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Quantum-Chemical Study of Adducts of Germanium Halides with Nitrogen-Containing Donors

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Abstract—Structural and thermodynamic characteristics of adducts $GeX_4 \cdot nL$ (n = 1, 2; X = F, Cl, Br; L = NH_3, py, bipy, phen) have been calculated by the B3LYP density functional theory method. The enthalpies of sublimation of complexes *trans*-$GeX_4 \cdot 2py$ and the adduct $GeCl_4 \cdot bipy$ have been estimated for the first time. The rearrangement energies of the donor and acceptor fragments and the Ge–N bond energies for the 1 : 1 and 1 : 2 complexes have been calculated. While the rearrangement energy for germanium halides is lower by 19–63 kJ mol^{-1} than that for silicon halides, the energy of the donor–acceptor bond in the former case is slightly lower. As a result, germanium adducts are slightly more stable than silicon adducts.

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Proceeding with quantum-chemical research [1–5] on Group IV halide adducts with nitrogen-containing donors, we turned to complexes formed by germanium tetrahalides with nitrogen-containing donors. It was previously shown that, in spite of the fairly high energies of Si–N donor–acceptor bonds (76–225 kJ mol^{-1}), the enthalpies of gas-phase dissociation of a number of silicon chloride and bromide adducts are low or even negative. The main reason for this phenomenon is the high rearrangement energy of the acceptor, which contributes most in the difference between the dissociation energy and the energy of the Si–N donor–acceptor bond. It should be expected that the increase in the size of the central atom in going from silicon to germanium will decrease the rearrangement energy of tetrahalides and increase stability of their gas-phase complexes.

The present work is devoted to a quantum-chemical study of adducts of germanium tetrahalides (F, Cl, and Br) with ammonia, pyridine (py), 2,2'-bipyridyl (bipy), and 1,10-phenanthroline (phen). The resulting data, most of which were obtained for the first time, allowed us to analyze the influence of the nature of the central atom, halogen, and ligand on the structural and energy characteristics of a wide range of complexes.

Of adducts of germanium tetrahalides with the above nitrogen-containing donors, $GeF_4 \cdot NH_3$ has been the only studied by quantum-chemical methods, specifically B3LYP/631G(d) [6].

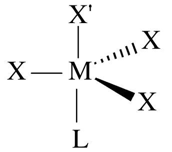
The IR spectral characteristics of the $GeF_4 \cdot NH_3$ complex synthesized in an argon matrix let McNair and Ault [7] to assume that the germanium atom in this compound has a trigonal bipyramidal surrounding and ammonia is in the axial position, which agrees with quantum-chemical calculations [6].

Experimental structural data have been available for crystalline complexes *trans*-$GeF_4 \cdot 2$ py [8], *trans*-GeCl4 · 2 py [9], and $GeF_4 \cdot$bipy [10], and thermochemical data obtained by calorimetry [11–13] and tensimetry [14], for adducts $GeX_4 \cdot 2$ py (X = F, Cl, Br) and $GeCl_4 \cdot$bipy.

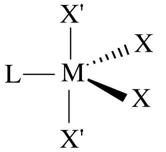
In the present work we performed B3LYP calculations of the structural and thermodynamic characteristics of adducts $GeX_4 \cdot nL$ (n = 1, 2; X = F, Cl, Br; L = NH_3, py, bipy, phen), the rearrangement energies of the donors and acceptors on complex formation, and the energies of Ge–N donor–acceptor bonds. All calculations were performed at the Theoretical Chemistry Department of the Philipps University of Marburg (Germany) using a standard GAUSSIAN-98 software package [15], by the B3LYP density functional method with Becke's exchange functional (B3) [16] and Lee–Yang–Parr's correlation functional (LYP) [17]. For H, N, F, Si, and Cl atoms we used the d95** full-electron basis set with polarization functions [18] and for Br and Ge atoms, the pVDZ full-electron basis set [19]. The calculation procedure has been described in [1].

The geometry of all the compounds was fully optimized, after which vibrational analysis was performed. The reaction enthalpies were calculated with zero-point corrections and reduced to standard conditions using thermal corrections. The energies of Ge–N bonds were calculated with allowance for rearrangement energies of the fragments and basis set superposition errors, as described in [2].

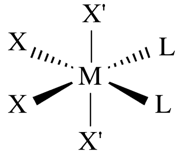
Structural characteristics of adducts. Germanium tetrahalides are capable of forming complexes in which the coordination number of the central atom is 5 and 6. With monodentate ligands (ammonia and pyridine), both 1:1 (coordination number 5) and 1:2 (coordination number 6) complexes are possible. Bidentate ligands (2,2'-bipyridyl and 1,10-phenanthroline) form only 1:1 adducts with MX_4 (coordination number 6). Therewith, $GeX_4 \cdot nL$ complexes with monodentate ligands can exist as various isomers: axial (**A**) and equatorial (**B**) for 1:1 adducts and *cis* (**C**) and *trans* (**D**) for 1:2 adducts. The bidentate ligands under consideration form *cis* isomers (**E**) exclusively, by structural reasons.



