Experimental and quantum-chemical study of complexation of carbene analogs with dinitrogen. Direct IR-spectroscopic observation of $Cl_2Si \cdot N_2$ complexes in low-temperature argon-nitrogen matrices*

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Interaction of dichlorosilylene with dinitrogen in mixed Ar—N_2 matrices at 9 - 10 K was studied by IR spectroscopy. A donor-acceptor complex $Cl_2Si \cdot N_2$ was found and characterized by six bands of symmetric (at 511.2, 508.9, and 506.5 cm^{-1}) and antisymmetric (at 500.1, 496.9, and 495.1 cm^{-1}) stretching vibrations of Si—Cl bonds in the most abundant isotopomers. Two bands at 498.7 and 493.5 cm^{-1} observed in mixed matrices were tentatively assigned to $Cl_2Si \cdot (N_2)_2$ complex. Several stretching vibration bands of minor isotopomers of $SiCl_2$ were detected for the first time in argon matrices. Assignment has been done for the isotopic structure of $SiCl_2$ associates with dinitrogen observed in N_2 matrices. Dimerization of $SiCl_2$ and its complexation with one and two N_2 molecules were studied by quantum-chemical DFT calculations (PBE and B3LYP functionals). The structures, energies, and vibrational frequencies of the $Cl_2Si \cdot N_2$ and $Cl_2Si \cdot (N_2)_2$ complexes and the Si_2Cl_4 dimer were determined. The energies of $SiCl_2$ complexation with one and two N_2 molecules obtained from PBE and B3LYP calculations are 0.3 and 0.6 kcal mol^{-1}, respectively. More accurate G2(MP2,SVP) calculations using the B3LYP geometries have predicted a higher stability of the $Cl_2Si \cdot N_2$ complex (1.2 kcal mol^{-1}). The calculated and experimental vibrational frequencies of reagents and complexes are in good agreement. A correlation has been established between the PBE calculated energies of complexation of $EHal_2$ (E = Si, Ge, Sn, Pb) with N_2 and the experimentally observed shifts of E—Hal stretching vibrations in $EHal_2$ upon complexation. The strength of the complexes with N_2 increases on going from dihalosilylenes to dihaloplumbylenes.

Key words: dinitrogen, dichlorosilylene, dichlorogermylene, dichlorostannylene, hexachlorodisilane, complexes of carbene analogs with nitrogen, tetrachlorodisilene, matrix IR spectroscopy, quantum-chemical calculations, density functional theory, G2(MP2,SVP) computational scheme.

Complexation plays an important role in chemistry of dicoordinated silicon derivatives (silylenes).[1] Several examples of direct UV-spectroscopic observation in solutions and low-temperature hydrocarbon matrices of labile silylene complexes with relatively strong Lewis bases like ROH, R_2O, R_2S, $R_2C{=}X$ (X = O, S), R_3N, RC≡N, R_3P have been reported.[1] The complexes with alcohols subsequently rearranged into insertion products R'_2SiHOR,[2] while the complexes with carbonyl and thiocarbonyl compounds experienced a reversible isomerization into silaoxiranes and silathiiranes, respectively.[3] Recently,[4] the first examples of stable complexes of sterically hindered silylenes with isocyanides bearing bulky substituents were reported. The interaction of sterically less strained silylenes and isocyanides, which produces silaketenimines,[5,6] also implies an intermediate formation of similar complexes in the first stage of the reaction.

The data on the formation of silylene complexes with essentially weaker Lewis bases are scarce. For instance, the formation of labile complex between dimethylsilylene and $CHBr_3$ was shown by flash photolysis technique and confirmed by quantum-chemical calculations.[7] This was the first example of experimentally observed complex of silylene with organohalide. Kinetic data and results of quantum-chemical calculations[8] indicate unequivocally an intermediate formation of weak pre-reaction complexes in the course of insertion of the most reactive silylenes (SiH_2, SiHMe, $SiMe_2$) into Si—H bonds. Being added to unsaturated organic compounds, silylenes behave like electrophilic species,[8] and, according to quantum-chemical calculations,[9] the first stage of SiF_2 interaction with ethylene also involves formation of a weak pre-reaction complex. Complexes of various silylenes with CO were

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* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 504—516, March, 2003.

1066-5285/03/5203-526 $25.00 © 2003 Plenum Publishing Corporation

detected[10,11] by UV spectroscopy. A complex of dimethylsilylene with CO was detected by the method of IR spectroscopy in low-temperature inert matrices.[11]

Dinitrogen is often used as a matrix material in studies of the spectral properties and reactivity of silylenes in low-temperature matrices. Due to the presence of lone electron pairs in the N_2 molecule it can be considered as a Lewis base, though undoubtedly it is one of the weakest bases. However, it was shown earlier by matrix IR spectroscopy that heavier silylene analogs, namely, SnF_2,[12] $SnCl_2$, and PbF_2 [13] do form complexes with N_2. The possibility of complexation of silylenes with dinitrogen was not studied yet.

In this work we present the results of experimental and theoretical studies of the interaction between one of the simplest silylenes — dichlorosilylene, $SiCl_2$, with dinitrogen. Besides, quantum-chemical calculations were carried out for dinitrogen complexes with heavier carbene analogs, $GeCl_2$ and $SnCl_2$. All calculations were performed for the singlet state, which is the ground state of all carbene analogs.

Experimental

Dichlorosilylene was generated according to the known procedure[14] by passing Si_2Cl_6 vapors through a pyrolyzer — a quartz tube (internal diameter 2 mm, heating zone length 100 mm) coupled to a vacuum shroud of cryostat. The temperature was measured with a chromel-alumel thermocouple positioned between a heater (a quartz tube with nichrome wire wound around it) and the pyrolyzer. In most of the experiments pyrolysis was carried out at 850 °C, though in the preliminary experiments performed to determine the optimum temperature of pyrolysis, the temperature of the pyrolyzer was varied in the range 770—1100 °C. The pressure of Si_2Cl_6 vapors near the pyrolysis zone (~10^{-2} Torr) was measured by a PMT-2 manometer converter. The consumption of Si_2Cl_6 was estimated from the weight loss of a sample after several experiments, taking into account the time factor. The average flow rate of Si_2Cl_6 was 0.04 mmol h^{-1}.

The products of Si_2Cl_6 pyrolysis and Ar—N_2 mixtures containing from 0 to 100 mol.% N_2 and brought *via* an independent pipeline were codeposited on the mirror surface of a copper plate cooled to 10—15 K and located inside the cryostat 80 mm from the pyrolysis zone and at a distance of 50 mm from an outlet of the matrix gas introduction pipeline. The pressure in the cryostat was measured by a PMI-2 manometer converter. It was ~2×10^{-5} Torr during the deposition of the matrices and ~2×10^{-6} Torr after the deposition. Ar—N_2 mixtures of prescribed compositions were prepared several hours prior to the deposition and stored in a glass vessel. A mercury free gauge was used to measure the pressure of the components. The mixture consumption (8—12 mmol h^{-1}) was controlled by a manometer. The duration of deposition varied from 30 to 100 min. The $SiCl_2$: (Ar + N_2) molar ratio varied from 1 : 200 to 1 : 300, based on the assumption of total conversion of Si_2Cl_6 into $SiCl_2$ + $SiCl_4$. After the matrix deposition the temperature of the copper plate was lowered to 9—10 K. The plate was cooled by a Displex-CSW-208R microcryogenic closed-cycle refrigerator (APD Cryogenics, Inc.). The temperature of the plate was measured by a DT-470-SD12 silicon diode soldered to the plate and was preset by a Lake Shore Model 330-11 temperature controller (Lake Shore Cryotronics, Inc.).

IR spectra of the matrices prepared were recorded using the reflection scheme on a Bruker IFS 113v IR Fourier spectrometer in the range of 4000—400 cm^{-1} with a resolution of 0.25 or 0.5 cm^{-1}. The reproducibility of the frequency measurements was ±0.1 cm^{-1}.

