

Nature of Coordination Bond in 1-Chlorogeriatrane and Dynamic of its Formation Based on Ab Initio Calculations

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ABSTRACT

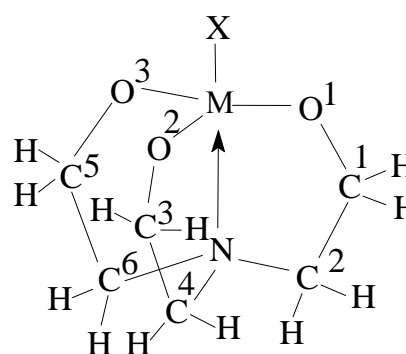
Quantum-chemical calculations were performed for the 1-chlorogeriatrane at the MP2/6-31G(d) level with total optimization of its geometry and at different fixed Ge...N distances (from 2.0 to 3.8 Å) and fixed rights (90°) CNGe angles. The coordination bond in this molecule is a result of participation of different AO's of N and Ge atoms (along with orbitals of other atoms of the molecule) in the formation of a series of MO's. Formation of MO existing only at the Ge...N distance of the totally optimized molecule plays the most essential role. On formation of the coordination bond, electron density shifts from the electron-donor fragment of a molecule to the electron-acceptor one, but not from "electron-donor center" on the "electron-acceptor" one. At this point, a negative charge of the N atom increases. Coordination centers serve as conductors of this electron density. Populations of s- and p-orbitals of the N atom depend essentially on CNGe angles.

Keywords: 1-Chlorogeriatrane, coordination bond, nature and dynamic of formation, ab initio calculations, molecular orbitals, electron density

INTRODUCTION

Currently, various ideas on the nature of intra- and intermolecular coordination bonds continue existing. In most cases, these ideas are too much simplified (see, e.g., [1, 2]). We are of opinion that, while ascertaining the nature of coordination bonds, all the bonds in polyatomic molecules including coordination bonds are to be regarded as many-centric ones. Therefore, interaction between orbitals of either two atoms as coordination centers, or three atoms of the axial fragment of the molecule (see, e.g., [1-4]) may hardly be talked about when discussing this nature. It is necessary to analyze a series of molecular orbitals (MO) of molecules with coordination bonds is to be necessarily analyzed. However, the analysis appears to be problematic, since the MOs participating in formation of such a bond can usually hardly be ascertained. Nevertheless, these difficulties can be avoided. Coordination compounds of elements from the 14th group of the Mendeleev table (M=Si, Ge, Sn) with the N atom as an "electron-donor center" are convenient objects to study the coordination bond. In these molecules, the unshared electron pair of the N atom directed towards an M atom necessarily

interacts with the latter. Atranes (1), for example, appear to be such compounds with the intra-molecular coordination bond.



In these molecules, the coordination polyhedron of the M atom is structured as a trigonal bipyramid, with the nitrogen atom at one of its axial positions [3-8]. The X, M and N atoms in these molecules are located on the straight line X-M←N. If, in quantum-chemical calculations, the X atom were taken as the origin of the coordinate system, all the three atoms would be located on the Z axis of this system, since this axis is directed along the X-M bond. The orbital of the unshared electron pair of the N atom would be the p_z-orbital of this atom. When

studying the nature of the coordination bond, it is necessary to analyze the MOs formed with participation of p_z -orbitals of the N and M atoms are to be necessarily analyzed. With this background, we have studied 1-hydro- [9] and 1-chlorosilatranes [10] by the MP2/6-31G(d) method. In these molecules, the coordination bond is shown as a result of how different AO's of the N and Si atoms, along with orbitals of other atoms of the molecule, participate in formation of a series of MO's. The number of these MO's increases with decreasing distance between the N and Si atoms. This phenomenon leads to a decrease in total energy of the molecule. With decreasing distance between the N and Si atoms, electron density shifts from the N and Si atoms to the X atom. We believe (see, While continuing investigation in the nature of coordination bonds and in dynamics of their formation, we performed quantum-chemical calculations at the MP2/6-31G (d) level of the 1-chlorogermetrane molecule [molecule (1) with X=Cl and M=Ge] with total optimization of its geometry and at various Ge...N distances, as well as at the right (90.0°) CNGe angles, at which the three C-N bonds lie on one plane. In