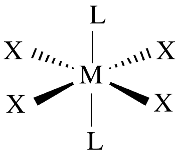
A



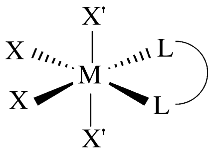
B



C



D



E

With adducts $GeX_4 \cdot nL$ ($L = NH_3$, py), a trigonal bipyramidal structure was optimized, with both an axial and the equatorial ligand. The resulting structural data are given in Table 1. In ammonia complexes, the initial equatorial structure of C_s symmetry converts into the more stable axial isomer of C_{3v} symmetry during optimization. In the case of pyridine adducts, a different pattern is observed: In axial $GeX_4 \cdot py$ isomers (X = Cl, Br), the calculated Ge–N distances are larger than the sum of the van der Waals radii (3.54 Å), the Ge–X distances coincide with r(Ge–X) in the starting molecules, and the XGeX valence angles are close to tetrahedral. Together these findings suggest that $GeX_4 \cdot py$ (X = Cl, Br) species with an axial position of the donor are meaningless to consider as independent molecular formations.

By contrast, the isomers with the equatorial position of pyridine in the trigonal bipyramidal configuration have the Ge–N distance smaller than the sum of the van der Waals radii. Furthermore, the halides noticeably rearrange: Ge–X distances increase, XGeX valence angles between equatorial halogen atoms also increase, whereas the corresponding angles between equatorial and axial atoms decrease. This evidence points to the presence of a donor–acceptor bond in these complexes.

The fluoride complex $GeF_4 \cdot py$ is a special case. The structural characteristics of this complex (Ge–N and Ge–X distances and valence angles) suggest that it can have pyridine both in the axial and in the equatorial position, but the Ge–N distance in the equatorial isomer is shorter by 0.092 Å than in the axial isomer.

Thus, our calculations showed that pyridine complexes, unlike ammonia ones, prefer the equatorial position of the ligand in the trigonal bipyramidal configuration over axial, first of all by steric reasons. The small ammonia molecule can occupy the axial position, whereas the bulkier pyridine is arranged in the equatorial plane, where bond angles are larger and atomic repulsion is weaker. An analogous situation has been observed in silicon complexes [1, 4].

For $GeX_4 \cdot 2L$ we optimized the *cis* and *trans* isomers. It is necessary to note that Ge–N distances in six-coordinate $GeX_4 \cdot 2NH_3$ adducts are commonly slightly shorter than in five-coordinate $GeX_4 \cdot NH_3$ adducts. By contrast, with pyridine, the Ge–N distance in 1:2 adducts increases as compared to 1:1 adducts.

In all the *cis* complexes (Table 1), the Ge–N distance, while increasing the series F–Cl–Br, is essentially shorter than the sum of the van der Waals radii of germanium and nitrogen. The lengths of germanium–halogen bonds are larger than in the starting halides, Ge–X distances being shorter than Ge–X'. Valence angles in the *cis* adducts only slightly vary with halogen. In the pyridine complexes, the plane formed by the nitrogen atoms and equatorial halogen atoms is slightly distorted (the $X^1N^1N^2X^2$ angle is 0.1–0.8°, depending on halogen).

The Ge–N distance for all the *trans* isomers (Table 1) is even shorter than in the respective *cis* isomers and increases in the series F–Cl–Br. Note that unlike *trans*-$SiX_4 \cdot 2NH_3$ [1], *trans*-$GeX_4 \cdot 2NH_3$ have an eclipsed conformation in the ground state. This conformation is probably stabilized by nonbonded interactions of H and X atoms.

For the *trans* complexes with pyridine (except for germanium tetrafluoride), D_{2d} (pyridine rings are perpendicul to each other) and D_{2h} structures (pyridine rings are parallel to each other) are possible. The energy gap between the D_{2d} and D_{2h} complexes is very small (0.04 and –0.61 kJ mol^{-1} for $GeCl_4 \cdot 2py$ and $GeBr_4 \cdot 2py$, respectively). In the case of $GeF_4 \cdot$

Table 1. Structural parameters of $GeX_4 \cdot nL$ adducts[a]

