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Coordination compounds of tetravalent silicon, germanium and tin: the structure, chemical bonding and intermolecular interactions in them †

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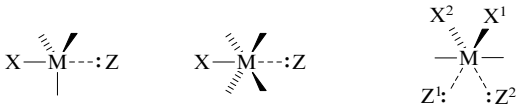
The review is devoted to analysis and generalization of the results of (i) quantum chemical studies on the structure, chemical bonding and intermolecular interactions in coordination compounds of tetravalent silicon, germanium and tin in crystals, in solutions and in the gas phase and (ii) experimental investigations of the electron density distribution in these systems. The bibliography includes 147 references.

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I. Introduction

Improvement of experimental methods and theoretical approaches in organic chemistry facilitated progress in ideas of chemical bonding in organosilicon, organogermanium and organotin compounds with weak coordination bonds. Formally, these are compounds containing a chemical bond between the Si (Ge, Sn) atom and the atom Z (Z = O, N), the bond being longer than conventional covalent bonds.[1] Usually, the Z atom is treated as electron density donor. Main forms of coordination polyhedra of the atoms of Group 14 elements (M = Si, Ge and Sn) in this type of compounds include a trigonal bipyramid and an octahedron[1–3] provided that the atoms of these elements have a formal oxidation state of +4. The formation of an M---Z coordination bond leads to weakening of the M---X bond (usually, X = Hal, Ar, Alk) in *trans*-position to the coordination bond.[1]



Structural studies of silatranes, the simplest representatives of the title compounds, revealed considerable differences between the lengths of the M---Z coordination bonds in crystals and in the gas phase (in free molecules). For many other compounds of silicon, germanium and tin, this was demonstrated by comparing the results of quantum chemical calculations with the X-ray diffraction data.

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Changes in the length of the M···Z coordination bond in the coordination compounds of tetravalent silicon, germanium and tin on going from free molecules to solids are similar to the changes observed for donor-acceptor complexes of Group 5 and 8 elements, mainly boron and sulfur compounds. In the last-mentioned case, a huge data array is available. It was studied using modern theoretical concepts including Bader's quantum topological theory[4] called 'Atoms in Molecules'. A great body of information was also obtained for the title compounds; however, there are almost no reviews devoted to generalization and systematization of these data. Here, we made an attempt to bridge the gap.

The Cambridge Structural Database[5] includes information on nearly a thousand structures of coordination compounds of tetravalent silicon, germanium and tin. These data were widely used in reviews on the chemistry of atranes,[6] quasi-atranes (metal ocanes),[7,8] as well as chelate complexes of silicon, germanium and tin[9–11] (all of them were published in the last 15 years). However, experimental structural data for the gas phase and moreover solutions are very few. Situation in the gas phase is mainly approximated using quantum chemical calculations of isolated (free) molecules. Molecular geometry in solution can be studied by quantum chemical calculations within the framework of the self-consistent reaction field model[12] (or similar approximations) or using cluster models. For these systems, one can calculate a number of spectroscopic parameters (chemical shifts in NMR spectra and vibrational frequencies). Comparison of the results obtained with experimental data makes it possible to draw reliable conclusions about the geometry of the coordination sites in atoms of Group 14 elements in solution or in the crystal. Finally, by analyzing information on the electronic structure of crystals, isolated molecules and cluster models one can establish some common features related to the nature of the M···Z bond.

This review is focused on the studies carried out in the last decade. The reasons are as follows. First, two reviews reported in 1989 and in 1997 (see Refs 13 and 14, respectively) are available, both being devoted to the problem in question. They included a comparison of the experimental data on the structure of the title compounds in the crystalline and gas phases available at that time. Next, it is the last decade that is characterized by a higher level of research activity and by an increase in the number of studies containing results of quantum chemical calculations and experimental data on the electron density distribution. The authors of the two reviews mentioned above considered quantum chemical calculations as an auxiliary method of investigation aimed to refine information obtained by microwave spectroscopy and electron diffraction (this characterizes the research profile of the authors).

Wide use of computational methods made it possible to partially fill the deficiency of experimental information and to carry out detailed studies of specific features of the electronic structure of Group 14 compounds containing the M···Z coordination bonds.

II. Theoretical concepts proposed to describe specific features of the M···Z coordination bond. Role of intermolecular interactions

The dependence of the M...Z interatomic distance on the phase state is a salient feature of all types of the compounds in question. For the same molecule, the M...Z interatomic distance is minimum in the crystal, being the longest in the gas phase; in solutions, this distance is usually intermediate between the gas-phase and solid-state values and depends on the dielectric constant (ε) of the solvent. The M...Z interatomic distance varies in different polymorphs of the same compound. An example is provided by 1-phenylsilatrane, *viz*., the Si...N interatomic distances in three polymorphs of this compound lie in the range from 2.132 to 2.155 Å.[15–17] Haaland and Leopold[13,14,18] discussed the reasons underlying changes in the M...Z interatomic distance taking donor-acceptor complexes of boron and sulfur as examples. According to Haaland, the larger the dipole moment of a molecule the more pronounced the difference in the M···Z bond lengths in the molecule in the crystal and in the gas phase. The structures of nonpolar molecules in these phases differ insignificantly. In his review Haaland[13] considered polar molecules containing the M atom bearing a large positive charge and the X and Z atoms with large negative charges; therefore, the dipole moments of the molecules were also rather large, *e.g*., from 5 to 9 D for the complexes of haloboranes with SO_3.[13,14,18–20] A mechanism of shortening of the M···Z bond on going from the crystal to the gas phase (Fig. 1) was reported.[14,21] Such molecules were called partially bonded, which characterizes weakness of the M···Z bonds. According to this model, stabilization of the crystal structure (and, therefore, weaker intermolecular repulsion) requires an increase in the dipole moments of the interacting molecules and shortening of the M···Z bond, *i.e*., electron density redistribution between the M and Z atoms.

Going from an isolated complex to its dimer is accompanied by shortening of the B–N bond from 1.662 to 1.637 Å for $BH_3 \cdot NH_3$ (**1**)[22] and from 1.679 to 1.629 Å for $BF_3 \cdot NH_3$ (**2**). It the tetramer of **2**, this bond is even shorter. The B–N bond length in crystals **1** and **2** is 1.564 and 1.604 Å, respectively. According to MP2/6-31G(d) calculations,[23] an increase in the number of complexes **1** in the associate to nine is followed by shortening of the B–N bond by 0.27 Å as compared to the bond length in the isolated complex studied at the same level of theory. HF/6-31G(d) calculations predict that the B–N bond in the associate containing twenty eight complexes **1** is longer than in the associate comprising a total of twenty molecules (1.623 *vs*. 1.609 Å), being at the same time much shorter than in the isolated complex (1.689 Å).

However, the model associates give no means to determine the dipole moment of an individual molecule and the polarity of the medium. The influence of the latter parameter on the former one was studied using the self-consistent reaction field (SCRF) model and complex **1** as an example.[23] As the dielectric constant increases from 1 to 200, the dipole moment increases by 0.7 D and the B...N interatomic distance decreases from 1.689 to 1.663 Å. This is good agreement with the conclusion drawn in the studies of associates (see above).

Molecular association is also characteristic of the gas phase (microsolvation). This was experimentally demonstrated by microwave spectroscopy (in this method, it is hard to maintain the stoichiometric ratios of the reactants used to prepare donor-acceptor complexes). For instance, in the presence of excess HCN the B...N distance in the complex $HCN \cdot BF_3$ is 0.18 Å shorter than at the stoichiometric ratio of the reactants.[24] Taking into account this

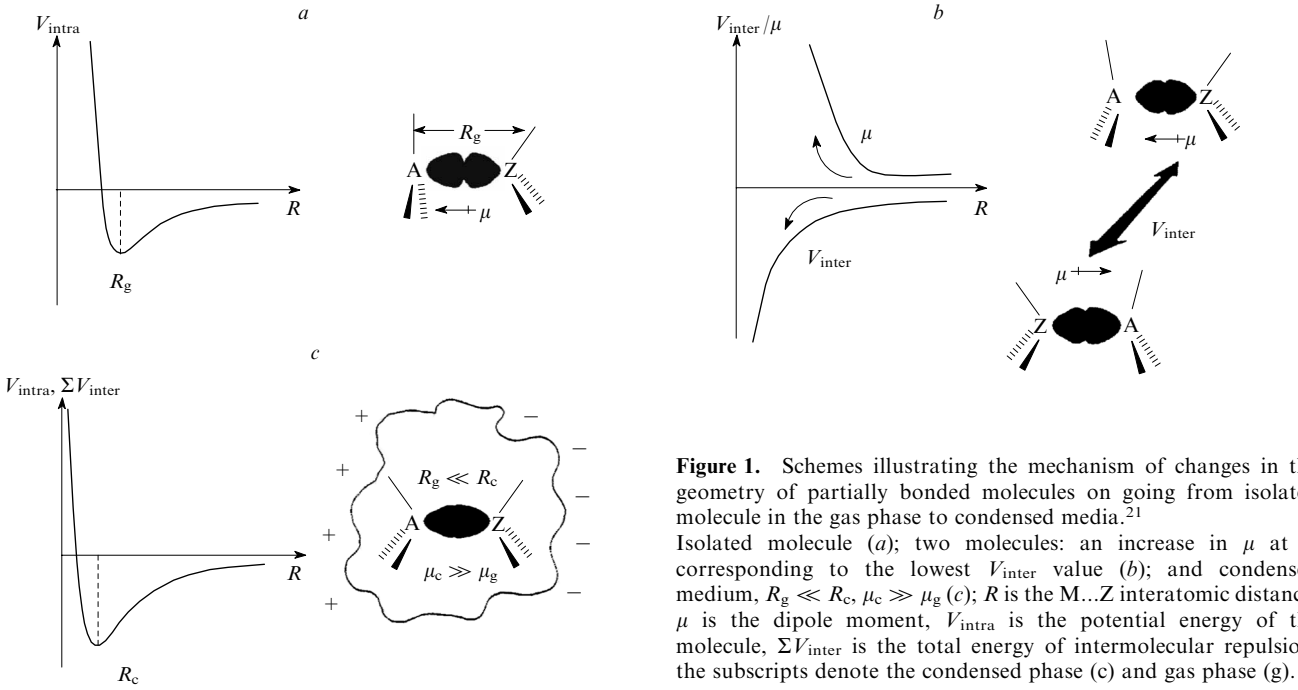


Figure 1. Schemes illustrating the mechanism of changes in the geometry of partially bonded molecules on going from isolated molecule in the gas phase to condensed media.[21]
Isolated molecule (*a*); two molecules: an increase in μ at R corresponding to the lowest V_{inter} value (*b*); and condensed medium, $R_g \ll R_c$, $\mu_c \gg \mu_g$ (*c*); R is the M...Z interatomic distance; μ is the dipole moment, V_{intra} is the potential energy of the molecule, ΣV_{inter} is the total energy of intermolecular repulsion, the subscripts denote the condensed phase (c) and gas phase (g).

fact, the existence of a weak van der Waals complex $HCN\cdots HCN\cdot BF_3$ in the gas phase was suggested. This complex was studied by quantum chemical calculations similarly to the complex $HCN\cdots HCN\cdot SO_3$[25] in which the N...S interatomic distance is 0.1 Å shorter than in $HCN\cdot SO_3$. In the latter case, shortening of the N...S distance was accompanied by an increase in the experimentally determined dipole moment from 7.4 to 8.64 D. Calculations[26] also predicted that sulfamic acid mainly exists in the form of a van der Waals complex $NH_3\cdots H_3N\cdot SO_3$.