Quantum-chemical calculations of the structures and vibrational frequencies were carried out using the B3LYP [15] and PBE [16] density functionals. The energies of reagents and $Cl_2Si \cdot N_2$ complex were also calculated using the G2(MP2,SVP) modification[17] of precise Gaussian-2 computational scheme.[18] Both G2(MP2,SVP) and B3LYP calculations were performed with the GAUSSIAN-94 program package[19]. All B3LYP calculations were done using the 6-311+G(d) basis set. They included geometry optimization and frequency calculations. Energy computations according to the G2(MP2,SVP) procedure[18] consisted of several steps, including geometry optimization at the B3LYP/6-311+G(d) level and energy calculations using the QCISD and MP2 methods with various basis sets. The final value of energy obtained by the G2(MP2,SVP) method was an approximation to that of the single point QCISD(T)/6-311+G(3df,2pd) calculation. Zero-point vibrational energy correction, ZPE, calculated with the B3LYP/6-311+G(d) method was used without scaling of frequencies.

PBE calculations were carried out using the PRIRODA program.[20] These computations, which included full geometry optimization and vibrational frequency calculations, were performed using the triple-zeta type basis sets: (5s2p) [3s2p] for H, (11s6p2d) [6s3p2d] for C, (15s11p2d) [10s6p2d] for Si and Cl, (18s14p9d) [13s10p5d] for Ge, and (21s17p12d) [15s12p8d] for Sn. Here, the primitive gaussian basis sets are given in parentheses, while the contracted basis sets are given in brackets. The program employs the electron density expansion[21] over an auxiliary uncontracted basis set: (5s2p) for H, (10s3p3d1f) for C, (14s3p3d1f1g) for Si and Cl, (18s3p3d1f1g) for Ge, (23s3p3d1f1g) for Sn. The nature of the stationary points located was determined by calculating the eigenvalues of the matrix of the second derivatives of energy. Thermodynamic functions were calculated using the harmonic oscillator—rigid rotor model.

Calculations using the PRIRODA program were done on personal computers with Pentium©-III 800 and Celeron© 433 CPUs. Calculations using the GAUSSIAN-94 program were performed on a SGI POWER CHALLENGE L supercomputer at the Computer Center, Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

Results and Discussion

Hexachlorodisilane, Si_2Cl_6, was used in this work as a precursor of labile dichlorosilylene. Earlier,[14,22] pyrolysis of Si_2Cl_6 was successfully used for generation of $SiCl_2$ which was then stabilized in low-temperature inert matrices. In the temperature range 600—1100 °C pyrolysis of Si_2Cl_6 proceeds exclusively as follows[14,23]

$$Si_2Cl_6 \rightarrow SiCl_2 + SiCl_4. \qquad (1)$$

According to the experimental data,[23] the enthalpy change of reaction (1) is 48 kcal mol^{-1}. However, MP2/6-31+G(2df,p) calculations predicted a somewhat smaller value (ΔH_{298} = 35.4 kcal mol^{-1}).[24] An alternative route of thermal decomposition of Si_2Cl_6 into two trichlorosilyl radicals is much more endothermic (77 kcal mol^{-1}).[23] Thus this channel of thermal decomposition of Si_2Cl_6 can became significant only at temperatures above 1200 °C.[23] The activation energy for reaction (1) was determined in kinetic studies. Different authors reported the values of 49.6,[25] 48.0 [26] or 49.2 [27] kcal mol^{-1}. These values are in good agreement with the calculated height of the activation barrier (48.8 kcal mol^{-1}).[24]

The IR spectrum of Si_2Cl_6 isolated in Ar matrix was recorded during preliminary experiments. Vibrational spectra of Si_2Cl_6 were reported in several studies.[28—35] In particular, the IR spectra of this compound were recorded in the liquid[31—35] and gas[30,33] phases. It was shown[33] that the set of vibrational frequencies observed in the IR and Raman spectra agrees best with D_{3d} symmetry of this molecule. The presence of two chlorine isotopes with comparable natural abundances (75.53% for ^{35}Cl and 24.47% for ^{37}Cl in unenriched samples) should result in noticeable splitting of most of the bands on the chlorine isotopes. However, the isotope splitting was earlier observed[33] only for the ν_2(Si—Cl) stretching vibration band in the Raman spectrum of a solid sample of Si_2Cl_6. No vibrational spectra of Si_2Cl_6 in low-temperature matrices were reported to date.

The IR spectrum of Si_2Cl_6 isolated in argon matrix exhibited three isotopically split bands with maxima at 631.6 (very weak, poorly resolved, ν_1(Si—Si)[33] or $\nu_6+\nu_8+\nu_{11}$),[32] 609.5 (very strong, ν_{10}(Si—Cl)[32,33]), and 462.4 cm^{-1} (strong, ν_5(Si—Cl)[32,33]) and a very weak single band at 528.9 cm^{-1} ($\nu_2+\nu_{11}$).[32,33] The band near 462 cm^{-1} corresponding to a nondegenerate vibration of a_{2u} type consists of seven well-resolved components separated by 1.4 cm^{-1}. The relative intensities of the components correspond to the natural abundances of chlorine isotopes. The intense band near 609 cm^{-1} corresponds to a doubly degenerate e_u type vibration which strongly complicates its isotopic structure. Detailed analysis of the isotopic structure of this band was not undertaken in this work. The isotopic structure of the band near 631 cm^{-1} is very similar to that of the band near 462 cm^{-1}, which implies that the latter belongs to a nondegenerate vibration or to transition to a composite level which consists of nondegenerate vibrations only. It precludes the possibility of its assignment to a combination transition $\nu_6+\nu_8+\nu_{11}$,[32] but agrees with the assignment to ν_1(Si—Si).[33,35] Noticeable isotopic splitting (interval between individual components is ~0.8 cm^{-1}) indicates a significant participation of Si—Cl bond in this vibration. The absence of isotopic splitting of the band in the region 529 cm^{-1} could be explained by very low intensity due to which only the most intense component of the isotopic structure was registered.

Besides the bands of Si_2Cl_6, the spectra recorded exhibit a number of very weak bands of H_2O [36,37] and CO_2,[38] which get into the matrix in small quantities due to desorption from inner walls of the cryostat and micro leaks in the system; HCl [39] — the product of insignificant hydrolysis of the sample, as well as $SiCl_4$ [40,41] and $SiHCl_3$ [42] — from micro impurities in the initial sample. The above-mentioned impurity compounds, as well as complexes of dinitrogen with H_2O,[43] HCl,[44] and CO_2 [38] formed in mixed argon-dinitrogen matrices, exhibit no bands near the $SiCl_2$ absorption. No interaction of these compounds with dichlorosilylene was observed in further experiments, due to their insignificant concentration, and their presence did not interfere with the study of $SiCl_2$ interaction with dinitrogen.

IR spectra of $SiCl_2$ in argon matrix. Dichlorosilylene was generated by pyrolysis of Si_2Cl_6 at 850 °C (the lowest temperature at which a complete decomposition of Si_2Cl_6 takes place). Two IR bands in the region of stretch vibrations of Si—Cl bonds characterize dichlorosilylene isolated in argon matrix. Both bands show well-resolved isotopic structure (Fig. 1, *b*). The isotopic components of the bands of antisymmetric stretching vibration are additionally split into doublets. The high frequency components of the doublets are almost three times less intense than the low frequency ones. The ratio of the intensities of these components remains unchanged after short-term warming up of the matrices. These facts indicate the presence of two positions of $SiCl_2$ in the matrices studied, which are close in energy but differ in concentrations, *i.e.* the observed splitting could be interpreted as a matrix effect. The matrix splitting of $SiCl_2$ bands in Ar matrix was previously observed[45] when $SiCl_2$ was generated by the action of $SiCl_4$ on metallic silicon at 1000 °C in a flow pyrolyzer.

The vibrational frequencies of $SiCl_2$ measured in this work are presented in Table 1. Due to the use of a more sensitive spectrometer with higher resolution compared to earlier studies,[14,45] a number of isotopic components of $SiCl_2$ bands not observed earlier was revealed in the IR spectra at 504.8, 502.8, and 500.2 cm^{-1} (ν_{sym}), and at 490.5 and 485.7 cm^{-1} (ν_{as}). The frequencies of these components agree well with the values previously calculated using an empirical force field.[14] Other frequency values of $SiCl_2$ given in Table 1 for the main matrix site coincide with those published earlier[14] within the limits of measurement error and are also in good agreement with the data from Ref. 45 for the main matrix site. An exception is the $\nu_{sym}(^{29}Si^{35}Cl_2)$ frequency which proved to be 0.4 cm^{-1} higher than that reported earlier.[14] In the previously published spectra this component was not fully resolved from the $\nu_{sym}(^{28}Si^{37}Cl_2)$ component; therefore, the value given in Table 1 looks more reliable.