Adduct	r(Ge–N), Å	r(Ge–X), Å	r(Ge–X'), Å	XFeX, deg	X'GeX', deg	XGeX', deg	NGeN, deg
$GeF_4 \cdot NH_3$ (ax)	2.158 (2.159)	1.736 (1.740)	1.732 (1.733)	118.4		97.4	
$GeCl_4 \cdot NH_3$ (ax)	2.273	2.198	2.207	118.2		97.7	
$GeBr_4 \cdot NH_3$ (ax)	2.325	2.365	2.384	118.1		98.0	
trans-$GeF_4 \cdot 2NH_3$	2.054	1.787, 1.789		89.9			179.8
trans-$GeCl_4 \cdot 2NH_3$	2.094	2.290, 2.294		89.8			178.8
trans-$GeBr_4 \cdot 2NH_3$	2.121	2.466, 2.417(2), 2.476		89.8			178.7
cis-$GeF_4 \cdot 2NH_3$	2.163	1.759	1.783	100.0	158.7	96.8	91.4
cis-$GeCl_4 \cdot 2NH_3$	2.185	2.245	2.303	99.4	161.3	96.0	86.8
cis-$GeBr_4 \cdot 2NH_3$	2.198	2.423	2.491	99.8	161.2	96.0	85.5
$GeF_4 \cdot$ py (ax)	2.156	1.736, 1.740	1.737	117.8		96.8	
$GeF_4 \cdot$ py (eq)	2.064	1.775	1.733	124.3	171.2	92.1, 93.0	
$GeCl_4 \cdot$ py (eq)	2.078	2.199	2.285	128.0	170.7	91.9, 92.1	
$GeBr_4 \cdot$ py (eq)	2.092	2.369	2.470	127.5	169.5	92.4, 92.8	
trans-$GeF_4 \cdot$ 2py (D_2)	2.057 (2.014)	1.793 (1.768, 1.770)		90.0 (89.96)			180.0 (180.0)
trans-$GeCl_4 \cdot$ 2py (D_{2h})	2.137 (2.02)	2.299 (2.27)		89.9			180.0
trans-$GeBr_4 \cdot$ 2py (D_{2h})	2.177	2.482		89.6			180.0
trans-$GeCl_4 \cdot$ 2py (D_{2d})	2.138	2.298		90.0			180.0
trans-$GeBr_4 \cdot$ 2py (D_{2d})	2.179	2.481		90.0			180.0
cis-$GeF_4 \cdot$ 2py	2.172	1.755	1.792	99.8	162.7	94.8, 96.3	87.6
cis-$GeCl_4 \cdot$ 2py	2.250	2.246	2.299	99.1	168.0	93.8, 94.0	83.9
cis-$GeBr_4 \cdot$ 2py	2.286	2.426	2.483	99.0	168.8	83.5, 93.7	82.7
$GeF_4 \cdot$ bipy	2.144 (2.023, 2.029)	1.760 (1.757, 1.761)	1.778 (1.777)	104.4 (95.9)	164.5 (173.6)	94.7 (92.0)	75.4 (79.3)
$GeCl_4 \cdot$ bipy	2.193	2.251	2.284	98.8	165.5	94.7	74.4
$GeBr_4 \cdot$ bipy	2.214	2.432	2.467	97.6	165.1	94.9	73.9
$GeF_4 \cdot$ phen	2.166	1.758	1.776	104.8	163.2	95.1	76.0
$GeCl_4 \cdot$ phen	2.209	2.248	2.281	100.1	164.8	94.9	75.0
$GeBr_4 \cdot$ phen	2.371	2.427	2.463	99.1	164.4	95.1	74.3

[a] For $GeF_4 \cdot NH_3$(ax), parenthesized are B3LYP/6-31G(d) results [6]; for *trans*-$GeF_4 \cdot$2py [8], *trans*-$GeCl_4 \cdot$2py [9], and $GeF_4 \cdot$bipy [10], parenthesized are experimental data for crystalline adducts.

2py, the D_{2d} and D_{2h} configurations appear to be transition states (one and two imaginary frequencies, respectively), and the minimum on the potential energy surface corresponds to a D_2 structure.

For $GeX_4 \cdot$bipy and $GeX_4 \cdot$phen we optimized the *cis* structure of C_{2v} symmetry. It should be noted that free 2,2'-bipyridyl has the nitrogen atoms *trans* to each other because of the repulsion between their lone electron pairs. The *cis* structure of C_{2v} symmetry is a transition state with respect to rotation about the C–C bond. The rotation barrier is 32 kJ mol^{-1}. In 1,10-phenanthroline, such rotation is impossible, and it has a *cis* structure of C_{2v} symmetry [5]. As seen from Table 1, the Ge–N distance in $GeX_4 \cdot$bipy and $GeX_4 \cdot$phen complexes is essentially shorter than the sum of the van der Waals radii of germanium and nitrogen atoms (3.54 Å); therewith, the donor–acceptor bond

Table 2. Charge transfer to GeX_4 (q_{CT}), effective atomic charges in complexes (q_i), and changes in atomic charges on complex formation (Δq_i)

