Matrix IR-spectroscopic and quantum-chemical study of difluorostannylene complexation with dinitrogen*

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Complexes of difluorostannylene with dinitrogen of composition 1 : 1 and 1 : 2 were stabilized in Ar matrix (12 K) and characterized by IR spectra. The bands at 588, 565, and 583, 557 cm^{-1}, respectively, were assigned to these complexes. Potential energy surfaces of the systems SnF_2+N_2 and SnF_2+2N_2 were studied by the *ab initio* MP2/3-21G(d2)//HF/3-21G(d2) method using the basis set including polarization functions at Sn, F, and N atoms. Equilibrium structures of the complexes have C_s and C_{2v} symmetry and correspond to coordination of lone electron pairs of nitrogen molecules with vacant p-AO of the carbenic center. The calculated complexation energies are equal to 4.6 and 8.9 kcal mol^{-1}, respectively. Based on results of quantum-chemical calculations an interpretation of the IR spectra of the complexes was given and it was shown that cycloaddition of SnF_2 to a triple N≡N bond with formation of *cyclo*-SnF_2N_2 is energetically unfavorable. The absorption band belonging to $SiF_4 \cdot N_2$ complex in Ar matrix was detected and assigned.

Key words: difluorostannylene, dinitrogen, donor-acceptor complex; matrix IR spectra; quantum-chemical calculations, *ab initio* calculations.

Carbene analogs (CAs) — silylenes, germylenes and stannylenes — are important intermediates in organometallic chemistry. Their formation is postulated in many reactions. The number of publications devoted to studies of physicochemical properties of compounds of two-coordinated silicon, germanium, and tin has grown steadily.[1–3]

In the singlet state, which is the ground state of all CAs studied, they have a low lying vacant p-orbital that allow them to behave like Lewis acids. Reactivity of stable complexes formed by CAs with relatively strong Lewis bases[4–8] can differ significantly from that of free CAs thus allowing one to control their reactions.[9] Weak Lewis bases can, in principle, also form similar complexes. For example, the blue shift of absorption maxima of germylenes observed in hydrocarbon matrices in the presence of cyclohexyl, phenyl, or allyl chlorides was explained by the formation of the complexes.[10,11]

Recently, strong experimental and theoretical evidence of complex formation in the course of the reaction of Me_2Si with $CHBr_3$ was reported and complexes of SnF_2 with MeCl,[13] alkenes,[14] and alkynes[15,16] were detected and stable complexes of stannylenes of the formulas $Sn(SO_3F)_2 \cdot MesH$, $Sn(SbF_6)_2 \cdot 2MesH$ (Mes is 2,4,6-trimethylphenyl),[17] and $R_2Sn \cdot SnCl_2$ (R = $CH(SiMe_3)C_9H_6N$-8)[18] were identified. In the latter case the structure of the complex was unequivocally established by the X-ray diffraction method. Evidently, the formation of complexes with substrates or molecules from reaction media where CAs are generated is, in general, the first and often underestimated step of many reactions involving carbene analogs. Hence, studies of stability, structure, and reactivity of complexes of CAs appear to be important.

Due to the presence of two lone electron pairs in the N_2 molecule it can be considered as a weak Lewis base. This is confirmed by its ability to form complexes with different Lewis acids[19,20], as well as formation of hydrogen bonds with such molecules as H_2O,[21] HCl,[21] HF,[21–23] HNO_3,[24] ROH.[25] Earlier, it was shown[26] by matrix IR spectroscopy that $SnCl_2$ and PbF_2 forms complexes with N_2. The complex of silylene, $(Me_5C_5)_2Si \cdot N_2$, was characterized[27] by the vibration frequency of the N≡N bond in liquid Xe and in liquid N_2. However, detailed experimental and theoretical studies of the stability and structure of CA complexes with dinitrogen have not been reported yet.