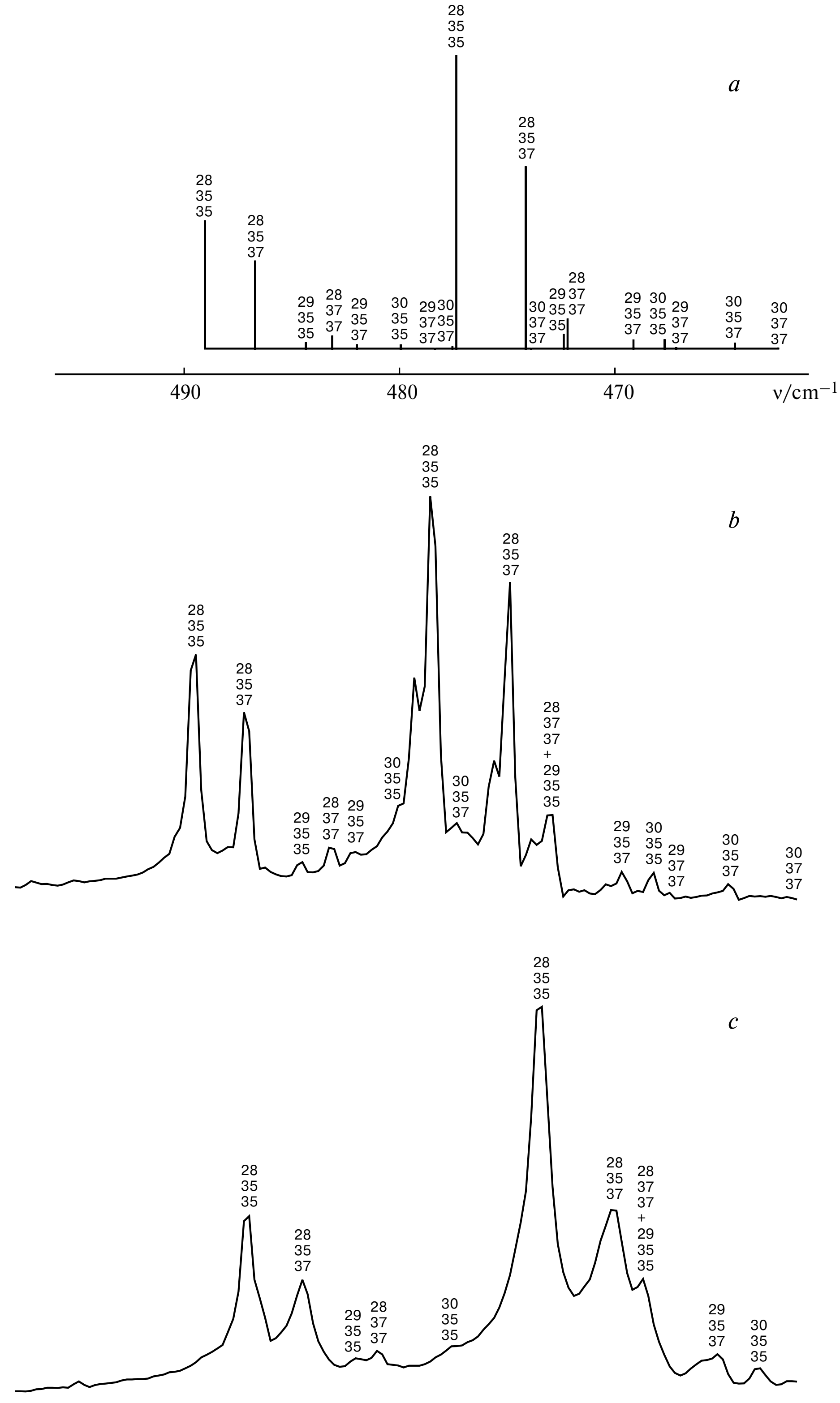


Fig. 1. IR spectra of $SiCl_2$ in the region of stretch vibrations of Si—Cl bonds: Theoretical IR spectrum obtained from B3LYP/6-311+G(d) calculations (*a*). IR spectrum of $SiCl_2$ in Ar matrix (*b*). IR spectrum of $SiCl_2$ in N_2 matrix (*c*). The isotopic composition of each isotopomer (Si, Cl, Cl) corresponding to particular band is shown above the absorption band.

Table 1. Experimental frequencies of various isotopomers of $SiCl_2$ and $Cl_2Si \cdot N_2$ in the region of stretch vibrations of Si—Cl bonds

Isotopomer	$SiCl_2$ in Ar			$Cl_2Si \cdot N_2$		$Cl_2Si \cdot (N_2)_2$ ν_{as}(Si—Cl)	$Cl_2Si \cdot (N_2)_2$ in N_2	
	ν_{sym}(Si—Cl) main*	ν_{as}(Si—Cl)		ν_{sym}(Si—Cl)	ν_{as}(Si—Cl)		ν_{sym}(Si—Cl)	ν_{as}(Si—Cl)
		main*	minor*					
$^{28}Si^{35}Cl_2$	512.2	501.3	502.1	511.2	500.1	498.7	509.6	496.4
$^{28}Si^{35}Cl^{37}Cl$	509.8	497.8	498.5	508.9	496.9	—	507.4	493.0
$^{28}Si^{37}Cl_2$	505.9	495.9	496.8	—	495.1	493.5	503.8	491.7
$^{29}Si^{35}Cl_2$	507.2	495.9	496.8	506.5	495.1	493.5	504.8	491.7
$^{29}Si^{35}Cl^{37}Cl$	504.8	492.7	493.3	—	—	—	—	488.3
$^{29}Si^{37}Cl_2$	—	490.5	—	—	—	—	—	—
$^{30}Si^{35}Cl_2$	502.8	491.3	—	—	—	—	500.4	486.4
$^{30}Si^{35}Cl^{37}Cl$	500.2	487.7	—	—	—	—	—	—
$^{30}Si^{37}Cl_2$	—	485.7	—	—	—	—	—	—

* Main and minor matrix sites.

IR spectra of $SiCl_2$ in mixed argon-dinitrogen and dinitrogen matrices. Complexes $Cl_2Si \cdot N_2$ and $Cl_2Si \cdot (N_2)_2$. The frequencies of $SiCl_2$ vibrations measured in Ar matrices actually do not change on going to mixed argon-dinitrogen matrices until $[N_2]$ = 13 mol.%. New bands at 511.2 and 508.9 cm^{-1} in the region of symmetric and at 501.1 and 496.9 cm^{-1} in the region of antisymmetric stretch vibrations appear in mixed argon-dinitrogen matrices (Fig. 2, *b—e*) starting with $[N_2]$ = 1 mol.%. These bands have the same relative intensities as the corresponding components of the $SiCl_2$ bands. The intensities of these bands compared with those of $SiCl_2$ increase with an increase in the N_2 concentration until 13 mol.%. This indicates the formation in mixed matrices of a new intermediate, a product of the interaction of $SiCl_2$ with N_2 which is characterized by virtually the same force field parameters as free $SiCl_2$. This intermediate is apparently a $Cl_2Si \cdot N_2$ complex. The presence of only one N_2 ligand in the complex follows from its formation at relatively low concentration of N_2. Thus, four new absorption bands mentioned above could be surely assigned to symmetric and antisymmetric stretch vibrations of Si—Cl bonds in the most abundant isotopomers of $Cl_2Si \cdot N_2$ (see Table 1).

Starting from N_2 concentration of 3 mol.%, two new very weak bands appear in the matrix IR spectra at 495.1 and 493.5 cm^{-1}, both at the low-frequency side of the antisymmetric component of the $SiCl_2$ stretch vibration at 495.9 cm^{-1}. The former band was not observed at higher N_2 concentrations because of the overlap with more intense $SiCl_2$ band at 495.9 cm^{-1} due to broadening of the bands upon increase in N_2 concentration. The band at 495.1 cm^{-1} is shifted by 0.8 cm^{-1} from the third (in intensity) isotopic component of the antisymmetric band of initial $SiCl_2$ at 495.9 cm^{-1}. The frequencies of the most intense isotopic components of $Cl_2Si \cdot N_2$ differ from the corresponding frequencies of $SiCl_2$ by approximately the same value. Thus, the band at 495.1 cm^{-1} was assigned to the third isotopic component of antisymmetric vibration of Si—Cl bond in the $Cl_2Si \cdot N_2$ complex (Table 1). Using similar arguments, a weak band at 506.5 cm^{-1}, which appears in the matrix IR spectra starting with N_2 concentrations of 5 mol.%, was assigned to the third isotopic component of the symmetric vibration of the Si—Cl bond in the $Cl_2Si \cdot N_2$ complex (Table 1). Other isotopic components of the bands of the $Cl_2Si \cdot N_2$ complex were not revealed probably due to their smaller intensity and overlapping with the bands of initial $SiCl_2$.