RESULTS AND DISCUSSION

Calculation of the 1-chlorogermetrane molecule with total optimization of its geometry indicates practical equivalence of its three cycles. The Cl, Ge and N atoms are practically on one line, the ClGeN angle is close to 180°. Basic geometrical characteristics of the molecule are presented in Table 1. These values are close to the experimental data [8, 14] and to the results derived from calculations of this molecule at the

Table 1. Bond lengths (d), valence (α) and dihedral (β) angles in molecule (1) with X=Cl and M=Ge, calculated at the MP2/6-31G(d) level

Bond	$d, \text{Å}$	Angle	α, deg	Angle	β, deg
Cl-Ge	2.155	ClGeO	97.61-97.64	ClGeOC	156.47-156.52
O-Ge	1.811	GeOC	114.99-115.01	GeOCC	48.38-48.47
O-C	1.419	OCC	108.98-109.0	OCCN	50.16-50.22
C-C	1.524	CCN	106.94-106.96	CNGeO	5.44-5.48
C-N	1.474	CNC	113.96-113.97		
Ge...N	2.235	OGeO	118.25-118.30		
		CNGe	104.47-104.48		
		ClGeN	179.99-180.02		

This contribution is insignificant. While passing from ϕ_{62} to ϕ_{59} , ϕ_{56} , ϕ_{55} and ϕ_{52} this contribution decreases. In the MOs ϕ_{62} , ϕ_{59} and ϕ_{52} contribution of the p_z -orbital of the Ge atom is insignificant, whereas in the MOs ϕ_{56} and ϕ_{55} this value is significant. The p_z -orbital of the Cl atom markedly contributes to the MOs ϕ_{62} , ϕ_{56}

e.g., [1, 11, 12]) the coordination bond in compounds with intra- and intermolecular coordination, including atranes, to be initiated by electrostatic interaction of coordination centers that results in a reduced distance between them, polarization of the molecule components containing these centers and, at a sufficiently small distance between them, in the transfer of electron density from electron-donor fragment of a molecule to the electron-acceptor one (but not from electron-donor center on the electron-acceptor one). At this point, the transfer of electron density is not the reason for the coordination bond's formation. The transfer only manifests the bond and is its consequence. Coordination centers serve as a conductor of this electron density.

all calculations, the origin of the coordinate system coincided with the chlorine atom nucleus. The Z axis of this system was directed along the Cl-Ge bond. In accord with these calculations, the stereo electronic structure of this molecule, its molecular orbitals and their changes at various Ge...N distances were analyzed. All calculations were performed with use of the Gaussian 03W program [13].

B3LYP/6-311G (d,p) level [14]. The molecule contains several MOs with a marked contribution of the valence p_z -orbital of the nitrogen atom. For instance, this orbital essentially contributes to the MOs with energies -11.439 eV (ϕ_{62}), -12.493 eV (ϕ_{59}), -13.237 eV (ϕ_{56}) and -14.83 eV (ϕ_{55}). In the MO with energy -15.196 eV (ϕ_{52}),

and ϕ_{55} , whereas its contribution to the MOs ϕ_{59} and ϕ_{52} is insignificant. The s-orbitals of these atoms and d-orbitals of the Ge atom contribute to these MOs, to some extent as well. The orbitals of other atoms of the molecule variously contribute to these MOs, too [see, eg., equations (1) – (4)]. The p_z -orbital of the N atom markedly

contributes to other MOs, for example, to the MOs with energies -18.535 eV (ϕ_{44}), -20.312 eV (ϕ_{41}) and -22.231 eV (ϕ_{40}). The upper occupied MO (ϕ_{64}) and its neighbouring orbital ϕ_{63} with close energy values (~ 11.230 eV) do not form the coordination bond, since the coefficients at atomic orbitals of Ge and N atoms are close to zero.