Adduct	q_{CT}	q_{Ge}	q_X	$q_{X'}$	q_N	Δq_{Ge}	Δq_X	$\Delta q_{X'}$	Δq_N
$GeF_4 \cdot NH_3$ (ax)	0.255	1.488	–0.440	–0.423	–0.671	–0.093	–0.044	–0.027	0.042
$GeCl_4 \cdot NH_3$ (ax)	0.224	0.825	–0.263	–0.260	–0.678	0.060	–0.072	–0.069	0.035
$GeBr_4 \cdot NH_3$ (ax)	0.204	0.703	–0.225	–0.232	–0.683	0.077	–0.069	–0.076	0.030
trans-$GeF_4 \cdot 2NH_3$	0.583	1.352	–0.484		–0.659	–0.230	–0.083		0.054
trans-$GeCl_4 \cdot 2NH_3$	0.598	0.948	–0.387		–0.645	0.183	–0.195		0.068
trans-$GeBr_4 \cdot 2NH_3$	0.548	0.845	–0.348		–0.660	0.219	–0.192		0.053
cis-$GeF_4 \cdot 2NH_3$	0.445	1.462	–0.464	–0.489	–0.685	–0.120	–0.068	–0.093	0.028
cis-$GeCl_4 \cdot 2NH_3$	0.467	0.972	–0.321	–0.399	–0.669	0.207	–0.130	–0.208	0.044
cis-$GeBr_4 \cdot 2NH_3$	0.441	0.898	–0.294	–0.375	–0.676	0.272	–0.138	–0.219	0.037
$GeF_4 \cdot$ py (ax)	0.283	1.452	–0.432, –0.439(2)	–0.426	–0.098	–0.130	–0.036 –0.043(2)	–0.030	–0.045
$GeF_4 \cdot$ py (eq)	0.336	1.428	–0.421	–0.461	–0.160	–0.154	–0.025	–0.065	–0.107
$GeCl_4 \cdot$ py (eq)	0.353	0.813	–0.225	–0.338	–0.099	0.048	–0.034	–0.147	–0.046
$GeBr_4 \cdot$ py (eq)	0.348	0.658	–0.194	–0.310	–0.092	0.032	–0.038	–0.154	–0.039
trans-$GeF_4 \cdot$ 2py (D_2)	0.575	1.305	–0.470		–0.047	–0.277	–0.074		0.006
trans-GeCl4 · 2py (D_{2h})	0.578	0.933	–0.378		–0.052	0.168	–0.187		0.001
trans-GeBr4 · 2py (D_{2h})	0.514	0.871	–0.346		–0.058	0.245		–0.190	–0.005
trans-$GeCl_4 \cdot$ 2py (D_{2d})	0.563	0.957	–0.380		–0.054	0.192	–0.189		–0.001
trans-$GeBr_4 \cdot$ 2py (D_{2d})	0.501	0.888	–0.347		–0.058	0.262	–0.191		–0.005
cis-$GeF_4 \cdot$ 2py	0.442	1.404	–0.445	–0.478	–0.093	–0.178	–0.049	–0.082	–0.040
cis-$GeCl_4 \cdot$ 2py	0.435	0.933	–0.315	–0.370	–0.089	0.168	–0.124	–0.179	–0.036
cis-$GeBr_4 \cdot$ 2py	0.396	0.884	–0.294	–0.346	–0.089	0.258	–0.138	–0.190	–0.036
$GeF_4 \cdot$ bipy	0.468	1.383	–0.459	–0.466	–0.109	–0.199	–0.063	–0.070	–0.022
$GeCl_4 \cdot$ bipy	0.438	0.940	–0.323	–0.366	–0.121	0.175	–0.132	–0.175	–0.034
$GeBr_4 \cdot$ bipy	0.391	0.888	–0.302	–0.337	–0.131	0.262	–0.146	–0.181	–0.044
$GeF_4 \cdot$ phen	0.452	1.392	–0.457	–0.464	–0.100	–0.190	–0.061	–0.068	–0.079
$GeCl_4 \cdot$ phen	0.428	0.941	–0.321	–0.364	–0.113	0.176	–0.130	–0.173	–0.092
$GeBr_4 \cdot$ phen	0.381	0.890	–0.300	–0.336	–0.122	0.264	–0.144	–0.180	–0.101

in fluorides is shorter than in chlorides and bromides. The equatorial halogen and nitrogen atoms are in the same plane (the $X^1N^1N^2X^2$ dihedral angle is zero). The Ge–X distances are longer than in the starting tetrahalides, and r(Ge–X') > r(Ge–X). The Ge–X and Ge–X' bond lengths increase in the series F ≪ Cl < Br. Valence angles in the adducts only slightly vary with halogen, and the X'GeX' angle differ from 180° by 14.5–17°.

Thus, we can note that, irrespective of the composition and structure of the adduct, the Ge–N, Ge–X, and Ge–X' bond lengths increase in the series F–Cl–Br. Therewith, Ge–N distances in the *trans* isomers are shorter by 0.035–0.115 Å than in the *cis* isomers.

The donor–acceptor charge transfers (q_{CT}), atomic charges in complexes (q_i), and changes in atomic charges compared to the starting components (Δq_i) are presented in Table 2. The data obtained show that q_{CT} differently varies along the F–Cl–Br series: It decreases in some complexes or has a maximum for the chlorine atom in others.