In contrast to the absorption band of $Cl_2Si \cdot N_2$ complex at 495.1 cm^{-1}, the band at 493.5 cm^{-1} is present at $[N_2] > 3$ mol.%. It could not be assigned to the $Cl_2Si \cdot N_2$ complex, since its shift relative to the nearest high frequency isotopic component of $SiCl_2$ (495.9 cm^{-1}) is too large (2.4 cm^{-1}). It is natural to suggest that the band at 493.5 cm^{-1} belongs to $Cl_2Si \cdot (N_2)_2$ complex. Really, the shifts of E—Hal bond antisymmetric stretch vibration frequencies in the complexes of SnF_2 and $SnCl_2$ with two N_2 molecules relative to the frequencies of free $SnHal_2$ are approximately twice as large as the shifts of the same frequencies in the complexes of SnF_2 and $SnCl_2$ with one N_2 molecule[12,13] (Table 2). So, one can expect that the shift of antisymmetric stretch vibration frequencies of the Si—Cl bonds in the complex $Cl_2Si \cdot (N_2)_2$ should be ~2 cm^{-1}, which is in good agreement with the experimentally observed value (2.4 cm^{-1}). More intense isotopic components of the same band in the complex $Cl_2Si \cdot (N_2)_2$, which are expected at 498.9 and 495.4 cm^{-1}, overlap with intense components of $SiCl_2$ at 498.5 and 495.9 cm^{-1}. However, with an increase in N_2 concentration in matrices from 0 to 7 mol.% one observes a steady shift of maximum of the $SiCl_2$ band at 498.5 cm^{-1} toward 498.7 cm^{-1}. At $[N_2] > 7$ mol.%, the intensity of this band in the matrix IR spectra increases significantly, which testifies a contribution of the absorption band of the $Cl_2Si \cdot (N_2)_2$ complex. Thus, the absorption band at 493.5 cm^{-1} could be

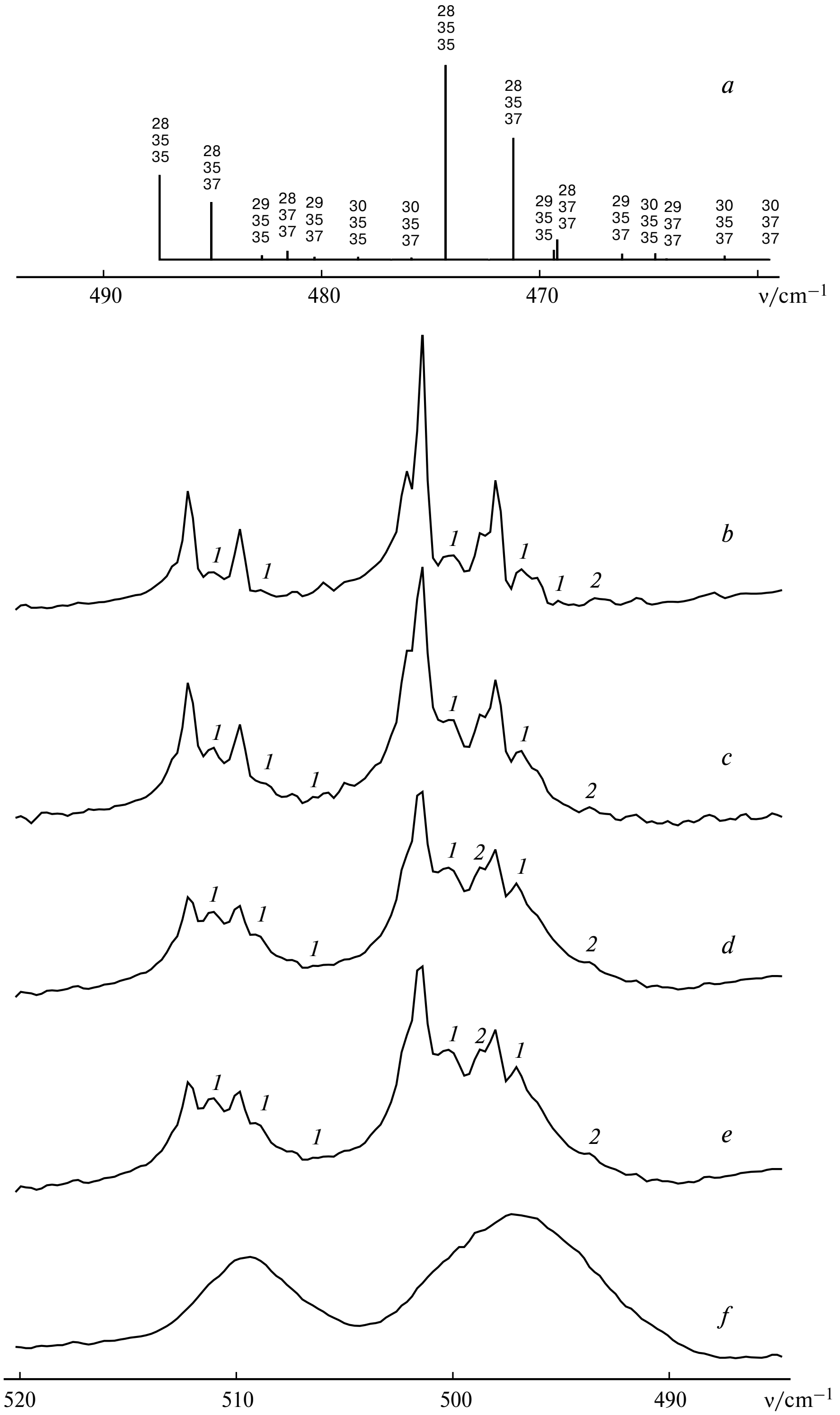


Fig. 2. IR spectrum of $Cl_2Si \cdot N_2$ in the region of stretch vibrations of Si—Cl bonds: Theoretical IR spectrum obtained from B3LYP/6-311+G(d) calculations (isotopic composition of isotopomer (Si, Cl, Cl) corresponding to particular band is shown above the absorption band) (*a*). Fragments of the IR spectra of Ar—N_2 matrices containing $SiCl_2$ in the region of stretch vibrations of Si—Cl bonds; N_2 concentration in matrices : 3 (*b*), 5 (*c*), 8 (*d*), 10 (*e*), and 20 mol.% (*f*). Shown are the bands of $Cl_2Si \cdot N_2$ (*1*) and $Cl_2Si \cdot (N_2)_2$ (*2*).

Table 2. Comparison of frequency shifts of dihalosubstituted carbene analogs upon formation of complexes with dinitrogen in argon matrices[a]

Species	ν_{sym}	ν_{as}	$\Delta\nu_{sym}$[b] ($\Delta\nu_i/\nu_i$ (%))	$\Delta\nu_{as}$[b] ($\Delta\nu_i/\nu_i$ (%))	Reference
	cm^{-1}				
$SiCl_2$	512.2	501.3			c
$Cl_2Si \cdot N_2$	511.2	500.1	1 (0.2)	1.2 (0.2)	c
$Cl_2Si \cdot (N_2)_2$		498.7	—	2.6 (0.5)	c
SnF_2	593	571			12
$F_2Sn \cdot N_2$	588	565	5 (0.8)	6 (1.1)	12
$F_2Sn \cdot (N_2)_2$	583	557	10 (1.7)	14 (2.5)	12
$SnCl_2$	354.1	334.2			13
$Cl_2Sn \cdot N_2$	—	329.9		4.3 (1.3)	13
$Cl_2Sn \cdot (N_2)_2$	—	326.1		8.1 (2.4)	13
PbF_2	531.4	507.2			13
$F_2Pb \cdot N_2$	526.6	502.2	4.8 (0.9)	5 (1)	13

[a] Listed are the frequencies of isotopomers with the most abundant isotopes.

[b] $\Delta\nu_i$/cm^{-1} = ν_i (free carbene analog) − ν_i (complex).

[c] This work.

tentatively assigned to the third isotopic component of antisymmetric Si—Cl bond vibration in the complex $Cl_2Si \cdot (N_2)_2$. A value of 498.7 cm^{-1} (Table 1) could be attributed to a frequency of the first isotopic component of $Cl_2Si \cdot (N_2)_2$ complex .