Considering studies on quantum chemical calculations of associates (molecular clusters), one can conclude that forces leading to shortening of the M...Z interatomic distance in condensed media are short-range in character, *i.e.*, some change in the distance is due to the influence of weak interactions between neighbouring molecules, which are often called dipole–dipole interactions. The energy of the dipole–dipole interactions between neighbouring molecules in the structure of $HCN\cdot BF_3$ (8.5 kcal mol^{-1}) was estimated at about one third of the crystal packing energy (23.7 kcal mol^{-1}).[27]

Some authors (see, *e.g.*, Refs 28–30) ignore the term 'dipole–dipole interactions'. When studying the crystal structure, one deals with a rather large number of intermolecular interactions that can hardly be classified exactly. The simplest example is provided by the structure of $BH_3\cdot NH_3$. Here, only H···H interactions with an average energy of 1.5 kcal mol^{-1} occur.[29] This value was calculated from the sublimation energy (18.1 kcal mol^{-1}) obtained from quantum chemical calculations of a crystal of complex **1**. It would be a delightful prospect to represent the crystal lattice energy (or the solvation energy) as the sum of the energies of weak two-centre interactions. The determination of the energy of each interaction using conventional approaches which treat the total energies of isolated molecules or their associates is a stubborn problem.

By and large, the rules established for simple donor-acceptor complexes of Group 13 and 16 elements hold for the coordination compounds of silicon, germanium and tin. The changes in the geometric parameters, spectroscopic characteristics and electron density distribution observed for the title class of compounds are due to the influence of intermolecular interactions.

III. Intermolecular interactions in crystals of coordination compounds of tetravalent silicon, germanium and tin

Crystals of coordination compounds of tetravalent silicon, germanium and tin are characterized by a large number of different-type intermolecular interactions because even simple compounds contain atoms with significantly different electronegativities and van der Waals radii. Since most atoms in molecules of the coordination compounds in question are carbon, hydrogen, oxygen and nitrogen atoms, the most plausible assumption is that main types of intermolecular interactions in the crystals of such compounds are the same as those in crystals of organic compounds.

Of particular interest is to answer the question as to does the M atom participate in intermolecular interactions? To answer the question, a total of 3346 silicon-containing and 718 germanium-containing compounds were studied.[31] The necessary information was retrieved from the Cambridge Structural Database. Among these compounds, nearly 600 can be treated as coordination compounds with the coordination number (CN) of the central atom M equal to 5 or 6. The search for weak intermolecular interactions involving the M atom was carried out using Blatov's stereoatomic model of the crystal structure.[32,33] It was shown that in compounds with CN = 6 the M atom is not involved in the intermolecular interactions with neighbouring molecules in the crystal except a polymeric structure of $(^nBu_2N)_2(GeI_4)$.[34] Among the compounds with CN = 4 and CN = 5, only fifteen contain the M atom involved in weak intermolecular interactions with oxygen, nitrogen or

halogen atoms. Thus, intermolecular interactions with participation of the M atoms can not be responsible for shortening of the M---Z bond.

According to Desiraju,[35] C–H···O hydrogen bonds are the main structure-forming interactions in organic crystals. Also, a significant role is played by 'nonclassical' interactions involving hydrogen atoms, *viz*., H···H or C–H···π.[36] Probably, it is these interactions that either directly or indirectly influence the length of the M---Z bond in the crystal. The energies of these interactions can be evaluated using topological analysis of the electron density distribution within the framework of Bader's theory 'Atoms in Molecules'. To this end, one should locate the (3,−1) critical points for all intermolecular interactions and to calculate the potential energy density [$V^e(\mathbf{r})$] at these points.

Espinosa, Molins and Lecomte[37] reported a correlation between the energy of a hydrogen bond (E_b) and the potential energy density at the (3,−1) critical point

$$E_b = 313.75\, V^e(\mathbf{r}) \text{ kcal mol}^{-1}. \quad (1)$$

This expression is widely used to estimate the energies of all types of intermolecular interactions,[38,39] the sublimation energies[40] and the energies of the M---Z coordination bonds (see Section IX). According to calculations of the electron density distribution in the crystal of 1-hydrosilatrane (**3a**),[41] the C–H···O and H···H interactions make comparable contributions (55% and 45%, respectively) to the sublimation energy which equals 17.5 kcal mol^{-1}. The presence of halogen atoms in the coordination environment of the M atom is responsible for the occurrence of nonclassical intermolecular interactions of the Hal···C(N,O) type.[42]

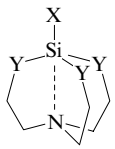
Intermolecular interactions in crystals can be revealed by analyzing the crystal packing or the electron density distribution. As to solutions, the nature of intermolecular interactions with solvent molecules and their influence on the M---Z bond length can be studied only by spectroscopic methods or quantum chemical calculations.

IV. Modelling the structure of coordination compounds of tetravalent silicon, germanium and tin in solutions

Molecules of coordination compounds of tetravalent silicon, germanium and tin usually have a complex structure and are of low symmetry. This precludes obtaining reliable experimental data on their gas-phase structure. Indeed, experimental gas-phase structures are available only for the three simplest silatranes **3a**–**c**.[43–45] They can with a reasonable accuracy be reproduced by quantum chemical methods, such as MP2,[46,47] B3PW91,[48] and PBE.[49] These methods also seem to be appropriate for calculating molecules with unknown gas-phase structures (*e.g*., compounds **3d**–**h**).

Studies on the molecular geometry in solutions require taking account of solvation effects. This is done using two types of models, (i) cluster (or supermolecule) and (ii) continuum ones. To study intermolecular interactions using the first type of models, one should calculate model associates comprised of solute and solvent molecules. In the continuum models, the solute molecule interacts with an electric field produced by the system of point charges (SCRF theory by Onsager)[12] or dipoles (Polarized Continuum Model, PCM).[50] The polarity of a solvent is characterized by its dielectric permittivity. Clearly, comprehensive elucidation of the nature of intermolecular interactions using these models is impossible; therefore, combined models with associates placed in the solvent field are often used.

Structures 3



3a–h

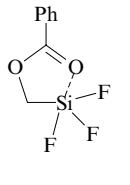
Compound **3**	X	Y	Compound **3**	X	Y
a	H	O	**e**	F	NH
b	F	O	**f**	F	CH_2
c	Me	O	**g**	Me	NH
d	Cl	O	**h**	Me	CH_2

The use of the models described above with inclusion of account solvation effects leads to considerably smaller M---Z bond lengths and to more realistic values of spectroscopic parameters, as shown by comparing the results of calculations and experimental data.

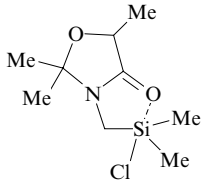
To study the molecular geometries of compounds **4**–**8** containing pentacoordinate Si atoms in solutions, quantum chemical calculations using the SCRF model were performed.[46,51–53] The authors of all publications varied the dielectric constant value, ε, of the solvent. An increase in ε was followed by shortening of the Z...Si distance, which in some cases became shorter than in the crystal. By varying ε one could monitor the changes in the dipole moment of the molecule upon a change in the Z...Si interatomic distance. The dipole moment of the five-membered monochelate **7** with a 'soft' coordination site C_3OSiCl is directly related to the Si...O interatomic distance; shortening of this distance from 2.35 to 2.05 Å causes the dipole moment to increase by 2 D.[52] Interestingly, it was concluded[46,51–53] that the decrease in the Si...O and Si...N interatomic distances is a consequence of weakness of the corresponding bonds.

An example of quantum chemical calculations of associates of cyclic compounds with the M---Z bond is provided by the molecular clusters of 1-chlorosilatrane (**3d**). The crystal structure of **3d** was used as the starting point.[54] The central molecule of the associate was calculated by the

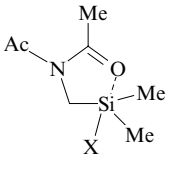
Structures 4–8



4

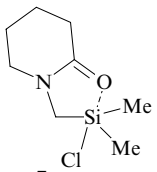


5

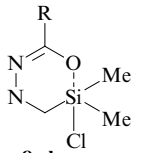


6a–e

X = Cl (**a**), OC(O)CF_3 (**b**), Br (**c**), F (**d**), OAc (**e**)



7



8a,b

R = CF_3 (**a**), Me (**b**)

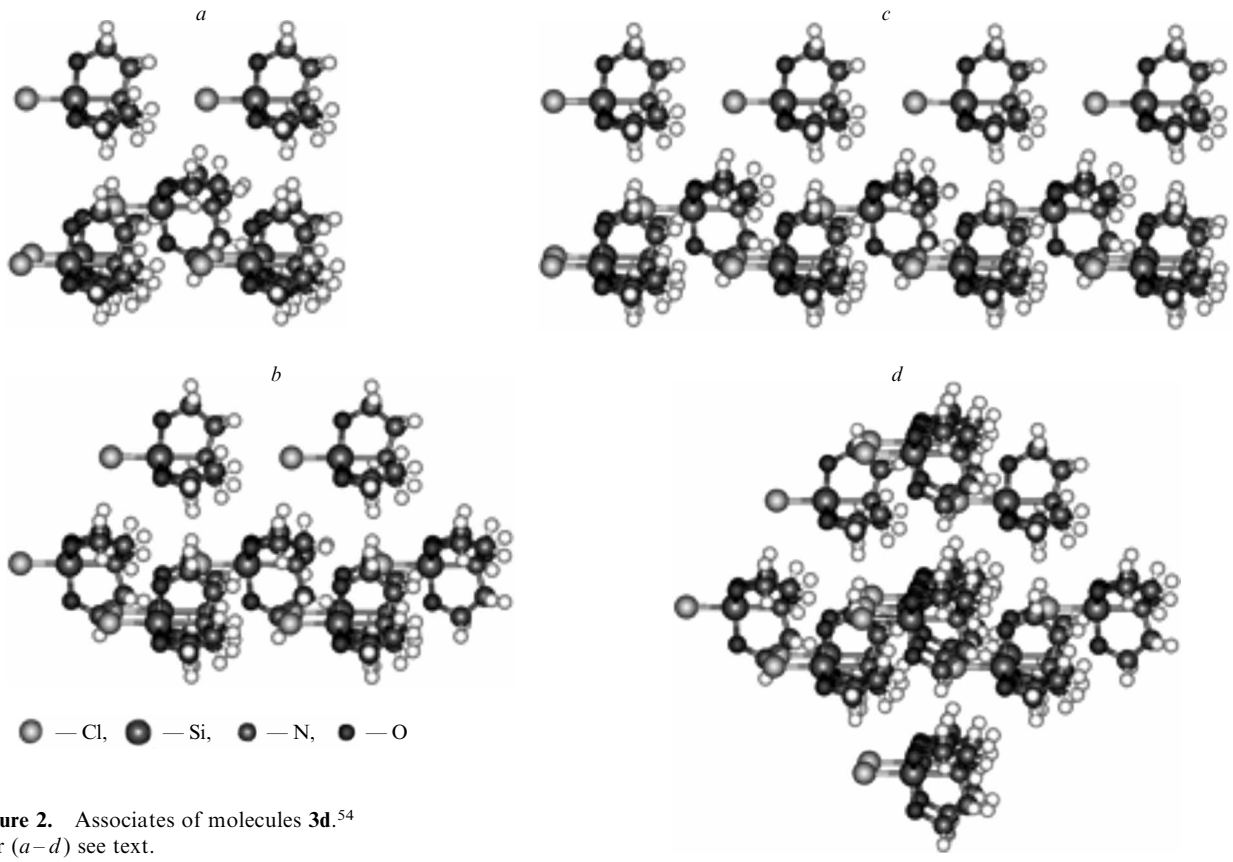
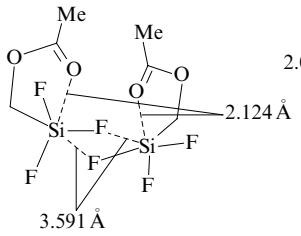


Figure 2. Associates of molecules **3d**.[54]
For (*a*–*d*) see text.