In the study of the complexes of $SnCl_2$ and PbF_2 with dinitrogen[26] it was assumed that they are formed *via* interaction with one of the lone electron pairs of the N_2 molecule, although based on the data reported,[26] one could not in principle exclude an alternative structure with the SnF_2 molecule coordinated to a triple N≡N bond, similar to that found by us[15] in the case of π-complex of SnF_2 with hept-1-yne. Because dinitrogen is usually considered to be an inert compound and is

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often used as a medium where unstable short-lived intermediates, in particular, carbene analogs, are studied, the question of possible complexation of a CA with N_2 is of great importance. Moreover, the formation of complexes is directly related to the problem of chemical fixation of nitrogen.[20]

In this work we studied in detail the complexation of carbene analog (SnF_2) with dinitrogen using matrix IR spectroscopy and quantum-chemical calculations. This work is a part of our systematic studies of formation of complexes by SnF_2.[13,15,16] Combined use of both theoretical and experimental methods allows us not only to detect the $SnF_2 \cdot N_2$ and $SnF_2 \cdot (N_2)_2$ complexes but to determine their structure and stability.

Experimental; procedures of quantum-chemical calculations

A sample of SnF_2 (Aldrich, 99% purity) was evaporated from a graphite Knudsen cell with orifice diameter 1 mm positioned inside a quartz pyrolyzer, coupled to a vacuum optical helium cryostat. Heating was done by an electrical coil wound around the pyrolyzer above the asbestos isolation coat. The temperature was measured with a chromel-alumel thermocouple positioned on the external wall of the pyrolyzer under the insulating coat and was varied in the range 515—550 °C.

The products of SnF_2 evaporation together with the mixtures of Ar—N_2 were deposited on the surface of a mirror copper plate cooled to 12 K, located inside the cryostat 80 mm from the orifice of the Knudsen cell and at a distance of 50 mm from an outlet of the mixture introduction pipeline. The plate was cooled by a Displex-CSW-208R closed-cycle refrigerator. The working pressure in the cryostat was $\sim 10^{-5}$ Torr.

The amount of frozen SnF_2 was estimated from the weight loss of the Knudsen cell after the experiment, taking into account the geometrical factor of the pyrolyzer, equal to 0.5. The molar ratio of SnF_2 : (Ar+N_2) was varied from 1 : 150 to 1 : 550.

The mixtures of argon with dinitrogen were prepared the day before the beginning of experiment in a glass vessel; the composition of the mixtures was measured by a mercury gauge. Mixtures of the following composition were used: pure argon; N_2—Ar with molar ratio of 1 : 206, 1 : 92, 1 : 36, 1 : 5; pure dinitrogen. The mixtures were brought into the cryostat *via* an unheated pipeline and, in parallel, through the quartz pyrolyzer where evaporation of SnF_2 took place (to reduce the interaction of SnF_2 vapor with its walls). Total consumption of the mixture was ~16 mmol h^{-1}. The time of deposition varied from 20 to 40 min. IR spectra were recorded in the range of 4000—400 cm^{-1} on an IKS-24-LOMO spectrophotometer using the reflection scheme.

Quantum-chemical calculations were done with the GAUSSIAN 92W, GAUSSIAN-94,[28] and GAMESS[29] programs. Optimization of geometry and vibrational frequency calculations were done using the 3-21G(d)[30,31] basis set with additional polarization d-functions on N and F atoms denoted below as 3-21G(d2). For d-functions of N and F atoms the same exponents were used, as in 6-31G(d)[31] basis. The nature of the calculated stationary points (minima, transition states) was determined by calculations of the eigenvalues of the matrix of second derivatives of energy. Energies of stationary points optimized at the HF/3-21G(d2) level were corrected by second-order Moller—Plesset MP2/3-21G(d)//HF/3-21G(d2)[32] single point calculations. Calculations using GAUSSIAN-92W and GAMESS programs were done with a Pentium-120 computer, and using GAUSSIAN-94* — with the SGI POWER CHALLENGE L supercomputer at the computer center of IOC RAS.

