

Quantum-Chemical Study the Nature of Coordination Bond in $\text{SiCl}_4 \leftarrow \text{N}(\text{CH}_3)_3$ Complex

Valentin Petrovich Feshin^{*}, Elena Valentinovna Feshina

Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences, Perm, Russian Federation

Email address:

vpfeshin@mail.ru (V. P. Feshin)

^{*}Corresponding author

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Abstract: Quantum-chemical calculations were performed for the system $\text{SiCl}_4 \leftarrow \text{N}(\text{CH}_3)_3$ using the MP2/6-31+G(d) level with total optimization of its geometry and at different fixed Si...N distances (from 1.9 to 4.5 Å). The coordination bond in the complex is a result of participation of different AO's of N and Si atoms (along with orbitals of other atoms of the molecule) in the formation of a series of MO's, the number of which increases on convergence of coordination centers. This coordination bond is of the same nature as covalent bond is. Formation of such bond results in variations in partial charges of atoms and in populations of their orbitals.

Keywords: Nature of Coordination Bond, $\text{SiCl}_4 \leftarrow \text{N}(\text{CH}_3)_3$ Complex, AbInitio Calculations, MP2/6-31G(d) Level, Nuclear Quadrupole Resonance, Molecular Orbitals

1. Introduction

Various ideas on the nature of coordination bond in compounds with intra- and intermolecular coordination continue circulating. One of most prevalent hypotheses says that two electrons requisite to form such a bond in accord with valence scheme are supplied by electron-donor center on the vacant orbital of electron-acceptor center (donor-acceptor bond) [1, 2]. Intermolecular transannular interaction in atranenes of X=B, Al, Ga elements is assumed to have markedly covalent character [3], whereas the $(\text{R})\text{X} \leftarrow \text{N}$ interaction in atranenes with X=C, Si and Ge is due to donor action of the unshared electron pair of the N atom to the antibonding orbital $\sigma^*\text{XR}$ [4]. The Si \leftarrow O coordination bond in the (benzoyloxymethyl)trifluorosilane molecule is believed to be high-polar covalent bond [5]; interaction of zwitterion coordination compounds in the axial fragment $\text{O} \rightarrow \text{Si-X}$ "... varies from dative to three-center four-electron ($3c4e$)" [6]; in isolated molecules of N-(trifluorosilylmethyl)succinimide and of N-(trifluorosilylmethyl)phthalimide, this bond is weak donor-acceptor bond, etc. [7]. At the same time in the molecular orbital method, "... a complex is considered as an integrated

quantum-mechanical system in which separate atoms and molecules lose their individual traits. Valence electrons of the system are located in multi-centered molecular orbitals uniting nuclei of complex-forming agent and of all ligands the complex is comprised of" [2]. Taking into account such a variety of ideas on the nature of coordination bond, we have continued its investigation while using non-empirical methods of quantum chemistry.

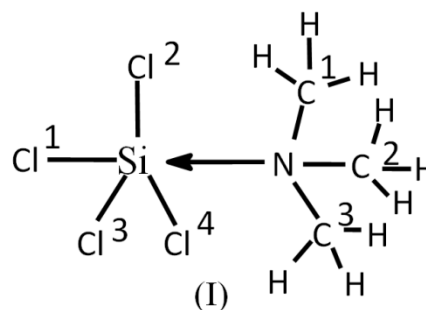


Figure 1. $\text{SiCl}_4 \leftarrow \text{N}(\text{CH}_3)_3$ complex (I)

The $\text{SiCl}_4 \leftarrow \text{N}(\text{CH}_3)_3$ complex (I) appears to be a convenient model to investigate in the nature of coordination bond and in dynamics of its formation. In accord with the

^{35}Cl NQR spectrum (at 77 K) [8, 9], this complex has a trigonal-bipyramidal structure. Three chlorine atoms occupy equatorial positions of the trigonalbipyramid, the fourth atom and ligand – axial positions. Two high-frequency lines in the NQR spectrum (21.502 and 21.296 MHz, with 1:2 ratio of line intensity) are assigned to equatorial chlorine atoms, the low-frequency line (18.857 MHz) – to axial chlorine atom. Such a structure is confirmed also by asymmetry parameters of the electric field gradient (EFG) at ^{35}Cl nuclei [9] which have large values for equatorial chlorine atoms (42.1 ± 7.2 and $36.6 \pm 4.0\%$, respectively), and a value close to zero (1.7%) – for axial atom.

