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Stable Hexacoordinated Neutral Complexes between Silyl Halides and Two Water or Two Ammonia Molecules: SiX_4Y_2 (X = H, F, Cl; Y = H_2O, NH_3)

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Potential energy surfaces for $SiH_{4-n}Hal_n + 2NH_3$ (**I**) and $SiH_nHal_{4-n} + 2H_2O$ (**II**) systems ($n = 2, 4$; Hal = F, Cl) were explored using the B3LYP and MP2 methods with 6-311+G(d,p) and DZP+diff basis sets in search of stable tightly bound complexes with hexacoordinate silicon. Despite discrepancies in values of the complexation energies, all methods employed predict a similar order of stability of isomers. In contrast to monohalosilanes, where tight complexes are metastable, the energies of all low-entropy complexes in **I** are below those of the reactants. However, only for the SiH_2Cl_2, SiF_4, and $SiCl_4$ complexes were the tight structures found to be global minima. The predicted SiN bond lengths in these species are in a good agreement with experimentally determined parameters for complexes of these three halosilanes with pyridines. In the water systems (**II**), the tight octahedral complexes (with water molecules in axial and equatorial positions) are predicted to lie below reactants only for the $SiF_4 + 2H_2O$ system. A loosely bound complex is the global minimum for this system, as well as for complexes of SiH_2F_2 and SiH_2Cl_2 with two water molecules. No minimum with energy below those of the reactants was found for the $SiCl_4 + 2H_2O$ system.

Introduction

In a previous study,[1] we found that the hexacoordinate complexes of silyl fluoride and chloride with two ammonia or water molecules exist as local minima on the potential energy surfaces of these systems, as proposed from analyses of the kinetics of the racemization and hydrolysis reaction of halosilanes.[2−7] However, these metastable minima tend to convert to transition states in going from SiH_3F to SH_3Cl and from ammonia to water. Since hydrogen f halogen substitution in silyl halides increases the positive charge on silicon, one may suppose that this substitution may lead to more stable hexacoordinate complexes. Indeed, stable neutral complexes of SiF_4 with two ammonia molecules[8] and with two water molecules[9] have been characterized. Infrared spectra of different halosilanes with bases, including two pyridine and trimethylamine molecules, have been reported,[10−12] but the complexity of the vibrational spectra prevented any definitive conclusions about their structure. The first X-ray diffraction studies of molecular crystals formed as complexes of two pyridine molecules with SiF_4[13] and $SiCl_4$[14] have shown that these complexes have a centrosymmetric octahedral configuration with the pyridine molecules in axial positions. Recently, this structure was confirmed by X-ray studies of complexes of SiH_2Cl_2[15,16] and silicon tetrahalides with methyl and dimethylpyridines.[17,18] All these structures and those described in our previous study[1] are characterized by octahedral coordination of the H, Hal, O, and N atoms around silicon and comparatively short Si−N bonds (ca. 2 Å).

However, no structural information for such complexes with simpler bases such as ammonia and water exists. The aim of this study was to determine whether such complexes are stable for di- and tetrahalosilanes and to provide structural and vibrational spectroscopic information for their future identification by experimental methods.

Theoretical Methods

The computational methods employed in this work included some description of electron correlation. These were the hybrid DFT method, combining Becke's three-parameter exchange functional[19] with the LYP correlation functional[20] (B3LYP) and second-order Moller−Plesset perturbation theory (MP2)[21] as implemented in the GAUSSIAN 94 program.[22] The basis sets were the standard 6-311+G(d,p) set and the basis set constructed from the double-ζ set of Huzinaga, Hay, and Dunning, [23]namely, Si and Cl (11s7p/6s4p), N, O, and F (9s5p/4s2p), and H (4s/2s). The latter basis set was augmented with one set of *d* polarization functions with [$\alpha_d(Si) = 0.5$, $\alpha_d(Cl) = 0.75$, $\alpha_d(N) = 0.8$, $\alpha_d(O) = 0.85$ $\alpha_d(F) = 1.00$] and p polarization functions at H, as well as one set of diffuse functions for H, F, N, and O [$\alpha_s(H) = 0.048273$, $\alpha_p(F) = 0.0826$, $\alpha_p(N) = 0.048$, $\alpha_p(O) = 0.059$] and two sets of diffuse functions for Cl [$\alpha_s(Cl) = 0.05048$ and $\alpha_p(Cl) = 0.05087$]. This basis set is designated as DZP+diff. At the MP2/ DZP+diff level, the core 1s-like orbitals and corresponding virtuals were excluded from the correlation treatment for Si and Cl.

The "tight" option as a criterion for optimization was used in GAUSSIAN, and in some cases, in which the low accuracy of the default integration grid prevented the B3LYP optimization convergence and/or calculated vibrational frequencies were very low (below 10 cm^{-1}), the larger integration grid of 99 radial shells and 434 angular points in each shell (99434) was used. Vibrational frequencies were evaluated for all stationary points at all theory levels. Zero-point vibrational energy (ZPVE) corrections, thermal corrections, and entropies cited in the tables refer to those obtained by B3LYP/ DZP+diff, since vibrational frequencies obtained by this method are closest to the available experimental values.

