Inversion of ν(MHal) stretching frequencies in the spectra of dihalosilylenes, -germylenes, -stannylenes, and their complexes with Lewis bases*

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The vibrational spectra of tetravalent metal halides (M = Si, Ge, Sn) and the corresponding dihalocarbene analogs $M^{II}Hal_2$, obtained by the authors, and the relevant published data are compared. The spectra of the $M^{II}Hal_2$ species exhibit inversion of the M—Hal stretching frequencies ($\nu^s(M^{II}Hal) > \nu^{as}(M^{II}Hal)$). This can be used for analytical purposes and allows one to distinguish between the spectra of the M^{IV} and M^{II} halides. The IR and Raman spectra of the complexes of dihalogermylenes and -stannylenes with triphenylphosphine and 1,4-dioxane also exhibit inversion of the ν(MHal) stretching frequencies. This confirms the conclusion drawn earlier based on the analysis of the geometric parameters and reactivities of the complexes in question that the divalent state of the M atom in these species is retained.

Key words: dihalosilylenes, -germylenes, and -stannylenes, donor-acceptor complexes, vibrational spectra, metal—halogen stretching frequencies.

Carbene analogs (CAs) of the MRR′ (M = Si, Ge, Sn) type are highly reactive intermediates. The vibrational (IR and Raman) spectra of such species are usually recorded under low-temperature matrix isolation conditions. The results obtained for dihalogen-substituted CAs ($M^{II}Hal_2$) have been reviewed.**[1—3]** Analysis of these data and comparison with the spectra of the di-, tri-, and tetrahalides (R_2MHal_2, $RMHal_3$, and $MHal_4$, respectively; Hal = Cl, Br)**[4—6]** suggest that the spectra of all $M^{II}Hal_2$ species studied exhibit inversion of the ν(MHal) stretching frequencies. Indeed, the frequencies of the symmetrical stretching metal—halogen (ν^s(MHal)) vibrations in the spectra of the $R_nM^{IV}Hal_{4-n}$ (n = 0—2) molecules are always lower than the frequencies of the antisymmetrical vibrations (ν^{as}(MHal)). At the same time, the reverse is observed in the spectra of dihalogen-substituted CAs, namely, $\nu^s(M^{II}Hal) > \nu^{as}(M^{II}Hal)$. Apparently, this inversion characterizes specific features of the divalent state of the M atom (*via* the off-diagonal force constant of the M—Hal interaction, which changes its sign on going from M^{IV} to M^{II} halides).

It is well known that the central atoms M in the singlet CAs have vacant p_z-orbitals; because of this, CAs can act as Lewis acids and form rather stable complexes with Lewis bases. Reduced reactivity of such complexes compared to free CAs allows them to be used as CA sources in various reactions. For instance, a 1 : 1 complex of dichlorogermylene with dioxane ($Cl_2Ge\cdot C_4H_8O_2$)**[7,8]** has found wide application in organogermanium chemistry as a source of dichlorogermylene (see, *e.g.*, Ref. 9). In this connection, it was interesting to study the behaviour of the ν(MHal) frequencies in the vibrational spectra of the $M^{II}Hal_2$ complexes with Lewis bases (triphenylphosphine and 1,4-dioxane) and to analyze, from this point of view, the published data.**[10]** In this study we for the first time report the vibrational spectra of the complexes $Cl_2Ge\cdot PPh_3$ (**1**), $Br_2Ge\cdot PPh_3$ (**2**), $Cl_2Sn\cdot PPh_3$ (**3**), $Cl_2Ge\cdot C_4H_8O_2$ (**4**) and $Cl_2Sn\cdot C_4H_8O_2$ (**5**); for some of them we performed quantum-chemical calculations of geometric parameters and normal coordinate analysis. The ν(MHal) vibrational frequencies in the spectra of the compounds under study are shown in Tables 1 and 2.

Complexes of carbene analogs with triphenylphosphine

In a recent X-ray study**[11]** of complex **1**, the data obtained earlier**[12]** were refined and it was confirmed that the complex exists in monomeric form (nonbonding distance

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Table 1. The ν(GeHal) frequencies in the spectra of divalent and tetravalent germanium compounds and complexes **1**, **2**, and **4**

