35}Cl frequencies and asymmetry parameters of the electric field on ^{35}Cl nuclei. The experimental NQR parameters were compared with the populations of the 3*p* components of valence *p* orbitals of Cl atoms, obtained by ab initio quantum-chemical calculations for the corresponding complexes and by Eqs. (1) and (2) [11]. Such procedure for estimation NQR parameters we proposed earlier (e.g., see [12–14]).

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

$$\eta = |3(Np_x - Np_y)/(2Np_z - Np_x - Npy)|. \quad (2)$$

Here e^2Qq_{at} is the atomic quadrupole interaction constant; *h*, Plank's constant; and N_x, Ny, and Nz, orbital populations of valence px, py, and p_z orbitals of the indicator atom. The e^2Qq_{at} value was found from the experimental NQR of Cl^2 and calculated populations of the 3*p* components of valence *p* orbitals of the Cl atoms in this molecule.

This procedure was used to calculate the ^{35}Cl NMR frequencies and asymmetry parameters of the electric field gradient on ^{35}Cl nuclei at a varied distance between the coordination centers. The NQR parameters and populations of chlorine valence *p* orbitals and their 3*p* components are listed in Tables 2 and 3. For the Cl atom of system **I**, which in the complex become axial, the populations of the p_x and p_y orbitals and their 3*p* components are equal at a given Ge←O distance. For this reason, we give in Table 2 the populations of the p_x orbitals and their 3*p* components only. We also omit from Table 2 the asymmetry parameters for this Cl atom, since they equal zero at all Ge←O distances due to equal populations of the 3*p* components of the p_x and p_y orbitals, which is characteristic of such atoms. The experimental asymmetry parameter of the axial Cl atom in the $GeCl_4$–HMPA complex, too, is close to zero (3.4 ± 0.5% at 77 K [2]). The calculated asymmetry parameters of the Cl atoms which in the trigonal-bipyramidal complex become equatorial are also close to zero at a large distance between the coordinatrion centers in system **I** also near zero, which is characteristic of Cl atoms bonded with sp^3 atoms of Group IVA elements. For example, the asymmetry parameter for $SiCl_4$ is 2.9 ± 0.5% and for $GeCl_4$, 2.2 ± 0.5% [2]. As the Ge←O distance decreases, the asymmetry of the electron distribution of these Cl atoms increases and, as a result, the asymmetry parameters also increase. At the Ge←O distance of 1.965 Å, when $GeCl_4$ forms complex with HMPA, the calculated asymmetry parameter of the electric field gradient asymmetry on ^{35}Cl nuclei of the equatorial Cl atoms (Table 2) is close to the experimental values: 28.0 ± 4.3, 28.0 ± 4.3, and 31.8 ± 5.0% (at 77 K) [2]. At larger Ge←O distances in system **II**, the asymmetry parameters are close to zero, as would be expected. As this distance decreases, the asymmetry parameters increase (Table 3) and, beginning with the Ge←O distance of 3.0 Å, they

Table 3. Populations of Cl valence *p* orbitals (ΣNp) and 3*p* components of these orbitals ($N3p$) in system **II**, calculated by the RHF/6-31G(*d*) method with varied Ge←O distance, and the ^{35}Cl NQR frequencies (ν) and asymmetry parameters of the electric field gradient on ^{35}Cl nuclei (η), calculated from the latter populations

Ge←O	Orbital	Np_x, e	Np_y, e	Np_z, e	ν, MHz	η, %
8.0	$N3p$	1.282	1.283	1.013	25.11	0.42
	ΣNp	1.917	1.917	1.370		
5.0	$N3p$	1.282	1.285	1.011	25.354	2.01
	ΣNp	1.918	1.920	1.372		
3.0	$N3p$	1.278	1.299	1.005	26.467	11.13
	ΣNp	1.930	1.939	1.390		
2.5	$N3p$	1.282	1.296	1.000	26.912	7.20
	ΣNp	1.941	1.948	1.406		
1.914	$N3p$	1.270	1.259	1.048	20.197	7.68
	ΣNp	1.958	1.957	1.529		

Table 4. Atomic charges in system **I** and charges transferred from the ligand on electron acceptor $GeCl_4$ (Δq), calculated by the RHF/6-31G(*d*) method with varied Ge←O distance

Atom	*q*, e					
Ge←O, Å	1.965	2.5	3.0	5.0	8.0	∞
Cl^1	–0.255	–0.224	–0.194	–0.167	–0.157	–0.151
Cl^2	–0.263	–0.191	–0.171	–0.149	–0.151	–0.151
Cl^3	–0.252	–0.191	–0.171	–0.152	–0.148	–0.151
Cl^4	–0.256	–0.202	–0.182	–0.153	–0.150	–0.151
Ge	0.780	0.716	0.678	0.621	0.606	0.604
O	–0.843	0.816	–0.782	–0.752	–0.749	–0.749
P	1.782	1.750	1.709	1.677	1.676	1.676
N^1	–0.763	–0.771	–0.771	–0.771	–0.771	–0.771
N^2	–0.761	–0.772	–0.771	–0.771	–0.771	–0.771
N^3	–0.772	–0.771	–0.771	–0.774	–0.774	–0.774
6C	–1.825	–1.817	–1.801	–1.789	–1.788	–1.788
18H	3.427	3.289	3.227	3.180	3.177	3.177
Δq, e	0.246	0.092	0.040	0.000	0.000	0.000