Results and Discussion

IR spectra of the matrix produced by codeposition of SnF_2 evaporation products with argon (Fig. 1, *a*) have revealed absorption bands of monomeric SnF_2 (593 and 571 cm^{-1}),[33,34] its dimer $(SnF_2)_2$ (580 cm^{-1}),[33,34] which exists in equilibrium with monomeric difluorostannylene in the gas phase at the evaporation temperatures used[35], SiF_4, which is the product of SnF_2 interaction with the quartz pyrolyzer walls (the band at 1027 cm^{-1} of the most abundant ^{28}Si isotope and at 1017, and 1009 cm^{-1} of ^{29}Si and ^{30}Si isotopes),[36] trace quantities of water (3776, 3755, 1624, 1608 cm^{-1}),[37–39] desorbed from cryostat walls and frosted in the matrix, as well as trace quantities of HF (3963 and 3953 cm^{-1}),[40] which is the product of hydrolysis of SnF_2 vapor. Unfortunately, the cryostat setup does not allow us to exclude the formation of SiF_4. The bands belonging to tin oxides,[41–43] which should arise from SnF_2 hydrolysis, were absent due to the relatively low temperature of the pyrolyzer, insufficient for evaporation of oxides from the walls.[41–43] The absorption bands of the compounds observed in the matrices were positioned in different parts of the spectrum; no interaction between this compounds was detected, thus their simultaneous presence in the matrix does not hinder the subsequent studies.

Upon codeposition of the products of SnF_2 evaporation and the mixtures of argon with dinitrogen the following changes were observed in the matrix IR spectra.

At molar ratios of N_2 : Ar equal to 1 : 206 and 1 : 92 (Fig. 1, *b*, *c*) two new bands appeared in the region of Sn—F bond stretching vibrations at 588 and 565 cm^{-1}, the intensity of which grew with increase in dinitrogen concentration in the mixture. Simultaneously, a shoulder at 1022 cm^{-1} arose and grew, as well as a band at 3882 cm^{-1} in the region of H—F vibrations. The latter belongs to a known complex $N_2 \cdot HF$.[22]

Further increase in concentration of dinitrogen (N_2 : Ar = 1 : 36; Fig. 1, *d*) led to disappearance of the bands belonging to monomeric SnF_2 and to emergence of one more band with a maximum at 558 cm^{-1} (as a poorly resolved shoulder on the band at 565 cm^{-1}). The maximum of the absorption band of $(SnF_2)_2$ under these circumstances shifts from 580 to 578 cm^{-1}, the intensity of the shoulder at 1022 cm^{-1} increases, and instead of two bands in the region of deformation vibrations and two bands in the region of antisymmetric stretching vibrations two intense bands arise at 3731 and

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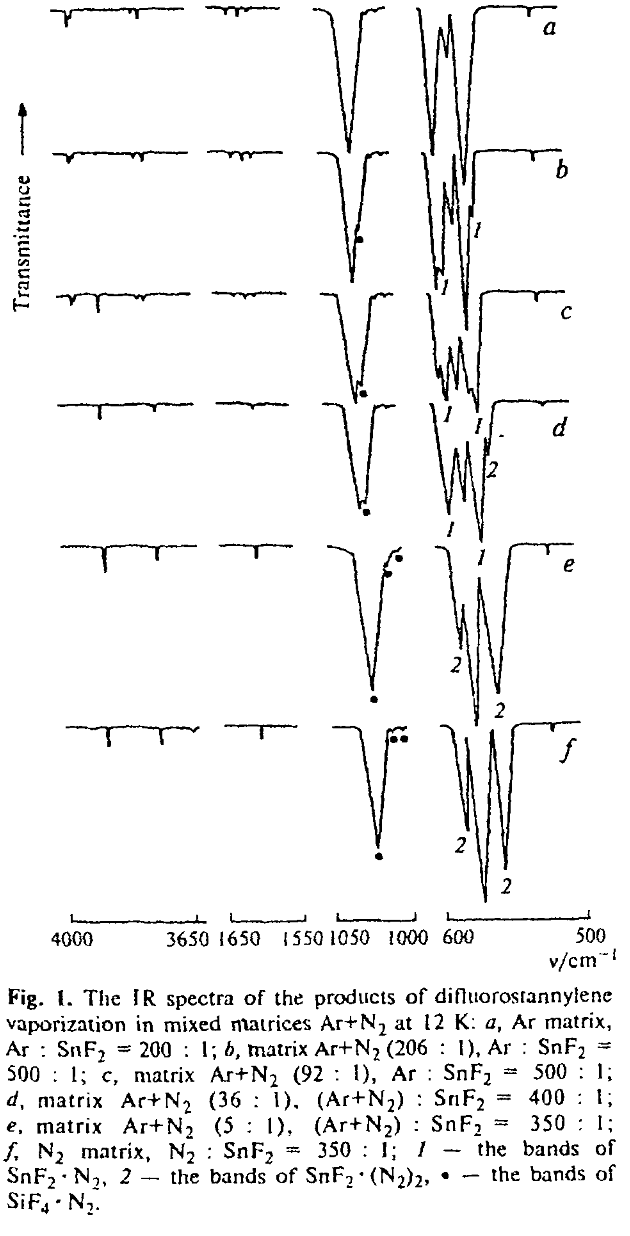