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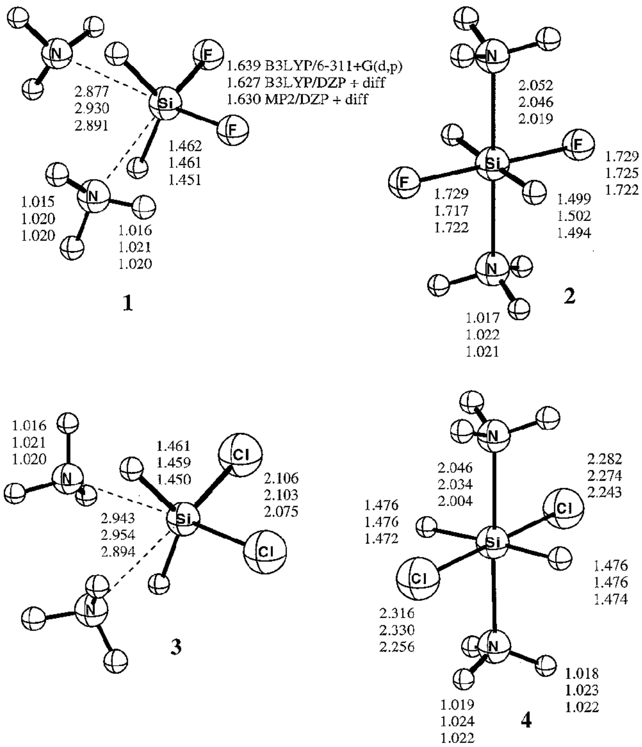

Figure 1. Equilibrium structures (bond lengths in Å) of energy minima for the SiH_2F_2 + $2NH_3$ and SiH_2Cl_2 + $2NH_3$ systems.

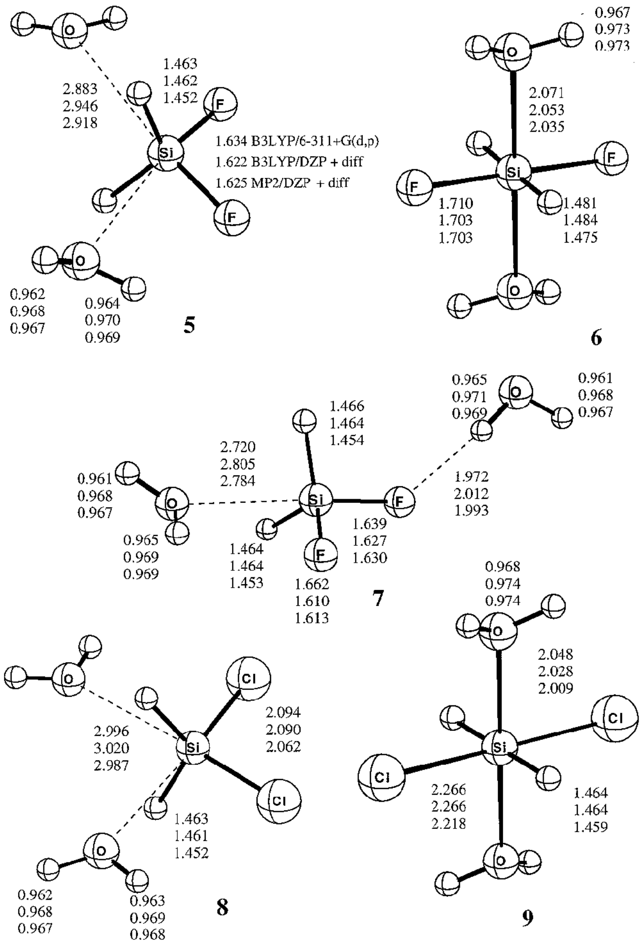

Figure 2. Equilibrium structures (bond lengths in Å) of energy minima for the SiH_2F_2 + $2H_2O$ and SiH_2Cl_2 + $2H_2O$ systems.

Results and Discussion

A. Complexes of Two Ammonia Molecules with Difluoro and Dichlorosilanes. Two types of complexes have been found for the monohalosilanes: one with large SiN separations (ca. 2.5 Å for the backside position and 3.5 Å for the frontside position) and the tight octahedral complex (both SiN bonds ca. 2.0 Å).[1] Similar structures are found as minima on the potential energy surface (PES) of the SiH_2Hal_2 + $2NH_3$ (Hal = F,Cl) systems (structures **1**−**4**, Figure 1). However, in contrast to the monohalosilanes, the presence of two halogen atoms provides the possibility for both ammonia molecules to reside in the position backside to the halogen atoms. This structure of C_{2v} symmetry (**1**) is the global minimum for the SiH_2F_2 + $2NH_3$ system with all theory levels employed (Table 1). Although the other energy minimum, corresponding to the tightly bound octahedral structure with two ammonias in axial positions (complex **1** may be also regarded as a distorted octahedron with two hydrogens in axial positions), gains stability (ca. 10 kcal/mol) compared to monofluorosilane, it still remains the second most stable isomer. Complex **2** is a minimum within the C_{2h} point group, with ammonia molecules bisected by the SiH_2N_2 plane at B3LYP/6-311+G(d,p) and MP2/DZP+diff, but at B3LYP/DZP+diff, the symmetry is lowered to C_2 by the rotation of the ammonia molecules out of the plane. Both **1** and **2** have positive complexation energies (E_e below reactants) at all levels of theory, but while 1 has negative ΔH_{298} (ΔE_e +