Trimethylamine has a pyramidal structure. Methyl groups are located in the base of pyramid, the nitrogen atom – at vertex of pyramid. On formation of the SiCl_4 complex with trimethylamine, the orbital of the unshared electron pair of the nitrogen atom of trimethylamine is directed to the Si atom and, certainly, partakes in formation of the $\text{Si} \leftarrow \text{N}$ coordination bond. If, in quantum-chemical calculation, the axial chlorine atom were chosen as point of origin of coordinates system, the Z axis of which coincides with the Cl-Si axial bond, the orbital of the unshared electron pair of the nitrogen atom would be located on this axis. Among a variety of molecular orbitals, this would give an opportunity to identify molecular orbitals formed with participation of s - and p_z -orbital functions of the axial fragment's atoms in molecule of the complex (Cl, Si, N) which mainly contribute to formation of the $\text{Si} \leftarrow \text{N}$ coordination bond, and to monitor formation dynamics of such bond.

2. Methods

Earlier [10], we had calculated the $\text{SiCl}_4 \leftarrow \text{N}(\text{CH}_3)_3$ system (I) at the RHF/6-31G(d) and B3LYP/6-311G(d) levels with full optimization of its geometry and at various $\text{Si} \dots \text{N}$ distances. The obtained results were compared with experimental data on electron and spatial structure of such complex. However, this comparison was made not with full optimization of its geometry, but at a fixed $\text{Si} \leftarrow \text{N}$ distance appraised from experimental data. These calculations have evinced that, on convergence of the system's components, the following phenomena take place: (a) mutual polarization of the components, (b) a transfer of electron density from H atoms of the donor to chlorine atoms of the acceptor. The C, N, and Si atoms of the system serve only as conductors of this electron density. In this work, we unfortunately did not analyze molecular orbitals of the system and their dynamics during formation of the $\text{Si} \leftarrow \text{N}$ coordination bond. Our previous works [11-13] had shown such analysis to be necessary to ascertain the nature of coordination bond and dynamics of its formation. Therefore, we have calculated this system with the use of the Hartree-Fock method, while taking into account electron correlation in accord with the Moeller-Plesset method of the 2nd order, and of the 6-31+G(d) basis set using diffuse functions, with subsequent analysis of molecular orbitals. Calculations were made with the use of the Gaussian 03 program [14], with full optimization of geometry of the system

and at various fixed $\text{Si} \leftarrow \text{N}$ distances. All calculations were performed without limitations in symmetry.

3. Results and Discussion

The structure (I) calculated with full optimization of its geometry (Table 1) corresponds to minimum on the potential energy surface, since imaginary frequencies of valence vibrations are absent in this structure. At this point, however, the $\text{Si} \dots \text{N}$ distance (3.207 Å) in it is only slightly less as compared with the sum of van-der-Waals radii of the Si and N atoms (≈ 3.4 Å [15]). In addition, the structure of coordination polyhedron of its Si atom markedly differs from the trigonal-bipyramidal structure expected on the basis of the ^{35}Cl NQR spectrum (see above). The Cl^1 -Si bond in this structure is only non-significantly longer as compared with other Cl-Si bonds having same lengths; valence angles are closer to tetrahedral ones than to angles typical for trigonal-bipyramidal coordination polyhedron of the Si atom. The $\text{Si} \dots \text{N}$ distance resulting from calculation of the (I) structure with the use of the RHF/6-31G(d) and B3LYP/6-311G(d) levels is appreciably larger (3.95 Å and 3.67 Å, respectively [10]) than the one calculated at the MP2/6-31+G(d) level.

Table 1. Lengths (Å) and valence angles (deg.) in the (I) structure calculated at the MP2/6-31+G(d) level, with full optimization of geometry ($\text{Si} \leftarrow \text{N}$ 3.207 Å) and at various $\text{Si} \leftarrow \text{N}$ distances (Å).