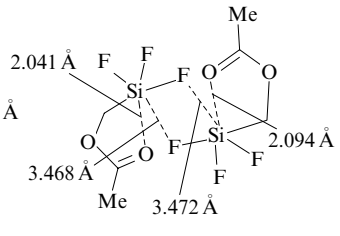
B3LYP/6-31G(d) method and the environment was described by a universal force field.[55] The number of molecules **3d** in the associates varied from 7 to 15; the molecular geometry was analyzed for the central molecule only. In the associates whose structures are shown in Fig. 2 *a*–*c* the molecules of 1-chlorosilatrane form a helix along the 6_3 pseudoaxis. As the number of molecules increases, the Si...N interatomic distance in these structures decreases from 2.26 to 2.07 Å (*cf.* 2.571 Å for the isolated molecule). In the associate whose structure is shown in Fig. 2 *d*, the $Si^+...N^-$ dipoles are aligned and molecules **3d** are stacked. In spite of the larger number of molecules **3d** in this associate (15), the Si...N interatomic distance appeared to be the longest (2.38 Å); apparently, dipole–dipole interactions in the associate destabilize the Si---N coordination bond.

According to B3LYP/6-311G(d,p), the length of the Si---O coordination bond in isolated (O---Si)-acetoxytrifluorosilane molecule is 2.201 Å.[56] Dimerization of the molecule causes the M---Z bond to shorten. The symmetric dimer **9a** contains two shortened Si···F contacts and two weak coordination bonds Si---O which are almost as long as the bonds in the isolated molecule. The dipole moment of **9a** is 4.8 D, the Si^+-O^- dipoles being nearly aligned. In the asymmetric dimer **9b**, the Si---O coordination bonds are stronger than in **9a** but differ in length. The dipole moment of **9b** (1.2 D) is much lower than that of **9a** due to different direction of Si^+-O^- dipoles. Isolated dimer **9a** is energetically less favourable than **9b**, namely, the energy of formation calculated with inclusion of zero-point energy correction is 8.7 and 10.0 kcal mol^{-1}, respectively. Probably, additional stabilization of the asymmetric dimer is due to the presence of a weak hydrogen bond H···F. Calculations using the SCRF model ($\varepsilon = 36$) change the picture, namely, both dimers become energetically unfavourable, **9b** (with the smaller dipole moment) being destabilized to a greater extent compared to **9a** ($\Delta H = 1.4$ and 2.1 kcal mol^{-1}).

Structures 9



9a

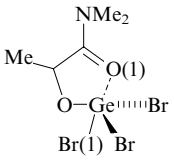


9b

The role of intermolecular interactions was studied in relation to associates of monochelate germanium complex **10**.[57] Quantum chemical calculations of seven solvate clusters **10**·*n*MeCN·X containing from two to six MeCN molecules, H_2O and HBr molecules and an H_3O^+ cation were carried out. The Ge---O bond in isolated molecule **10** is 2.213 Å long and shortens to 2.040 Å as the number of MeCN molecules increases to 6. This is accompanied by elongation of the Ge–Br axial bond from 2.344 to 2.411 Å. Changes in the Ge–O and Ge–Br bond lengths with increasing number of MeCN molecules are followed by the formation of weak hydrogen bonds C–H···Br, C–H···N and C–H···O between the solvent and molecule **10** and between MeCN molecules. Augmentation of the associate

10·6 MeCN with one more water molecule and HBr molecule capable of forming intermolecular bonds between hydrogen atom and bromine atoms of the tribromogermyl fragment causes no marked elongation of the Ge–Br(1) bond. However, the addition of H_3O^+ cation capable of forming a strong hydrogen bond with the axial bromine atom causes dissociation of molecule **10** to HBr and germylium cation. The Ge...Br(1) distance thus increases to 4.573 Å while the Ge–O bond is shortened to 1.845 Å.

Structure 10



10

The Espinosa–Molins–Lecomte correlation was used to calculate the energies of all weak interactions between solvent molecules and complex **10**. The total energy of these interactions (E_{solv}) regularly increases with the number of solvent molecules. In the limiting case, it can be treated as the solvation energy at 0 K. For two solvate clusters, **10**·2 MeCN (E_{solv} = 3.3 kcal mol^{-1}) and **10**·4 MeCN (E_{solv} = 9.3 kcal mol^{-1}), the contribution of C–H···Br intermolecular interactions to E_{solv} is 2.2 and 3.8 kcal mol^{-1}, respectively. In the solvate clusters of more complex structure the contribution of C–H···Br interactions is even smaller, while E_{solv} is much higher

Cluster	E_{solv}/kcal mol^{-1}
10·6 MeCN	15.6
10·6 MeCN·H_2O	18.4
10·6 MeCN·HBr	19.7

The influence of intermolecular interactions on the Ge---O(1) coordination bond can be illustrated by the dependence between the relative strengthening of this bond (change in the length Δ_{Ge-O} compare to the length in free molecule **10**) and E_{solv} values. This dependence (Fig. 3) can be described by a linear equation (correlation coefficient is 0.96)

$$\Delta_{Ge-O} = 0.05 + 0.0744\,E_{solv}$$

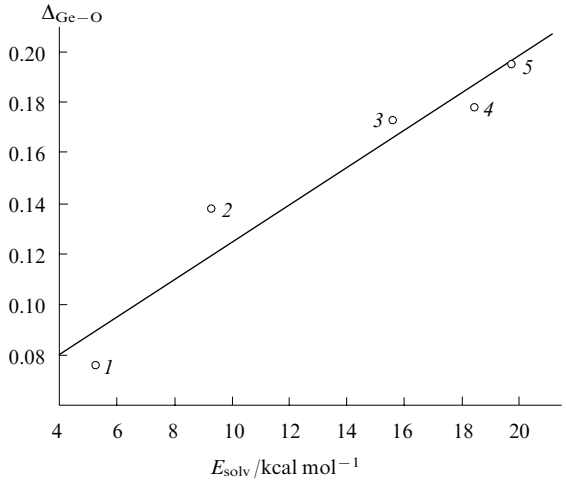


Figure 3. Plot of Δ_{Ge-O} *vs.* energy of solvation of clusters **10**·2 MeCN (*1*), **10**·4 MeCN (*2*), **10**·6 MeCN (*3*), **10**·6 MeCN·H_2O (*4*), **10**·6 MeCN·HBr (*5*).[57]

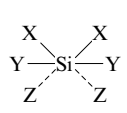
V. NMR and IR spectroscopic parameters of solutions and solids: estimates based on results of quantum chemical calculations

Interest in quantum chemical calculations of spectroscopic parameters of molecules containing the M---Z coordination bond is due to the lack of structural data for solutions. Quantum chemical calculations make it possible to determine the vibrational frequencies and chemical shifts of atomic nuclei (δ), which can be compared with experimentally determined values. There is a huge body of experimental data for compounds of Group 14 elements (see, *e.g.*, reviews [3, 11, 58–60]). Nevertheless, the number of publications devoted to comparison of the calculated and experimental spectroscopic data are few. Quantum chemical calculations of various complexes of substituted silanes **11**–**17** (Refs 61–64) and atranes (Refs 46, 54 and 65–67) predict a shift of the ν(M---Z) frequency of isolated molecules with respect to corresponding vibrational frequencies in crystals and solutions.

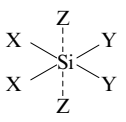
Differences between the calculated and experimental vibrational frequencies can be of different origin. First, experimental studies of silanes were carried out in inert matrices that could contain complexes of different composition as well as unreacted reactants. Next, computational methods are far from being perfect. Also, the geometry of complexes can be influenced by the medium. By and large, at least reasonable agreement between the results of calculations and experimental data was pointed out.[61–64]

For associates of molecules **3d** [54] calculated using the cluster model, the frequencies of the normal modes with the maximum contribution of bending vibrations of the Si---N bond changed by 35 cm^{-1} on going from free molecule to the crystal. Dillen [54] reported that the accuracy in determination of the frequency shift is limited by complexity in selection of normal modes corresponding to the Si---N stretching vibrations and by the impossibility of calculations using complex basis sets (owing to large size of associates). Although the coordination bond involving the Ge atom is usually stronger than the bond involving the Si atom, selection of normal modes remains a complicated

Structures 11, 12



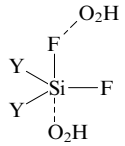
11a–h



12a–h

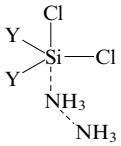
Compounds **11**, **12**	Z	X	Y	Compounds **11**, **12**	Z	X	Y
a	NH_3	F	H	**e**	NH_3	F	F
b	NH_3	Cl	H	**f**	NH_3	Cl	Cl
c	H_2O	F	H	**g**	H_2O	F	F
d	H_2O	Cl	H	**h**	H_2O	Cl	Cl

Structures 13–17



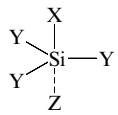
13a,b

Y = H (**a**), F (**b**)



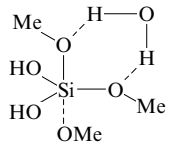
14a,b

Y = H (**a**), Cl (**b**)

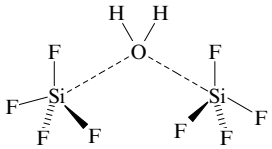


15a–g

Compound **15**	X	Y	Z
a	OMe	OMe	NH_3
b	OH	OMe	NH_3
c	OMe	OMe	OH
d	OH	OMe	OH
e	F	F	H_2O
f	F	F	MeOH
g	F	F	MeOMe



16



17

task. According to quantum chemical calculations of a number of germatranes,[66, 67] an increase in the vibrational frequency with the greatest contribution of deformation of the Ge---N coordination bond in the solid compared to a free molecule can be estimated at 20–30 cm^{-1}.