TABLE 1: Total Energies (E_e, in Hartrees) for the Reactants in the SiH_2X_2 + $2NH_3$ and SiH_2X_2 + H_2O (X = F, Cl) Systems and Relative Energies (with Respect to Reactants), as well as Zero-Point Vibrational Energy (ΔZPVE) and Thermal Corrections (ΔTHERM) for These Complexes[a]

	B3LYP		MP2	B3LYP	
	6-311+G(d,p)	DZP+diff	DZP+diff	DZP+diff	
complexes	E_e (ΔE_e)	E_e (ΔE_e)	E_e (ΔE_e)	ΔZPVE	ΔTHERM
SiH_2F_2 + $2NH_3$	−603.75446	−603.72390	−602.49493	0	0
1	−9.7	−8.4	−11.6	2.7	2.9
2	−6.5	−4.5	−9.2	6.1	4.7
SiH_2Cl_2 + $2NH_3$	−1324.43040	−1324.33154	−1322.48394	0	0
3	−7.4	−7.4	−11.4	2.6	3.0
4	−11.7	−13.7	−16.4	6.6	6.3
SiH_2F_2 + $2H_2O$	−643.50610	−643.47642	−642.19045	0	0
5	−8.5	−7.4	−10.0	2.6	2.8
6	11.4	13.8	11.5	5.2	3.9
7	−8.4	−7.2	−9.2	2.3	2.8
SiH_2Cl_2 + $2H_2O$	−1364.18204	−1364.08406	−1362.17946	0	0
8	−6.5	−6.4	−9.6	2.3	2.7
9	9.4	8.4	9.0	5.2	4.0

[a] Note that ΔTHERM includes ΔZPVE.

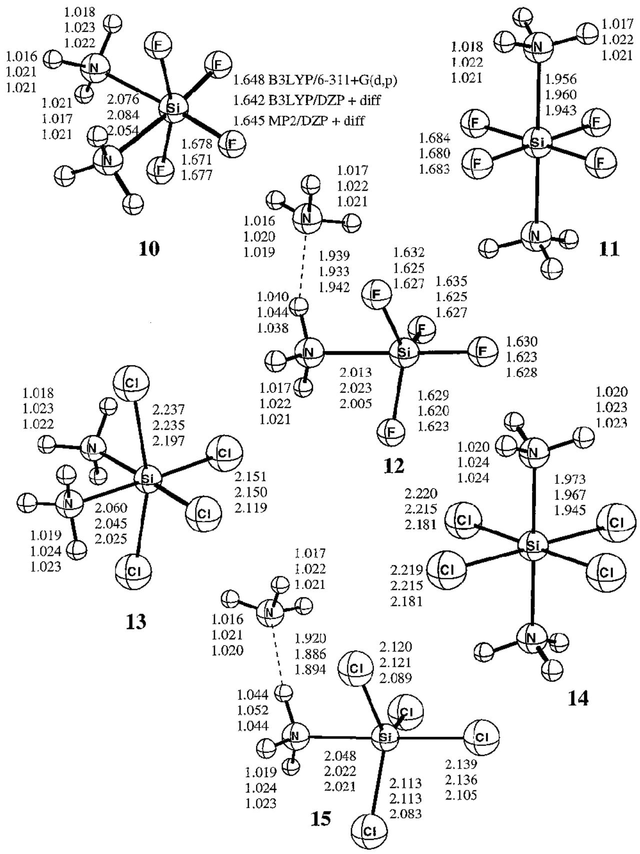

Figure 3. Equilibrium structures (bond lengths in Å) of energy minima for the $SiF_4 + 2NH_3$ and $SiCl_4 + 2NH_3$ systems. The geometry for 10 optimized with the MP2/DZP+diff method has C_s symmetry, and the SiN bond lengths are 2.050 and 2.057 Å. The averaged SiN bond length is shown.

THERM) at all levels of theory, this value at the B3LYP/DZP+diff for complex **2** lies above reactants. (Table 1).

Similar structures have been found to be the energy minima for SiH_2Cl_2. Note that in the $SiH_3Hal + 2NH_3$ (Hal = F,Cl) system structures of the tight complexes for Hal = F and Cl differ significantly: the fluorine complex has the octahedral arrangement of atoms around Si, while the chlorine analogue has a structure close to trigonal bipyramidal.[1] In contrast to this, both **2** and **4** have structures close to octahedral. The complex **4**, however, appears to be a transition state in the C_{2h} point group; however, a minimum at the B3LYP/6-311+G(d,p) and B3LYP/DZP+diff levels of theory was found for C_{2v} symmetry. At the MP2/DZP+diff level, rotation of the ammonias lowers the symmetry to C_s.