$\text{Si} \leftarrow \text{N}$	1.9	2.14	2.5	3.0	3.207	3.6	4.0	4.5
$\text{Si}-\text{Cl}^1$	2.161	2.131	2.091	2.051	2.041	2.033	2.028	2.028
$\text{Si}-\text{Cl}^2$	2.105	2.084	2.056	2.032	2.029	2.027	2.027	2.027
N-C	1.518	1.500	1.480	1.465	1.461	1.457	1.456	1.457
Cl^1SiCl^2	90.60	93.40	98.07	104.45	106.39	108.59	109.41	109.48
Cl^1SiCl^3	90.60	93.41	98.08	104.44	106.39	108.60	109.41	109.48
Cl^1SiCl^4	90.62	93.40	98.07	104.40	106.39	108.60	109.42	109.49
Cl^2SiCl^3	119.99	119.65	118.06	114.01	112.36	110.35	110.15	109.46
Cl^2SiCl^4	119.99	119.65	118.08	114.03	112.37	110.36	109.54	109.47
Cl^1SiN	179.99	179.99	179.99	179.96	179.98	179.98	179.99	179.99
Cl^2SiN	89.41	86.60	81.92	75.52	-	71.39	70.59	70.52
Cl^3SiN	89.40	86.60	81.93	75.54	-	71.42	70.6121	70.53
Cl^4SiN	89.37	86.60	81.93	75.53	-	71.40	70.57	70.50
Cl^1NC^2	104.84	106.29	107.83	109.34	109.95	110.75	111.07	110.99

Table 2. Populations (N) of 3p-components of valence p-orbitals of Cl atoms in the (I) structure calculated with full optimization of geometry (3.207 Å) and at fixed $\text{Si} \dots \text{N}$ distances; ^{35}Cl NQR frequencies (ν_{Cl}) and asymmetry parameters (η_{Cl}) of EFG at ^{35}Cl nuclei calculated from these populations.

$\text{Si} \dots \text{N}$, Å	Atom	N3p _{xy} , e	N3p _{xz} , e	N3p _{yz} , e	ν_{Cl} , MHz	η_{Cl} , %
1.9	Cl^1	1.274	1.274	1.060	19.337	0.0
	Cl^2	1.303	1.254	1.063	19.847	34.11
2.14	Cl^1	1.275	1.275	1.062	19.247	0.0
	Cl^2	1.303	1.259	1.056	20.621	29.33
2.3	Cl^1	1.276	1.276	1.062	19.337	0.0
	Cl^2	1.303	1.262	1.052	21.074	26.68
2.5	Cl^1	1.277	1.277	1.062	19.427	0.0
	Cl^2	1.302	1.266	1.049	21.421	22.98
2.7	Cl^1	1.277	1.277	1.061	19.518	0.0
	Cl^2	1.299	1.269	1.048	21.454	19.07
3.0	Cl^1	1.278	1.278	1.059	19.789	0.0
	Cl^2	1.293	1.272	1.050	21.073	13.55
3.207	Cl^1	1.279	1.279	1.058	19.970	0.0
	Cl^2	1.290	1.274	1.052	20.821	10.43

While using Eqs (1) and (2) [16] and populations of less diffusive $3p$ -components of valence p -orbitals of chlorine atoms [17, 18] obtained from calculation of the (I) system at the MP2/6-31+G(d) level, ^{35}Cl NQR frequencies (ν) and asymmetry parameters (η) of EFG at ^{35}Cl nuclei were appraised (Table 2).

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

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

Here, $e^2 Q q_{\text{at}}$ – 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 chlorine indicative atom, respectively. The $e^2 Q q_{\text{at}} / 2h$ value was found with the use of experimental Cl_2 NQR frequency at 77 K and of populations of $3p$ -components of valence p -orbitals of the Cl atoms of this molecule obtained from its calculation with the use of the respective method [17, 18].

Calculated and experimental NQR frequencies of the chlorine atoms in the (I) system somewhat differ between themselves. The asymmetry parameter of EFG at the nucleus of the Cl^1 atom had appeared to be equal to zero (as was to expect), whereas asymmetry parameters of other three atoms was considerably less than their experimental values.