Upon short-term annealing of nitrogen-containing matrices the intensities of the bands of the complexes somewhat increase compared to the $SiCl_2$ bands. This is due to diffusion of N_2 molecules and the formation of new molecular complexes.

As mentioned above (see Fig. 2), with an increase in N_2 concentration all bands in the IR spectra are gradually broadened due to an increase in heterogeneity of matrix-isolated molecules environment. As a result, the band structure in the region of $SiCl_2$ stretch vibrations, which is due to both isotopic splitting and complexation, disappears at dinitrogen concentrations in the range of 13—16 mol.%. At dinitrogen concentrations between 20 and 50 mol.%, only two broad bands were observed, assigned to symmetric and antisymmetric vibrations of Si—Cl bonds in $SiCl_2$ and its complexes. However, the isotopic structure of these bands appears again in the N_2 matrix (see Fig. 1, *c*). The assignment of the frequencies observed in the N_2 matrix is given in Table 1. Taking into account the ability of $SiCl_2$ to complexation with N_2 found in this work, these frequencies obviously belong to the $Cl_2Si \cdot (N_2)_2$ complex or to associates containing more N_2 molecules. A noticeable difference of their values from the corresponding frequency values of $Cl_2Si \cdot (N_2)_2$ complex recorded in mixed Ar—N_2 matrices, can be due to a change in the matrix composition rather than a change in the composition of the complexes. Thus, the experimental data obtained do not allow to differ $Cl_2Si \cdot (N_2)_n$ complexes with $n \geq 2$. Therefore the frequencies observed in N_2 matrix are presented in Table 1 as frequencies of the $Cl_2Si \cdot (N_2)_2$ complex in the N_2 matrix.

The IR spectrum of $Cl_2Si \cdot (N_2)_2$ (or $Cl_2Si \cdot (N_2)_n$ associates, with $n > 2$) in N_2 matrix was previously recorded during generation of $SiCl_2$ by reaction of $SiCl_4$ with metallic silicon.[45] The authors of the study[45] interpreted this spectrum as a spectrum of free $SiCl_2$ in N_2 matrix. In this case, as well as in the case of Ar matrices,[45] a strong matrix splitting of bands was found. The method of $SiCl_2$ generation used in this work allows avoiding the splitting of bands in the N_2 matrix, which resulted in significant simplification of the spectra and recognition of a close analogy between the spectra recorded in the Ar and N_2 matrices. The assignment of the $Cl_2Si \cdot (N_2)_2$ bands in the N_2 matrix (see Table 1) is based on this analogy. It differs from the assignment made earlier.[45] We assigned a number of the bands assigned earlier[45] to minor matrix sites, to vibrations of minor isotopomers. This assignment is favored by the fact that the frequency shifts of all $SiCl_2$ isotopomers on going from Ar to N_2 matrix for every vibration mode coincide and are ~2.5 cm^{-1} for ν_{sym} and ~4.5 cm^{-1} for ν_{as}.

One could expect that the IR spectra of the complexes of $SiCl_2$ with N_2 should exhibit not only the bands of Si—Cl stretch vibrations but also bands of N≡N bond vibration. However, we failed to record these bands, probably, because of weak interaction of $SiCl_2$ with N_2 and, hence, small polarization of the N≡N bonds. The bands of stretch vibration of the N≡N bond were also not observed for previously studied complexes of SnF_2,[12] $SnCl_2$, and PbF_2 [13] with N_2. Nevertheless, for a complex of dinitrogen with bis-(pentamethylcyclopenta-1,3-dienyl)silicon, which could be considered as a compound related to silylenes, an IR band of the N≡N bond vibration was recorded in cryosolutions of Xe and of N_2 (at 2046 cm^{-1} in liquid Xe and at 2053 cm^{-1} in liquid N_2) owing to the use of cuvettes with a long optical path.[46]

The main by-product, which is always present in matrices besides dichlorosilylene, is $SiCl_4$. In principle, it could also interact with dinitrogen. However, our special experiments showed that neither $SiCl_4$ nor Si_2Cl_6 (precursor of dichlorosilylene) do not form complexes with dinitrogen or any products which are stable under conditions of low-temperature matrix. It worth to note, $SiCl_4$ is able to form complexes in low temperature matrices, but with stronger bases like NH_3 [47] and Me_2HN.[48] A complex of SiF_4 with dinitrogen was also registered previously in mixed argon-nitrogen matrices.[12]

Quantum-chemical calculations on the potential energy surfaces of $SiCl_2$+N_2 and $SiCl_2$+2 N_2 systems. Density functional PBE calculations revealed energy minima for the complexes $Cl_2Si \cdot N_2$ and $Cl_2Si \cdot (N_2)_2$ (Fig. 3). No minima were located on the potential energy surfaces (PES) of these systems for other orientations of N_2 mol-

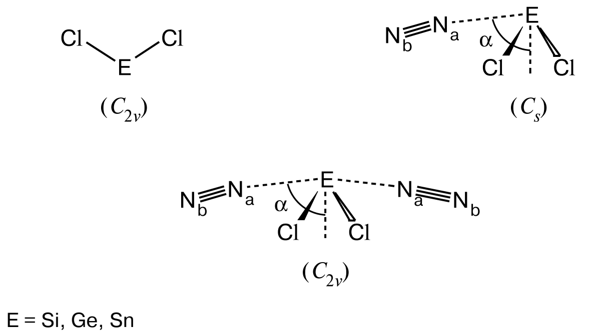


Fig. 3. Structures of carbene analogs ECl_2 (E = Si, Ge, Sn) and their complexes with N_2 calculated by the PBE/TZ2P and B3LYP/6-311+G(d) methods. The symmetry groups are given in parenthesis.

ecule relative to $SiCl_2$, e.g., π-complexes. This agrees with results of the PES calculations for the SnF_2+N_2 system.[12] Complex $Cl_2Si \cdot N_2$ was also calculated by the B3LYP method. The calculated geometric parameters of the complexes and initial $SiCl_2$ and N_2 molecules are presented in Table 3. The calculations reproduce well the bond length in the N_2 molecule (1.103 Å, PBE/TZ2P; 1.096 Å, B3LYP; and 1.098 Å, experiment[49]) and somewhat overestimate the Si—Cl bonds length in $SiCl_2$ (2.116 Å, PBE and 2.109 Å, B3LYP; *cf.* experimental value of 2.0653 Å [50]).

As follows from the data of Table 3, the geometry of the reagents remains virtually unchanged upon complexation. The Si—N_a distance in the complexes is rather long (~3.5 Å), being slightly longer in the complex with two N_2 molecules than in the complex with one N_2 molecule. Both PBE and B3LYP density functional calculations give for $Cl_2Si \cdot N_2$ complex the same values of the energy of formation (0.3 kcal mol^{-1}, Table 4). The formation of $Cl_2Si \cdot (N_2)_2$ complex is nearly two times more energetically favorable compared to $Cl_2Si \cdot N_2$ complex (Table 4). G2(MP2,SVP) calculations give a higher estimate of the strength of $Cl_2Si \cdot N_2$ complex (1.2 kcal mol^{-1}) compared to those given by density functional methods. Taking into account higher accuracy of the G2(MP2,SVP) method, this estimate looks more reliable. In brief, the characteristics of the molecules calculated by different methods agree well.

Complexation results in small change in the dipole moment (see Table 3), which shows an insignificant transfer of electron density in the complexes.

