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Ab initio Calculations of Complexes of Group IVA Tetrachlorides: VI.[1] Structure and Dynamics of Formation of a Complex of $GeCl_4$ with Tetramethylurea

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Abstract—RHF/6-31G(*d*) calculations of the $GeCl_4 \leftarrow OC[N(CH_3)_2]_2$ system were done with full geometry optimization and at varied Ge←O distances. The calculated structure of the complex $GeCl_4 \leftarrow OC[N(CH_3)_2]_2$ and its ^{35}Cl NQR parameters were consistent with the experimental data not at the fully optimized geometry of the system but at the Ge←O distance fixed at 2.0 Å, at which the total energy of the system is higher by 0.264 eV. With a decrease in the Ge←O distance from ∞ to 1.9 Å, the electron density of the Cl atoms increases as a result of the electron density transfer from the H atoms and polarization of the Ge–Cl bonds under the action of the electron-donor fragment. The O, C, and N atoms of this fragment are merely conductors of the electron density from the H atoms of the methyl groups to the Cl atoms of the electron acceptor.

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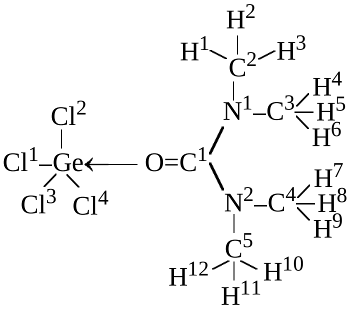
The quadruplet ^{35}Cl NQR spectrum of the complex of $GeCl_4$ with tetramethylurea (**I**) suggests its trigonal-bipyramidal structure. In this spectrum, the high-frequency triplet (25.094, 24.858, and 24.341 MHz) belongs to three equatorial Cl atoms, and the low-frequency line (20.668 MHz), to the axial atom [2, 3]. This structure is also confirmed by the asymmetry parameters of the electric field gradient on the ^{35}Cl nuclei. The asymmetry parameters corresponding to the three high-frequency NQR lines are high (26.4 ± 5.0, 25.3 ± 4.2, and 27.0 ± 3.8%, respectively), and that corresponding to the low-frequency line is low (5.6 ± 1.0%), indicating that the symmetry of the electron distribution of the Cl atom giving this line is close to axial [3, 4].



I

In this study, the structure, mechanism, and dynamics of formation of this complex were studied by the restricted Hartree–Fock method using the 6-31G(*d*) split and polarized valence basis set. The structure of **I** was calculated with full geometry optimization and at fixed Ge←O distances, using the GAUSSIAN 94W program [5]. In the calculations, the origin of the coordinate system coincided with the nucleus of the axial Cl^1 atom. To estimate the populations of valence *p* orbitals of the equatorial Cl atoms, the calculations were repeated with the origin coinciding with the Cl^2 nucleus. As judged from the experimental NQR frequencies and asymmetry parameters of the electric field gradient for the equatorial Cl atoms, the electron distributions on these atoms differ insignificantly. Therefore, the populations of the valence *p* orbitals of the equatorial Cl atoms will also differ insignificantly. In both cases, the *Z* axis of the coordinate system is directed along the corresponding Cl–Ge bond.

At full geometry optimization, we obtained the structure of **I** essentially different from the ideal trigonal-bipyramidal structure, with a Ge←O distance of 3.376 Å (Table 1). Similar structure with an unrealistically long Si←O distance was also obtained previously by full optimization of the geometry of the $SiCl_4 \leftarrow OC[N(CH_3)_2]_2$ system [1]. According to the

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

Table 1. Bond lengths *d*, bond angles ω, and dihedral angles τ in system **I**, calculated by the RHF/6-31G(*d*)) method at various Ge←O distances