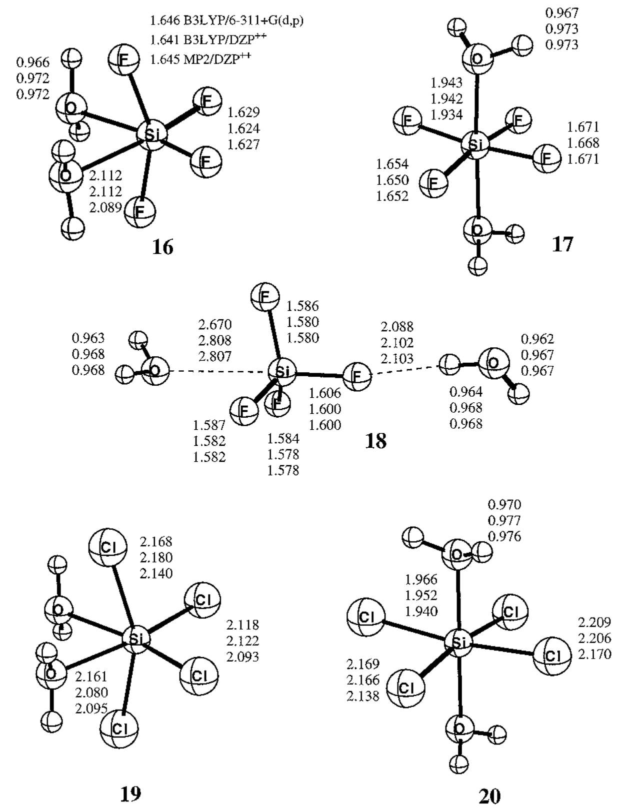

Figure 4. Equilibrium structures (bond lengths in Å) of energy minima for the $SiF_4 + 2H_2O$ and $SiCl_4 + 2H_2O$ systems.

However, the important difference between **2** and **4** is that the latter complex is the global minimum on the $SiH_2Cl_2 + 2NH_3$ PES. The complexation energy of **4** (16.4 kcal/mol, MP2/DZP+diff, Table 1) exceeds that of the loose complex **2** by 5 kcal/mol. This is in agreement with the fact that the stable complexes between SiH_2Cl_2 and two base molecules (pyridines) were characterized experimentally.[15,16] The SiN bond lengths found in the X-ray diffraction studies of these complexes (1.969

TABLE 2: Total Energies (E_e, in Hartrees) for the Reactants in the $SiX_4 + 2NH_3$ and $SiX_4 + H_2O$ (X = F, Cl) Systems and Relative Energies (with respect to reactants), as Well as Zero-Point Vibrational Energy (ΔZPVE) and Thermal Corrections (ΔTHERM) for Complexes[a]

	B3LYP		MP2	B3LYP	
	6-311+G(d,p)	DZP+diff	DZP+diff	DZP+diff	
complexes	E_e (ΔE_e)	E_e (ΔE_e)	E_e (ΔE_e)	ΔZPVE	ΔTHERM
$SiF_4 + 2NH_3$	−802.43405	−802.40734	−800.76703	0	0
10	−19.4	−15.2	−20.5	6.1	4.5
11	−27.3	−22.4	−28.1	6.6	4.8
12	−21.1	−18.9	−22.1	5.1	3.9
$SiCl_4 + 2NH_3$	−2243.77668	−2243.61156	−2240.74078	0	0
13	−5.2	−7.0	−14.1	6.7	5.1
14	−12.2	−14.4	−20.3	6.6	5.1
15	−9.9	−11.5	−16.3	5.2	4.1
$SiF_4 + 2H_2O$	−842.18569	−842.15986	−840.46255	0	0
16	−6.8	−3.1	−6.2	5.3	3.7
17	−1.4	−2.8	−0.2	5.7	3.7
18	−6.7	−5.3	−7.6	2.1	2.7
$SiCl_4 + 2H_2O$	−2283.52832	−2283.36408	−2280.43630		
19	11.0	10.1	6.4	5.1	3.6
20	17.3	15.9	14.1	5.2	3.5

[a] Note that ΔTHERM includes ΔZPVE.

TABLE 3: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Equilibrium Bond Lengths (in Å) for Di- and Tetrahalosilanes Compared to Experimental Data