Let us consider in more detail how charge transfer from donor to acceptor occurs. As seen from Table 2, the charge transfer on germanium Δq_{Ge} on complex formation always increases in the series F–Cl–Br. It is important that at X = F a certain negative charge flows on the metal atom, whereas at X = Cl, Br germanium becomes more electropositive than in pure tetrahalides.

As to changes in the charges on halogen atoms, the Δq_X value decreases (becomes more negative) in the series F–Cl–Br, the charge on fluorine atoms changing much weaker than on chlorine and bromine atoms. This is probably explained by the fact that the fluorine atom, being electron-saturated, cannot accept additional electron density.

According to [1, 4, 5, 20], the only function of the complex-forming centers Si and N in silicon tetra-

Table 3. Components of the donor–acceptor bond energy (all values are in kJ mol^{-1})

Adduct	E^{r}		E^{BSSE}		E^{dis}	$E^{\mathrm{b,r}}_{\mathrm{M–N}}$	$E^{\mathrm{b,r+BSSE}}_{\mathrm{Ge–N}}$	$E^{\mathrm{b}}_{\mathrm{M–N}}$
	L	MX_4	L	MX_4				
$GeF_4 \cdot NH_3$ (ax)	0.4	62.3	–9.7	–6.3	82.7	145.4	129.4	137 ± 8
$GeCl_4 \cdot NH_3$ (ax)	0.5	58.0	–8.0	–6.0	24.9	83.5	69.4	76 ± 7
$GeBr_4 \cdot NH_3$ (ax)	0.6	51.4	–7.8	–5.5	13.8	65.7	52.4	59 ± 7
trans-$GeF_4 \cdot 2NH_3$	1.2	209.3	–9.8	–15.3	167.2	189.5	172.0	181 ± 9
trans-$GeCl_4 \cdot 2NH_3$	1.5	227.7	–9.6	–13.1	81.3	156.0	139.8	148 ± 8
trans-$GeBr_4 \cdot 2NH_3$	1.5	221.6	–9.5	–11.9	56.0	140.3	124.9	133 ± 8
cis-$GeF_4 \cdot 2NH_3$	1.1	150.0	–9.4	–13.8	142.5	147.4	131.1	139 ± 8
cis-$GeCl_4 \cdot 2NH_3$	1.6	165.0	–8.8	–12.6	58.5	113.3	98.3	106 ± 8
cis-$GeBr_4 \cdot 2NH_3$	1.8	155.4	–8.8	–11.3	39.9	99.4	84.9	92 ± 7
$GeF_4 \cdot$ py (ax)	2.2	76.9	–6.6	–10.2	75.6	154.7	137.9	146 ± 11
$GeF_4 \cdot$ py (eq)	3.9	172.4	–6.9	–11.8	55.9	232.2	213.4	223 ± 10
$GeCl_4 \cdot$ py (eq)	4.1	178.2	–7.2	–9.9	–26.9	155.4	138.2	147 ± 9
$GeBr_4 \cdot$ py (eq)	4.0	166.1	–7.6	–9.0	–41.8	128.3	111.7	120 ± 8
trans-$GeF_4 \cdot$ 2py (D_2)	3.5	211.2	–7.7	–25.6	158.2	188.2	167.6	178 ± 10
trans-$GeCl_4 \cdot$ 2py (D_{2h})	2.7	231.1	–7.9	–20.3	52.9	144.7	126.5	136 ± 9
trans-$GeBr_4 \cdot$ 2py (D_{2h})	2.4	225.2	–8.2	–17.5	23.6	126.8	109.8	118 ± 9
trans-$GeCl_4 \cdot$ 2py (D_{2d})	2.7	230.8	–7.8	–20.5	53.0	144.6	126.5	136 ± 11
trans-$GeBr_4 \cdot$ 2py (D_{2d})	2.4	225.2	–8.2	–17.5	23.0	126.5	109.5	118 ± 9
cis-$GeF_4 \cdot$ 2py	2.3	171.3	–7.7	–21.6	136.4	156.1	137.7	147 ± 10
cis-$GeCl_4 \cdot$ 2py	1.9	193.0	–7.9	–19.6	26.5	111.7	93.9	103 ± 9
cis-$GeBr_4 \cdot$ 2py	1.7	185.4	–8.4	–17.6	0.1	94.4	77.3	86 ± 9
$GeF_4 \cdot$ bipy	40.2	166.8	–10.4	–18.8	100.4	153.7	139.1	146 ± 7
$GeCl_4 \cdot$ bipy	37.3	180.0	–10.3	–18.2	10.4	113.8	99.6	107 ± 7
$GeBr_4 \cdot$ bipy	36.6	170.0	–10.7	–17.0	–11.3	97.6	83.8	91 ± 7
$GeF_4 \cdot$ phen	9.1	158.8	–9.7	–18.5	124.1	146.0	131.8	139 ± 7
$GeCl_4 \cdot$ phen	6.7	173.5	–9.7	–18.0	38.7	109.5	95.6	103 ± 7
$GeBr_4 \cdot$ phen	5.9	163.3	–10.1	–16.8	18.0	93.6	80.1	87 ± 7