Fig. 1. The IR spectra of the products of difluorostannylene vaporization in mixed matrices Ar+N_2 at 12 K: *a*, Ar matrix, Ar : SnF_2 = 200 : 1; *b*, matrix Ar+N_2 (206 : 1), Ar : SnF_2 = 500 : 1; *c*, matrix Ar+N_2 (92 : 1), Ar : SnF_2 = 500 : 1; *d*, matrix Ar+N_2 (36 : 1), (Ar+N_2) : SnF_2 = 400 : 1; *e*, matrix Ar+N_2 (5 : 1), (Ar+N_2) : SnF_2 = 350 : 1; *f*, N_2 matrix, N_2 : SnF_2 = 350 : 1; *1* — the bands of $SnF_2 \cdot N_2$, *2* — the bands of $SnF_2 \cdot (N_2)_2$, • — the bands of $SiF_4 \cdot N_2$.

1600 cm^{-1} corresponding to vibrations of water molecules observed in the dinitrogen matrix[44] and assigned to its complex with dinitrogen.[17] Starting from this concentration of dinitrogen the absorption bands of free isolated HF were absent in the spectrum and only the band corresponding to complex $N_2 \cdot HF$ was observed.

At the ratio N_2 : Ar = 1 : 5 (Fig. 1, *e*), bands at 583, 572, and 557 cm^{-1} were observed in the region of stretching vibrations, and the absorption band of SiF_4 at 1027 cm^{-1} disappeared; the band at 1022 cm^{-1} was preserved. No changes were observed in the region of H_2O and HF absorption.

Upon codeposition of the products of SnF_2 evaporation and pure dinitrogen the following new bands were observed in the spectrum (Fig. 1, *f*): at 3878 cm^{-1} ($N_2 \cdot HF$ in dinitrogen matrix),[22] at 3728, 3638, 1600 cm^{-1} ($H_2O \cdot N_2$),[11,44] at 1022 cm^{-1}, together with weak low frequency satellites, and at 583, 569 and 557 cm^{-1} (Table 1).

Altogether, it is worth mentioning that the resolution of bands in the matrix spectra of the mixtures of argon with dinitrogen was poorer than the resolution of bands in the spectra of the matrix which consisted of dinitrogen or argon only, which is evidently related to inhomogeneity of the mixed matrices. However, the total transmittance of the matrices does not decreased appreciably.

The new bands in the matrix IR spectra arise from the products of interaction of codeposited substances with dinitrogen. One should mention that this interaction is a specific one, because the majority of new bands appears at sufficiently low concentrations of nitrogen in the matrix, when the nonspecific influence of dinitrogen should be small. The persistence of the observed bands in a relatively wide range of dinitrogen concentrations up to a pure dinitrogen matrix suggests that these bands belong to compounds of fixed rather than variable composition that are stable under the matrix conditions, *i.e.*, to complexes.