Thus, the calculated characteristics of the (I) structure somewhat do not correspond to the structure of the crystalline $\text{SiCl}_4\leftarrow\text{N}(\text{CH}_3)_3$ complex ascertained with the use of the ^{35}Cl NQR method. Apparently, in crystalline complex the $\text{Si}\dots\text{N}$ distance is markedly less than the one calculated with full optimization of geometry of the (I) structure. To ascertain probabilistic structure of this complex, to study dynamics of its formation and the nature of coordination bond in it, the (I) structure was calculated at variable fixed $\text{Si}\dots\text{N}$ distances (from 1.9 Å to 4.5 Å). Calculations were performed also for 2.14 Å distance which is by 0.05 Å less than the $\text{Ge}\dots\text{N}$ distance (2.19 Å) in the $\text{GeCl}_4\leftarrow\text{N}(\text{CH}_3)_3$ complex determined with use of X-rayanalysis [15, 19]. This value, being the difference between covalent radii of Si and Ge atoms.

As the $\text{Si}\dots\text{N}$ distance decreases, the following phenomena take place: (a) lengths of all Si-Cl, of N-C, and especially of

Si- Cl^1 bonds increase; (b) the difference between the latter bond and remaining Si-Cl bonds increases; (c) values of Cl^1SiCl angles decrease from tetrahedral to practically right angle values; (d) values of Cl^2SiCl^3 , Cl^2SiCl^4 , and Cl^3SiCl^4 angles increase from tetrahedral to $\sim 120^\circ$ (Table 1). At the given $\text{Si}\dots\text{N}$ distance, lengths of the three bonds (Si- Cl^2 , Si- Cl^3 and Si- Cl^4) are practically same. Therefore, only length of the Si- Cl^1 bond is presented in Table 1. At minor $\text{Si}\dots\text{N}$ distances, coordination polyhedron of the Si atom in the (I) structure is structured as trigonalbipyramid, in accord with the ^{35}Cl NQR spectrum. Appraisal of NQR frequencies and of asymmetry parameters of EFG at ^{35}Cl nuclei, in accord with Eqs (1) and (2) and with populations of $3p$ -components of valence p -orbitals of the Cl^1 and Cl^2 atoms, evinces that their values calculated at $\text{Si}\dots\text{N}$ distances from 2.14 Å to 2.7 Å (Table 2) are most close to experimental NQR parameters (see above).

As the $\text{Si}\dots\text{N}$ distance in the $\text{SiCl}_4\leftarrow\text{N}(\text{CH}_3)_3$ system decreases, partial negative charges of all chlorine atoms and of the N atom, as well as partial positive charges of the Si and H atoms increase (Table 3). At this point: (a) the charge of axial chlorine atom increases more rapidly, as compared with each equatorial atom; (b) the sum of partial negative charges of all chlorine atoms increases more rapidly than the positive charge of the Si atom. As a result, the sum of negative charges of chlorine atoms (at minor $\text{Si}\dots\text{N}$ distances, e.g. -0.954 e at 1.9 Å) is appreciably larger than that of the positive Si atom (Table 3); at the $\text{Si}\dots\text{N}$ distance equaling 4.5 Å these two values are practically equal. In the electron-donor fragment of the system, the sum of partial positive charges of H atoms increases more rapidly, as compared with the sum of negative charges of the C and N atoms. As a result, at minor $\text{Si}\dots\text{N}$ distances the sum of positive charges of H atoms in this fragment (e.g. 2.322 e at 1.9 Å) is considerably larger than the sum of negative charges of the C and N atoms (2.031 e), at the $\text{Si}\dots\text{N}$ distance equaling 4.5 Å these two values are practically equal. Consequently, at minor $\text{Si}\dots\text{N}$ distances, electron density is transferred from the electron donor to the electron acceptor (0.29 e at 1.9 Å). With full optimization of geometry of the system, this value equals solely 0.025 e .

Table 3. Mulliken charges (q) of atoms in the (I) structure calculated at the MP2/6-31+G(d) level, at various $\text{Si}\dots\text{N}$ distances (Å).