$$\phi_{62} = -0.082N_s + 0.636N_{p_z} - 0.081Ge_s + 0.025Ge_{p_z} - 0.049Ge_{d_z^2} + 0.053C^2_s + 0.101Cl_s - 0.408Cl_{p_z} - 0.013Cl_{d_z^2} - 0.266O^1_{p_x} - 0.272O^1_{p_y} - 0.092O^1_{p_z} + 0.104C^1_{p_y} + 0.111C^1_{p_z} - 0.022C^2_{p_x} - 0.158C^2_{p_z} - 0.103O^2_{p_x} + 0.366O^2_{p_y} - 0.092O^2_{p_z} + 0.071C^3_s + 0.099C^3_{p_x} - 0.037p_y + 0.112C^3_{p_z} + \dots \quad (1)$$

$$\phi_{59} = -0.211N_s + 0.567N_{p_z} + 0.025Ge_{p_z} + 0.035Cl_s + 0.036Cl_{p_z} - 0.127O^1_{p_x} + 0.468O^1_{p_y} + 0.199O^1_{p_z} + 0.045C^1_s - 0.046C^1_{p_x} - 0.093C^1_{p_y} + 0.025C^1_{p_z} + 0.065C^2_s - 0.117C^2_{p_x} + 0.087C^2_{p_y} - 0.053C^2_{p_z} + 0.472O^2_{p_x} - 0.124O^2_{p_y} + 0.201O^2_{p_z} + 0.045C^3_s - 0.059C^3_{p_x} + 0.087C^3_{p_y} + 0.025C^3_{p_z} + \dots \quad (2)$$

$$\phi_{56} = -0.128N_s + 0.388N_{p_z} + 0.022Ge_s - 0.313Ge_{p_z} + 0.016Ge_{d_x^2} + 0.016Ge_{d_y^2} + 0.084Ge_{d_z^2} - 0.248Cl_s + 0.694Cl_{p_z} - 0.047O^1_s + 0.114O^1_{p_x} - 0.128O^1_{p_y} + 0.037O^1_{p_z} + 0.038C^1_s - 0.132C^1_{p_x} + 0.09C^1_{p_y} = 0.076C^2_s - 0.068C^2_{p_y} - 0.158C^2_{p_z} - 0.047O^2_s - 0.168O^2_{p_x} - 0.034O^2_{p_y} + 0.037O^2_{p_z} + 0.038C^3_s + 0.144C^3_{p_x} + 0.069C^3_{p_y} + \dots \quad (3)$$

$$\phi_{55} = -0.017N_s + 0.102N_{p_z} + 0.171Ge_s - 0.103Ge_{p_z} + 0.133Ge_{d_x^2} - 0.031Cl_s + 0.176Cl_{p_z} + 0.083Ge_{d_x^2} + 0.083Ge_{d_y^2} - 0.184O^1_s - 0.224O^1_{p_x} - 0.140O^1_{p_y} + 0.354O^1_{p_z} + 0.026C^1_s + 0.139C^1_{p_x} + 0.094C^1_{p_y} - 0.155C^1_{p_z} - 0.086C^2_s - 0.060C^2_{p_x} + 0.084C^2_{p_y} + 0.172C^2_{p_z} + \dots \quad (4)$$

Thus, a series of MOs formed with participation of various orbitals not only of “coordination centers” (N and Ge atoms) or of the three atoms of axial fragment of the molecule (N, Ge and Cl atoms), but of its other atoms as well, results in the coordination bond.

To further study the nature of coordination bond and dynamics of its formation, the

quantum-chemical calculations of the 1-chlorogermetrane molecule were performed at the MP2/6-31G(d) level with total optimization of its geometry and at different fixed Ge...N distances, as well as at fixed CNGe angles (90°), when all three C-N bonds lie on one plane and the unshared electron pair of the N atom is perpendicular to it (in the latter case, the Ge...N distance equals 2.897 Å). The Ge...N distance was varied from 2.0 Å to 3.8 Å, so as to direct the unshared electron pair of the nitrogen atom to the Ge atom and from it, respectively. Calculation of the 1-chlorogermetrane molecule at different Ge...N distances (from 2.0 Å to 3.8 Å) confirms the Cl-Ge-N angle within it to always be practically equal to 180° (179.99° - 180.02°). Therefore, the Cl, Ge and N atoms are practically located on the Z axis of the coordination system. This fact enables discussing populations of their atomic orbitals located on this axis (s-, p_z - and d_z^2 -orbitals). With a decrease of the Ge...N distance from 3.8 Å to 2.0 Å, the Cl-Ge-O angles decrease from 115.3° to 94.0° , and the length of the Ge-Cl bond exponentially (not linearly) increases from 2.089 Å to 2.176 Å. Partial negative charges of both N and Cl atoms increase, whereas the charges of the oxygen atoms decrease. A partial positive charge of the Ge atom at first increases insignificantly (up to the plane state of the N atom), and markedly decreases with further decrease of the Ge...N distance. Therefore, the transfer of electron density to the Ge atom and to the Cl atom actually takes place, but not from the N atom usually meant as the “electron-donor centre”. As for the latter, its electron density increases with decreasing distance between coordination centers as well (Table 2).