DFT calculations underestimate the stretch vibration frequencies of Si—Cl bonds both in the initial $SiCl_2$ molecule and its complexes by ~20 cm^{-1} (Tables 1 and 5). The difference between the frequencies of symmetric and antisymmetric vibrations in $SiCl_2$ is underestimated by 3.6 cm^{-1} in the PBE calculations compared to the experimental value and almost coincides with experiment in the B3LYP calculations (the difference is –0.8 cm^{-1}). Both methods somewhat overestimate the shifts of the Si—Cl bond stretch vibrations frequencies upon complexation. The shifts obtained from B3LYP calculations are closer to the experimental values (Table 2 and 5). Both methods also predict a decrease in these frequencies upon the formation of complexes, the shift of symmetric stretch vibration frequency upon complexation being slightly smaller than the shift of the antisymmetric vibration, which is consistent with the experimental data. Noteworthy is that the intensities of the stretch vibration bands remain nearly unchanged upon the formation of the $Cl_2Si \cdot N_2$ com-

Table 3. Geometric parameters (interatomic distances and angles) and dipole moments (μ/D) of carbene analogs ECl_2 (E = Si, Ge, Sn) and their complexes with N_2 calculated using the PBE/TZ2P and B3LYP/6-311+G(d) (figures in parentheses) methods

Species	E—Cl/Å	Cl—E—Cl /deg	N_a—N_b/Å	E—N_a/Å	N_a—E—N_a /deg	α	μ
				E = Si			
$SiCl_2$	2.116 (2.109)	101.8 (102.1)					1.1 (1.5)
$Cl_2Si \cdot N_2$	2.119 (2.111)	101.6 (102.0)	1.103 (1.095)	3.489 (3.540)		87.4	1.2 (1.6)
$Cl_2Si \cdot (N_2)_2$	2.230	101.5	1.103	3.525	169.5	87.0	1.2
				E = Ge			
$GeCl_2$	2.221	100.9					2.1
$Cl_2Ge \cdot N_2$	2.225	100.8	1.103	3.311		86.9	2.2
$Cl_2Ge \cdot (N_2)_2$	2.229	100.7	1.103	3.327	169.2	84.0	2.3
				E = Sn			
$SnCl_2$	2.409	98.8					3.0
$Cl_2Sn \cdot N_2$	2.415	98.7	1.102	3.313		79.7	3.1
$Cl_2Sn \cdot (N_2)_2$	2.420	98.6	1.102	3.326	154.3	76.9	3.0

* For definition of the α angle and the atom numbering, see Fig. 3.

Note. The bond length in the N_2 molecule is 1.103 Å (PBE/TZ2P), 1.096 Å (B3LYP/6-311+G(d)), and 1.098 Å (experiment[49]). The experimental bond length and bond angles are 2.065310 Å and 101.324° for $SiCl_2$,[50] 2.169452 Å and 99.882° for $GeCl_2$,[51] and 2.335 Å and 99.1° for $SnCl_2$.[52]

Table 4. Total energies (*E*) of ECl_2, $Cl_2E \cdot N_2$, and $Cl_2E \cdot (N_2)_2$ (E = Si, Ge, Sn) and energy differences (ΔE) for the complexation reactions calculated by the DFT and G2(MP2,SVP) methods

Species	Method[a]	$-E$[b] /au	$-\Delta E$[b] /kcal mol^{-1}
$SiCl_2$	B3LYP	1210.02904	—
	G2	1208.59507	—
	PBE	1209.49976	—
$Cl_2Si \cdot N_2$[c]	B3LYP	1319.58368	0.3[d]
	G2	1317.98969	1.2
	PBE	1318.94503	0.3
$Cl_2Si \cdot (N_2)_2$[c]	PBE	1428.39028	0.6
$GeCl_2$	PBE	2996.90348	—
$Cl_2Ge \cdot N_2$[c]	PBE	3106.34932	0.7
$Cl_2Ge \cdot (N_2)_2$[c]	PBE	3215.79470	1.0
$SnCl_2$	PBE	6945.10803	—
$Cl_2Sn \cdot N_2$[c]	PBE	7054.55433	0.9
$Cl_2Sn \cdot (N_2)_2$[c]	PBE	7164.00000	1.5

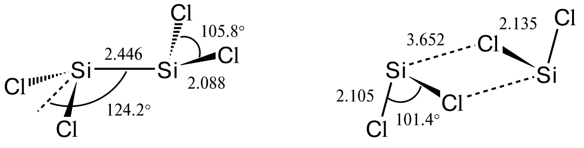
[a] Notations of computational methods: B3LYP = B3LYP/6-311+G(d), G2 = G2(MP2,SVP), and PBE = PBE/TZ2P.

[b] Calculated for $T = 0$ K with inclusion of ZPE correction.

[c] The total energy of the N_2 molecule calculated with the B3LYP/6-311+G(d), G2(MP2,SVP), and PBE/TZ2P methods is −109.55412, −109.39267, and −109.44479 au, respectively.

[d] $\Delta G = 4.3$ kcal mol^{-1}; calculated with inclusion of ZPE correction for $p = 1$ atm. and $T = 298$ K.

plex and decrease by ~6% upon the formation of the $Cl_2Si \cdot (N_2)_2$ complex. This allows estimation of the relative quantities of $SiCl_2$ associates in the matrix by comparing the intensities of their bands (see below). Formation of complex results in insignificant polarization of the N≡N bond. As a result, the stretch vibration intensity of this bond differs from zero but remains approximately three orders of magnitude lower than the stretch vibrations intensities of the Si—Cl bonds. Just for this reason the band was not detected in experiments.



1 (C_{2h}) **2** (C_i)

Fig. 4. Structures of Si_2Cl_4 dimer calculated with the B3LYP/6-311+G(d) method. Interatomic distances are given in Å. The symmetry groups are given in parentheses.

The isotopic structure of the stretch vibration bands of the $SiCl_2$ and $Cl_2Si \cdot N_2$ molecules was calculated by the B3LYP method. The calculated frequencies and intensities of the isotopic components are presented in Table 6 as well as the theoretical and experimental isotopic shifts. These data show that calculations excellently reproduce the experimental shifts of isotopic components relative to each other within each band. According to calculations, the frequency differences between the isotopic components of the bands do not change upon complex formation. This, especially, supports correctness of our assignment of two weak bands to the $Cl_2Si \cdot N_2$ complex, based on their shifts relative to the corresponding isotopic components of $SiCl_2$. The calculated spectra of $SiCl_2$ and $Cl_2Si \cdot (N_2)_2$ are shown in Fig. 1, *a* and 2, *a*, respectively. As is seen from comparison of the calculated and experimental spectra, the observed isotopic structure of the stretch vibration bands of Si—Cl bonds agrees well with the theoretical one.

Possibility of formation of Si_2Cl_4 dimer. During deposition of matrices the $SiCl_2$ molecules could interact not only with N_2 but also between themselves, thus producing Si_2Cl_4 dimers. Calculations of probable structures of the dimer and their vibration spectra were carried out to investigate the possibility of superimposition of the Si_2Cl_4 bands on the bands of monomeric $SiCl_2$ or on the bands of the complexes observed. B3LYP/6-311+G(d) calculations showed that two configurations of the Si_2Cl_4 dimer

Table 5. Some vibration frequencies (δ and ν/cm^{-1}) and their IR intensities (I/km · mol^{-1}) of the structures, corresponding to minima on the potential energy surfaces of $SiCl_2+N_2$ and $SiCl_2+2N_2$ systems calculated using the B3LYP/6-311+G(d) and PBE/TZ2P methods

Structure	Method[a]	ν(N≡N)[b]/I	ν_{sym}(Si—Cl)/I	$\Delta\nu_{sym}$(Si—Cl)[c]	ν_{as}(Si—Cl)/I	$\Delta\nu_{as}$(Si—Cl)[c]	δ(ClSiCl)/I
$SiCl_2$	B3LYP	—	489.0/95	—	477.4/217	—	194.4/2.3
	PBE	—	490.0/71	—	482.7/182	—	182.5/1
$Cl_2Si \cdot N_2$	B3LYP	2447.0/0.3	487.4/92	1.6	474.3/211	3.1	193.6/1.9
	PBE	2344.1/0.2	487.2/69	2.8	478.4/178	4.3	184.0/1.1
$Cl_2Si \cdot (N_2)_2$	PBE	2342.5/0.1, 2342.4/0.1	487.1/67	2.9	476.5/174	6.2	182.1/0.8

[a] B3LYP = B3LYP/6-311+G(d) method , PBE = PBE/TZ2P method.

[b] Calculated value ν(N≡N) for free N_2: 2330.8 cm^{-1} (PBE/TZ2P) and 2444.9 cm^{-1} (B3LYP/6-311+G(d)).

[c] $\Delta\nu_i = \nu_i$ (free carbene analog) $- \nu_i$ (complex).