$\text{Si}\dots\text{N}$, Å	$q(\text{Cl}^1)$, e	$q(\text{Cl}^2)$, e	$q(\text{Si})$, e	$q(\text{N})$, e	$q(\text{C})$, e	$q(\text{H}^1)$, e	$q(\text{H}^2)$, e	$q(\text{H}^3)$, e
1.9	-0.345	-0.203	0.664	-0.825	-0.402	0.275	0.223	0.276
2.14	-0.326	-0.187	0.685	-0.783	-0.401	0.257	0.213	0.259
2.3	-0.307	-0.175	0.685	-0.738	-0.403	0.246	0.206	0.246
2.5	-0.281	-0.161	0.673	-0.634	-0.418	0.231	0.199	0.231
2.7	-0.250	-0.157	0.667	-0.521	-0.437	0.218	0.193	0.218
3.0	-0.202	-0.159	0.652	-0.363	-0.462	0.204	0.185	0.204
3.207	-0.174	-0.160	0.629	-0.272	-0.477	0.197	0.181	0.197
3.6	-0.141	-0.153	0.578	-0.167	-0.494	0.191	0.176	0.191
4.0	-0.128	-0.143	0.543	-0.154	-0.493	0.188	0.172	0.188
4.5	-0.128	-0.132	0.524	-0.196	-0.480	0.188	0.170	0.188

Thus, in the (I) structure calculated with full optimization of its geometry, a weak interaction between electron-donor and electron-acceptor fragments is possible. The $\text{Si}\dots\text{N}$ distance in this system is only negligibly less than the sum of

van-der-Waals radii of Si and N atoms. Such system is energetically more advantageous. However, in accord with experimental ^{35}Cl NQR spectrum of the system at 77 K and fulfilled calculations, the stable $\text{SiCl}_4\leftarrow\text{N}(\text{CH}_3)_3$ complex is

formed at a considerably lesser Si...N distance. To form this complex, total energy of the system is to be enhanced (Table 4). This state is attainable at a lowered temperature (77 K), at increasing of intermolecular interactions and deformation of the Si atom coordination polyhedron. At the study a comprehensive set of Lewis acid-base adducts of silanes by means of the density functional theory calculations it is inferred that the existence of some of the silicon complexes in the solid state or in solution is caused by stabilizing intermolecular forces [20].

Table 4. Populations of valence orbitals of Cl^I , Si and N atoms (e) in the (I) structure calculated at the MP2/6-31+G(d) level with full optimization of its geometry ($\text{Si} \leftarrow \text{N}$ 3.207 Å) and at various Si←N distances X (Å); difference (ΔE , eV) between total energy values of the structure (I) with Si ← N distance 3.207 Å [$E(3.207 \text{ Å}) = -62627.611 \text{ eV}$] and other distances [$E(X)$] $\Delta E = E(3.207 \text{ Å}) - E(X)$.

Si←N	ΔE , eV	$\text{Cl}^I(\text{s})$	$\text{Cl}^I(\text{p}_z)$	Si(s)	Si(p_z)	Si(dz^2)	N(s)	N(p_z)
1.9	0.461	1.958	1.474	1.009	0.492	0.151	1.674	1.423
2.14	0.139	1.959	1.467	0.948	0.536	0.117	1.720	1.492
2.3	0.90	1.957	1.461	0.917	0.561	0.100	1.738	1.527
2.5	0.83	1.951	1.453	0.885	0.591	0.088	1.714	1.560
2.7	0.57	1.943	1.445	0.849	0.616	0.083	1.670	1.588
3.0	0.13	1.927	1.433	0.818	0.650	0.085	1.592	1.621
3.207	0.0	1.915	1.426	0.818	0.672	0.087	1.541	1.640
3.6	0.44	1.900	1.419	0.840	0.703	0.091	1.469	1.670
4.0	0.140	1.895	1.416	0.862	0.714	0.094	1.442	1.690
4.5	0.253	1.896	1.415	0.878	0.713	0.094	1.451	1.705

The Cl^ISiN angle of the (I) structure is close to 180° with both full and partial optimization of geometry of the molecule, at variable fixed Si...N distances (Table 1). This gives an opportunity to monitor: (a) variations in populations of valence s - and p_z -orbitals of axial fragment of the molecule, as well as of d -orbitals of the Si atom (Table 4), and (b) degree of participation of these functions in formation of molecular orbitals during the complex formation.