halide adducts is to initiate and mediate charge transfer. The same is true of germanium complexes. In fact, the electron density leaving the nitrogen atom of the donor molecule in the chloride and bromide is localized not on the central atom but is transferred on halogen atoms. As a result of enhanced polarization of the molecule, not only the electron density transferred from the ligand, but also part of the electron density of the metal atom is localized on the halogen atoms. By contrast, in the case of tetrafluorides, the electron density is accepted by the central atom and scarcely transferred on the electron-saturated fluorine atoms.

Calculation of the donor–acceptor bond energy and thermodynamic characteristics of adducts. The most important characteristics of a donor–acceptor interaction is the energy of the donor–acceptor bond, which we calculated by Eqs. (1) and (2) (for more detail, see [2]).

$$nE^{\mathrm{b,r}}_{\mathrm{Ge–N}} = E^{\mathrm{dis}} + [nE^{\mathrm{r}}(\mathrm{L}) + E^{\mathrm{r}}(\mathrm{GeX_4})], \qquad (1)$$

$$nE^{\mathrm{b,r+BSSE}}_{\mathrm{Ge–N}} = E^{\mathrm{dis}} + [nE^{\mathrm{r}}(\mathrm{L}) + E^{\mathrm{r}}(\mathrm{GeX_4})] + [nE^{\mathrm{NSSE}}(\mathrm{L}) + E^{\mathrm{BSSE}}(\mathrm{GeX_4})]. \qquad (2)$$

Here n is the number of bonds; $E^{\mathrm{b,r}}_{\mathrm{Ge–N}}$, bond energy calculated with allowance for the rearrangement energy of the donor and acceptor; E^{dis}, dissociation energy of the complex into components in the gas phase; $E^{\mathrm{r}}(\mathrm{L})$, rearrangement energy of the ligand; $E^{\mathrm{r}}(\mathrm{GeX_4})$, rearrangement energy of the germanium tetrahalide; $E^{\mathrm{b,r+BSSE}}_{\mathrm{Ge–N}}$, bond energy calculated with allowance for the rearrangement energy of the donor and acceptor, as well as basis set superposition error; and E^{BSSE}, basis set superposition error.

In Eq. (1), $E^{\mathrm{b,r}}_{\mathrm{Ge–N}}$ represents the upper, and $E^{\mathrm{b,r+BSSE}}_{\mathrm{Ge–N}}$ in Eq. (2), lower limit of possible $E^{\mathrm{b}}_{\mathrm{Ge–N}}$ values [2].

The E^{r}, E^{BSSE}, and E^{dis} values, and the energies of the Ge–N bond ($E^{\mathrm{b}}_{\mathrm{Ge–N}}$), calculated by Eqs. (1) and (2), are given in Table 3. The bond energies calculated

Table 4. Thermodynamic characteristics of the dissociation of adducts by Eq. (4)

Adduct	ΔH^0_{298}, kJ mol^{-1}	ΔS^0_{298}, J mol^{-1} K^{-1}	ΔG^0_{298}, kJ mol^{-1}
$GeF_4 \cdot NH_3$ (ax)	73.2	131.2	34.1
$GeCl_4 \cdot NH_3$ (ax)	15.7	132.5	–23.8
$GeBr_4 \cdot NH_3$ (ax)	5.0	130.6	–33.9
trans-$GeF_4 \cdot 2NH_3$	153.0	307.5	61.4
trans-$GeCl_4 \cdot 2NH_3$	61.9	263.8	–16.7
trans-$GeBr_4 \cdot 2NH_3$	37.0	269.2	–43.2
cis-$GeF_4 \cdot 2NH_3$	125.0	268.2	45.1
cis-$GeCl_4 \cdot 2NH_3$	40.5	264.1	–38.2
cis-$GeBr_4 \cdot 2NH_3$	22.3	265.2	–56.7
$GeF_4 \cdot$ py (ax)	68.3	136.3	27.7
$GeF_4 \cdot$ py (eq)	48.3	144.2	5.3
$GeCl_4 \cdot$ py (eq)	–34.1	139.4	–75.6
$GeBr_4 \cdot$ py (eq)	–49.1	137.7	–90.1
trans-$GeF_4 \cdot$ 2py (D_2)	143.8	304.1	53.2
trans-$GeCl_4 \cdot$ 2py (D_{2h})	37.8	338.0	–62.9
trans-$GeBr_4 \cdot$ 2py (D_{2h})	8.6	336.9	–91.8
trans-$GeCl_4 \cdot$ 2py (D_{2d})	37.9	337.8	–62.8
trans-$GeBr_4 \cdot$ 2py (D_{2d})	8.0	336.0	–92.1
cis-$GeF_4 \cdot$ 2py	122.1	318.2	27.3
cis-$GeCl_4 \cdot$ 2py	11.7	328.3	–86.1
cis-$GeBr_4 \cdot$ 2py	–14.5	325.5	–111.5
$GeF_4 \cdot$ bipy	92.7	181.5	38.6
$GeCl_4 \cdot$ bipy	2.1	180.7	–51.7
$GeBr_4 \cdot$ bipy	–19.7	178.0	–72.7
$GeF_4 \cdot$ phen	115.8	178.8	62.5
$GeCl_4 \cdot$ phen	29.7	179.8	–23.9
$GeBr_4 \cdot$ phen	9.0	179.1	–44.4