		B3LYP		MP2		
symmetry and type of vibration		6-311+G(d,p)	DZP+diff	6-311+G(d,p)	DZP+diff	expt
			SiH_2F_2			
A_1	SiH_2 s-str	2299	2304	2392	2409	2246[a]
	SiH_2 scis	981	998	1023	1046	982
	SiF_2 s-str	833	848	852	855	870
	SiF_2 scis	305	311	316	317	322
A_2	SiH_2 twist	725	738	757	771	730
B_1	SiH_2 a-str	2315	2317	2402	2418	2250
	SiH_2 rock	705	714	738	733	730
B_2	SiH_2 wag	960	977	994	1007	981
	SiF_2 a-str	881	893	909	910	903
	r (Si−H)	1.471	1.470	1.461	1.458	1.471[b]
	r (Si−F)	1.614	1.605	1.608	1.607	1.577[b]
			SiH_2F_2			
A_1	SiH_2 s-str	2281	2294	2375	2387	2224[c]
	SiH_2 scis	957	966	995	1007	954
	$SiCl_2$ s-str	506	510	540	544	527
	$SiCl_2$ scis	186	185	196	195	188
A_2	SiH_2 twist	712	720	745	755	710
B_1	SiH_2 a-str	2300	2311	2389	2398	2237
	SiH_2 rock	594	598	624	624	602
B_2	SiH_2 wag	882	893	930	944	876
	$SiCl_2$ a-str	563	569	602	612	590
	r (Si−H)	1.473	1.470	1.462	1.460	1.480[b]
	r (Si−Cl)	2.065	2.064	2.041	2.039	2.033[b]
			SiF_4			
A_1	s-str	763	774	779	778	800[c]
E	d-def	252	252	261	258	268
F_2	d-str	997	1011	1012	1016	1032
	d-def	367	373	377	380	389
	r (Si−F)	1.584	1.580	1.577	1.581	1.552[b]
			$SiCl_4$			
A_1	s-str	405	408	435	436	424[c]
E	d-def	147	145	156	154	150
F_2	d-str	599	609	639	647	621
	d-def	220	219	231	229	221
	r (Si−Cl)	2.043	2.041	2.019	2.019	2.017[b]

[a] Ref 24. [b] Ref 25. [c] Ref 26.

Å for pyridine,[15] 1.974 Å for methylpyridine,[15] and 2.016 Å for dimehylpyridine[16]) are close to the SiN distance (2.004 Å, MP2/DZP+diff) predicted for 4 in the present study. The experimental SiCl bond lengths (2.288 Å for pyridine,[15] 2.292 Å for methylpyridine,[15] and 2.134 Å for dimethylpyridine[16]) are also in good agreement with our predictions (see 4 in Figure 1).

B. Complexes of Two Water Molecules with Difluoro and Dichlorosilanes. In addition to the two types of the complexes described in the previous section in which two nucleophiles (in the current case, water molecules) are in positions backside to the fluorine atoms (**5**) and in the axial octahedral positions (**6**), one more minimum was found in the $SiH_2F_2 + 2H_2O$ system, the structure of which is analogous to the global minimum structures for monofluorosilane. This isomer **7** is formed by one water attached to silicon in the backside position of one of the fluorine atoms and the second water molecules bound to the same fluorine by a hydrogen bond (Figure 2). This structure has practically the same complexation energy as that of the symmetric complex **5** (Table 1). Both these complexes are ca. 10 kcal/mol below reactants, while the octahedral complex is at roughly the same energy above them (Table 1).

The complex analogous to **7** was not located for the $SiH_2Cl_2 + 2H_2O$ system, but the symmetric loose complex **8** and tight octahedral structure **9** were found as minima. Similar to the $SiH_2F_2 + 2H_2O$ system, the loose complex **8** is the global minimum with complexation energy 10 kcal/mol, and the tight complex **9** is predicted to lie 9 kcal/mol above reactants (Table 1).

C. Complexes of Two Ammonia Molecules with Tetrafluoro and Tetrachlorosilanes. Three energy minima are found in the $SiF_4 + 2NH_3$ system. The complex **10** has a structure similar to the global minimum for the difluorosilane system, i.e., 1; however the complex (**10**) has substantially stronger SiN bonds (Figure 3). This structure may be described as an octahedron with two NH_3 groups in equatorial positions. The symmetry of the heavy atom skeleton is C_{2v}, but the overall symmetry of the minimum is reduced to C_2 due to rotation of the NH_3 groups.

In contrast to the $SiH_2F_2 + 2NH_3$ system, the structure with two ammonia molecules in equatorial positions in the $SiF_4 + 2NH_3$ system is not a global minimum (nor even the second most stable isomer). The global minimum (Table 2) corresponds to the complex **11** with two ammonias in axial positions, and the second most stable isomer is the tetrafluorosilane-ammonia complex with the second ammonia molecule hydrogen bonded to the first (**12**, Figure 3).

The three complexes in the $SiF_4 + 2NH_3$ system have the highest complexation energies among the systems studied. However, some discrepancy in the estimates of this complexation energy exists between the B3LYP/6-311+G(d,p) and MP2/DZP+diff methods on one hand and B3LYP/DZP+diff on another: the latter systematically gives lower energies by several

TABLE 4: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and IR Intensities (in km mol^{-1}) of the Stable Hexacoordinate Complex $SiH_2Cl_2{\cdot}2NH_3$ (4) Predicted at the B3LYP/DZP+Diff Level of Theory