Table 2. The Mulliken charges (q) of atoms and lengths of the Ge-Cl bonds (d) in molecule (1) with $M=Ge$ and $X=Cl$ calculated at the MP2/6-31G(d) level at different Ge...N distances

$d(Ge..N), \text{Å}$	$d(Ge-Cl), \text{Å}$	$q(N), e$	$q(Ge), e$	$q(Cl), e$	$q(O^1), e$	$q(C^1), e$	$q(C^2), e$
2.0	2.176	-0.743	1.474	-0.292	-0.754	0.027	-0.167
2.234 ^a	2.155	-0.741	1.514	-0.274	-0.763	0.015	-0.147
2.4	2.140	-0.731	1.539	-0.262	-0.773	0.011	-0.136
2.6	2.126	-0.717	1.563	-0.247	-0.786	0.008	-0.125
2.897 ^b	2.120	-0.702	1.564	-0.236	-0.791	0.009	-0.110
3.2	2.106	-0.658	1.562	-0.196	-0.807	-0.008	-0.118
3.4	2.100	-0.624	1.551	-0.180	-0.810	-0.011	-0.134
3.6	2.095	-0.589	1.545	-0.167	-0.814	-0.011	-0.154
3.8	2.089	-0.561	1.542	-0.155	-0.818	-0.008	-0.172

^a The Ge...N distance at total optimization of molecular geometry. ^b At the CNGe angles of 90° .

Thus, the commonly accepted notions about electron-donor and electron-acceptor centers in coordination compounds are to be regarded as incorrect. The data presented in this work and obtained earlier (see, e.g., [1, 11, 12]) evince that, on formation of the coordination bond, the electron density of the so-termed “electron-donor center” does not decrease but, on the contrary, increases. This density decreases on atoms adjacent to this center and on more

Analysis of populations of valence orbitals of N, Ge and Cl atoms in the molecule (1) evinces (Table 3) the following phenomena taking place with decreasing distance between the N and Ge atoms: the most considerable changes occur in population of the N atom p_z -orbital, markedly less changes occur in populations of s-orbital of the N atom, of s-, p_z - and d_z^2 -orbitals of the Ge

remote atoms. The electron density is not localized on the “electron-acceptor center”, but is shifted to adjacent atoms. Hence, on formation of the coordination bond, the electron density is shifted not from the “electron-donor center” to the “electron-acceptor center”, but from the electron-donor molecular fragment to the electron-acceptor one. The coordination centers serve as conductors of this electron density.

atom, and of p_z -orbital of the Cl atom as well. Population of s-orbital of the Cl atom practically does not change. Population of the d_z^2 -orbital of the Ge atom at all the Ge...N distances is appreciable higher as compared with its p_z -orbital. Evidently, this d_z^2 -orbital markedly contributes to formation of the coordination bond in 1-chlorogermetrane.

Table 3. Populations of valence orbitals of N, Ge and Cl atoms in the (1) structure with $M=Ge$ and $X=C$ calculated at the MP2/6-31G(d) level at different Ge-N distances $d(Ge...N)$, total energies of the molecule ($E=-8293X eV$)

$d(Ge...N), \text{Å}$	X, eV	N(s),e	N(p_z),e	Ge(s),e	Ge(p_z),e	Ge(d_z^2),e	Cl(s),e	Cl(p_z),e
2.0	5.007	1.638	1.573	1.039	0.354	1.233	1.943	1.463
2.234 ^a	5.182	1.642	1.659	1.030	0.382	1.189	1.941	1.454
2.4	5.132	1.628	1.717	1.021	0.402	1.159	1.941	1.447
2.6	4.983	1.597	1.778	1.006	0.423	1.133	1.941	1.438
2.897 ^b	4.652	1.550	1.844	0.981	0.447	1.124	1.939	1.432
3.2	4.447	1.543	1.842	0.964	0.461	1.130	1.934	1.403
3.4	4.266	1.571	1.806	0.967	0.467	1.132	1.933	1.391
3.6	4.008	1.610	1.759	0.976	0.467	1.130	1.933	1.381
3.8	3.611	1.652	1.709	0.988	0.462	1.127	1.934	1.371

^a The Ge...N distance at total optimization of molecular geometry. ^b At the CNGe angles of 90°.

