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Ab Initio Calculations of Group IVA Tetrachloride Complexes: IV.[1] Dynamics of the Formation of the Complex of SiCl_4 with Trimethylamine

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Abstract—Quantum-chemical calculations of the system $\text{SiCl}_4\leftarrow\text{N(CH}_3)_3$ were fulfilled by the RHF/6-31G(d) and B3LYP/6-311G(d) methods with full geometry optimization at varied Si←N distances. The experimental electronic and steric structure of the complex were fit not on full geometry optimization but on the geometry optimization with the Si←N distance fixed at the experimental estimate. The calculations showed that the components polarize each other as come closer together. Furthermore, the electron density is transferred from the H atoms of the donor onto the Cl atoms of the acceptor. The C, N, and Si atoms serve only as electron density conductors.

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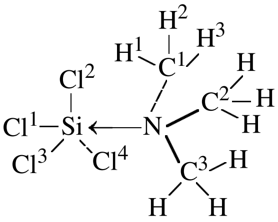
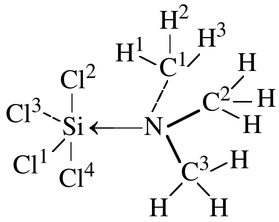
Quantum-chemical calculations of the complex of SiCl_4 with trimethylamine in the MNDO approximation [2] agree with the ^{35}Cl NQR experimental data for this complex, which point to its trigonal-bipyramidal structure **I** with the ligand in an axial position of the bipyramid. The NQR spectrum contains two high-frequency lines at 21.502 and 21.296 MHz (intensity ratio ~1 : 2), corresponding to three equatorial Cl atoms, and one low-frequency line at 18.857 MHz, belonging to an axial Cl atom [3, 4]. The frequencies of the first two lines are much higher than those for pure SiCl_4 (20.464, 20.415, 20.408, and 20.273 MHz [3, 4]), whereas the frequency of the third line is lower. Therefore, as compared to pure SiCl_4, the electron density of the axial Cl atom in the complex is higher and that of the equatorial atoms is lower. The asymmetry parameters of the electric field gradient at ^{35}Cl for the equatorial Cl atoms in this complex are fairly large (42.1 and 36.6%, respectively [4]), whereas that for the axial Cl atom is close to zero (1.7% [4]), implying that the electron distribution has an almost axial symmetry.



I



II

According to MNDO calculations [2], the formation heat of complex **I** is a minimum (*F* –125.7 kcal mol^{-1}) at a Si←N distance of 2.25 Å, and that of complex **II** with an equatorial ligand, at a Si←N distance of 2.0 Å (*F* –119.9 kcal mol^{-1}).

In the present work we studied complex **I** by higher level quantum-chemical methods, viz. the restricted Hartree–Fock method (RHF) with split-valence and polarized 6-31G(d) basis in which each valence orbital is presented as a combination of two orbitals of different size, as well as by the B3LYP density functional theory method with the 6-311G(d) basis in which each valence orbital is presented as a combination of three orbitals of different size. The latter method takes partial account for electron correlation and is recommended for better fitting properties of compounds (see, for example, [5]). The former method was chosen because it fairly reproduces experimental ^{35}Cl NQR parameters, as we showed, for example, in [6–8]) when estimating ^{35}Cl NQR frequencies (η) and asymmetry parameters of the electric

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

field gradient at ^{35}Cl (ν) for organic and organoelement molecules from the populations of less diffuse 3*p* components of valence *p* orbitals of Cl atoms, found from RHF/6-31G(d) calculations and from Eqs. (1) and (2) [9], respectively.

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

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

Here e^2Qq_{at} is the atomic quadrupole coupling constant; *h*, Planck's constant; and N_x, N_y, and N_z, populations of the p_x, p_y, and p_z valence orbitals of an indicator atom, respectively. The e^2Qq_{at} value was found from the experimental NQR frequency of Cl_2 and from the calculated valence 3*p* orbital populations of the Cl atoms of this molecule.

Structure **I** was calculated using the GAUSSIAN 94W program [10] with full geometry optimization and with varied coordinate of the complex formation reaction. The axial Cl^1 atom was taken as the coordinate origin. To estimate the populations of valence *p* orbitals of the equatorial Cl atoms, the calculations were carried out repeatedly with the coordinate origin system put on the equatorial Cl^2 atom. In this case, the *X* axis is perpendicular to the equatorial plane of the trigonalbipyramidal complex and the *Y* axis lies in this plane. In both coordinate systems, the *Z* axis coincides with the corresponding Cl–Si bond.