ω	symmetry	description
3582 (0)	A_2	NH_3 str
3582 (80)	B_1	NH_3 str
3571 (87)	A_1	NH_3 str
3571 (3)	B_2	NH_3 str
3447 (2)	A_1	NH_3 str
3446 (19)	B_2	NH_3 str
2243 (3)	B_1	SiH_2 a-str
2164 (0)	A_1	SiH_2 s-str
1646 (0)	A_2	NH_3 d-def
1645 (59)	B_1	NH_3 d-def
1638 (49)	A_1	NH_3 d-def
1635 (2)	B_2	NH_3 d-def
1279 (0)	A_1	NH_3 s-def
1275 (501)	B_2	NH_3 s-def
1028 (0)	A_2	SiH_2 a-def (in-plane)
1021 (226)	B_2	SiH_2 s-def (in-plane)
968 (568)	A_1	SiH_2 a-def (out-of-plane)
921 (1)	B_1	SiH_2 s-def (out-of-plane)
789 (50)	B_1	NH_3 translation-like
745 (100)	A_1	NH_3 translation-like
698 (12)	B_2	NH_3 translation-like
613 (0)	A_2	NH_3 translation-like
448 (158)	B_2	NH_3 translation-like (SiN_2 a-str)
345 (0)	A_1	NH_3 translation-like (SiN_2 s-str)
286 (278)	A_1	$SiCl_2$ a-str
277 (0)	B_1	NH_3 rotation-like
229 (87)	A_1	$SiCl_2$ s-str
180 (1)	B_2	NH_3 rotation-like
162 (4)	A_1	NH_3 rotation-like
150 (16)	B_2	$SiCl_2$ def
150 (27)	B_1	NH_3 rotation-like
48 (0)	A_2	NH_3 rotation-like
44 (2)	B_1	NH_3 rotation-like

TABLE 5: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and IR Intensities (in km mol^{-1}) of the Stable Hexacoordinate Complex $SiF_4{\cdot}2NH_3$ (11) Predicted at the B3LYP/DZP+Diff Level of Theory

ω	symmetry	description
3595 (0)	A_g	NH_3 str
3595 (108)	A_u	NH_3 str
3592 (0)	A_g	NH_3 str
3592 (106)	A_u	NH_3 str
3470 (0)	A_g	NH_3 str
3469 (23)	A_u	NH_3 str
1650 (60)	A_u	NH_3 d-def
1651 (0)	A_g	NH_3 d-def
1639 (0)	A_g	NH_3 d-def
1636 (52)	A_u	NH_3 d-def
1300 (0)	A_g	NH_3 s-def
1295 (477)	A_u	NH_3 s-def
901 (397)	A_u	NH_3 translation-like
900 (396)	A_u	NH_3 translation-like
766 (0)	A_g	NH_3 translation-like
765 (0)	A_g	NH_3 translation-like
730 (36)	A_u	SiF_4 d-str
729 (35)	A_u	SiF_4 d-str
641 (0)	A_g	SiF_4 a-str
596 (370)	A_u	NH_3 translation-like (SiN_2 a-str)
522 (0)	A_g	SiF_4 s-str
428 (80)	A_u	SiF_4 out-of-plane def
408 (0)	A_g	SiF_4 in-plane def
388 (0)	A_g	NH_3 translation-like (SiN_2 s-str)
385 (11)	A_u	SiF_4 in-plane def
385 (11)	A_u	SiF_4 in-plane def
272 (0)	A_g	NH_3 rotation-like
272 (0)	A_g	NH_3 rotation-like
198 (9)	A_u	SiF_4 out-of -plane def
192 (32)	A_u	NH_3 rotation-like
190 (24)	A_u	NH_3 rotation-like
13 (0)	A_g	NH_3 rotation-like
11 (1)	A_u	NH_3 rotation-like

kilocalories per mole (Table 2). There exists an experimental estimate of enthalpy of formation of this complex from the dissociation pressure measurements in the 352−422 K temperature range,[8] namely, 18.2 kcal/mol. The ΔH^0_{298} value of 17.6 kcal/mol obtained by B3LYP/DZP+diff is in good agreement with the experimental estimate.

Analogously, three isomers were found for the $SiCl_4 + 2NH_3$ system, and the order of their stability is the same as that for the tetrafluorosilane system. The most stable isomer is the tightly bound octahedral complex with ammonias in axial positions **14**, the second isomer is the hydrogen bound complex **15**, and the third is the complex with ammonias in equatorial positions (**13**). Both **15** and **13** have comparatively short SiN bonds, but the SiN bond lengths in **14** are the shortest among chlorosilane−diammonia complexes. This is in agreement with the shortening of the experimental SiN bond lengths in going from SiH_2Cl_2 (2.016 Å with dimethylpyridine[16]) to $SiCl_4$ (1.984 Å with methylpyridine,[17] 1.990 Å with dimethylpyridine[18]).