Geometric parameter	Ge←O, Å							
	1.9	2.0	2.15	3.0	3.376	4.0	6.0	∞
Bond	*d*, Å							
Ge–XCl$_1$	2.247	2.234	2.213	2.144	2.133	2.125	2.120	2.116
Ge–XCl$_2$	2.186	2.170	2.153	2.117	2.115	2.115	2.115	2.116
Ge–XCl$_3$	2.183	2.168	2.152	2.118	2.117	2.116	2.115	2.116
Ge–XCl$_4$	2.161	2.153	2.143	2.118	2.116	2.115	2.115	2.116
O=C^1	1.245	1.239	1.231	1.209	1.206	1.203	1.202	1.202
C^1–XN$_1$	1.342	1.346	1.352	1.370	1.374	1.378	1.380	1.380
C^1–XN$_2$	1.340	1.345	1.352	1.375	1.378	1.378	1.380	1.380
N^1–XC$_2$	1.456	1.455	1.453	1.451	1.451	1.451	1.451	1.451
N^1–XC$_3$	1.457	1.456	1.455	1.453	1.453	1.454	1.453	1.453
N^2–XC$_4$	1.458	1.457	1.456	1.455	1.454	1.454	1.453	1.453
N^2–XC$_5$	1.461	1.459	1.456	1.452	1.451	1.451	1.451	1.451
Angle	ω, deg							
Cl^{1}GeCl^2	91.87	93.30	95.42	104.80	106.95	108.40	109.18	109.49
Cl^{1}GeCl^3	92.23	93.63	95.70	104.91	106.93	108.35	109.15	109.46
Cl^{1}GeCl^4	94.25	95.01	96.62	104.96	106.96	108.44	109.16	109.46
Cl^{2}GeCl^3	128.62	126.20	123.86	114.01	111.97	110.48	109.78	109.46
Cl^{2}GeCl^4	117.24	118.07	118.13	114.19	112.14	110.57	109.79	109.46
Cl^{2}GeO	84.44	83.41	81.68	73.09	71.55	71.36	69.65	
Cl^{3}GeO	85.91	85.00	83.20	76.59	74.28	72.44	72.12	
Cl^{4}GeO	92.23	90.25	87.75	75.70	73.35	71.01	70.74	
OC^{1}N^1	121.58	121.79	122.03	121.66	121.73	121.85	121.97	121.97
OC^{1}N^2	119.37	119.74	120.17	121.78	121.84	121.92	121.97	121.97
C^{1}N^{1}C^2	120.58	120.23	119.58	116.94	116.28	115.67	115.51	115.51
C^{1}N^{1}C^3	122.42	122.44	122.40	122.12	121.64	120.94	120.72	120.72
C^{1}N^{2}C^4	122.69	122.63	122.54	120.86	120.73	120.88	120.72	120.72
C^{1}N^{2}C^5	119.75	119.33	118.71	115.89	115.62	115.66	115.51	115.51
Angle	τ, deg							
OC^{1}N^{1}C^2	–19.23	–18.07	–16.04	–7.55	–6.72	–6.73	–6.70	–6.70
OC^{1}N^{1}C^3	143.20	142.94	142.31	142.19	140.17	137.23	136.47	136.47
OC^{1}N^{2}C^4	148.10	146.94	145.30	135.81	135.76	136.91	136.50	136.50
OC^{1}N^{2}C^5	–11.12	–10.60	–9.91	–8.46	–7.67	–6.92	–6.70	–6.70

^{35}Cl NQR spectra, complexes of $SiCl_4$ and $GeCl_4$ with trimethylamine also have a trigonal-bipyramidal structure [2, 3]. In their RHF/6-31G(*d*) calculations with full geometry optimization, we also obtained a structure essentially different from the trigonal-bipyramidal structure, with an unrealistically long distance between the coordination centers [6, 7].

The correctness of quantum-chemical calculations of the geometries of complexes of Group IVA element tetrachlorides with organic ligands and of the electron distribution of the Cl atoms in these complexes was checked [1, 6–9] by determining the populations of the 3*p* constituents of the valence *p* orbitals of the Cl atoms, calculating the ^{35}Cl NQR frequencies and asymmetry parameters of the electric field gradient on the ^{35}Cl nuclei by Eqs. (1) and (2) [10], and comparing the results obtained with the experimental data:

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

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

where e^2Qq_{at} is the atomic quadrupole interaction constant; *h*, Planck constant; N_x, N_y, and N_z, populations of the p_x, p_y, and p_z orbitals of the indicator atom, respectively. The quantity e^2Qq_{at} was found from the experimental NQR frequency of Cl_2 and populations of the 3*p* constituents of the valence *p* or-

Table 2. Populations of the valence *p* orbitals of the Cl^1 and Cl^2 atoms (ΣNp) and of their 3*p* constituents ($N3p$) in system **I**, calculated by the RHF/6-31G(*d*) method at various Ge←O distances, and the ^{35}Cl NQR frequencies ν and asymmetry parameters η of the electric field gradient on the ^{35}Cl nuclei, calculated from these populations