NMR studies of the strength of M---Z bonds seem to be more informative. For many nuclei (*e.g.*, ^{73}Ge), obtaining experimental data is difficult, but one can establish correlations between the chemical shift and the Z...M interatomic distance. Of course, the situation is complicated if polytopic rearrangements,[68] as well as association, dissociation and solvolysis proceed in solution. Nevertheless, correlations between the ^{15}N chemical shift and the Si---N bond length for such rigid molecules as silatrane were reported.[58, 59, 69] Similar correlations can also be found for germatranes. By and large, the spectroscopic parameters differ insignificantly, but the ^{15}N chemical shifts in 1-halogermatrane molecules are shifted downfield by 14 ppm compared to the corresponding chemical shifts in the isostructural silatranes.[65] The experimental ^{29}Si chemical shifts also correlate with the Si—O bond length in various monochelates.[70–73] These correlations are of particular interest for quantum chemists.

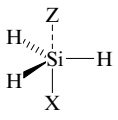
High-precision calculations of the magnetic shielding tensor require a split-valence basis set. The ^{29}Si NMR spectra can be calculated using the IGLO-II extended basis set.[74] In the case of the ^{73}Ge and ^{119}Sn NMR spectra of the simplest germanes and stannanes, the magnetic properties were calculated using basis sets of different complexity.[75–80] Despite the variety of basis sets and functionals used for calculating the magnetic shielding tensor and the exchange-correlation functionals, the calculated chemical shifts and magnetic shielding constants often differ appreciably from corresponding experimental values. Taking into account this fact, it seems reasonable to use the calculated values to illustrate changes in the molecular and electronic structure relative to those of the known molecular and electronic structure of a same-class compound rather than to compare the experimental and calculated chemical shift values.

Up to date, no detailed calculations of chemical shifts in the coordination compounds of tin and germanium are available. Corresponding studies on the coordination compounds of silicon are also few. The most detailed study[81] involved an attempt to predict the properties of silylium cations and solvate complexes using results of quantum chemical calculations. The authors carried out HF/6-311G(d,p)/IGLO-II calculations of the chemical shifts of silylium cations and solvate complexes **18–21** containing a SiR_3 (R = H, Me) group for the gas phase and a dielectric continuum. Based on the analysis of the results obtained, it was concluded[81] that the systems under study form a coordination bond with the solvent molecules and the ^{29}Si chemical shift is determined by the atomic charge of silicon, which depends on the nature of substituents. According to published data,[81] a large upfield shift of the ^{29}Si signal is an indicator of the formation of a coordination bond. Yet another important conclusion drawn in Ref. 81 is that the spectroscopic parameters of isolated and solvated complexes or cations differ appreciably (^{29}Si chemical shifts can differ by 100 ppm!). In polar solvents, silylium cations should exist only as tightly bound complexes. Further studies[82] using experimental data showed that R_3Si^+ cations (R = Alk) can form coordination bonds only with the solvents characterized by high electron-donating ability (*e.g.*, with hexamethylphosphoramide or pyridine). But even in this case one deals with an equilibrium between the complex, on the one hand, and the unbound solvent and free silylium ions, on the other hand.

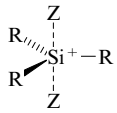
If two coordination modes, $Si(OCN)_6^{2-}$ and $Si(NCO)_6^{2-}$, are possible for the same anionic fragment in the crystal, the structure of the coordination site of Si atom in solution is hard to determine. B3LYP/SVP/IGLO calculations[83] of the chemical shifts[83] in solution revealed only the $Si(NCO)_6^{2-}$ anion, the calculated ^{29}Si chemical shift being different from the experimental value by 9 ppm [*cf.* 53 ppm for $Si(OCN)_6^{2-}$].

Interpretation of ^{29}Si NMR spectra of solids requires a correct reproduction of components of the magnetic shield-

Structures 18–21



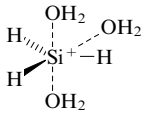
18a–f



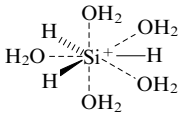
19a–e

Compound **18**	X	Z
a	CN	NH_3
b	OH	NH_3
c	Cl	NH_3
d	Cl	H_2O
e	Cl	HCl
f	ClO_4	NH_3

Compound **19**	R	Z
a	H	HCN
b	H	NH_3
c	H	H_2O
d	Me	NH_3
e	Me	H_2O



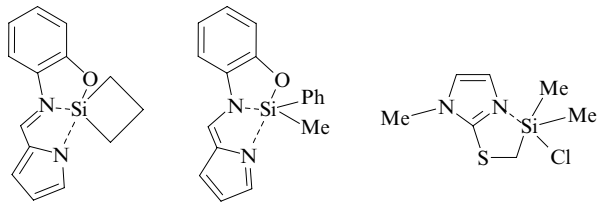
20



21

ing tensor. For instance, the presence of two independent molecules in the structure of pyrrole-2-*N*-(*o*-hydroxyphenyl)carbaldimine derivatives **22** and **23** leads to a multiple-line ^{29}Si NMR spectrum of single crystals.[84] PBE/IGLO-III calculations of components of the magnetic shielding tensor from the experimental coordinates of each independent molecule gave unsatisfactory results. Optimization of the molecular geometry led to better agreement between theory and experiment, although quantum chemical calculations predict that the molecular geometry in the gas phase is somewhat different from that in the crystal. This suggested that the directions of the tensor components are almost independent of the type of crystal packing, being mainly determined by the nature of the coordination site of Si atom. A similar conclusion was also drawn in another study[85] carried out using a molecular cluster (fragment of crystal packing) rather than molecule **24** as the starting system.

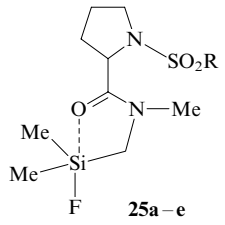
Structures 22–24



22 **23** **24**

Quantum chemical calculations using the IGLO-III high-precision basis set were performed to estimate the ^{29}Si chemical shifts in the series of complexes **25a–e** containing a proline dimethylamide residue and the $SiMe_2F$ group. Almost quantitative agreement between the results of calculations and experiment was achieved for both solution and the solid phase. Earlier,[73] an exponential correlation was found between the experimental δ ^{29}Si values and the Si---O bond lengths in solids. Quantum chemical calculations of this series of molecules using their geometric parameters in the crystal as well as geometry optimization within the framework of the PCM model with the ε values corresponding to chloroform, pyridine and acetone showed that in a wide range of δ ^{29}Si values and Si---O bond lengths these parameters are linearly related (Fig. 4),[86] the experimental and calculated values being different by at most 1 ppm for δ ^{29}Si and 1–3 ppm for pyridine and acetone. Statistically valuable deviation from the linear dependence obtained for chloroform suggested a hydrogen bond between the complexes and the solvent.

Structures 25



25a–e

R = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-BrC_6H_4 (**d**), 4-$O_2NC_6H_4$ (**e**)

Quantum chemical calculations made it possible to determine the configuration of the coordination site of Si

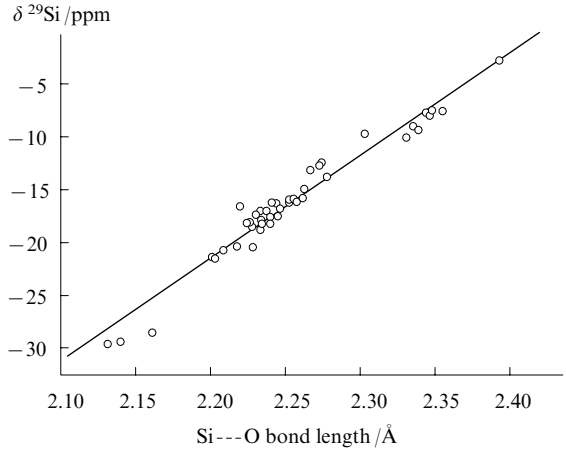
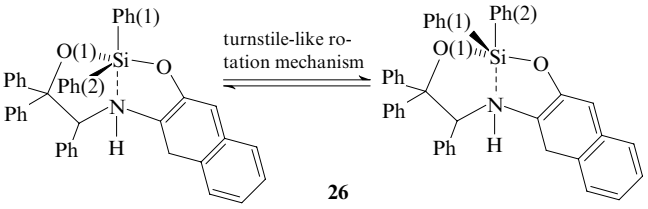


Figure 4. Plot of δ ^{29}Si *vs.* Si---O bond length according to results of quantum chemical calculations of molecules **25**.[86]
Upper right open circles correspond to crystals and bottom left open circles correspond to isolated molecules.

atom in complex **26** which can crystallize as a mixture of two epimers with different arrangement of substituents (Scheme 1).‡ In solution, the epimers undergo interconversion by the turnstile-like rotation mechanism. B3LYP/6-31++G(d) density functional calculations well reproduce the δ ^{29}Si difference between the two epimers (16.1 ppm for the solid state *vs.* 14.1 ppm for the gas phase); this is sufficient for reliable signal assignment.

Scheme 1



26

Associates of molecules containing the M---Z coordination bond with various solvent molecules seem to be the best model for the description of the solvation shell. However, only a few examples of such calculations are available. The cluster model may not work to reproduce the experimental δ ^{29}Si values. For instance, calculations[87] of associates of *N*-methyl-*N*-[1-(3′,7′,10′-trimethylsilatranyl)-methyl]acetamide (**27**) with four chloroform molecules predict that the upfield ^{29}Si chemical shift is only 2–5 ppm compared to isolated molecule (−64.3 and −63.4 ppm for two stereoisomers shown in Fig. 5). It should be noted that the Si---N bond in the associates is 0.08 Å shorter than in the isolated molecule. At the same time, the experimental δ ^{29}Si values for compound **27** representing a mixture of two stereoisomers in solution are −76.7 and −79.2 ppm. Thus, four chloroform molecules in the associate are insufficient to reproduce the experimental δ ^{29}Si value.

‡ S Schlecht, M Finze, R Bertermann, W Frank, A Domann, M Braun *Eur. J. Inorg. Chem.* 1488 (2013)

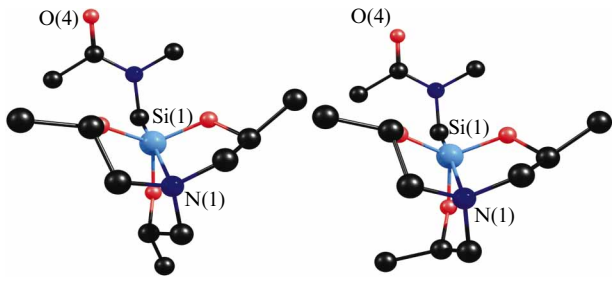
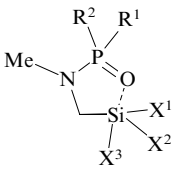


Figure 5. Stereoisomers of molecule **27**: a general view.[87]

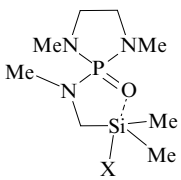
Calculations of a large number of monochelate complexes (phosphoric acid derivatives) with inclusion of solvation effects were carried out using the continuum (PCM) and cluster models.[88] Experimental δ^{29}Si values were obtained for seven compounds only, namely, **28a–e** and **29a,b**. Experimental chemical shift values showed that compounds **28b,c** and **26a,b** exist in solution in the acyclic (non-chelate) form. Taking account of solvation effects within the framework of the PCM model (with chloroform as solvent) led to a very good agreement between theoretical and experimental values of δ^{29}Si (within 1 ppm) only for compounds **28a,d,e**. Solvation causes the Si---O coordination bond in the molecules of all seven compounds to systematically shorten (by 0.1–0.2 Å) compared to free molecules. For compounds **28b,d** and **29b** the difference between the experimental data and results of quantum chemical calculations was at least 5 ppm The experimental value of δ ^{29}Si was reproduced by quantum chemical calculations of molecular complexes **28**, **29** with one chloroform molecule taking into account solvation effects. This led to agreement between the calculated and experimental chemical shift values within 1 ppm for all seven compounds. In the complex, the chloroform molecule is bonded to the chelate oxygen atom, therefore, the Si---O coordination bond in many compounds was somewhat longer than in the isolated molecules. Therefore, the inclusion of specific solvation, which is impossible when using the continuum model, appeared to be of importance for calculations of compounds **28** and **29**.