The bands observed by us in the region of stretching vibrations of Sn—F bonds (600—550 cm^{-1}, see Table 1) could be divided into four groups. In each group the intensities of bands change simultaneously in matrices

Table 1. Assignment of bands in matrix IR spectra observed in the experiments on codeposition of SnF_2 and SiF_4 with N_2

Matrix	ν/cm^{-1}								
	$SnF_2 \cdot (N_2)_2$	$SnF_2 \cdot N_2$	SnF_2	$(SnF_2)_2$	$SiF_4 \cdot N_2$	SiF_4	H_2O	$N_2 \cdot HF$	HF
Ar			571, 593	580		1027	1608, 1624, 3755, 3776		3953, 3963
Ar+N_2, (206—92) : 1		565, 588	571, 593	580	1022	1027	1608, 1624, 3755, 3776	3882	3953, 3963
Ar+N_2, 36 : 1	558	565, 588		578	1022	1027	1600, 3731	3882	
Ar+N_2, 5 : 1	557, 583			572	1022		1600, 3731	3882	
N_2	557, 583			569	1022		1600, 3638, 3728	3878	

of different composition, which indicate that every group belongs to an individual compound. One of them, the monomeric SnF_2 (571 and 593 cm^{-1}), was present in matrix in appreciable quantities until the ratio of N_2 : Ar = 1 : 92 (~1% dinitrogen). In the range of N_2 concentrations from 0.5 to 3% (from 1 : 206 to 1 : 36) in the matrix another particle appeared, which was characterized by two bands in the region of stretching vibrations of Sn—F bonds (565 and 588 cm^{-1}). As this particle appeared in noticeable quantities even at dinitrogen concentrations equal to ~0.5%, when the presence of two N_2 molecules in a cell containing the SnF_2 molecule is statistically unlikely, one may consider it to be a complex of SnF_2 with N_2 of the simplest composition of 1 : 1.

The third particle, which has bands at 557 and 583 cm^{-1}, is formed only at dinitrogen concentrations >2% (the decline in resolution is the reason why at N_2 : Ar = 1 : 36 only one band appeared at 557 cm^{-1}). Quantum-chemical calculations show (see below) that SnF_2 could form a donor-acceptor complex with no more than two dinitrogen molecules, coordinated at the different sides of the difluorostannylene molecular plane. That is why this particle should be a complex of composition $SnF_2 \cdot (N_2)_2$. Characteristically, the positions of the bands of this complex do not changed upon further increase in N_2 concentration and persist even in a pure dinitrogen matrix. The constancy of vibration frequency values upon transition from argon to dinitrogen matrices is a characteristic of compounds having a small dipole moment.[45] The SnF_2 molecule has a significant dipole moment, but its coordination with two N_2 molecules could significantly lower this value, which is one more argument in favor of the accuracy of assignment of the observed bands. As could be expected, an increase in the coordination number of Sn atom owing to complexation with N_2 results in lowering of the stretching vibrations frequencies of Sn—F bonds.

Upon controlled annealing of the matrices studied (35—40 K, 10—30 min) the following transformations of $SnF_2 \cdot (N_2)_n$ (n = 0—2) compounds took place. The annealing of matrices with ratio of N_2 : Ar = 1 : 92 at the first stage led to a synchronous decrease of intensities of the absorption bands of monomeric SnF_2, a small growth of bands belonging to $SnF_2 \cdot N_2$, and to appearance of bands belonging to $SnF_2 \cdot (N_2)_2$. Upon further annealing, a decrease of intensities of SnF_2, as well as of $SnF_2 \cdot N_2$, took place with a simultaneous growth of intensities of $SnF_2 \cdot (N_2)_2$ bands. Annealing of matrices with the ratio of N_2 : Ar = 1 : 36, which have no bands corresponding to free SnF_2, led to a lowering of intensities of the bands corresponding to $SnF_2 \cdot N_2$, and an increase of intensities of the bands corresponding to $SnF_2 \cdot (N_2)_2$. Upon increase in annealing time (up to 60 min) the intensities of the bands of $SnF_2 \cdot (N_2)_2$ also decreased. The transformations observed upon annealing of the matrix are explained by a diffusion of nitrogen molecules and their complexation with free SnF_2 (with formation of the complex $SnF_2 \cdot N_2$) or with $SnF_2 \cdot N_2$ (resulting in $SnF_2 \cdot (N_2)_2$), and this indicates the thermodynamic feasibility of these processes under the matrix conditions. More prolonged annealing resulted in transformation of complexes into oligomers transparent in the middle IR region, which in turn indicates lability of the complexes.