As the Si...N distance decreases from 4.5 Å to 1.9 Å, populations of valence s - and p_z -orbitals of the Cl^I atom as well as population of s -orbital of the N atom increase (by 0.062 e , 0.059 e and 0.223 e , respectively), populations of p_z -orbitals of the Si and N atoms decrease markedly (by 0.221 e and 0.282 e , respectively). As the Si...N distance decreases, populations of s - and dz^2 -orbitals of the Si atom slightly decrease up to the Si...N distance equaling $\sim 2.7 - 3.0$ Å and starts rapidly increasing, as this distance decreases. Diminution of populations of p_z -orbitals of the Si and N atoms is much more considerable, as compared with enhancement of populations of s - and p_z -orbitals of the Cl^I atom, s -orbital of the N atom, as well as of dz^2 -orbital of the Si atom (as the Si...N distance decreases from 2.7 Å to 1.9 Å) (Table 3). Thus, on convergence of the $\text{SiCl}_4 \leftarrow \text{N}(\text{CH}_3)_3$ system's components, the following phenomena take place: (a) populations of p_z -orbitals of the Si and N atoms decrease markedly; (b) population of s -orbital of the N atom increases, populations of s - and p_z -orbitals of the Cl^I atom increase comparatively moderately, just as populations of s - and dz^2 -orbitals of the Si atom at certain Si...N distances do. These data evince the coordination bond to be formed not only with participation of the aforementioned orbitals of axial fragment

of the complex. The nature of coordination bond may not be judged by these data. Variations in these populations, as well as variations in atom charges, on convergence of the system's components, are caused by participation of atom orbitals (AO) of the system in its various molecular orbitals (MO). All these molecular orbitals are multi-centered. Among them, there is no one formed with participation of only one orbital from either the Si and N atoms, or Cl^I , Si and N atoms, as is evidenced by coefficients at atom orbitals in molecular orbitals. For example, in the (I) structure calculated at the Si...N distance equaling 1.9 Å, formation of MO ϕ_{56} with energy of 11.645 eV is assisted by participation of the p_z -orbital of the N atoms; moreover, orbitals of the Si atom, of axial and equatorial chlorine atoms etc. appreciably contribute to this formation (Eq. 3).

$$\begin{aligned} \phi_{56} = & -0.025\text{Cl}^I(\text{s}) + 0.739\text{Cl}^I(\text{p}_z) + 0.042\text{Cl}^I(\text{dz}^2) - \\ & 0.035\text{Si}(\text{s}) - 0.168\text{Si}(\text{p}_z) - 0.049\text{Si}(\text{dx}^2) - 0.049\text{Si}(\text{dy}^2) + \\ & 0.104\text{Si}(\text{dz}^2) + 0.531\text{N}(\text{s}) - 0.250\text{N}(\text{p}_z) - 0.072\text{Cl}^I(\text{s}) + \\ & 0.267\text{Cl}^I(\text{p}_x) - 0.024\text{Cl}^I(\text{p}_y) + 0.424\text{Cl}^I(\text{p}_z) - 0.072\text{Cl}^I(\text{s}) - \\ & 0.155\text{Cl}^I(\text{p}_x) - 0.217\text{Cl}^I(\text{p}_y) + 0.424\text{Cl}^I(\text{p}_z) - 0.072\text{Cl}^I(\text{s}) - \\ & 0.113\text{Cl}^I(\text{p}_x) + 0.243\text{Cl}^I(\text{p}_y) + 0.425\text{Cl}^I(\text{p}_z) - 0.162\text{Cl}^I(\text{s}) + \\ & 0.021\text{Cl}^I(\text{p}_x) + 0.078\text{Cl}^I(\text{p}_z) + \dots \quad (3) \end{aligned}$$