Thus, joint use of the cluster and continuum models appears to be more appropriate for the description of solvation effects than each model separately.

Structures 28, 29



28a–e



29a, b

X = F (**a**), Cl (**b**)

Compound **28**	X^1	X^2	X^3	R^1	R^2
a	F	F	F	NMe_2	NMe_2
b	Me	Me	F	NMe_2	NMe_2
c	Me	Me	F	OMe	OMe
d	Me	Me	Cl	NMe_2	NMe_2
e	F	F	F	OMe	OMe

Next steps in studies of the structure of coordination compounds of silicon, germanium and tin in solutions involve simulation of the pathways of S_N2-reactions or stereodynamic processes in solution, as well as estimation of spectroscopic parameters and energy barriers followed by comparison with experimental data. The results of such studies are available (see, *e.g.*, Refs 89–92), but it should be noted that the solvent effect was included only within the framework of the continuum model (see Refs 91 and 92), because the number of atomic configurations to be quantum chemically calculated was rather large. However, the key point is to include specific solvation which requires huge improvement of computing power.

VI. The 'Atoms in Molecules' theory and the nature of the M---Z bond

The nature of the M---Z bond in coordination compounds of silicon, germanium and tin has been studied and debated over a period of a few decades. There is a number of theoretical models proposed to describe the electron density redistribution upon formation of the M---Z bond. The most widespread is the model of a three-centre four-electron (3c–4e) bond [93, 94] involving an electron pair of the Z atom and two electrons of the central atom M and the substituent X in *trans*-position. Depending on the electronegativity of the M, Z and X atoms, two types of electron density transfer to the M---Z–X fragment are possible, namely, from the lone electron pair of the Z atom to the region of the M and X atoms and in the opposite direction. Some authors (see Refs 46 and 95) describe chemical bonding in the Z---M–X fragment as analogue to the $n \rightarrow \sigma^*$ interactions, *viz.*, donation of an electron pair by the Z atom to the antibonding orbital of the M–X bond (dative bond).

The possibility of existence of an 'inverted' dative bond formed through donation of an electron pair of the X atom to the antibonding orbital of the M---N bond in 1-halogermatranes was reported.[96] The model for the 3c–4e bond and the model for the dative bond were primarily formulated for compounds with CN = 5 and for the trigonal-bipyramidal environment of the central atom. Unfortunately, these models are inappropriate to directly include the influence of other substituents at the M atom. Zabalov and co-workers [97] treated chemical bonding in the coordination site of the M atom in atranes as the interaction of valence electrons of the M atom with the system of ligand orbitals. Similar ideas were suggested in another study.[98]

All models mentioned above are to a great extent speculative and equally correctly predict changes in the geometry of the coordination site of the M atom upon a change in the electron-withdrawing ability of substituent X or in the electron-donating ability of nitrogen atom. Bader's quantum topological theory 'Atoms in Molecules' [4] was widely used to test various models for chemical bonding in the Z---M–X fragment.[4] By analyzing the electron density distribution within the framework of this theory one cannot only establish the existence of a chemical bond or the occurrence of weak interatomic interactions, but also obtain quantitative data ('topological parameters') which describe the nature, properties and energy of these interactions. The potential of the theory is well known; examples of recent publications are provided by, *e.g.*, a monograph [99] and a review.[100]

However, large data arrays generated when applying the 'Atoms in Molecules' theory often do not help researchers to come to a consensus on the nature of the M---Z bond; rather, they give rise to contradictions. The reason is the inconsistency between Bader's classification of chemical bonds and the commonly accepted concepts of ionic and covalent bonds and nonvalence interactions. Therefore, we have to precede an analysis of the results obtained by different research groups with a brief survey of the most important characteristics of the electron density distribution that are basic to understanding of the nature of the M---Z bond.

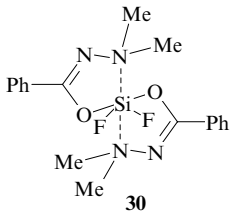
According to Bader, the sign of the Laplacian of the electron density, $\nabla^2\rho(\mathbf{r})$, at the (3, −1) critical point (main indicator of the occurrence of a bonding interaction) plays a key role in the description of the nature of a chemical bond. Almost all quantum chemical calculations [49, 51, 53, 54, 81, 97, 101–107] and experimental studies [48, 108–115] demonstrate that the M---Z coordination bonds are characterized by positive values of $\nabla^2\rho(\mathbf{r})$. This substantiates the assumption of mainly ionic nature of the M---Z bond.

It was proposed to estimate the 'deformation' of the electron pair of the Z atom upon the formation of the M---Z bond by analyzing the cross sections of $\nabla^2\rho(\mathbf{r})$ along the bond lines.[116] The Laplacian of the electron density at the (3, −1) critical point is defined as the algebraic sum of the three eigenvalues of the matrix of the second derivatives of the electron density function:

$$\nabla^2\rho(\mathbf{r}) = \lambda_1 + \lambda_2 + \lambda_3$$

For ionic bonds, the curvature along the bond line (described by the λ_3 eigenvalue of the Hessian matrix) is positive, being larger than the other eigenvalues in magnitude. It is believed [116] that weak coordination bond are characterized by 'compression' of the electron density on the M---Z bond along the direction towards the M atom. An analysis of the curvature of the cross section of $\nabla^2\rho(\mathbf{r})$ in the N---Si---N fragment of difluorobis[*N*-(dimethylamino)phenylacetimidato-*N*,*O*]silane **30** revealed [108] additional polarization through the influence of the crystal packing (Fig. 6). However, it should be noted that a direct comparison of the λ_3 values obtained from topological analysis of the experimental electron density distribution and from quantum chemical calculations should be performed with care. The character of the electron density distribution near the atom of the Group 14 element can be affected by experimental errors, especially in the case of germanium and tin complexes.

Structure 30



30

N···Si = 1.9703 Å (experiment), 1.9998 Å [calculations B3LYP/6-311G(d, p)]

Bader and Essen [117] showed that ionic and covalent bonds are characterized by different eigenvalues of the Hessian matrix, which describe the curvature of the electron density function along the bond line and in the plane lying normal to this line. The $|\lambda_1|/\lambda_3$ eigenvalue ratio was used for additional description of the type of the chemical bond. For ionic bonds, this ratio lies between 0.16 and 0.25. Covalent nonpolar bonds are characterized by $|\lambda_1|/\lambda_3 > 0.76$. The range from 0.25 to 0.76 corresponds to polar bonds. According to calculations,[96] for various atranes and their analogues one has $|\lambda_1|/\lambda_3 < 0.41$, which indicates at least a high polarity of the M---Z bond. Assuming that the $|\lambda_1|/\lambda_3$ ratio is a measure of bond polarity, the N---Ge bond in germatranes is of higher polarity than the Si---N bond in silatranes. In this case, shortening of the M---N bond leads to a decrease in its polarity.

The local virial theorem [4] relates the Laplacian to the kinetic and potential energy density [$G^e(\mathbf{r})$ and $V^e(\mathbf{r})$, respectively]. Cremer and Kraka [118] showed that the kinetic-to-potential energy ratio [local energy density $E^e(\mathbf{r})$] at the (3, −1) critical point can be used as a criterion for the existence of a covalent bond

$$\frac{\hbar}{4m}\nabla^2\rho(\mathbf{r}) = 2G^e(\mathbf{r}) + V^e(\mathbf{r}) \quad (2)$$

$$G^e(\mathbf{r}) - \frac{\hbar}{4m}\nabla^2\rho = -E^e(\mathbf{r}) \quad (3)$$

(m is the mass of an electron).

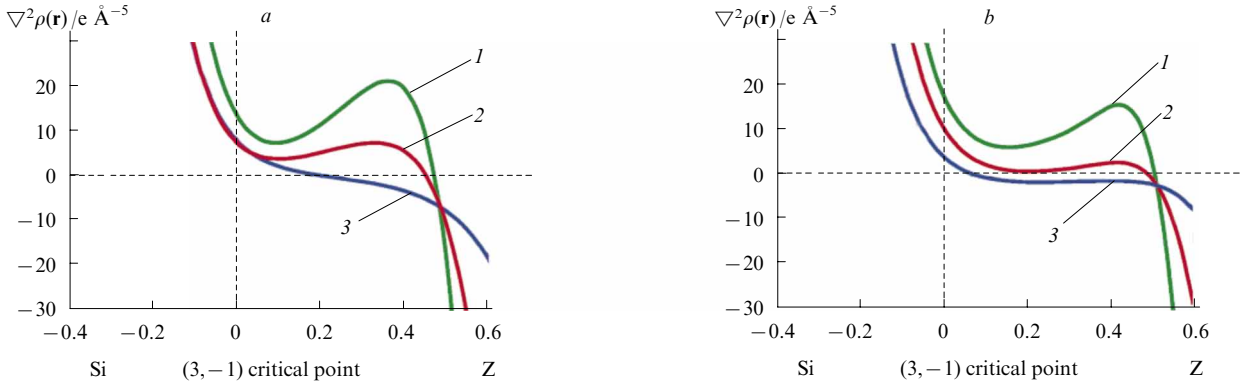
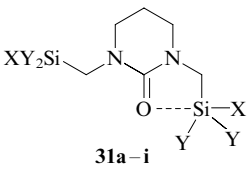


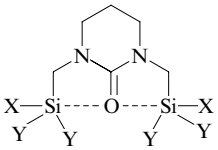
Figure 6. The $\nabla^2\rho(\mathbf{r})$ distribution along the Si–Z [Z = F (*1*), O (*2*), N (*3*)] bond paths in the crystal and in isolated molecule **30**.[108] Experiment (*a*) and results of B3LYP/6-311G(d,p) quantum chemical calculations (*b*).

The $E^e(\mathbf{r})$ values reported for the M---Z bonds are negative and close to zero (in the atomic unit system). Following Cremer and Kraka,[118] the bond can be treated as covalent, but this contradicts the opinion of the ionic nature of the M---Z bond. Based on the results of analysis of the $\nabla^2\rho(\mathbf{r})$ cross sections and on the $|\lambda_1|/\lambda_3$ ratio for molecule **28b**, Kocher *et al.*[108] reported a full domination of the ionic component in the case of the N---Si bond. Only a small covalent contribution was reported for the Si—F and Si—O bonds. Zabalov *et al.*[97] led to similar conclusions, but their terminology is still unclear. For instance, the N---Si and N---Ge bond were called 'closed-shell type interactions with large ionic component'; this seems to be an awkward combination of conventional chemical concepts and the 'Atoms in Molecules' theory. The $E^e(\mathbf{r})$ value was in fact ignored because it was nearly zero (in the atomic unit system).