Compound	ν(GeHal)/cm^{-1}	
	ν^{s}	ν^{as}
$GeCl_4$	396 (A_1)	456 (F_2)^{4}
$MeGeCl_3$	399 (A_1)	424 (E)^{4}
Me_2GeCl_2	385 (A_1)	402 (B_2)^{4}
$MeEtGeCl_2$	384 (A_1)	400 (B_2)^{6}
$Bu^n{}_2GeCl_2$	372 (A_1)	388 (B_2)^{5}
$GeCl_2$ (gas phase)	392 (A_1)	372 (B_2)^{1}
$GeCl_2$ (Ar matrix)	399	373^{1}
$Cl_2Ge \cdot PPh_3$ (**1**)	335 (A_1)	311 (B_2)
$[Cl_2Ge \cdot C_4H_8O_2]_n$ (**4**) (crystals)	313 (A_1)	281 (B_2)
$[Cl_2Ge \cdot C_4H_8O_2]_n$ (**4**) (dioxane solution)	351	
$GeBr_4$	236 (A_1)	329 (F_2)^{4}
$MeGeBr_3$	261 (A_1)	311 (E)^{4}
Me_2GeBr_2	269 (A_1)	293 (B_2)^{4}
$Bu^n{}_2GeBr_2$	231 (A_1)	266 (B_2)^{5}
$GeBr_2$ (gas phase)	288 (A_1)	267 (B_2)^{1}
$GeBr_2$ (Ar matrix)	286	276^{1}
$Br_2Ge \cdot PPh_3$ (**2**)	230 (A_1)	—

Table 2. The ν(SnHal) vibrational frequencies in the spectra of divalent and tetravalent tin compounds and complexes **3** and **5**

Compound	ν(SnHal)/cm^{-1}	
	ν^{s}	ν^{as}
$SnCl_4$	369 (A_1)	408 (F_2)^{4}
Me_2SnCl_2	344 (A_1)^{4}	—
$Bu^n{}_2SnCl_2$	314 (A_1)	341 (B_2)^{5}
$SnCl_2$ (gas phase)	358 (A_1)	340 (B_2)^{1}
$SnCl_2$ (Ar matrix)	353	332^{1}
$Cl_2Sn \cdot PPh_3$ (**3**)	307 (A_1)	290 (B_2)
$[Cl_2Sn \cdot C_4H_8O_2]_n$ (**5**) (crystals)	263 (A_1)	—
$[Cl_2Sn \cdot C_4H_8O_2]_n$ (**5**) (dioxane solution)	311	
$SnBr_4$	222 (A_1)	284 (F_2)
$MeSnBr_3$	234 (A_1)	260 (E)^{4}
Me_2SnBr_2	232 (A_1)	260 (B_2)^{4}
$SnBr_2$ (Ar matrix)	244 (A_1)	231 (B_2)^{1}

between the Ge and Cl atoms is 6.098 Å). The complexation energy of **1** is 10.7±0.4 kcal mol^{-1}.[13]

The Raman spectra of "free" PPh_3 and complexes **1** and **3** are shown in Fig. 1. The lines at 334 and 311 cm^{-1} in the spectrum of complex **1** and the lines at 307 and 290 cm^{-1} in the spectrum of complex **3** were assigned to the ν^{s}(MCl) and ν^{as}(MCl) vibrations, respectively. The assignment was made based on the band intensities in the IR and Raman spectra, comparison with the spectra of free CAs, and the results of normal coordinate analysis performed in the course of quantum-chemical and model (using a phenomenological force field) calculations. For complex **1**, this assignment is also confirmed by disappearance of the lines mentioned above in the Raman spectrum of the corresponding bromide **2**. Thus, it is clear that inversion of the ν(MCl) frequencies found in the spectra of CAs also occurs in the spectra of their complexes with PPh_3. The ν(MHal) frequency shifts due to complexation are ~60 cm^{-1} for complex **1** and ~45 cm^{-1} for complex **3**.

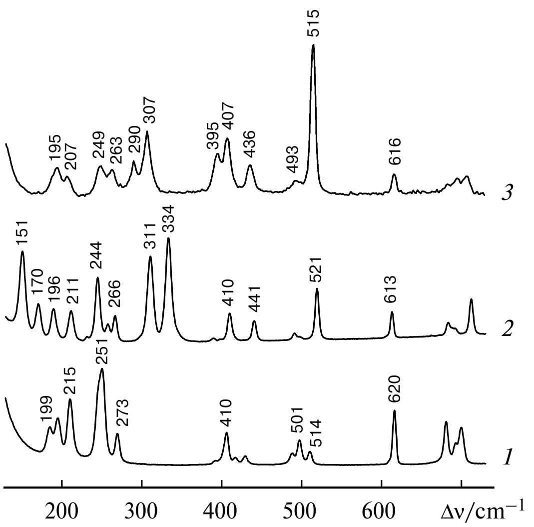

Fig. 1. Raman spectra of PPh_3 (*1*) and its complexes with $GeCl_2$ (*2*) and $SnCl_2$ (*3*).

Complexes of carbene analogs with 1,4-dioxane (1 : 1)

The most accurate structure determinations of complex **4** were reported recently.[11,14] The structure of a bromine-containing analog, $Br_2Ge \cdot C_4H_8O_2$, was also established.[15] Both complexes were described as polymers with infinite chains in which each Ge atom is linked to two dioxane molecules. The geometries of the dihalogermylene fragments in the complexes are only slightly changed compared to those of "free" species, which indicates a weak Ge...O coordination bond. Indeed, the energy of this bond in solid complex **4** is 7.1 kcal mol^{-1} [13] (*cf.* a ~3 kcal mol^{-1} estimate[16] of the dissociation enthalpy of this complex in solution). According to the X-ray data,[17] the dichlorostannylene complex **5** is structurally similar to **4** and characterized by analogous changes in the structural parameters.