With a decrease in the Ge...N distance from 3.8 Å to 2.897 Å, populations of s-orbitals of both N and Ge atoms decrease, whereas, on further decreasing distance between Ge and N atoms, they increase. Contrary to that, population of p_z -orbital of the N atom increases at first, then, having passed the plane state of this atom, it decreases. Populations of p_z - and d_z^2 -orbitals of the Ge atom change insignificantly and

Thus, the change in populations of orbitals of the N, Ge and Cl atoms significantly depends on how the unshared electron pair of the N atom (its p_z -orbital) is oriented towards the Ge atom. With this orbital directed to the Ge atom and the N and Ge atoms closely spaced, its population decreases. At this point, population of p_z -orbital of the Ge atom decreases, populations of s-orbitals of both N and Ge atoms increase, as well as those of both d_z^2 -orbital of the Ge atom and p_z -orbital of the Cl atom do. These data enable supposing that, in case of the unshared

irregularly, until the N atom passes the plane state. With further decrease of the Ge...N distance, population of p_z -orbital of the Ge atom decreases, whereas that of the d_z^2 -orbital increases. As the Ge...N distance decreases from 3.8 Å to 2.0 Å population of s-orbital of the Cl atom changes insignificantly and irregularly, but population of its p_z -orbital increases significantly (Table3)

electron pair's orbital of the N atom directed towards the Ge atom, the transfer of electron density from p_z -orbital of the N atom to s- and d_z^2 -orbitals of the Ge atom and from p_z -orbital of the Ge atom to p_z -orbital of the Cl atom appears to be possible. However, with the Ge...N distance < 2.897 Å, populations of s- and p_z -orbitals of the N atom change as significantly as they do on increase of the distance over this value. Therefore, populations of these orbitals of the N atom are appreciable dependent on the CNGe angles. Maximal

population of p_z -orbital of the N atom is observed in case of the plate state of the N atom, minimal population of its valence s -orbital is observed when this atom is near this state (at the Ge...N distance 3.2 Å).

Analysis of 1-chlorogermetrane MO's shows, that, as the distance Ge...N being decreased, all the MOs rearrange, their energies and contributions of AOs thereto change. At this point, atomic orbitals of N, Ge and Cl atoms participate in formation of the ϕ_{62} orbital only when the molecular geometry is totally optimized (Ge...N distance equals 2.234Å, and less, 2.0 Å). These atomic orbitals participate in formation of MOs ϕ_{56} and ϕ_{55} in the interval of Ge...N distances varying from 2.0 Å to 3.4 Å. They inconsiderably contribute to formation of the MO ϕ_{52} in the interval of Ge...N distances from 2.0 Å to 3.6 Å. Their contribution to formation of the MOs ϕ_{59} , ϕ_{44} , ϕ_{41} and ϕ_{40} is observed in all interval of variable Ge...N distances. Table 4 summarizes the coefficients at certain AOs of these atoms.

Thus, atomic orbitals of the N, Ge and Cl atoms contribute to formation of the ϕ_{62} orbital only at

the Ge...N distance at which molecular geometry becomes totally optimized and at less Ge...N distance, when p_z -orbital of the N atom is directed to the Ge atom. These AOs contribute to formation of all other above-mentioned MOs when p_z -orbital of the N atom is directed both to the Ge atom, and conversely. Consequently, these latter MOs contribute not only to formation of coordination bond in this molecule. The reason is that the donor and acceptor fragments of the molecule are bonded not only by the coordination bond, but by covalent bonds as well.