Ge←O, Å	Orbital	Cl^1					Cl^2				
		Np_x, e	Np_y, e	Np_z, e	ν, MHz	η, %	Np_x, e	Np_y, e	Np_z, e	ν, MHz	η, %
6.0	$N3p$	1.281	1.281	1.015	24.765	0.00	1.283	1.282	1.013	25.117	0.98
	ΣNp	1.919	1.919	1.378			1.918	1.917	1.371		
4.0	$N3p$	1.280	1.280	1.017	24.511	0.00	1.287	1.280	1.011	25.368	4.22
	ΣNp	1.921	1.921	1.381			1.922	1.918	1.372		
3.376	$N3p$	1.280	1.279	1.019	24.250	0.21	1.293	1.277	1.009	25.734	8.39
	ΣNp	1.923	1.923	1.384			1.926	1.919	1.373		
3.0	$N3p$	1.279	1.278	1.022	23.820	0.50	1.298	1.274	1.006	26.123	12.47
	ΣNp	1.926	1.925	1.397			1.929	1.919	1.374		
2.15	$N3p$	1.273	1.269	1.030	22.426	0.39	1.303	1.264	1.011	25.563	21.37
	ΣNp	1.941	1.939	1.425			1.946	1.926	1.402		
2.0	$N3p$	1.271	1.266	1.029	22.298	3.26	1.301	1.260	1.017	24.75	23.20
	ΣNp	1.946	1.942	1.429			1.950	1.927	1.418		
1.9	$N3p$	1.272	1.265	1.028	22.366	4.25	1.300	1.252	1.021	24.035	27.95
	ΣNp	1.272	1.265	1.028			1.957	1.927	1.430		

bitals of the Cl atoms of this molecule, obtained by appropriate calculation.

By the same procedure, we calculated the ^{35}Cl NQR parameters for system **I** (Table 2). From the populations found by a quantum-chemical calculation with the full geometry optimization, we obtained the ^{35}Cl NQR frequencies and asymmetry parameters of the electric field gradient on ^{35}Cl nuclei; the results we obtained, however, appreciably differ from the experimental data (see above).

For all the trigonal-bipyramidal complexes, the structure close to a trigonal bipyramid and the ^{35}Cl NQR parameters close to the experimental values were obtained when the distance between the coordination centers was fixed at a considerably smaller value than that corresponding to the fully optimized goemetry. This fixed distance for the complex of $GeCl_4$ with trimethylamine was taken [7] from X-ray diffraction data [11]; for the complex of $SiCl_4$ with trimethylamine, it was estimated from the above data and the difference between the covalent radii of the Si and Ge atoms [6]; and for the complex of $SiCl_4$ with tetramethylurea (2.1 Å), it was estimated from the previous value and the difference between the covalent radii of the N and O atoms [1]. As the covalent radius of the Ge atom is larger than that of the Si atom by 0.05 Å, the distance between the coordination centers in the complex of $GeCl_4$ with tetramethylurea can be assumed to be 2.15 Å. Therefore, the calculations for system **I** were performed at the distance between the coordination centers fixed at this level and the other geometric parameters optimized. In this case, the axial Cl–Ge bond, as expected, becomes appreciably longer than the equatorial bonds (Table 1). The lengths between the axial and equatorial Cl–Ge bonds approach 90°, and those between the equatorial Cl–Ge bonds, 120°, i.e., the values characteristic of a trigonal-bipyramidal structure. Furthermore, the ^{35}Cl NQR frequencies and asymmetry parameters of the electric field gradient on the ^{35}Cl nuclei approach the corresponding experimental values, although the disagreement is still appreciable (Table 2).

At a Si←O distrance of 2.0 Å in the complex of $SiCl_4$ with tetramethylurea, the agreement with the experimental NQR data is still better than at the distance of 2.1 Å. Therefore, in the complex of $GeCl_4$ with tetramethylurea the distance between the coordination centers may be also shorter than 2.15 Å. To check this assumption, we performed calculations for system **I** at a Ge←O distance of 2.0 Å. In this case, the axial Cl–Ge bond becomes still longer relative to the equatorial bonds, and the bond angles in the acceptor moiety become still closer to those in an ideal trigonal bipyramid. The NQR frequency of the axial Cl atom somewhat decreases, but becomes considerably higher than the experimental value, as in the calculations of other trigonal-bipyramidal complexes [1, 6, 7]. The NQR frequency of the equatorial Cl atoms virtually coincides with the experimental value. The asymmetry parameters of the electric field gradient on the ^{35}Cl nuclei of the axial and equatorial Cl atoms are close to the experimental values (Table 2). At the Ge←O distance decreased further to 1.9 Å, some of the geometric parameters of the Ge coordination polyhedron somewhat approach the values characteristic of an ideal trigonal bipyramid, but the other parameters show larger deviations (Table 1). The same concerns the ^{35}Cl NQR parameters (Table 2).