For the $SiCl_4$ [11] and $GeCl_4$ [12] complexes with pyridine, which have the same *trans*-octahedral structures, the results of the RHF/6-31G(d) calculations with full geometry optimization agree with the ^{35}Cl NQR spectra [3, 4]. The Si←N distance in the first complex (2.038 Å) is shorter by 0.05 Å than the Ge←N distance in the second (2.088 Å), which coincides with the difference between the covalent radii of the Si and Ge atoms [12]. The ^{35}Cl NQR spectra of the $SiCl_4$ and $GeCl_4$ complexes with trimethylamine point to their similar trigonalbipyramidal structures [3, 4]. It can be assumed that the Si←N and Ge←N distances in these complexes will differ by the same value as the covalent radii of the Si and Ge atoms (by analogy with *trans*-octahedral complexes). The results of the RHF/6-31G(d) calculations of the $GeCl_4$ complex with trimethylamine are given in [1]. The optimized geometry [1] essentially differ from X-ray diffraction data, according to which the Ge←N distance is 2.19 Å [13]. In the completely optimized system this distance is 3.41 Å [1]. The RHF/6-31G(d) calculation of structure **I** with full geometry optimization, as well as of the similar $GeCl_4$ structure [1], do not fit the experimental NQR data for the complex, indicative of its trigonal-bipyramidal structure (see above). According to the calculation, the most energetically favorable structure of **I** has the Si←N distance of 3.95 Å, which is even longer than in the similar germanium structure. The Si–Cl^1 bond is only slightly longer than the Si–Cl^2, Si–Cl^3, and Si–Cl^4 bonds (Table 1). The angles between the first and last bonds are closer to tetrahedral than to right angles characteristic of a trigonal-bipyramidal molecule. The B3LYP/6-311G(d) method does not provide qualitatively better results. The Si←N distance (3.67 Å) decreases only slightly. The results of calculations of the geometric parameters of structure **I** with various fixed Si←N distances by both methods do not differ essentially from each other (Table 1).

The results of the RHF/6-31G(d) calculations for the $GeCl_4$ complex with trimethylamine [1] with a fixed Ge←N distance taken from X-ray diffraction data agree with these data. The NQR frequencies of the equatorial Cl atoms and also the asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei of the equatorial and axial Cl atoms are close to experimental values. The calculated NQR frequency of the axial Cl atom still essentially differs from the experimental value.

For the complex of $SiCl_4$ with trimethylamine, X-ray diffraction data are absent. However, we can assume that the Si←N distance in it should be close to the Ge←N distance in the corresponding $GeCl_4$ complex. Therefore, we fulfilled calculations with the Si←N distance fixed at 2.14 Å, which is shorter by 0.5 Å than the Ge←N distance in the $GeCl_4$ complex, and also with the Si←N distance fixed at 2.25 Å, which gave the minimal formation heat of this complex in the MNDO approximation [2]. With the Si←N distance of 2.14 Å, system **I** has a structure close to trigonal-bipyramidal: The calculated axial Si–Cl^1 bond length is essentially larger than the lengths of the equatorial Si–Cl bonds, the angles between the axial and equatorial Si–Cl bonds are close to 90°, and the angles between the equatorial Si–Cl bonds are close to 120°. With the Si←N distance of 2.25 Å, the structure of the complex corresponds to trigonal-bipyramidal to a lesser degree. The structure of system **I** is closest to ideal trigonal-bipyramid at the Si←N distance of 1.9 Å (Table 1).

Table 2 lists the valence 3*p* orbital populations of the Cl atoms in structure **I**, calculated by the RHF/6-31G(d) method with varied Si←N distances, and also the ^{35}Cl NQR frequencies and the asymmetry parameters of the electric field gradient at ^{35}Cl, calculated from these populations by Eqs. (1) and (2) [9]. For the Cl^1 atom at any Si←N distances, the populations