In some studies the sign of $E^e(\mathbf{r})$ was used as main criterion for the determination of the nature of the M---Z bond. The length of the Si---O bond in chelate *N*,*N*′-bis(silylmethyl)propylene ureas **31** and **32** varies from 2.014 to 2.344 Å; also, one has $E^e(\mathbf{r}) < 0$; this made it possible to conclude that the Si---O bond in these compounds is covalent in nature in spite of its high polarity.[103] The longest Si---O bonds characterized by $E^e(\mathbf{r}) < 0.04$ a.u. were treated as ionic. A similar conclusion was also drawn for the monochelate derivatives **4**–**8** containing a pentacoordinate silicon atom.[51] All bonds formed by silicon atom and characterized by negative $E^e(\mathbf{r})$ values were treated as covalent ones.[81]



31a–i



32a–i

Structures 31, 32

Compounds **31**, **32**	X	Y
a	Cl	Me
b	Cl	H
c	Cl	F
d	Cl	Cl
e	Cl	Br
f	OH	H
g	F	H
h	Br	H
i	Me	H

Summing up, although the authors who analyzed the nature of the M---Z bond within the framework of the 'Atoms in Molecules' theory used the same topological parameters, they described the Si---O bond from different points of view. A possible reason is the intention of researchers to present the results obtained in a language that is understandable to a wide range of chemists. At the same time, the authors of all studies cited above reported an increase in the topological parameters $\rho(\mathbf{r})$ and $V^e(\mathbf{r})$ with decreasing M---Z bond lengths; this allows one to use the 'Atoms in Molecules' theory to describe changes in the electronic structure on going from isolated molecules to condensed phase.

VII. Electron density redistribution between the M and Z atoms on going from isolated molecules to crystals and solutions

Often, studies of the electron density distribution in the Z---M—X fragment involve a qualitative analysis of the valence-electron localization functions. This first of all concerns the deformation electron density (DED) and the Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$. A qualitative analysis of these functions is to some extent complicated by errors introduced during experimental data processing or in the course of multipole refinement. The results of calculations also include errors due to inappropriate choice of the method or basis set. It should also be noted that the results of calculations carried out using localized basis sets (either of Gaussian or Slater type) are hardly comparable with the results of calculations performed with basis sets of augmented plane waves.

Nevertheless, in many cases a qualitative comparison of the results of calculations and experimental data gives a clear illustration of differences in chemical bonding in the crystal and in isolated molecule.

An example is provided by molecule **8a**. In the crystal, the Si---O coordination bond is 1.879(1) Å long, being 0.24 Å longer than in the isolated molecule. The Si—Cl bond lengths in the crystal and in isolated molecule differ by about the same value [2.432(1) and 2.223 Å, respectively]. In spite of considerable changes in the geometry of the O---Si—X fragment on going from isolated molecule to the crystal, the character of the DED distribution (Fig. 7) in the region of the Si---O bond remains almost unchanged. At the same time, the distribution of the $-\nabla^2\rho(\mathbf{r})$ function changes on going from the crystal to isolated molecule. The region where the experimental function $-\nabla^2\rho(\mathbf{r})$ has a maximum near the oxygen atom is extended along the Si---O bond path towards the Si atom (Fig. 8). More pronounced are differences between the crystal and isolated molecule in the region of the Si—Cl bond. An analysis of the DED and $\nabla^2\rho(\mathbf{r})$ distributions suggests that in the crystal, electron pairs of chlorine atom are oriented in different manner compared to isolated molecule. Probably, weak intermolecular interactions induce a shift of maxima of the DED and $-\nabla^2\rho(\mathbf{r})$ functions from the Si—Cl bond path.

The distribution of the Laplacian of the electron density in molecule **3d** (Fig. 9)[54] on going from isolated molecule to crystal (this was simulated using a molecular cluster comprised of sixteen molecules) changes analogously to its distribution in molecule **8a**. The region of negative values of the $\nabla^2\rho(\mathbf{r})$ function in the vicinity of the nitrogen atom in the crystal is extended along the Si---N bond path towards the silicon atom. Some changes in the region of the Si—Cl bond are also visible.

The observed differences between the distributions of the $\nabla^2\rho(\mathbf{r})$ functions on going from isolated molecule to the crystal (or solution) in the region of the M---Z coordination bond indicate changes in electron density transfer between molecular fragments. In this connection, evaluation of the electron density transferred between the M and Z atoms is of importance. It seems logical to use corresponding atomic charges as a measure of the degree of electron density transfer.

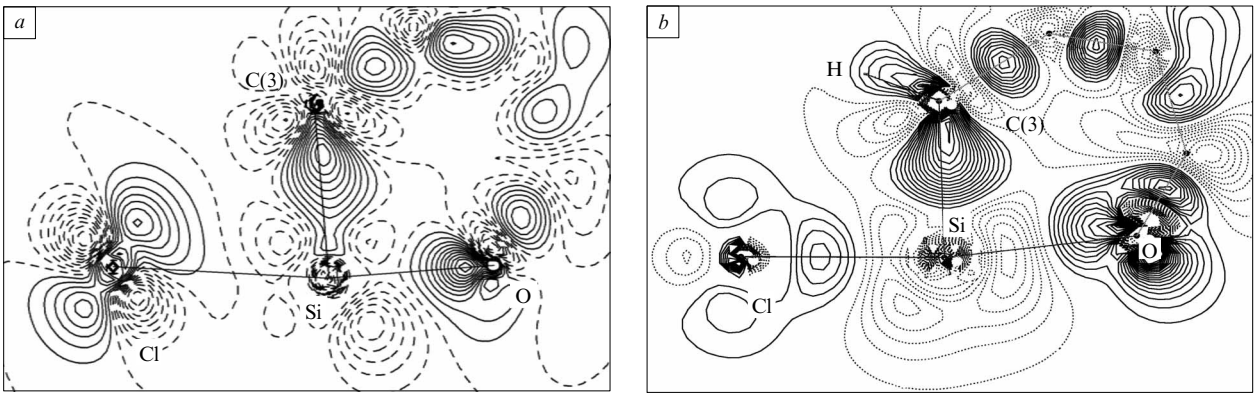


Figure 7. Distribution of the experimental (*a*) and calculated (*b*) DED in the C(3)SiCl plane in molecule **8a**.[110]
Crystal (*a*) and isolated molecule (*b*). Isolines in the maps are drawn at 0.05 e Å^{-3} intervals for the experimental DED and at 0.034 e Å^{-3} intervals for the calculated DED; negative DED values are shown by dashed lines.

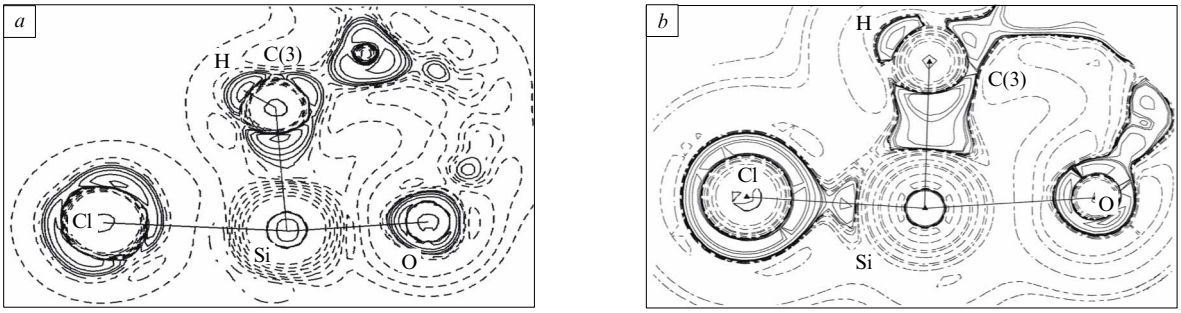


Figure 8. Distribution of the experimental (*a*) and calculated (*b*) functions $-\nabla^2\rho(\mathbf{r})$ in the C(3)SiCl plane for molecule **8a**.[110]
Crystal (*a*) and isolated molecule (*b*). Negative $-\nabla^2\rho(\mathbf{r})$ values are shown by dashed lines.

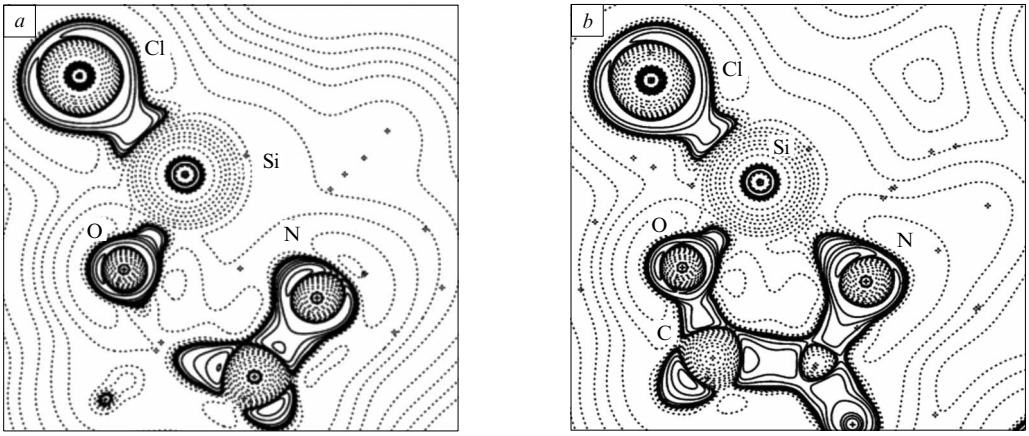


Figure 9. Distribution of the calculated function $\nabla^2\rho(\mathbf{r})$ in the NSiO plane of molecule **3d** in the gas phase (*a*) and in the crystal (*b*).[54]
Positive $\nabla^2\rho(\mathbf{r})$ values are shown by dotted lines and negative $\nabla^2\rho(\mathbf{r})$ values are shown by thick solid lines.

Atomic charges in isolated molecule **3d** and its associates[54] were determined within the framework of the natural bond orbitals (NBO) formalism.[119] It was found that negative charges of the nitrogen and chlorine atoms and equatorial oxygen atoms increase with decreasing Si...N interatomic distance. The positive charge of the Si atom increases considerably from 1.565 to 1.771 e as the Si---N bond length decreases from 2.571 to 2.07 Å. In the coordination environment of the silicon atom, the atomic charge of chlorine changes to the greatest extent, from −0.372 to −0.546 e as the Si–Cl bond elongates from 2.058 to 2.129 Å. It should be noted that the negative charge of the

nitrogen atom increases by 0.07 e only, *i.e.*, the degree of electron density transfer between the silicon and nitrogen atoms increases insignificantly.

Similar conclusions were reported in a study of associates of molecule **10**.[57] The atomic charges were determined by integrating the electron density over atomic basins in accordance with the 'Atoms in Molecules' theory. The negative charge of the oxygen atom involved in the Ge---O coordination bond increased only slightly (by 0.01 e) on going from isolated molecule **10** to the associate **10**·6 MeCN·HBr with the shortest coordination bond Ge---O (2.018 Å). The negative charge of the axial bromine atom increased to a greater extent from −0.45 to −0.51 e. Shortening of the Ge---O coordination bond led to an increase in the positive atomic charge of Ge from 1.82 to 1.86 e.