as an average between $E^{b,r}_{Ge–N}$ and $E^{b,r+BSSE}_{Ge–N}$ are presented in the last column of Table 3. It is seen from the Table 3 that the donor fragment changes only slightly on complex formation, though bidentate ligands undergo stronger changes than monodentate. Nevertheless, the rearrangement energy of the donor does not exceed 9 kJ mol^{-1}. The rearrangement energy of bipyridyl is an exception, on account of the fact that this ligand changes configuration from *trans* in the free state to *cis* in complexes, which requires overcoming the barrier to rotation about the C–C bond (32 kJ mol^{-1}) and raises the rearrangement energy to ~40 kJ mol^{-1}.

The rearrangement energy of the acceptor varies from 51 to 231 kJ. It is minimal in the axial isomers of 1 : 1 adducts and maximal in the *trans* isomers of 1 : 2 adducts. Furthermore, $E^{r}_{MX_4}$, irrespective of the coordination number and isomer type, slightly changes in the series F–Cl–Br and reaches a maximum for the chlorine atom. The Ge–N bond energy decreases in the series F–Cl–Br for all types of complexes.

As the energy of a donor–acceptor bond cannot be determined experimentally, it is usually estimated on the basis of thermochemical data on the enthalpies of homogeneous gas-phase dissociation of the adduct into components [21] [in Eq. (3), n is the number of bonds].

$$nE^{b}_{M–N} \approx \Delta H^0_{298}. \tag{3}$$

Table 4 lists the enthalpies of dissociation of complexes (ΔH^0_{298}) by Eq. (4).

$$GeX_4 \cdot nL(gas) = GeX_4(gas) + nL(gas). \tag{4}$$

Comparison of the ΔH^0_{298} values for the *cis* and *trans* isomers shows that the *trans* configuration is more favored by energy than the *cis* configuration for all the halogens and ligands. In ammonia complexes, the difference in ΔH^0_{298} is 14–28 kJ mol^{-1}, and in pyridine complexes it is 21–26 kJ mol^{-1}.

As seen from Table 4, fluoride adducts differ from the others by large positive dissociation enthalpies and can be stable in the gas phase ($\Delta G^0_{298} > 0$). By contrast, the complexes of germanium chloride and bromide should dissociate spontaneously ($\Delta G^0_{298} < 0$). In fact, the adduct $GeCl_4 \cdot$bipy was not detected in the gas phase by tensimetry [14]. Comparison of the parameters of complete dissociation of gaseous adducts by Eq. (4) with the experimental data characterizing the dissociation of complexes by Eq. (5) allowed us to calculate ΔH^0_{subl} for a series of adducts and ΔS^0_{subl} for the adduct of germanium tetrachloride with bipyridyl (Table 5).

$$GeX_4 \cdot nL(cr.) \rightleftarrows GeX_4(gas) + nL(gas). \tag{5}$$

It should be noted that the sublimation enthalpies are slightly higher compared to those for Group III halide adducts (90–125 kJ mol^{-1} [22–24]). Similar pattern was observed for silicon adducts with pyridine and bipyridyl [4, 5]. Apparently, this can be explained by strong intermolecular interactions in the crystal state. The increase in the sublimation enthalpy in the series F–Cl–Br fully agrees with the regular trends characteristic of molecular compounds.

Table 5 also fives for the adduct $GeCl_4 \cdot$bipy the temperature found from the experimental data and corresponding to the equilibrium constant of reaction (5) equal to unit ($T_{K=1}$), as well as the temperature calculated for the sublimation pressure of 1 atm ($T_{p=1}$).

Table 5. Characteristics of dissociation and sublimation of complexes

Adduct	ΔH^0_{cr}(exp.), kJ mol^{-1}	ΔH^0_{298}(calc.), kJ mol^{-1}	ΔS^0_{298}(calc.), J mol^{-1} K^{-1}	ΔH^0_{subl}, kJ mol^{-1}
$GeF_4 \cdot 2py$	270	144	304	126
$GeCl_4 \cdot 2py$	246	38	338	208
$GeBr_4 \cdot 2py$	238	9	337	229
$GeCl_4 \cdot bipy$ [a]	248	2	181	246

[a] ΔS^0_{cr}(exp.) 431, ΔS^0_{subl} 250 J mol^{-1} K^{-1}; $T_{K=1}$ 575, $T_{p=1}$ 984 K.