Table 1. Bond lengths (*d*) and valence angles in structure **I** at various Si←N distances, calculated by the RHF/6-31G(d) and B3LYP/6-311G(d) methods

d, Å				Angle, deg								
Si←N	Si–Cl^1	Si–Cl^2	N–C^1	Cl^{1}SiCl^2	Cl^{1}SiCl^3	Cl^{1}SiCl^4	Cl^{2}SiCl^3	Cl^{1}SiN	Cl^{2}SiN	C^{1}NC^2	C^{2}NC^3	C^{3}NC^1
						RHF						
6.0	2.030	2.029	1.445	109.35	109.34	109.35	109.59	179.88	70.54	111.92	111.91	111.91
5.0	2.031	2.028	1.446	109.19	109.18	109.19	109.75	179.90	70.72	111.89	111.88	111.88
3.95	2.036	2.028	1.447	108.40	108.39	108.40	109.52	–	71.62	111.57	111.57	111.57
3.2	2.050	2.030	1.454	105.39	105.44	105.41	113.22	179.96	74.57	110.01	110.01	110.00
2.4	2.113	2.062	1.478	96.29	96.31	96.30	118.81	179.96	83.67	107.34	107.33	107.31
2.25	2.132	2.074	1.485	94.23	94.25	94.23	119.48	179.98	85.75	106.76	106.74	106.75
2.14	2.147	2.085	1.492	92.77	92.78	92.79	119.81	179.98	87.22	106.27	106.27	106.27
1.9	2.179	2.108	1.511	89.93	89.93	89.94	120.04	179.99	90.06	105.00	104.99	105.00
						B3LYP						
6.0	2.043	2.041	1.454	109.33	109.33	109.33	109.60	179.86	70.53	111.55	111.55	111.50
5.0	2.044	2.041	1.455	109.19	109.23	109.23	109.73	177.27	68.62	111.51	111.52	111.51
4.0	2.047	2.041	1.455	108.77	108.80	108.80	110.15	179.27	70.50	111.56	111.57	111.51
3.67	2.051	2.042	1.457	108.13	108.11	108.10	110.78	–	71.66	111.26	111.26	111.27
3.2	2.064	2.045	1.463	105.74	105.48	105.46	113.06	179.66	74.61	110.25	110.21	110.22
2.4	2.132	2.085	1.487	96.09	96.21	96.21	118.91	179.90	83.81	107.73	107.74	107.79
2.14	2.168	2.107	1.502	92.86	92.83	92.80	119.84	179.95	87.18	106.54	106.53	106.60
1.9	2.202	2.130	1.522	90.10	90.07	89.99	119.98	179.90	89.98	105.04	105.14	105.10

Table 2. Populations (*N*)[a] of the 3*p* components of valence *p* orbitals of the Cl atoms in structure **I**, calculated by the RHF/6-31G(d) method with varied Si←N distances and the ^{35}Cl NQR frequencies (ν) and asymmetry parameters of the electric field gradient on ^{35}Cl (η), calculated from these populations

d, Å	Cl^1			Cl^2				
Si←N	Np_x, e	Np_z, e	ν, MHz	Np_x, e	Np_y, e	Np_z, e	ν, MHz	η, %
6.0	1.280	1.053	21.157	1.281	1.280	1.052	21.277	0.71
5.0	1.280	1.053	21.111	1.282	1.279	1.052	21.308	1.53
3.95	1.279	1.054	21.005	1.285	1.278	1.051	21.464	4.69
3.2	1.278	1.055	20.772	1.291	1.275	1.049	21.800	10.72
2.4	1.274	1.057	20.222	1.301	1.265	1.049	22.005	23.51
2.25	1.273	1.057	20.152	1.302	1.262	1.051	21.702	26.19
2.14	1.272	1.056	20.138	1.302	1.260	1.054	21.414	27.92
1.9	1.271	1.054	20.221	1.301	1.255	1.059	20.701	31.80
1.8	1.270	1.052	20.307	1.301	1.253	1.062	20.407	33.17

[a] The populations of the components of the p_x and p_y orbitals of the Cl^1 atom are equal to each other at the same Si←N distance. The respective characteristics of the Cl^2, Cl^3, and Cl^4 atoms are close to each other.

of the p_x and p_y orbitals (Table 3) and of their less diffuse 3*p* components (Table 2) are equal. Therefore, the asymmetry parameters for these Cl atoms are equal to zero and are not given in Table 2.