Although different schemes for calculations of atomic charges give different results, all of them show that electron density transfer upon shortening of the M---Z coordination bond occurs from the M atom to substituents bonded to it. This contradicts the model for the 3c–4e bond and therefore the applicability of this model to coordination compounds of silicon, germanium and tin casts some doubt.[108] However, the results obtained by some other methods of analysis of the electronic structure, based on orbital analysis (NBO[110] and Boys localized orbitals[46]) or the electronic kinetic energy density (ELF function, see Ref. 88) do not contradict the model for the 3c–4e bond. It is still unclear which model for the description of chemical bonding in the Z---M–X fragment is best physically substantiated. Going from an isolated molecule to a crystal (or solution) is accompanied by not only shortening of the M...Z interatomic distance, but also by an increase in the degree of charge separation between these atoms (the charge of the central atom becomes more positive while the atomic charges of the environment become more negative). Undoubtedly, changes in the electronic structure of molecules are also accompanied by changes in the energy of the M---Z bond. Constructing correlations between the electron density redistribution between the M and Z atoms and the change in the energy of corresponding bond is difficult due to the lack of experimental data and results of calculations.

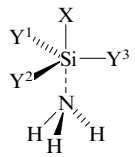
VIII. M---Z bond energies: estimates based on results of quantum chemical calculations

The energy of the M---Z bond (E_b) can be estimated by a number of experimental methods, *viz.*, using thermochemical data (heats of combustion), by IR spectroscopy (force constants) and by mass spectrometry. Nevertheless, a representative data set for the energies of the bonds in question is available for silatranes only. Experimentally determined energies of the Si---N bond in solid 1-substituted silatranes lie between 12.2 and 22.1 kcal mol^{-1}.[120] The E_b values calculated for isolated molecules of these compounds from thermochemical data taking into account the ring strain energy are much lower (7.4–11.7 kcal mol^{-1}).[121]

For most compounds, experimental determination of the energies of the M---Z bond in crystal or in the gas phase is impossible; therefore, quantum chemical calculations come to the fore. The energies of coordination bonds can be found from the results of quantum chemical calculations in different manner. First of all, it should be noted that all methods described in this Section were applied to isolated molecules only. Knowledge of the M---Z bond energy values is of importance for analysis of structural changes occurring on going from isolated molecules to the crystal and solution.

If a molecule represents an acyclic complex composed of some fragments and if each fragment can exist as an individual species, one can determine the dissociation energy at 0 K, which is treated as E_b. This requires carrying out quantum chemical calculations of the entire molecule and its fragments with inclusion of the zero-point vibrational energy correction and the basis set superposition error (BSSE). An example is provided by calculations of the dissociation energies of complexes **33a**–**n**.[101] By and large, a decrease in the N...Si interatomic distance was followed by an increase in the energy of the N...Si bond. For all complexes, the dissociation energies were at most 10 kcal mol^{-1}. However, the dissociation energy of the complex with the shortest N...Si interatomic distance (1.988 Å) appeared to be negative. This was explained[101] by drawbacks of the 6-31G(d) basis set used in the calculations. For all complexes studied, the changes in the Gibbs free energy are positive; this suggests a complete irreversible dissociation of the complexes in the gas phase due to domination of the entropy contribution $T\Delta S$ over the enthalpy of formation.

Structures 33



33a–n

Compound **33**	X	Y^1	Y^2	Y^3	Compound **33**	X	Y^1	Y^2	Y^3
a	H	H	H	H	**h**	OH	OH	OH	Me
b	OH	H	H	H	**i**	OH	OH	OH	OH
c	H	OH	OH	H	**j**	Cl	H	H	NH_2
d	OH	H	H	OH	**k**	NH_2	H	H	Cl
e	H	H	H	OH	**l**	NH_3	OH	OH	OH
f	OH	H	H	OH	**m**	NH_3	OH	OH	Me
g	H	OH	OH	OH	**n**	NH_2	H	H	H

The dependence of the results obtained on the level of theory can be illustrated taking complex **15e** as an example. Augmentation of the 6-311G basis set with polarization and diffuse functions has little effect on the calculated value of the dissociation energy of **15e**.[63] Also, the dissociation energy values obtained from Hartree–Fock calculations and using the B3LYP hybrid functional did not decrease as compared to the value obtained using the Møller–Plesset perturbation theory, namely, they varied in a narrow range from 4.3 kcal mol^{-1} [B3LYP/6-311++G(d,p)] to 7.7 kcal mol^{-1} [MP4(SDQ)/6-311G(df,p)]. Once BSSE correction was applied, the dissociation energy values decreased considerably, *viz.*, RHF/6-311G(d,p) and MP2/6-311G(d,p), calculations led to negative values; other methods gave positive values that were at most 2.9 kcal mol^{-1} [B3LYP/6-311G(d,p) calculations]. Complex **17** with

a bridging water molecule appeared to be more stable than complex **15e**. B3LYP and MP2 calculations of **17** using a basis set augmented with diffuse functions led to a higher dissociation energy value of 4.6 kcal mol^{-1} for both methods.

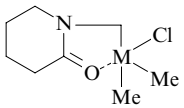
Detailed quantum chemical studies of the complexes of silanes **11**–**16** with H_2O and NH_3 molecules were also reported.[61] Potential energy minima were located for the structures with trigonal-bipyramidal environment of the silicon atom and NH_3 or H_2O molecule in *trans*-position relative to the X atom. The dissociation energies of these complexes lie between 4 and 8 kcal mol^{-1}. No BSSE correction was applied.[61]

Complexes of tin tetrahalides SnX_4 (X = Cl, Br) with two ligands are characterized by a wider interval of E_b values (0.6–37.6 kcal mol^{-1}).[122] The energy of the Sn---Z bond (Z = O, N, S) depends on the nature of the ligand donatinig an electron pair. The strongest Sn---Z bonds were found in the complexes with $Me_3P{=}O$ and pyridine, while the weakest ones were found in the complex with MeCN. Further analysis performed within the EPA (Ref. 123) and NBO (Ref. 119) formalisms showed that the contribution of electrostatic component to the bond energy is more than 50%. Estimation of the degree of electron density transfer from the ligand to the SnX_4 fragment led to unexpected results, *viz.*, no correlations with the bond energy were established at all. The maximum degree of transfer (0.68 e) was found for the complex with SMe_2; the bond energy is merely 11.7 kcal mol^{-1}. For the strongest bonds, the degree of electron density transfer is halved.

Calculations of acyclic complexes can be performed using improved computational methods with inclusion of zero-point energy and BSSE corrections; this makes it possible to obtain highly accurate results. Nevertheless, BSSE correction is not always applied in calculations of dissociation energies. Studies by Leopold[19, 24, 25, 124–126] prove that taking account of BSSE correction significantly influences the geometry of loosely bound complexes. An analysis of publications devoted to acyclic complexes suggests that their stability depends not only on the nature of the Z atom, but also mainly on the nature of other substituents at the M atom. For instance, acyclic complexes with the Z---Si bond and no Si–Hal bonds correspond to a transition state.[62, 63, 127]

Evaluation of the M---Z bond strength in cyclic compounds is difficult. The simplest way is to calculate the cyclic and acyclic forms of a molecule under study and thus obtain information on ring strain. This procedure was used in the pioneering determination of the energy of the M---Z bond in silatranes.[128] The ring strain energies can be estimated from the heats of combustion which, however, are not always available. Most probably, the energy of the M---Z bond calculated with no ring strain correction will be underestimated. For instance, the energy difference between the cyclic and acyclic forms of trifluorosilane **9** (Ref. 56) is merely 4.2 kcal mol^{-1} (calculated with BSSE correction applied). Also, the energy differences between the cyclic and acyclic forms of complexes of silicon derivatives of *N*-acetamide and *N*-piperidone derivatives **6b**–**e** and **34** (Refs 102 and 129) are treated as E_b. It should be noted that replacement of silicon atom by germanium atom causes E_b to increase from 7.2 to 9.7 kcal mol^{-1}, while replacement of germanium atom by tin atom leads to a further increase in the energy difference between two forms to 15.2 kcal mol^{-1}.

Structures 34



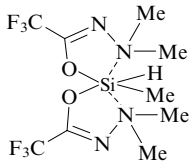
34a–**c**

M = Sn (**a**), Ge (**b**), Si (**c**)

The energy difference between chelate and acyclic non-chelate forms of compounds **28**, **29** and related complexes is 0.9–6.9 kcal mol^{-1}.[88] Interestingly, the authors of Ref. 88 tried to evaluate how the solvation effect included within the framework of the PCM model influences E_b. At $\varepsilon = 4.7$ (chloroform), the calculated E_b value appeared to be higher than for isolated molecules. In turn, the energy difference between the chelate and non-chelate forms of some molecules calculated for dimethyl sulfoxide (polar solvent with $\varepsilon = 46.7$) was smaller than for isolated molecules. In these cases, the Si---O bond was rather weak and longer than 2.4 Å. The whole series of compounds studied in Ref. 88 showed a clear correlation between the length and energy of the Si---O bond.

Among *N*,*N*′-bis(silylmethyl)propylene ureas **31** and **32**, the energy difference between acyclic and monochelate forms is 1.9–9.0 kcal mol^{-1} depending on the nature of substituents at the silicon atom.[103] The energy difference between monochelate and bischelate forms is 0.3–5.1 kcal mol^{-1}. The energy gain upon the formation of the second Si---O bond is smaller than upon the formation of the first bond. The energy difference between two forms of complex **35** with hexacoordinate silicon atom and two hydrazone ligands is 1.03 kcal mol^{-1}, being much lower than the experimental value of the Si---N bond dissociation energy (14.6 kcal mol^{-1}) determined in a NMR study of a related compound.[130] This points to a complex character of dissociation in solution.

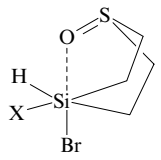
Structure 35



35

Even more complex picture was obtained for 4-bromo-4-silathiacyclohexane 1-oxide derivatives **36a**,**b**.[131] The boat conformer **36b** is stabilized by transannular interaction O···Si (2.146 Å) and its energy almost equals that of the most energetically favourable chair conformer with no additional coordination. The energy of the most unfavourable twist conformer (no O---Si interactions) is 6.1 kcal mol^{-1} higher. This difference cannot be explained by O---Si transannular interaction only. Calculations predict the existence of an isomerization pathway with a barrier of 4.3 kcal mol^{-1}, which is lower than the energy difference. Besides, taking into account the geometry of the conformer with O---Si transannular interaction, one can suggest a rather high ring strain.