Table 6. Frequencies (ν/cm^{-1}) and absolute intensities (I/km · mol^{-1}) of stretch vibrations of Si—Cl bonds in various isotopomers of $SiCl_2$ and $Cl_2Si \cdot N_2$ calculated using the B3LYP/6-311+G(d) method, and frequency differences (Δν/cm^{-1}) for various isotopomers (I — calculation, II — experiment)

Frequency	Isotope			$SiCl_2$		$Cl_2Si \cdot N_2$		Δν	Δν($SiCl_2$)		Δν($Cl_2Si \cdot N_2$)	
	Si	Cl	Cl	ν_{calc}	I*	ν_{calc}	I*		I	II	I	II
ν_{sym}	28	35	35	489.0	49.9	487.4	48.3	$\nu_{sym}(^{28}Si^{35}Cl_2) - \nu_{sym}(^{28}Si^{35}Cl^{37}Cl)$	2.3	2.4	2.3	2.3
	28	35	37	486.7	34.3	485.1	32.8	$\nu_{sym}(^{28}Si^{35}Cl^{37}Cl) - \nu_{sym}(^{28}Si^{37}Cl_2)$	3.6	3.9	3.5	—
	28	37	37	483.1	5.1	481.6	4.9	$\nu_{sym}(^{28}Si^{35}Cl_2) - \nu_{sym}(^{29}Si^{35}Cl_2)$	4.7	5.0	4.7	4.7
	29	35	35	484.3	2.5	482.7	2.4	$\nu_{sym}(^{29}Si^{35}Cl_2) - \nu_{sym}(^{29}Si^{35}Cl^{37}Cl)$	2.3	2.4	2.4	—
	29	35	37	482.0	1.7	480.3	1.6	$\nu_{sym}(^{29}Si^{35}Cl^{37}Cl) - \nu_{sym}(^{29}Si^{37}Cl_2)$	3.6	—	3.5	—
	29	37	37	478.4	0.3	476.8	0.2	$\nu_{sym}(^{29}Si^{35}Cl_2) - \nu_{sym}(^{30}Si^{35}Cl_2)$	4.4	4.4	4.4	—
	30	35	35	479.9	1.6	478.3	1.5	$\nu_{sym}(^{30}Si^{35}Cl_2) - \nu_{sym}(^{30}Si^{35}Cl^{37}Cl)$	2.4	2.6	2.4	—
	30	35	37	477.5	1.1	475.9	1.1	$\nu_{sym}(^{30}Si^{35}Cl^{37}Cl) - \nu_{sym}(^{30}Si^{37}Cl_2)$	3.6	—	3.6	—
	30	37	37	473.9	0.2	472.3	0.2					
ν_{as}	28	35	35	477.4	114.2	474.3	111.1	$\nu_{as}(^{28}Si^{35}Cl_2) - \nu_{as}(^{28}Si^{35}Cl^{37}Cl)$	3.3	3.5	3.1	3.2
	28	35	37	474.1	70.9	471.2	69.5	$\nu_{as}(^{28}Si^{35}Cl^{37}Cl) - \nu_{as}(^{28}Si^{37}Cl_2)$	1.9	1.9	2.0	1.8
	28	37	37	472.2	11.7	469.2	11.4	$\nu_{as}(^{28}Si^{35}Cl_2) - \nu_{as}(^{29}Si^{35}Cl_2)$	5.0	5.4	4.9	5.0
	29	35	35	472.4	5.7	469.4	5.5	$\nu_{as}(^{29}Si^{35}Cl_2) - \nu_{as}(^{29}Si^{35}Cl^{37}Cl)$	3.3	3.2	3.2	—
	29	35	37	469.1	3.5	466.2	3.5	$\nu_{as}(^{29}Si^{35}Cl^{37}Cl) - \nu_{as}(^{29}Si^{37}Cl_2)$	1.9	2.2	2.0	—
	29	37	37	467.2	0.6	464.2	0.6	$\nu_{as}(^{29}Si^{35}Cl_2) - \nu_{as}(^{30}Si^{35}Cl_2)$	4.7	4.6	4.7	—
	30	35	35	467.7	3.7	464.7	3.6	$\nu_{as}(^{30}Si^{35}Cl_2) - \nu_{as}(^{30}Si^{35}Cl^{37}Cl)$	3.3	3.6	3.2	—
	30	35	37	464.4	2.3	461.5	2.2	$\nu_{as}(^{30}Si^{35}Cl^{37}Cl) - \nu_{as}(^{30}Si^{37}Cl_2)$	2.0	2.0	2.0	—
	30	37	37	462.4	0.4	459.5	0.4					

* Taking into account the natural abundance of isotopomer.

are possible, namely, a *trans*-olefin type structure (**1**) and a less stable bridged structure (**2**) (Fig. 4, Table 7). The same order of the dimer structure stability was found earlier in MP2/6-31+G(2df,p) calculations.[53] According to calculations, the reaction 2 $SiCl_2 \rightarrow$ **1** occurs barrierlessly. At 0 K, the dimerization energy is 8.6 kcal mol^{-1} for structure **1** and only 1.2 kcal mol^{-1} for structure **2** (Table 7). This indicates that at low temperatures the dimer **1** is thermodynamically much more stable than complex $Cl_2Si \cdot N_2$ for which our calculations give a complexation energy of 0.3 to 1.2 kcal mol^{-1} (Table 4).

The IR spectrum of **1** calculated by the B3LYP/6-311+G(d) method shows two intense absorption bands at 468.2 and 526.5 cm^{-1} (Table 8). The latter band differs significantly from the bands of $SiCl_2$ and its complexes with N_2. No bands in the region 400—600 cm^{-1} which could be assigned to dimer **1** were found in the observed IR spectrum of $SiCl_2$, but at the same time the bands of thermodynamically less stable $Cl_2Si \cdot N_2$ complex were recorded. A reasonable explanation for this contradiction could be as follows. According to calculations, the changes in the Gibbs free energy at 298 K are such (Tables 4 and 7) that both complexation of $SiCl_2$ with N_2

Table 7. Total energies (E/au) and Gibbs free energies (G/au) of Si_2Cl_4 dimer structures and their differences (ΔE, ΔG/kcal mol^{-1}) for dimerization reaction 2 $SiCl_2 \rightarrow Si_2Cl_4$ calculated using the B3LYP/6-311+G(d) method

Dimer[a]	E [b]	ΔE [b]	G [c]	ΔG [c]
1	−2420.07179	−8.6	−2420.10899	2.3
2	−2420.06003	−1.2	−2420.10519	4.7

[a] The dimer structures are presented in Fig. 4.
[b] Calculated for T = 0 K with inclusion of ZPE correction.
[c] Calculated for p = 1 atm. and T = 298 K with inclusion of ZPE correction.

Table 8. Vibrational frequencies (ν/cm^{-1}) and their IR intensities (I/km · mol^{-1}) of structures **1** and **2** (see Fig. 4) calculated by the B3LYP/6-311+G(d) method

1		**2**	
ν	I	ν	I
37.6	0.6	4.5	0.5
55.5	0.4	16.4	0.0
100.8	10.8	19.4	1.8
110.4	0.0	35.7	0.0
132.5	0.0	40.8	18.0
191.3	8.0	72.6	0.0
221.9	0.0	191.5	0.0
274.3	0.0	192.3	3.6
468.2	345.1	445.6	0.0
513.9	0.0	461.5	372.3
526.5	307.0	486.7	0.0
530.9	0.0	491.8	214.8

(ΔG = 4.3 kcal mol^{-1}), and dimerization of $SiCl_2$ into **1** (ΔG = 2.3 kcal mol^{-1}) are thermodynamically unfavorable at $T > 298$K. According to calculations, the formation of $Cl_2Si \cdot N_2$ and dimer becomes thermodynamically favorable only at temperatures near the temperature of formation of the solid matrix. Under these conditions the probability of interaction of $SiCl_2$ with N_2 is significantly higher than with the second $SiCl_2$ molecule, because the concentration of dinitrogen in the matrix is higher than the concentration of $SiCl_2$ and in view of the fact that N_2 molecules have higher diffusion mobility.

Comparison of dinitrogen complexes of different carbene analogs. All known experimental data on the IR spectra of carbene analogs complexes with dinitrogen recorded in low-temperature inert matrices are collected in Table 2. As can be seen from Table 2, complexation of $EHal_2$ (E = Sn, Pb) with one N_2 molecule results in a decrease in the stretch vibration frequencies of E—Hal bonds by ~1%. In the complex with two N_2 molecules the frequency lowers by ~2%. In the case of $SiCl_2$ complexes with N_2 a decrease in the Si—Cl stretch vibration frequencies is also observed but it amounts to 0.2 and 0.5% for $Cl_2Si \cdot N_2$ and $Cl_2Si \cdot (N_2)_2$, respectively. Since the relative frequency shift upon complexation could be used as a measure[13] of strength of a particular complex, the values obtained suggest noticeable lowering of strengths of the complexes with N_2 on going from dihaloplumbylenes to dihalosilylenes.