The fourth species that absorbs in the region considered is difluorostannylene dimer. The position of its absorption band, unlike the bands corresponding to other compounds observed in the matrix, shifted gradually towards lower wave numbers upon an increase in N_2 concentration in the matrices (see Table 1). Upon annealing of the matrix with the ratio N_2 : Ar = 1 : 36 the band of the dimer (578 cm^{-1}) transformed into two not fully resolved bands with maxima at 580 and 571 cm^{-1}. The first belongs evidently to the $(SnF_2)_2$ molecule surrounded exclusively by Ar atoms, and the second corresponds to the wave number observed in matrices containing ≥20% of dinitrogen. Because under the same conditions monomeric SnF_2 was present only as complexes with dinitrogen, the formation of large dimer molecules not bound to dinitrogen contradicts the assumption of a specific interaction (complexation) of dinitrogen with the dimer. Nevertheless, this fact agrees with the assumption that the shift of the absorption band of the dimer is a result of nonspecific interaction only. Indeed, formation of microcrystals could take place upon annealing, which consist preferentially of Ar, or, on the contrary, are significantly enriched in N_2. An inclusion of $(SnF_2)_2$ into either microcrystals could explain the appearance of the two absorption maxima. The smooth shift of the absorption band maximum of $(SnF_2)_2$ upon increase in N_2 concentration also indicates the absence of stable dinitrogen complexes of a fixed composition. Thus, the shift of $(SnF_2)_2$ absorption band is due to nonspecific matrix environment effects.

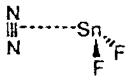
A decrease in intensity of the $(SnF_2)_2$ band took place only upon long-term annealing, which is caused by a small mobility of this polyatomic molecule in an annealed matrix. Additionally, some quantities of $(SnF_2)_2$ were formed under this conditions as a result of interaction of two molecules of monomeric SnF_2 (or its dinitrogen complexes) in the process of diffusion upon annealing.

Another compound, present in the matrices in noticeable quantities, was SiF_4,[36] characterized by the band of Si—F bond stretching vibrations (1027 cm^{-1}). Even in a N_2 : Ar mixture of composition 1 : 206 a shoulder arose at 1022 cm^{-1} on the band at 1027 cm^{-1}. Upon increase of N_2 concentration in the matrix the intensity of absorption at 1027 cm^{-1} decreases and the band at 1022 cm^{-1} grew. In the matrix containing 20% of dinitrogen and in the pure dinitrogen matrix only the band at 1022 cm^{-1} with low-frequency satellites from silicon isotopes was present. Appearance of the band at 1022 cm^{-1} even at low concentrations of N_2 allows one to assign it to a $SiF_4 \cdot N_2$ complex of the simplest composition 1 : 1, with a pentacoordinated Si atom, analogous to previously studied complexes of SiF_4 with amines.[46,47]

We found no bands which could be assigned to the $SiF_4 \cdot (N_2)_2$ complex.

Previously,[26] the complexes $SnCl_2 \cdot N_2$ (ν_3 329.9 and 326.7 cm^{-1}), $SnCl_2 \cdot (N_2)_2$ (ν_3 326.1 and 322.3 cm^{-1}) and $PbF_2 \cdot N_2$ (ν_1 526.6 and ν_3 502.2 cm^{-1}) were obtained in the Ar matrix and characterized by IR spectroscopy. The shifts of stretching vibration frequencies in CAs upon their complexation with N_2 relative to that of free CAs for $SnCl_2$ are equal to 1 and 1.3% (complex of composition 1 : 1), and 2.3 and 2.4% (complex of composition 1 : 2), and for PbF_2 they are equal to 1 and 1% (complex of composition 1 : 1).[26] With the complexes observed in this work the relative shifts of stretching vibration frequencies are equal to 0.8 and 1.1% for $SnF_2 \cdot N_2$, and 1.7 and 2.5% for $SnF_2 \cdot (N_2)_2$. Thus, complexation with N_2 influences the frequencies of SnX_2 (X = F, Cl) and PbF_2 in approximately the same degree. Thus, aforementioned complexes of the same composition (1 : 1 or 1 : 2) are apparently close in strength.