The NQR frequency of the Cl^1 atom, calculated with the Si←N distance of 3.95 Å (full geometry optimization), is only slightly lower than those for Cl^2, Cl^3, and Cl^4. It is essentially higher than the experimental frequency for the axial Cl atom. The calculated NQR frequencies of Cl^2, Cl^3, and Cl^4 practically coincide with experimental frequencies for the equatorial Cl atoms, but their electric field gradient asymmetry parameters considerably differ from ex-

Table 3. Populations (N)[a] of the $3p$ components of valence atomic p orbitals in structure **I**, calculated by the RHF/6-31G(d) and B3LYP/6-311G(d) methods with varied Si←N distances

d, Å	Cl^1		Cl^2			Si		N	
Si←N	Np_x, e	Np_z, e	Np_x, e	Np_y, e	Np_z, e	Np_x, e	Np_z, e	Np_x, e	Np_z, e
				RHF					
6.0	1.923	1.429	1.923	1.922	1.427	0.611	0.605	1.081	1.728
5.0	1.924	1.431	1.924	1.921	1.427	0.611	0.601	1.083	1.725
3.95	1.925	1.436	1.928	1.921	1.429	0.612	0.583	1.087	1.717
3.2	1.931	1.449	1.934	1.917	1.431	0.612	0.556	1.102	1.700
2.4	1.951	1.495	1.952	1.912	1.447	0.595	0.513	1.178	1.609
2.25	1.956	1.508	1.955	1.911	1.459	0.587	0.498	1.204	1.574
2.14	1.958	1.517	1.957	1.911	1.469	0.581	0.488	1.225	1.546
1.9	1.963	1.533	1.959	1.911	1.491	0.570	0.484	1.271	1.476
				B3LYP					
6.0	1.941	1.438	1.941	1.940	1.437	0.638	0.635	1.026	1.647
5.0	1.941	1.439	1.942	1.941	1.437	0.637	0.633	1.038	1.631
4.0	1.944	1.440	1.943	1.941	1.439	0.632	0.626	1.032	1.645
3.67	1.945	1.441	1.951	1.941	1.439	0.629	0.620	1.034	1.645
3.2	1.951	1.446	1.957	1.940	1.438	0.624	0.610	1.045	1.636
2.4	1.971	1.467	1.976	1.941	1.451	0.607	0.591	1.120	1.529
2.14	1.978	1.476	1.982	1.941	1.464	0.602	0.573	1.165	1.470
1.9	1.982	1.483	1.984	1.939	1.479	0.601	0.561	1.209	1.412

[a] The populations of the p_x and p_y orbitals of the Cl1 atom are equal to each other at the same Si←N distance. The same relates to the nitrogen and silicon atoms.

perimental (see above). At the same time, at the Si←N distance of 2.14 Å the calculated NQR frequencies of the equatorial Cl atoms and the electric field gradient asymmetry parameters on the ^{35}Cl nuclei of the axial and equatorial Cl atoms in structure **I** are close to the experimental values [3, 4]. The calculated NQR frequency of the axial Cl atom is essentially lower than for the equatorial atoms, as would be expected for a trigonal-bipyramidal complex, but noticeably higher than the experimental value (see above). Therefore, according to the RHF/6-31G(d) calculations of complex **I** with the Si←N distance fixed at 2.14 Å and the other geometric parameters optimized, the electronic distribution on its Cl atoms qualitatively and even quantitatively corresponds to experimental NQR data, except for the axial Cl atom, for which the quantitative correspondence is not fully satisfactory.

Thus, the trigonal-bipyramidal structure of complex **I**, found experimentally, is not reproduced on full geometry optimization. The electron distribution of the axial and equatorial Cl atoms poorly fits the ^{35}Cl NQR experimental data for this complex. Calculations with the Si←N distance fixed at 2.14 Å and less reproduce the trigonal-bipyramidal structure of the complex and the electron distribution on its Cl atoms, found by the ^{35}Cl NQR method. The total energy of the system at this distance is higher (by 0.758 eV) than in a fully optimized structure, like with the analogous $GeCl_4$ complex [1]. The fact that the calculation results obtained at a a certain fixed Si←N distance satisfactorily fit the experimental data allows us to discuss the mechanism and dynamics of this complex formation.