This conclusion was confirmed by the results of PBE/TZ2P calculations of $ECl_2 \cdot N_2$ and $ECl_2 \cdot (N_2)_2$ (E = Ge, Sn) systems. Energy minima were located on the PES of the complexes of $GeCl_2$ and $SnCl_2$ with one and two N_2 molecules (Fig. 3, Table 4). The geometric parameters of the stationary points found are presented in Table 3. The calculated values of the bond lengths and bond angles in the $GeCl_2$ and $SnCl_2$ molecules agree well with the known experimental values for the equilibrium configurations: 2.169452 Å and 99.8825° for $GeCl_2$ (determined by microwave spectroscopy[51]) and 2.335 Å and 99.1° for $SnCl_2$ (found from gas-phase electron diffraction data[52]). As in the case of $SiCl_2$, the geometry of $GeCl_2$ and $SnCl_2$ remains virtually unchanged upon complexation. On going from $SiCl_2$ to $GeCl_2$ and $SnCl_2$ the covalent radius of the central atom increases noticeably, which manifests itself in, *e.g.*, lengthening of the E—Cl bond (E = Si, Ge, Sn, Table 3). Therefore, one can expect a corresponding lengthening of the E—N distance in the series of complexes $Cl_2E \cdot N_2$ and $Cl_2E \cdot (N_2)_2$ on going from Si to Sn. However, calculations show (Table 3) that the E—N_a distances with E = Ge and Sn almost coincide (3.311 Å and 3.313 Å, respectively), being ~0.2 Å shorter than in $SiCl_2$ complexes. This variation of the distances indicates a strengthening of the complexes both with one and two N_2 molecules in the series $SiCl_2$—$GeCl_2$—$SnCl_2$. This is also confirmed by the calculated complexation energies (Table 4), which show a monotonous increase in the series $SiCl_2$—$GeCl_2$—$SnCl_2$.

Calculations correctly describe the vibrational frequencies of free $GeCl_2$ and $SnCl_2$ (Table 9). According to calculations, complexation results in a decrease in the stretch vibration frequencies of the E—Cl bonds. Earlier,[13] complexation of $SnCl_2$ with N_2 was studied by matrix IR spectroscopy.

The experimental shifts of the ν_{as} frequency upon the formation of $SnCl_2$ complexes with one and two N_2 molecules (Table 2) almost coincide with the calculated values

Table 9. Vibrational frequencies (δ and ν/cm^{-1}) and their intensities (I/km·mol^{-1}) of ECl_2 carbene analogs and their complexes $Cl_2E \cdot N_2$ and $Cl_2E \cdot 2N_2$ (E = Ge, Sn) calculated by the PBE/TZ2P method, and corresponding experimental values (in parentheses)

Species, complex	$\nu(N{\equiv}N)/I$	$\nu_{sym}(E—Cl)/I$	$\Delta\nu_{sym}(E—Cl)$[a]	$\nu_{as}(E—Cl)/I$	$\Delta\nu_{as}(E—Cl)$[a]	$\delta(ClECl)/I$
			E = Ge			
$GeCl_2$	—	380.4 (398.6[b])/43	—	361.1 (373.5[b])/114	—	143.2 (160[c])/1.6
$Cl_2Ge \cdot N_2$	2345.4/0.6	378.2/42	2.2	357.3/111	3.8	144.2/1.5
$Cl_2Ge \cdot (N_2)_2$	2343.8/0.4 2345.2/0.5	375.4/41	5.0	353.7/109	7.4	144.9/0.9
			E = Sn			
$SnCl_2$	—	338.8 (354.8[d])/42	—	325.5 (334.6[d])/88	—	113.3 (120[e])/2.6
$Cl_2Sn \cdot N_2$	2346.6/1	336.1/42	2.7	321.1 (329.9[f])/87	4.4	111.7/2.1
$Cl_2Sn \cdot (N_2)_2$	2346.1/0.8 2344.6/0.8	333.4/41	5.4	318.4 (326.1[f])/85	7.1	107.2/0.9

[a] Frequency shift in the complex.

[b] In argon matrix.[54]

[c] In the gas phase.[55—58]

[d] In argon matrix.[59]

[e] In the gas phase.[57,58,60—62]

[f] In argon matrix.[13]

(Table 9). The interaction of $GeCl_2$ with N_2 was not studied earlier.

In this connection it is worth to note that in case of dihalostannylenes and dihaloplumbylenes complete conversion of free carbene analogs into a complex with one dinitrogen molecule was observed already at N_2 concentrations of 3—4 mol.% and that appreciable amount of complexes with two N_2 molecules was noticed at the same concentrations.[12,13] In the case of $SiCl_2$, the bands of dichlorosilylene not bound to dinitrogen were observed even at N_2 concentration of 13 mol.%. Their intensities were comparable to those of $Cl_2Si \cdot N_2$ complex. On the contrary, the bands tentatively assigned to the $Cl_2Si \cdot (N_2)_2$ complex remained weak at all N_2 concentrations (up to 13 mol.%), for which the pattern of the stretch vibration bands of Si—Cl bonds in $SiCl_2$ and it complexes was unbroken.

In the case of matrices containing several reagents their interaction occurs mainly during the formation of the outer layer of the matrix *via* diffusion of 'hot' molecules in the surface layer prior to their rigid fixation in the crystal lattice of the matrix. This explains a significant (more than twofold) excess of the $[EHal_2 \cdot N_2]$: $[EHal_2]$ (E = Sn, Pb) ratio over the ratio of the number of matrix cells containing one N_2 molecule to the number of cells comprised of Ar atoms only (on the assumption of random distribution of N_2 molecules in Ar matrix).[13] The reverse was observed in the case of $SiCl_2$. The proportion of $Cl_2Si \cdot N_2$ complexes is markedly lower than that of the matrix cells containing one N_2 molecule. Therefore, in contrast to dihalostannylenes and dihaloplumbylenes, a significantly smaller number of diffusion collisions between $SiCl_2$ and N_2 molecules in the surface layer results in the formation of complexes. This fact indicates substantially lower energy gains from the formation of $Cl_2Si \cdot N_2$ complex compared to the formation of similar complexes of heavier carbene analogs, thus being in agreement with the conclusion of lowering of the strength of complexes with N_2 on going from dihaloplumbylene to dihalosilylene. Interaction of $SiCl_2$ and N_2 with unfavorable orientation within one matrix cell becomes impossible after the formation of the matrix and predefines a lower concentration of the complex compared to the concentration of N_2-containing cells. As mentioned above, controlled annealing of matrices lowers their rigidity, allows reorientation of molecules and their partial diffusion, and results in an increase in the concentration of the complex.

The problem of the relative ability of carbene analogs to form complexes with Lewis bases was considered earlier[63] in a theoretical study of complexation of EH_2 (E = Si, Ge, Sn) with the Group 15 and 16 elements hydrides. It was found that acidity of EH_2 decreases on going from silylene to stannylene. The authors[63] did not analyze the effect of substituents in carbene analogs on their acidity. An inversion of acidity series of $EHal_2$ toward N_2 found in this work could be explained both by the effect of the substituent at the carbenic center and by the nature of the base. Indeed, the calculated energies of EH_2 complexation with rather strong bases are most often >10 kcal mol^{-1}.[63] Although for the same base the complexation energies decrease on going from SiH_2 to SnH_2, this decrease depends strongly on the nature of the base and varies over in rather wide range, thus, probably reflecting specific features of the interaction with a particular base. For weaker bases, details of the interaction should be even more important. So the acidity series[63] towards weak Lewis bases can change dramatically even for EH_2 (E = Si, Ge, Sn).

The authors express their gratitude to D. N. Laikov for kindly providing a version of his PRIRODA program.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 00-15-97387, 00-03-33001, and 01-03-32630), Ministry of Industry, Science, and Technology of the Russian Federation (Federal Targeted Scientific and Technical Program "Priority Avenues of Scientific and Technological Research and Development"), Russian Academy of Sciences (Integrated Program "Physics and Chemistry of Extreme State of Matter," subprogram "Research into Chemical Bonding and Structure," project No. 1-20; VIIth Competition of projects of young researchers at the Russian Academy of Sciences), and the NATO (grant PST.CLG.975368).

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Received December 30, 2002