Based on general considerations on possible orbital and electrostatic interactions of carbene analogs with dinitrogen, the following probable configurations (**1**—**4**) of $SnF_2 \cdot N_2$ complex were considered:



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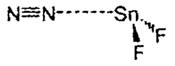

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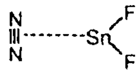

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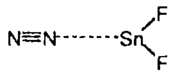

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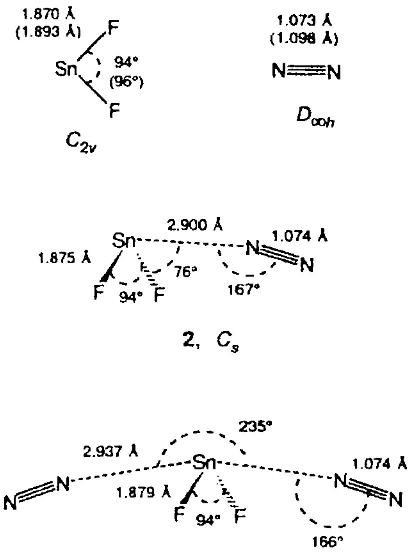
The structures **1** and **2** could be stabilized by interaction of the lowest unoccupied p-MO (LUMO) of the carbene analog with the occupied π-MO (p,π-interaction) and, respectively, with the lone electron pair of the N_2 molecule (p,n-interaction). Analogously, the structures **3** and **4** correspond to σ,π- and σ,n-interactions of σ-MO of the carbenic center. Earlier,[15,16] we have shown that interaction of SnF_2 with the triple C≡C bond of hept-1-yne results in the formation of a type **1** complex stabilized by p,π-interactions.



2, C_s

5, C_{2v}

Fig. 2. Main geometric parameters of PES stationary points for SnF_2+N_2 and SnF_2+$2N_2$ systems calculated by the *ab initio* method in the 3-21G(d2) basis. The symmetry group is presented beside the structure number. Experimental values for N_2 [48] and SnF_2 [49] are given in parentheses.

The results of the *ab initio* HF/3-21G(d2) calculations of the potential energy surface (PES) of the SnF_2+N_2 system show that there is only one sufficiently deep minimum corresponding to configuration **2** (Fig. 2).

Since according to the calculations structures **1**, **3** and **4** were found to be unstable in studies of $SnF_2 \cdot (N_2)_2$ complex we considered only the structure **5** constructed by analogy to **2** with two nitrogen molecules placed symmetrically relatively to CA and coordinated at its LUMO. Structure **5** was found to be a local minimum on the PES of SnF_2+$2N_2$ system (see Fig. 2).

SnF_2 complexation energies with one and two nitrogen molecules, calculated with corrections for correlation effects, zero point energy (ZPE), and basis set superposition error (BSSE), are equal to 4.6 and 8.9 kcal mol^{-1}, respectively (Table 2). One should note that the binding energies of the first (4.6 kcal mol^{-1})

Table 2. *Ab initio* calculated energies *(E)* and dipole moments (μ) of N_2, SnF_2, and complexes **2** and **5**

Structure	*E* (HF)	*E* (MP2)	Δ*E* (HF)	Δ*E* (MP2)	Δ*E* (MP2) + *ZPE* + + *BSSE*	μ/D
	au		kcal mol^{-1}			
N_2	−108.42595	−108.72214				0.00
SnF_2 [11]	−6194.75221	−6195.18141				2.38
$SnF_2 \cdot N_2$	−6303.18644	−6303.91605	5.2	7.8	4.6	2.26
$SnF_2 \cdot 2N_2$	−6411.61990	−6412.64976	9.9	15.1	8.9	1.57