Molecules of 1-hydro- [1, 9] and 1-chlorosilatane [1, 9] calculated at different Si...N distances contain one MO formed with participation of orbitals of N, Si, and H or Cl atoms accordingly, which exist only at Si..N distance obtained at total optimization of molecular geometry and at less distance (2.0Å). Other MO's formed with participation of orbitals of these atoms exist at the Si...N distances varying from

Table 4. Coefficients (c) at AO's of N, Ge and Cl atoms in MOs (ϕ) of the molecule (I) with $M=Ge$ and $X=Cl$, calculated at the MP2/6-31G(d) level at different Ge...N distances $d(Ge...N)$, as well energies (E) of these MO's

ϕ	$d(Ge...N), \text{Å}$	-E, eV	$c(Ns)$	$c(Np_z)$	$c(Ges)$	$c(Gep_z)$	$c(Ged_z^2)$	$c(Cl_s)$	$c(Cl p_z)$
ϕ_{62}	2.0	11.528	-0.10	-0.377	0.083	-0.107	0.084	-0.166	0.554
	2.234 ^a	11.439	-0.82	0.636	-0.081	0.025	-0.049	0.101	-0.408
	2.4	11.545	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ϕ_{56}	2.0	13.455	0.212	0.648	0.122	-0.110	0.140	-0.133	0.493
	2.234 ^a	13.237	-0.128	0.388	0.022	-0.313	0.084	-0.248	0.694
	2.4	13.437	-0.070	0.103	0.009	-0.329	0.056	-0.256	0.673
	2.6	13.760	-0.067	-0.032	-0.003	-0.328	0.029	-0.243	0.625
	2.897 ^b	14.051	-0.056	-0.065	0.004	-0.301	0.029	-0.225	0.586
	3.2	14.167	0.103	0.158	0.067	-0.007	0.060	-0.063	0.256
	3.4	14.127	0.000	0.000	0.000	0.000	0.000	0.000	0.001
ϕ_{55}	2.0	14.138	-0.056	0.373	-0.141	-0.223	-0.078	-0.067	0.112
	2.234 ^a	14.083	-0.017	0.102	0.171	0.103	0.133	-0.031	0.176
	2.4	14.181	-0.007	0.181	0.161	0.063	0.129	-0.058	0.239
	2.897 ^b	14.333	0.113	0.228	0.108	0.127	0.078	0.015	0.049
	3.2	14.277	-0.002	-0.003	-0.001	-0.006	0.000	-0.003	0.008
	3.4	14.127	0.001	0.001	0.000	0.000	0.000	0.000	0.000

^a The Ge...N distance at total optimization of molecular geometry. ^b At the CNGe angles of 90.

2 Å to the values when the N atom is plane or even to larger values [1, 9, 10]. Evidently, the latter orbitals contribute to formation not only of the coordination bond in the respective molecule. However, formation of a molecular orbital assisted by orbitals of coordination centers' atoms and of other atoms of the molecule, and existing only at the M...N distance (M=Si, Ge) when geometry of the molecule is totally optimized is, apparently, a critical factor for formation of the coordination bond. Complexes of MCl_4 (M=Si [2] and Ge [15]) with trimethylamine contain certain MOs existing only when the molecular geometry is totally optimized, and at smaller M...N distances. Other MOs exist at larger M...N distances, too. Apparently, the complex itself, and coordination bond start forming at these large distances. This formation discontinues upon attainment of a distance at which total optimization of molecular geometry occurs. This phenomenon is fair for compounds with both inter- and intra-molecular coordination.

CONCLUSION

The presented investigation shows the coordination bond in the 1-chlorogermetrane molecule to be formed with decreasing distance between the coordination centers as a result of formation of a series of MOs with participation of these centers and of other atoms of the molecule. At this point, formation of the MOs existing only at the Ge...N distances at which the molecular geometry is totally optimized plays an essential role. On formation of the coordination bond, electron density shifts from electron-donor fragment of the molecule to the electron-acceptor one (but not from electron-donor center to the electron-acceptor one). A decrease in electron density on the electron-donor fragment, an increase in it on the "electron-donor center", the shift of it from the "electron-acceptor center" to more remote atoms of the electron-acceptor fragment at this bond formation give evidence of this. Populations of s- and p_z -orbitals of the N atom in the 1-chlorogermetrane molecule depend essentially on the CNGe angles.

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