D. Complexes of Two Water Molecules with Tetrafluoro and Tetrachlorosilanes. Similar to the difluorosilane system, three energy minima are found in the $SiF_4 + 2H_2O$ system (**16**−**18**, Figure 4). However, the substitution of two axial hydrogens in the pseudo octahedral complex **5** by fluorines leads to a substantial shortening of the equatorial SiO bonds from ca. 2.9 Å in **5** to ca. 2.1 Å in **16**. Complex **5** is the global minimum for the $SiH_2F_2 + 2H_2O$ system. The complex with two water molecules in equatorial positions was also claimed to be the most stable isomer in the tetrafluorosilane system in a previous theoretical study.[27] However, in the present study, complex **18** was located, not found by Ignatov et al.[27] Structure **18** is close in energy to **16** but becomes lower in energy than **16** at higher levels of theory (Table 2). As with its analogue in the difluorosilane system, **18** is built from one water molecule in the position backside to one of the fluorine atoms and with the second water molecule forming a hydrogen bond with the same fluorine (**16**, Figure 4).

The octahedral complex with water molecules in axial positions becomes more stable by 12 kcal/mol in going from di- (**6**) to tetrafluorosilane (**17**), but still the latter remains the third most stable isomer. Note that in the earlier study[27] of this system, the energy minimum for this complex was found only in the C_1 point group. In the present study, the more symmetric structure (C_2) is found to be the minimum. Nevertheless, **17** cannot be be considered a stable complex, since its ΔH_{298} value is above those of the reactants (Table 2). Isomers **16** and **18** have similar complexation energies, but the loose complex **18** has a substantially lower ZPVE and lower thermal corrections due to smaller perturbations of the reactant vibrational frequencies on complex formation (Table 2). While for **16** the Δ ZPVE is 5.3 kcal/mol and is comparable to the complexation energy (6.2 kcal/mol MP2/DZP+diff), Δ ZPVE for **18** is only 2.1 kcal/mol and is substantially lower than the complexation energy (7.6 kcal/mol MP2/DZP+diff). This allows us to predict that the only complex of SiF_4 with two water molecules which may be identified experimentally is complex **18**. Since this complex was not found in the theoretical study of Ignatov et al.[27] but only the tight complexes **16** and **17**, they rejected the possibility that any complex with two water molecules might give rise to the bands observed in the matrix isolation study. This conclusion was based on the fact that the predicted shifts of vibrational frequencies of the tight complexes are much greater than observed. However, these observed bands may belong to the loose complex **18**.

For the $SiCl_4 + 2H_2O$ system, only octahedral structures were found to be minima (**19** and **20**, Figure 4). The loose complex analogous to **18** in the fluorine system was not located, in

TABLE 6: Harmonic Theoretical Vibrational Frequencies (in cm^{-1}) and IR Intensities (in km mol^{-1}) of the Stable Hexacoordinate Complex $SiCl_4{\cdot}2NH_3$ (14) Predicted at the B3LYP/DZP+Diff Theory Level

ω	symmetry	description
3562 (0)	A_g	NH_3 str
3562 (114)	A_u	NH_3 str
3555 (0)	A_g	NH_3 str
3555 (108)	A_u	NH_3 str
3436 (0)	A_g	NH_3 str
3435 (40)	A_u	NH_3 str
1637 (46)	A_u	NH_3 d-def
1636 (0)	A_g	NH_3 d-def
1621 (0)	A_g	NH_3 d-def
1614 (52)	A_u	NH_3 d-def
1339 (0)	A_g	NH_3 s-def
1330 (492)	A_u	NH_3 s-def
861 (233)	A_u	NH_3 translation-like
860 (231)	A_u	NH_3 translation-like
798 (0)	A_g	NH_3 translation-like
797 (0)	A_g	NH_3 translation-like
562 (95)	A_u	NH_3 translation-like (SiN_2 a-str)
413 (0)	A_g	NH_3 translation-like (SiN_2 s-str)
404 (220)	A_u	$SiCl_4$ d-str
403 (222)	A_u	$SiCl_4$ d-str
299 (0)	A_g	$SiCl_4$ a-str
292 (64)	A_u	$SiCl_4$ out-of-plane def
254 (3)	A_u	NH_3 rotation-like
253 (3)	A_u	NH_3 rotation-like
246 (0)	A_g	NH_3 rotation-like
238 (0)	A_g	$SiCl_4$ s-str
237 (0)	A_g	NH_3 rotation-like
221 (0)	A_g	$SiCl_4$ in-plane def
182 (8)	A_u	$SiCl_4$ in-plane def
174 (11)	A_u	$SiCl_4$ in-plane def
116 (0)	A_u	$SiCl_4$ out-of-plane def
37 (6)	A_u	NH_3 rotation-like
12 (2)	A_g	NH_3 rotation-like

contrast to the case of the $SiH_2Cl_2 + 2H_2O$ system. Both **19** and **20** lie substantially higher than reactants with all methods employed (Table 2).

E. Vibrational Frequencies. The tight octahedral complexes with short SiN bonds have been found to be the global minima for the $SiF_4{\cdot}2NH_3$, $SiH_2Cl_2{\cdot}2NH_3$, and $SiCl_4{\cdot}2NH_3$ systems. This opens the possibility for future experimental characterization of these complexes. Since the most common tool for such characterization is vibrational spectroscopy, here we shall discuss the main features of the vibrational spectra of the silicon hexacoordinate species not described before.