In all the examined systems Group IVA tetrachloride–ligand, at a fixed distance between the coordination centers, close to the actual distance in the trigonal-bipyramidal complex, the calculated NQR frequencies of the equatorial Cl atoms and asymmetry parameters of the electric field gradient on the ^{35}Cl nuclei of the axial and equatorial Cl atoms reasonably agree with the experimental values. The calculated NQR frequency of the axial Cl atom is always appreciably overestimated, whereas the trend toward its decrease with a decrease in the distance between the coordination centers is correct. The overestimation of the calculated NQR frequency of the axial Cl atom indicates that ab initio methods unsatisfactorily describe the electron distribution of axial atoms in complexes of such structure. The unrealistically long distance between the coordination centers, given by the quantum-chemical calculation of the system with full geometry optimization, indicates that the complex is not the form energetically most favorable. The total energy of system **I** calculated at a fixed Ge←O distance of 2.15 Å is 0.204 eV higher, and at a distance of 2.0 Å, 0.264 eV higher than that of the system with the fully optimized geometry.

The reasonable agreement between the experimental and calculated (at the Ge←O distance of 2.0 Å) NQR parameters of the complex of $GeCl_4$ with tetramethylurea allows us to analyze the mechanism and dynamics of formation of such complex on the basis of quantum-chemical data.

In Table 1, the geometric characteristics of system **I** at infinitely long Ge←O distance correspond to those of the individual components. With mutual approach of the components, all the Cl–Ge bonds become longer, especially the bond that becomes axial in the complex. The C^1=O bond length also increases, and the N–C^1 bond length decreases. The bonds of the N atoms with the C atoms of methyl groups remain essentially unchanged. As the Ge←O distance becomes shorter, the angles between the Cl–Ge bonds that become equatorial in the complex increase to ~120°, and the angles between the Cl–Ge bond that becomes axial and the Cl–Ge bonds that become equatorial, as well as the angles between the latter bonds and the Ge←O coordination bond, tend to 90°. The OC^1N bond angles are close to 120° and vary with the Ge←O distance insignificantly. The three N–C bonds of each N atom form a pyramid. The sum of the CNC angles is less than 360°: 349.87° for both N atoms at the Ge←O distance of 6.0 Å, and 357.15° and 356.75° for the N^1 and N^2 atoms, respectively, at a Ge←O distance of 2.0 Å. The changes in the geometric parameters of system I become significant at the Ge←O distance decreased to ~3 Å and below.

As the components of system **I** approach each other, the populations of the 3*p* constituents of the valence p_x and p_y orbitals of the axial Cl atom decrease, and the population of its p_z orbital increases. This leads to a decrease in the NQR frequency of this Cl atom with a decrease in the Ge←O distance to 2.0 Å. The asymmetry parameter of this Cl atom somewhat increases with a decrease in the Ge←O distance, approaching the experimental value (Table 2). As for the equatorial Cl atoms, the populations of the 3*p* constituents of their valence p_x orbitals increase, and those of the p_y orbitals, decrease with mutual approach of the components of system **I**. The populations of the 3*p* constituents of the p_z orbitals vary irregularly. The calculated NQR frequencies of these Cl atoms vary within narrow limits, and the asymmetry parameters appreciably increase, approaching the experimental values (see above), with a gradual decrease in the Ge←O distance.

In Table 3, the atomic charges in system **I** at infinitely long Ge←O distance correspond to those in the individual componentrs. With a decrease in the Ge←O distance, the partial negative charges of all the Cl atoms and the partial positive charge of the Ge atom of the acceptor increase. In the process, the partial positive charges of the C^1 atoms and of all the hydrogen atoms of the electron donor, and the partial negative charge of the O atom increase also. The partial negative charges of the N^1, C^2, C^3, C^4, and C^5 atoms slightly increase, and the charge of the N^2 atom remains essentially unchanged. At the Ge←O distance of 6.0 Å, the electron acceptor and donor remain neutral (Δq 0). As the Ge←O distance is decreased, the electron donor acquires a partial positive charge, and the acceptor, a negative charge. For example, at the distance of 2.0 Å the electron acceptor has a charge of -0.194 *e*, and the donor has a positive charge of the same value. This charge is mainly transferred from the hydrogen atoms of the electron donor to the Cl atoms of the acceptor. Some part of the electron density of the Cl atoms in the complex is also transferred from the Ge atom. In the complex, the carbonyl group is considerably more polarized than in the individual tetramethylurea molecule. Changes in the atomic charges in the donor fragment are the most pro-