Structures 36

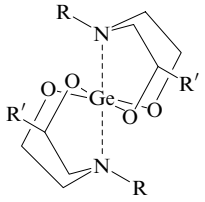


36a, b

a: X = H (O–Si = 2.120 Å); **b**: X = Br (O–Si = 2.146 Å)

Germaspirobis(ocanes) **37a–d** contain two coordination bonds Ge···N.[104] Isomerization of these compounds in solution can proceed by two mechanisms. One of them assumes cleavage of one Ge···N bond while the other involves no Ge···N bond dissociation. In the former case, the energy increases by 21.5–23.1 kcal mol^{-1}. Probably, this mechanism leads to a higher ring strain, all the more so because isomerization by the other mechanism is characterized by a lower energy barrier (13.4– 21.3 kcal mol^{-1}).

Structures 37



37a–d

R = Me: R′ = H (**a**), Ph (**b**); R = Ph: R′ = H (**c**), Ph (**d**)

A possible solution of difficulties related to inclusion of the ring strain is using the curve characterizing the changes in the potential energy of the M···Z bond upon variation of corresponding interatomic distance. In the case of weak coordination interactions, this curve (shallow parabola) was used to illustrate weakness of the Si···N bond in silatranes (Fig. 10).[132, 133]

More recently, an approximation of the potential curve by anharmonic Morse function was proposed [134]

$$V = E_b\{1-\exp[-\beta(R-R_e)]\}^2 \quad (4)$$

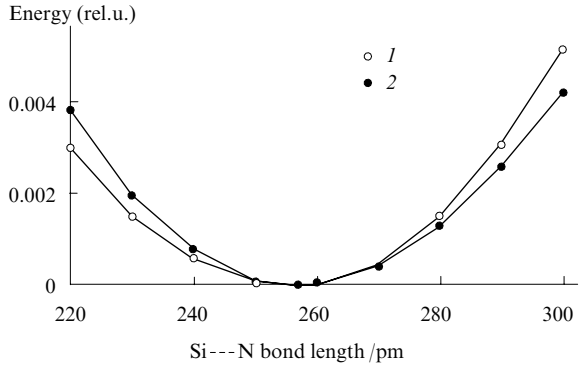


Figure 10. Potential energy of Si···N bond in 1-chlorosilatrane plotted *vs.* Si···N bond length.[132]
Basis set: 3-21G(d) (*1*) and 6-31G(d) (*2*). Energies in the ordinate axis are given relative to the energy minimum.

where β is the coefficient characterizing the width of the potential well and R_e is the equilibrium distance N...Si.

Using approximation (4), one can determine the dissociation energy E_b equal to the depth of the potential well. The energy of the Si–N bond in 1-methylsilatrane thus obtained is 18.7 kcal mol^{-1}, being in reasonable agreement with experimental data (12.2–22.1 kcal mol^{-1}).[120] This approach was also used to estimate the bond energies of a number of cage silaphosphanes with a Si···P dative bond [53] and phosphoric acid derivatives.[88]

Yet another method for estimating E_b in atranes is to carry out quantum chemical calculations of atrane ring opening and formation of acyclic products.[53, 134] The heat of this reaction differs from E_b by the ring strain energy.

Almost all energies of the M···Z coordination bonds presented in this Section are at most 30 kcal mol^{-1}, which indicates a common nature of the bonds. However, it should be noted that the methods described above are inconvenient for analysis of the influence of the medium (gas phase, crystal or solution) on E_b. This problem can be solved by using spectroscopic data taking into account feasible constraints or by using the results of topological analysis of the electron density.

IX. Espinosa–Molins–Lecomte correlation and the energy of the M···Z bond

In the case of molecules of complex structure, a very promising method is to use the Espinosa–Molins–Lecomte correlation between the potential energy density at the (3,–1) critical points and the energy of the chemical bond.[37, 135, 136]

The $V^e(\mathbf{r})$ value can be determined (i) analytically in the course of topological analysis of the distribution of the theoretical electron density or (ii) using the Kirzhnits formula [137] if the experimental electron density is available. The advantages of expression (1) include simplicity and versatility; it can be applied to compounds of any composition irrespective of the presence of the M···Z bond in the ring.

However, potential difficulties in using the Espinosa–Molins–Lecomte correlation should be pointed out. First, the correlation was obtained for hydrogen bonds and its applicability range is unknown. One can state with certainty that expression (1) is inapplicable to the covalent nonpolar or polar bonds formed by the exchange mechanism. Even for very strong hydrogen bonds O–H···O relation (1) predicts overestimated energy values.[138, 139] On the contrary, in the case of weak intermolecular interactions the use of expression (1) is justified. For instance, the sublimation energy values predicted for some simple organic and organoelement compounds using this relationship are in good agreement with experimental data. Also, expression (1) made it possible to predict the stability of the polymorphs of paracetamol [140] and $CaCO_3$ [141] and was successfully used to estimate the energy of the Au–P bond in $ClAuPPh_3$.[142]

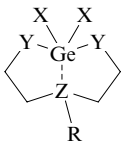
The energy of the M···Z coordination bond is intermediate between the energies of weak intermolecular interactions and covalent bonds; therefore, it is of great importance to determine the applicability range of expression (1). This can be done by comparing the values obtained using this expression with the results obtained using other computational methods and with experimental data. First

of all, it should be noted that the Espinosa–Molins–Lecomte correlation is suitable for reasonably correct reproduction of the energy of Si—O covalent bond. For instance, the energy of this bond in compounds **3a**,**b** varies in the range from 90 to 102 kcal mol^{-1}, which is close to the energy of the Si—O bond in cyclic siloxanes (100–120 kcal mol^{-1}). The energies of the Si---N coordination bonds in crystalline silatranes **3a**,**b** are 25.4 and 29.2 kcal mol^{-1}, respectively. This exceeds the upper bound of the interval obtained using thermochemical data (12.2–22.1 kcal mol^{-1}).[120] Using the $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ values from Ref. 97 and the Kirzhnits relation to approximate $V^e(\mathbf{r})$, the E_b values thus estimated for isolated molecules are 13.7 and 13.4 kcal mol^{-1}, being close to the experimental values (7.4–11.7 kcal mol^{-1}).[121] The value predicted by the Espinosa–Molins–Lecomte expression for isolated 1-methylsilatrane molecule (8.6 kcal mol^{-1}, calculated using the data from Ref. 48) is smaller than that obtained by approximating the potential curve of the Si---N bond by the Kirzhnits formula (16.4 kcal mol^{-1}). The energy of the Si---N bond in the crystal of 1-methylsilatrane calculated using the $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ values is 20.0 kcal mol^{-1}. The energy of the Sn---O bond in crystalline compound **34a** is 22 (experiment) and 26 kcal mol^{-1} according to calculations (*cf.* 16 kcal mol^{-1} for isolated molecule[115]). The estimate of the energy of the Sn---O bond in isolated molecule **34a** obtained using the Kirzhnits formula is in good agreement with the value found using expression (1). For compounds **34b**, **c** with much weaker Ge---O and Si---O bonds, the agreement is somewhat poorer. Analogously, the energy of the Si---P coordination bond in $P(CH_2CH_2O)_3SiF$,[53] found using the Espinosa–Molins–Lecomte correlation is about 13 kcal mol^{-1} lower than the estimate obtained by approximating the potential curve by the Kirzhnits formula. This can be due to the fact that the potential of weak bonds is not always correctly described by the Morse formula.

Other examples of application of expression (1) include evaluation of the energy of the M---Z bond in trimethylsilyl esters of phosphoric acids,[88] germocanes **38**,[106] chelates (**10** and **39**) with pentacoordinate germanium atom[143] and in complexes (**40** and **41**) of hexacoordinate silicon[113] and tin.[114] In principle, the parameters $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ determined either experimentally or from calculations can be used to determine the energy of all coordination bonds M---Z. For some compounds, the energies of coordination bonds in crystals and in isolated molecules were compared and it was shown that the bond energy varies with the bond length.[88, 113–115, 143]

Thus, the assumption that shortening of the M---Z bond on going from isolated molecule to the crystal or solution causes its energy to increase is unambiguously confirmed by the results of topological analysis of the electron density. Undoubtedly, certain specific features and drawbacks of the method used to determine the $\rho(\mathbf{r})$ function influence the final E_b values. Nevertheless, the energies of M---Z coordination bonds in different classes of silicon, germanium and tin compounds fall in the same range from a few to twenty or thirty kcal per mole as those obtained by other methods. Therefore, the Espinosa–Molins–Lecomte correlation can be used to estimate the energies of almost all types of coordination bonds in systems of different complexity for which the electron density distribution can be obtained.

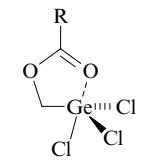
Structures 38



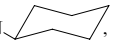
38a–j

Compound **38**	Z	R	Y	X
a	N	Ph	O	Cl
b	N	Me	O	Br
c	N	Me	O	C_4H_3S
d	N	H	O	OH
e	N	Me	O	OCH_2CH_2O
f	N	Me	O	$O(CH_2)_2NMe(OCH_2)_2O$
g	N	Ph	O	Cl
h	O	Me	S	Cl
i	S	Me	S	Cl
j	O	Me	S	$S(CH_2)_2S(OCH_2)_2S$

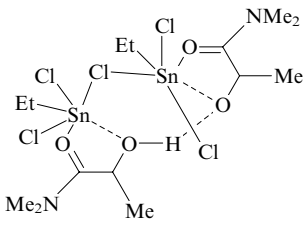
Structures 39–41



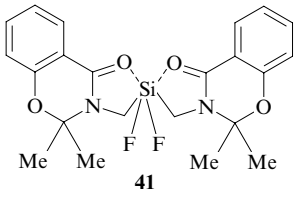
39a–c

a: R = HN ,

b: R = , **c**: R = NH_2



40



41

X. Conclusion

The spectroscopic parameters as well as characteristics of chemical bond in the coordination compounds of tetravalent silicon, germanium and tin considered in this review enable detailed and systematic description of the distinctions between the solid, solution and gas phase using modern quantum chemical methods and results of high-precision X-ray diffraction studies. Information on the molecular and electronic structures of the title class of compounds is systematized in order to help researchers in solving particular problems that require the inclusion of effects induced by intermolecular interactions, *e.g.*, the influence of crystal packing forces or the nature of a solvent. Methods and approaches described above can be useful in studies of almost all classes of compounds whose structures in the crystal or in solution differ from the gas-phase structure.

An analysis of original publications revealed not only an increase in the number of studies that involve quantum chemical calculations of coordination compounds of tetravalent silicon, germanium and tin, but also qualitative changes in the character of problems to be solved using quantum chemistry methods. Earlier studies usually illustrate research activity in the field of basic research and are devoted to various parameters of the M---Z bond. In the late decade, there has been a variety of publications concerned with solution of applied problems, in particular, interpretation of spectroscopic data. One can assume that determination of NMR and IR spectroscopic parameters of solutions and solids using quantum chemical methods will find application in the design of, *e.g.*, novel large-scale syntheses of organoelement compounds or in research on their biological activity.

To date, basic research on the nature of the M---Z bond remains topical. Progress in our views of chemical bonding offers novel prospects in the field. First of all, mention should be made of the theory of 'charge-shift bonds',[144] which represents a further development of the resonance theory and valence-bond theory. This approach enables quantitative characterization of chemical bonds using topological analysis of such functions, as ELF,[145] ELI-D,[146, 147] *etc*. At present, studies of coordination compounds of silicon, germanium and tin using this method are scarce,[88] but they seem to contribute to solution to the problem of specific features of the nature of the M---Z bond.

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