First, we will compare the theoretical vibrational spectra of the halosilanes with experimental data in order to evaluate the reliability of our predictions. Comparing theoretical and experimental vibrational frequencies in Table 3, one may notice that each method employed has its drawbacks. Thus, MP2 substantially overestimates the frequencies of the SiH stretching and deformation (to a lesser extent) vibrations (the same is true also for NH and OH vibrations). The harmonic vibrational frequencies cannot be directly compared to experiment, and the experimental estimation of the harmonic experimental frequencies cannot can be done for such a complex systems. Thus, for the practical purpose of the prediction of spectra, the B3LYP method, which gives XH (X = Si,N,O) vibrations much closer to experimental values, should be preferred. Within this method, the 6-311+G(d,p) basis set better describes SiH vibrations but exhibits a poorer reproduction of the Si−Hal vibrations. Thus, among the theoretical methods employed, B3LYP/DZP+diff should be chosen for the best overall performance.

The vibrational spectra of the octahedral $SiF_4{\cdot}2NH_3$, $SiH_2Cl_2{\cdot}2NH_3$, and $SiCl_4{\cdot}2NH_3$ complexes predicted with the B3LYP/DZP+diff method are presented in Tables 4−6. The description of vibrational modes is based on a scheme in which the 33 vibrational degrees of freedom of the systems discussed are divided into 9 vibrations of the central planar halosilane moiety, 12 internal vibrations of the two ammonia molecules, and 12 degrees of freedom which were translations and rotations of the free ammonia molecules but become hindered in the complex. The stretching NH vibrations and degenerate deformations are not significantly perturbed with formation of the SiN bond (theoretical frequencies for the free ammonia molecule are 3622, 3488, and 1662 cm^{-1}); however, the lowest-frequency vibration, i.e., the symmetric deformation, dramatically changes its frequency in the complex (the theoretical value in ammonia 1018 cm^{-1} and the experimental 950 cm^{-1}). Upon the formation of the tight complexes, this deformation frequency of ammonia grow to 1275 and 1279 cm^{-1} in the $SiH_2Cl_2{\cdot}2NH_3$ complex, 1295 and 1300 cm^{-1} in $SiF_4{\cdot}2NH_3$, and 1330 and 1339 cm^{-1} in $SiCl_4{\cdot}2NH_3$. Since these vibrations have the greatest IR intensity and reside in the region of spectra free from SiH_2Cl_2, SiF_4, and $SiCl_4$ bands as well as from the NH_3 vibrations, they may be a reliable tool for the identification of the tightly bound hexacoordinated species in the $SiH_2Cl_2(SiCl_4) + NH_3$ systems.

Conclusions

(i) Among 20 energy minima found in the $SiH_{4-n}Hal_n + 2NH_3$ and $SiH_nHal_{4-n} + 2H_2O$ ($n = 2, 4$; Hal = F, Cl) systems, only three correspond to global minima characterized by the tight octahedral structure with nucleophiles in axial positions. These are the complexes of SiH_2Cl_2, SiF_4 ,and $SiCl_4$ with two ammonia molecules. Analogous complexes of these three molecules with pyridines were experimentally identified by X-ray diffraction methods and the SiN and SiCl bond lengths obtained in the present studies are in a good agreement with our predictions for ammonia complexes.

(ii) In the $SiH_2F_2 + 2NH_3$ system, the tight octahedral complex is stable (energy below reactants), but the global minimum corresponds to the loosely bound structure, which is more stable than the tight one by ca. 2 kcal/mol.

(iii) Within the $SiH_nHal_{4-n} + 2H_2O$ ($n = 2, 4$; Hal = F, Cl) systems, tightly bound complexes are stable only for $SiF_4 + 2H_2O$. In this system, complexes with water molecules both in axial and equatorial positions are local minima, although the global minimum corresponds to the loose complex.

(iv) The stable water complexes of SiH_2F_2 and SiH_2Cl_2 are also the loose structures, and both energy minima found in the $SiCl_4 + 2H_2O$ lie substantially higher than reactants at all methods employed.

(v) Specific features of the vibrational spectra of the tightly bound diammonia complexes, by which they may be distinguished from the loose structures, include the presence of two modes (one of them with very high IR intensity) in the 1200−1300 cm^{-1} frequency range, which is free from features due the isolated reactant bands.

(vi)The relative stabilities of the tight octahedral complexes are influenced by two factors: (a) the basicity of the molecules in axial positions and (b) the energy difference between the tetrahedral and planar structures of SiH_2Hal_2 and $SiHal_4$. The effect of the former is obvious: the stronger base, i.e., ammonia, gives more stable complexes. The predicted increase of stability in going from $SiH_2F_2{\cdot}2NH_3$ to $SiH_2Cl_2{\cdot}2NH_3$ and its decrease from $SiF_4{\cdot}2NH_3$ to $SiCl_4{\cdot}2NH_3$ may be explained by the second factor. In the SiH_2Hal_2 molecules, the planarization energy is less for Hal = Cl, while in $SiHal_4$, the inversion barrier is higher for chlorine, due to the increased repulsion of the bulkier chlorine atoms in the planar form.

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