Table 3. Atomic charges *q* in system **I**, calculated by the RHF/6-31G(*d*) method at various Ge←O distances, and charges Δ*q* transferred from the ligands to the electron acceptor

Atom	Ge←O, Å							
	1.9	2.0	2.15	3.0	3.376	4.0	6.0	∞
				q, *e*				
Cl^{1}	–0.267	–0.261	–0.249	–0.195	–0.174	–0.167	–0.161	–0.151
Cl^{2}	–0.261	–0.240	–0.216	–0.169	–0.162	–0.156	–0.150	–0.151
Cl^{3}	–0.260	–0.242	–0.221	–0.178	–0.169	–0.158	–0.151	–0.151
Cl^{4}	–0.249	–0.236	–0.219	–0.174	–0.166	–0.155	–0.149	–0.151
Ge	0.806	0.785	0.760	0.684	0.652	0.628	0.611	0.604
O	–0.746	–0.742	–0.733	–0.660	–0.645	–0.634	–0.628	–0.627
C^{1}	1.111	1.100	1.084	1.013	1.001	0.992	0.984	0.984
N^{1}	–0.677	–0.677	–0.677	–0.671	–0.669	–0.668	–0.667	–0.667
N^{2}	–0.664	–0.665	–0.667	–0.668	–0.667	–0.668	–0.667	–0.667
C^{2}	–0.295	–0.292	–0.289	–0.281	–0.280	–0.279	–0.277	–0.277
C^{3}	–0.309	–0.307	–0.306	–0.305	–0.305	–0.304	–0.304	–0.304
C^{4}	–0.310	–0.309	–0.307	–0.306	–0.305	–0.304	–0.304	–0.304
C^{5}	–0.317	–0.312	–0.305	–0.283	–0.281	–0.279	–0.277	–0.277
H^{1}	0.224	0.220	0.216	0.210	0.208	0.204	0.203	0.203
H^{2}	0.205	0.199	0.192	0.170	0.167	0.165	0.164	0.164
H^{3}	0.183	0.181	0.177	0.165	0.164	0.162	0.161	0.161
H^{4}	0.207	0.206	0.205	0.204	0.203	0.202	0.201	0.201
H^{5}	0.187	0.184	0.181	0.173	0.172	0.173	0.172	0.172
H^{6}	0.204	0.200	0.194	0.176	0.173	0.170	0.169	0.169
H^{7}	0.189	0.186	0.182	0.175	0.174	0.172	0.172	0.172
H^{8}	0.205	0.200	0.194	0.175	0.172	0.171	0.169	0.169
H^{9}	0.206	0.205	0.204	0.201	0.201	0.202	0.201	0.201
H^{10}	0.206	0.200	0.192	0.170	0.168	0.165	0.164	0.164
H^{11}	0.187	0.183	0.179	0.166	0.164	0.162	0.161	0.161
H^{12}	0.237	0.233	0.228	0.208	0.206	0.204	0.203	0.203
Δ*q*, e	0.231	0.194	0.145	0.032	0.020	0.008	0.000	–

nounced. The N^{1}, N^{2}, C^{2}, C^{3}, C^{4}, and C^{5} atoms are merely conductors of the electron density from the H atoms of the methyl groups to the Cl atoms of the electron acceptor.

As judged from the populations of the valence *p* orbitals of the Cl atoms, the electron density of both axial and equatorial Cl atoms increases with mutual approach of the components of system **I**, mainly at the expense of an increase in the populations of their p_z (p_σ) orbitals (Table 2). Considerably smaller, and approximately equal, contribution to this increase is made by the p_x and p_y orbitals of the axial Cl atom. Changes in the populations of the p_x orbitals of the equatorial Cl atoms whose symmetry axes are perpendicular to the equatorial plane of the coordination polyhedron of the Ge atom also make a considerably smaller contribution, compared to the p_z orbitals, to an increase in the electron density of these Cl atoms, and the contribution of their p_y orbitals is negligible.

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