When the components of system **I** come together at a distance of 6.0–1.9 Å, the partial positive charges of the H atoms and the negative charges of the C and N atoms of the electron-donor ligand, as well as the partial positive charges of the Si atom and the negative charges of Cl atoms in the electron acceptor increase (Table 4). Increased opposite charges on the coordination centers (Si and N) promptthe system components to come closer and closer together. However, the strength this interaction allows the coordination centers to approach each other at a distance of 3.95 Å [RHF/6-31G(d)] or 3.67 Å [B3LYP/6-311G(d)] at which the complex is not yet formed. Its formation requires additional conditions to be met to increase the system energy, like with the the analogous $GeCl_4$ complex [1]. As the system components

Table 4. Atomic charges (q) in structure **I**, calculated by the RHF/6-31G(d) and B3LYP/6-311G(d) methods with varied Si←N distances (d)

d, Å	q, e							
Si←N	Cl^1	Cl^2	Si	N	C^1	H^1	H^2	H^3
				RHF				
6.0	–0.237	–0.233	0.936	–0.533	–0.286	0.167	0.130	0.167
5.0	–0.240	–0.235	0.941	–0.534	–0.287	0.168	0.131	0.168
3.95	–0.250	–0.242	0.964	–0.541	–0.290	0.171	0.133	0.171
3.2	–0.279	–0.251	1.005	–0.577	–0.298	0.178	0.143	0.178
2.4	–0.374	–0.282	1.086	–0.678	–0.327	0.212	0.174	0.212
2.25	–0.397	–0.298	1.119	–0.700	–0.335	0.222	0.181	0.222
2.14	–0.412	–0.311	1.144	–0.714	–0.342	0.230	0.186	0.230
1.9	–0.440	–0.337	1.166	–0.725	–0.351	0.242	0.197	0.249
				B3LYP				
6.0	–0.231	–0.228	0.914	–0.256	–0.508	0.210	0.173	0.210
5.0	–0.234	–0.232	0.919	–0.259	–0.509	0.212	0.173	0.212
4.0	–0.239	–0.242	0.937	–0.271	–0.510	0.216	0.177	0.216
3.67	–0.244	–0.245	0.947	–0.281	–0.513	0.218	0.180	0.218
3.2	–0.261	–0.250	0.963	–0.309	–0.522	0.227	0.189	0.226
2.4	–0.326	–0.284	0.990	–0.398	–0.545	0.261	0.219	0.261
2.14	–0.349	–0.304	1.011	–0.441	–0.551	0.276	0.229	0.276
1.9	–0.366	–0.319	1.019	–0.468	–0.558	0.285	0.237	0.293

come closer together, the charge on the axial Cl atom increases much faster than the charges on each of equatorial Cl atoms, and the sum of the partial negative charges of all Cl atoms increases faster than the positive charge of the Si atom (Table 4). The sum of the partial positive charges of the H atoms in the electron-donor fragment of the system increases faster than the negative charges of the C and N atoms. Therefore, the electron density is transferred from the electron donor onto acceptor. As a result, the donor starts to gain a greater and greater positive charge and the acceptor, the negative charge. At longer Si←N distances, their charges are close to zero.

Thus, the components of system **I** polarize each other as come closer together. Therewith, the electron density from the H atoms of the electron donor is displaced onto C and N, and from the Si atom of the acceptor, onto its Cl atoms. Furthermore, the electron density is transferred from the H atoms of the donor onto the Cl atoms of the acceptor. The C, N and Si atoms of the system are only conductors of this electron density.

As the components of system **I** come closer together, the population of the p_z orbital of the N atom whose symmetry axis coincides with the direction of the Si←N bond decreases, and the population of the p_x and p_y orbitals increases. The populations of the p_x, p_y, and p_z orbitals of the Si atom decrease, and those of the Cl^1 atom increase. The populations of the p_x orbitals of the Cl^2, Cl^3, and Cl^4 atoms with the symmetry axes perpendicular to the bonds of these atoms with the Si atom and to the equatorial plane of the complex increase, the populations of their p_z orbitals with the symmetry axes coinciding with the corresponding Cl–Si bonds increase only at short Si←N distances, and the populations of the p_y orbitals practically do not vary (B3LYP) or slightly decrease (RHF) (Table 3). Therefore, the partial negative charges of the axial Cl^1 atom increase upon complex formation (Table 4) due to increasing populations of its p_x, p_y, and p_z orbitals, the p_x and p_z orbitals of the Cl^2, Cl^3, and Cl^4 atoms, and the p_x and p_y orbitals of the N atom. The partial positive charge of the Si atom increases due to decreasing populations of its p_x, p_y, and p_z orbitals (Table 3).

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