Comparison of $T_{K=1}$ and $T_{p=1}$ shows that dissociation of $GeCl_4 \cdot bipy$ develops at lower temperatures than sublimation and, therefore, $GeCl_4 \cdot bipy$ should not pass in the gas phase, which completely agrees with experiment [14].

Comparison of silicon and germanium adducts. The element–nitrogen bond length increases in going from silicon to germanium complexes, but this increase is connected first of all with increasing size of the central atom. Therefore, in our opinion, it is necessary to consider not absolute, but relative M–N distances. One of such relative characteristics can be, for example, the value Δr, which represents the difference between the length of the donor–acceptor bond and the sum of the covalent radii of the central atom and nitrogen.

$$\Delta r = r_{M-N} - \Sigma r_{cov}.$$

The Σr_{cov} values for the Si–N and Ge–N bonds are 1.86 and 1.97 Å [25], respectively.

The Δr values are given in Table 6. As seen, in all the fluorides Δr decreases in going from silicon to germanium, implying strengthening of the donor–acceptor bond. On the contrary, in the chlorides (except for the *cis* and *trans* complexes with pyridine) and bromides Δr increases.

Table 6. Values of $\Delta r = r_{M-N} - \Sigma r_{cov}$ (Å)

Adduct	F	Cl	Br
$SiX_4 \cdot NH_3$ (ax)	0.251	0.290	0.301
$GeX_4 \cdot NH_3$ (ax)	0.188	0.303	0.355
trans-$SiX_4 \cdot 2NH_3$	0.106	0.119	0.130
trans-$GeX_4 \cdot 2NH_3$	0.084	0.124	0.151
cis-$SiX_4 \cdot 2NH_3$	0.226	0.206	0.204
cis-$GeX_4 \cdot 2NH_3$	0.193	0.215	0.228
$SiX_4 \cdot py$ (eq)	0.121	0.096	0.094
$GeX_4 \cdot py$ (eq)	0.094	0.108	0.122
trans-$SiX_4 \cdot 2py$	0.120	0.182	0.203
trans-$GeX_4 \cdot 2py$	0.087	0.167	0.207
cis-$SiX_4 \cdot 2py$	0.243	0.285	0.289
cis-$GeX_4 \cdot 2py$	0.202	0.280	0.316
$SiX_4 \cdot bipy$	0.203	0.220	0.222
$GeX_4 \cdot bipy$	0.174	0.223	0.244
$SiX_4 \cdot phen$	0.230	0.234	0.237
$GeX_4 \cdot phen$	0.196	0.239	0.261

Considering the changes in the bond energy in going from silicon to germanium (Table 7), we note that the E^b_{M-N} values are practically the same for all the fluorides within the calculation error (±10 kJ mol^{-1}), i.e. they are independent of the nature of the central atom. With the other tetrahalides, the energy of the donor–acceptor bond in germanium complexes is slightly lower than in silicon complexes, which is most pronounced in the case of bromide adducts.

Table 7. Changes in the bond energy in going from Si to Ge (kJ mol^{-1})

Adduct	Element	F	Cl	Br
trans-$MX_4 \cdot 2NH_3$	Si	187	169	158
	Ge	181	148	133
trans-$MX_4 \cdot 2py$	Si	180	147	132
	Ge	178	136	118
$MX_4 \cdot bipy$	Si	152	127	116
	Ge	146	107	91
$MX_4 \cdot phen$	Si	142	122	112
	Ge	139	103	87

Germanium adducts are thermodynamically more stable than analogous silicon complexes [1, 4, 5]. However, the enthalpies of dissociation of the majority of germanium complexes are still low and even negative. As a result, $\Delta G^0_{298} > 0$ only for fluoride adducts. It should be noted that our calculated dissociation enthalpy of the complex $GeF_4 \cdot NH_3$ is higher by 8.2 kJ mol^{-1} than the value given in [6], where the ΔH^0_{298} value was also calculated by the

B3LYP method but with another basis. However, within the framework of the chosen method and basis the relative pattern is preserved: F > Cl and Ge > Si.

Thus, our study showed that, in spite of the fact that the rearrangement energy of tetrahalides actually increases in going from silicon to germanium, the donor–acceptor bond energy also decreases. As a result, the dissociation enthalpy of germanium complexes is still low, and the adducts do not pass in the gas phase. Apparently, the situation may change in the case of tin complexes whose $E^{\mathrm{r}}_{\mathrm{MX_4}}$ value should be even lower, and the dissociation enthalpy (according to the available experimental data for solid adducts [11–13, 26–28]) is higher than for germanium tetrahalide complexes.

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