Table 3. Calculated vibrational frequencies of SnF_2, N_2,* and complexes **2** and **5**

SnF_2		SnF_2+N_2 (**2**)		SnF_2+2N_2 (**5**)	
Symmetry	ν_{calc}	Symmetry	ν_{calc}	Symmetry	ν_{calc}
				A_1	2756
		A'	2757	B_2	2756
A_1	749	A'	742	A_1	736
B_2	730	A''	723	B_1	717
A_1	251	A'	253	A_1	254
		A'	151	B_2	161
		A''	140	A_2	143
		A'	103	A_1	132
		A'	53	B_1	127
		A''	41	B_2	104
				A_1	90
				B_2	59
				A_2	45
				B_1	23
				A_1	23

* For N_2, the calculated value is 2743 cm^{-1} and the experimental one is 2328 cm^{-1} (from the Raman spectra).

and the second (4.3 kcal mol^{-1}) N_2 molecules differ little. Yet, the attachment of the second N_2 molecule results in a significant (by 0.037 Å) lengthening of $Sn\cdots N$ distances.

A comparison of calculated data on the structures of SnF_2, N_2, **2**, and **5** shows that complexation results in small lengthening of the Sn—F bonds (by 0.005 Å in **2** and 0.009 Å in **5**), but the lengths of the N≡N bonds and the valence angle F—Sn—F do not change in a significant degree. The calculations overestimate significantly the frequencies of valence vibrations of SnF_2 and N_2 (Table 3), but reproduce well the frequency shifts on formation of complexes with one and two N_2 molecules. The quasi-additivity of frequency shifts and the somewhat large shift of the antisymmetric B_2 vibration of SnF_2 molecule on going from complex of 1 : 1 composition to 1 : 2 complex are correctly reproduced. The calculations indicate a small polarization of the N_2 molecules in complexes **2** and **5**, resulting in nonzero intensities of the N≡N absorption band in IR spectrum. However, these effects are too small to be observed under our experiment conditions.

The calculations predict the transfer of electron density from nitrogen molecules to SnF_2, resulting in a lowering of the dipole moment of SnF_2 (see Table 2), small (by 0.1 D) in structure **2**, and significant (by 0.8 D) in structure **5**. The dipole moment is the only characteristic that changes in a non-additive manner on attachment of the second nitrogen molecule. The values of such characteristics as complexation energy, Sn—F bond length changes, and shifts of SnF_2 stretching vibration frequencies (see Table 3) in complex **5** with two N_2 molecules are approximately two times larger than in complex **2** with one N_2 molecule.

The possibility of SnF_2 to undergo p,n-interactions is fully realized in complex **5**, and upon addition of other N_2 molecules their interaction with SnF_2 should result in structures of types **1**, **3**, or **4**, which, as our calculations on the SnF_2+N_2 system have shown, are unlikely to result in a noticeable stabilization. This explains why increasing the dinitrogen concentration and going to a pure dinitrogen matrix do not result in additional bands that correspond to $SnF_2\cdot(N_2)_x$ complexes with $x > 2$. Additionally, the dipole moment of complex **5** is essentially smaller than that of free SnF_2, which also lowers its possibility to bind additional N_2 molecules as a result of electrostatic interactions.

The example of SnF_2 shows that formation of a type **2** complex with one N_2 molecule by a carbene analog practically does not affect its interaction with the second N_2 molecule. This means that despite the relatively high stability of complex **2**, its formation does not change dramatically the reactivity of SnF_2.

As was found previously[50] in the case of the $SnF_2+C_2H_2$ system, cycloaddition to a triple N≡N bond is energetically unfavorable, and according to our calculations the three-membered cycle SnF_2N_2 is unstable.

Thus, one can conclude that complexation with various types of compounds at low temperatures is a very characteristic reaction[20] of dinitrogen. Therefore, use of N_2 as a matrix material is undesirable in studies of molecules having Lewis acidity.

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