become close to the experimental values for Cl atoms in *trans*-octahedral Group IVA tetrachloride complexes. For example, the asymmetry parameters for the pairs of equivalent Cl atoms in the $SnCl_4$ complex with tetramethylurea of such structure are 8.4±0.5 and 6.7±1.9% [15]. The calculated ^{35}Cl NQR frequency of a trans-octahedral complex **II** (Table 3) is close to experiment (20.514, 20. 656, 20.784, and 21.101 MHz at 77 K [2]). The ^{35}Cl NQR frequencies of the Cl atoms which become equatorial in a trigonal-bipyramidal compex **I**, calculated at a varied Ge←O distance, vary in a narrow range (Table 2). They are close to experimental values for this complex (24.570, 24.663 and 24.916 MHz at 77 K [2]), while the NQR frequency of the Cl atom which in the complex becomes axial decreases with decreasing Ge←O distance (Table 2) but does not approach the experimental value (20.528 MHz at 77 K [2]) even at the distance of 1.965 Å. The same treads result from ab initio calculations of trigonal-bipyramidal complexes [1, 8–10]. Hence, the results obtained by these methods fail to describe adequately the electron distribution of axial Cl atoms in these complexes, the p_σ orbital populations first of all. At the same time, the calculated axial Ge–Cl bond length in complex **I** is quite reasonable (Table 1). It seems also strange that the partial negative charge on one of the equatorial Cl atoms in this complex is larger than that on the axial atom, while the latter has the same charge as the two other equatorial Cl atoms (Table 4). Earlier we

Table 5. Atomic charges in system **II** and charges transferred from the ligand on electron acceptor $GeCl_4$ (Δq), calculated by the RHF/6-31G(*d*) method with varied Ge←O distance

Atom	*q*, e				
Ge←O, Å	1.914	2.5	3.0	5.0	8.0
Cl^1	–0.415	–0.254	–0.210	–0.152	–0.149
Cl^2	–0.423	–0.249	–0.187	–0.152	–0.149
Cl^3	–0.414	–0.277	–0.216	–0.167	–0.156
Cl^4	–0.423	–0.286	–0.216	–0.167	–0.155
Ge	1.173	0.896	0.757	0.636	0.609
O^1	–0.827	–0.809	–0.772	–0.749	–0.748
O^2	–0.827	–0.809	–0.772	–0.749	–0.748
P^1	1.822	1.749	1.711	1.678	1.676
P^2	1.822	1.766	1.711	1.678	1.676
N^1	–0.769	–0.769	–0.772	–0.771	–0.771
N^2	–0.768	–0.767	–0.771	–0.771	–0.771
N^3	–0.774	–0.776	–0.772	–0.774	–0.774
N^4	–0.768	–0.770	–0.772	–0.771	–0.771
N^5	–0.774	–0.774	–0.771	–0.774	–0.774
N^6	–0.769	–0.777	–0.772	–0.771	–0.771
12C	–3.800	–3.664	–3.598	–3.577	–3.576
36H	6.934	6.570	6.422	6.353	6.352
Δq, e	0.502	0.170	0.072	0.002	0.000

showed that the partial charges on Cl atoms in chlorine-containing organic and organoelement molecules correlate with the ^{35}Cl NQR frequencies of the corresponding compounds: The higher the partial negative charge on an atom, the lower its NQR frequency [16]. Therefore, one would expect from the ^{35}Cl NQR spectrum of complex **I** that the partial negative charge on its axial Cl is substantially higher than the charges on equatorial Cl atoms. Such relation between the charges on the axial and equatorial Cl atoms occur in system **I** at Ge←O distances longer than 1.965 Å (Table 4).

In system **I** at large Ge←O distances, the atomic charges in the donor and acceptor molecules remain practically the same as in the individual molecules (in Table 4 they are listed in the "∞" column). As this distance decreases, the molecules mutually polarize: The partial negative charges on Cl and the positive charge on Ge increase in the electron acceptor, and the partial negative charges on O and C and the positive charges on P and H increase in the electron donor. To a certain Ge←O distance the donor and acceptor molecules remain neutral (the sum of the charges in each equals zero), the charges on the N atoms in the donor molecule scarcely vary with the Ge←O distance. When the Ge←O distance attains ~3 Å, electron density transfer, basically from H atoms of the donor onto Cl atoms of the acceptor, occurs. In complex **I**, the transfer is 0.246 e (Table 4). On the formation of complex **I** no electron density transfer occurs from the donor O atom onto the acceptor Ge atom: On the contrary, on complex formation the electron density on O increases and on Ge it decreases. These atoms behave as conductors in the electron density transfer from H atoms of the donor on Cl atoms of the acceptor. The same occurs on the formation of a trans-octahedral complex **II** (Table 5). The electron density is primarily transferred from H atoms of the electron-donor molecule on Cl atoms of the acceptor (a total of 0.502 e).

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