Therefore, the coordination bond $\text{Si} \leftarrow \text{N}$ in the (I) complex cannot be explained by either interaction between the unshared electron pair of the N atom and vacant orbitals of the Si atom, or formation of four-electron three-centered bond including orbitals of atoms of axial fragment's of the molecule. We assume all this to be related to other coordination bonds (intra- or intermolecular) in any coordination compounds. Coordination bond results from formation of a series of molecular orbitals with participation of atom orbitals as coordination centers of molecules, and is of the same nature as covalent bond is. Therefore, there is no sense to speak about a partially covalent character of coordination bond in coordination compounds (see above). On convergence of the (I) system's components, the number of molecular orbitals formed with participation of atom orbitals of axial fragment of the molecule, increases. Some of them are presented in Table 5. For example, these atoms partake at the Si...N distance ≤ 2.3 Å in formation of molecular orbitals ϕ_{56} and ϕ_{47} , at distance of ≤ 2.5 Å – in formation of ϕ_{55} , at distance of ≤ 2.14 Å – in formation of ϕ_{54} , ϕ_{44} and ϕ_{41} , and at distance of only 2.14 Å – in formation of ϕ_{49} . Orbitals of other atoms of the system also partake, to a certain extent, in formation of all these molecular orbitals. Earlier [11-13], we had shown an increase in the number of these molecular orbitals, on convergence of the system's components, to be accompanied by diminution of its total energy. However, in this particular case, an increase in the number of such molecular orbitals, on the contrary, leads to enhancement of total energy of the system (Tables 4, 5). In this case, the complex does not appear to be most advantageous form of the system. Consequently, an increase in the number of these molecular orbitals may be accompanied by both enhancement and diminution of total energy of the system.

Table 5. Coefficients (*c*) at atom orbitals of axial fragment of the (*l*) structure in various molecular orbitals (ϕ) formed with participation of atoms of this fragment, at various Si...N distances; energy values (*E*) of these molecular orbitals.

ϕ	Si...N, Å	-E, eV	cN(s)	cN(p _z)	cSi(s)	cSi(p _z)	cSi(dz ²)	cCl ¹ (s)	cCl(p _z)
ϕ_{56}	1.9	11.645	0.531	-0.250	-0.035	-0.168	0.104	-0.025	0.739
	2.14	12.047	0.347	-0.156	0.002	-0.098	0.095	-0.006	0.699
	2.3	12.040	-0.317	0.961	-0.224	-0.070	-0.059	0.062	-0.065
	2.5	11.831	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ϕ_{55}	1.9	12.337	0.052	-0.077	0.035	-0.019	0.010	-0.019	0.044
	2.14	12.446	-0.197	0.748	-0.133	0.055	-0.075	0.127	-0.181
	2.3	12.318	0.278	-0.251	0.044	-0.043	0.103	0.015	0.694
	2.5	12.637	0.145	-0.144	0.029	0.022	0.096	0.055	0.653
ϕ_{54}	2.7	12.767	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	1.9	12.850	-0.114	0.672	-0.075	0.280	-0.095	0.316	-0.218
	2.14	12.498	-0.115	0.493	-0.080	0.028	-0.078	0.086	-0.093
	2.3	12.576	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ϕ_{49}	1.9	15.022	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2.14	14.901	-0.006	0.365	0.067	-0.439	0.027	-0.362	0.429
	2.3	14.828	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2.5	15.227	-0.061	0.614	0.174	-0.312	-0.012	-0.270	0.370
ϕ_{47}	2.14	15.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2.3	14.922	0.022	0.217	0.050	-0.455	0.045	-0.379	0.471
	2.5	15.055	-0.001	-0.001	0.000	0.006	-0.001	0.005	-0.008
	2.7	14.783	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ϕ_{46}	2.3	15.372	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2.5	15.105	0.065	0.091	0.081	0.400	0.058	-0.366	0.522
	2.7	15.366	0.093	0.018	0.115	-0.400	0.062	-0.349	0.561
	3.0	15.249	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ϕ_{44}	1.9	15.986	-0.137	0.160	0.100	0.144	-0.002	0.072	0.013
	2.14	15.620	-0.026	0.065	0.049	0.083	-0.002	0.047	0.003
	2.3	15.666	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2.5	18.230	-0.417	0.166	0.630	0.065	0.000	-0.240	0.275
ϕ_{41}	2.14	18.466	-0.256	0.214	0.591	0.031	-0.004	-0.250	0.287
	2.3	18.389	0.000	0.000	0.000	0.000	0.000	0.000	0.000

4. Conclusions

Thus, quantum-chemical calculations at the MP2/6-31+G(d) level show that a coordination bond is a result of participation of atom orbitals of coordination centers (along with orbitals of other atoms of the molecule) in formation of a series of molecular orbitals, the number of which increases on convergence of coordination centers, or of components of the system.

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