The Raman spectra of solid complexes **4** and **5** at room temperature and the Raman spectrum of crystalline dioxane at −10 °C are shown in Fig. 2. Since the complexes with dioxane are weaker than the complexes with PPh_3, one could expect that the ν(MCl) frequencies in the spectra of complexes **4** and **5** would be higher than in

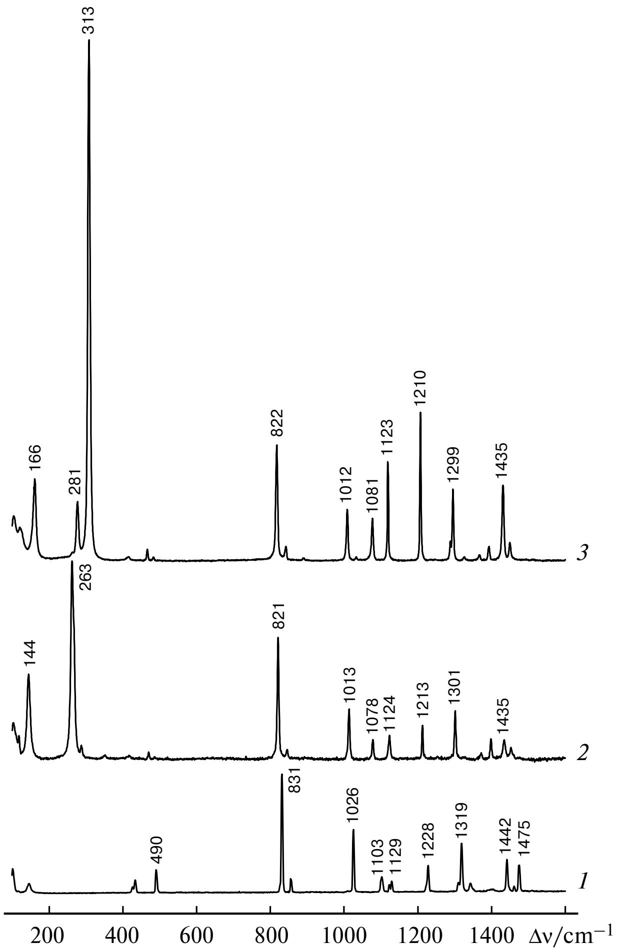

Fig. 2. Raman spectra of 1,4-dioxane at −10 °C (*1*) and its complexes with $SnCl_2$ (*2*) and $GeCl_2$ (*3*).

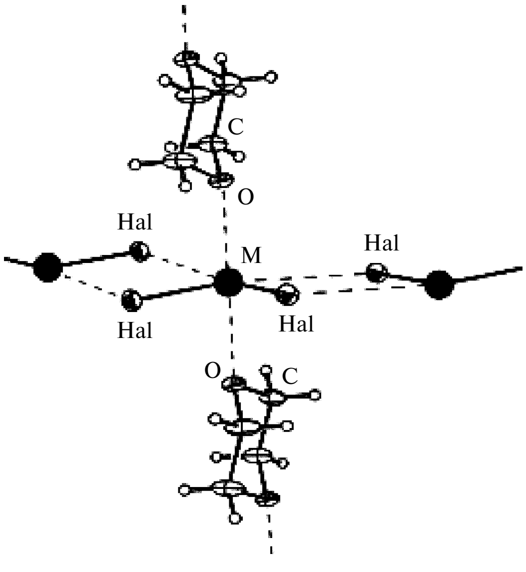

Fig. 3. Structures of crystalline complexes Hal_2M^{II} with 1,4-dioxane (M = Ge, Sn; Hal = Cl, Br).

the spectra of complexes **1** and **3**. However, the ν(GeCl) frequencies in the spectrum of complex **4** (313 and 281 cm^{-1}) are lower than those in the spectrum of complex **1** and the ν(SnCl) frequencies in the spectrum of complex **5** are lower than those in the spectrum of complex **3** (see Fig. 2). An unusually large decrease in the ν^s(MCl) frequency in the spectra of complexes **4** and **5** (by ~85 cm^{-1}!) can not be explained only by the formation of weak coordination bonds M...O. We assumed that this frequency can also decrease due to intermolecular coordination M...Cl. To confirm this hypothesis, we recorded the Raman spectra of solutions of complexes **4** and **5** in dioxane. Disappearance of the intense lines at 313 and 263 cm^{-1} in the spectra of complexes **4** and **5**, respectively, and the appearance of polarized lines at 351 and 311 cm^{-1} instead, *i.e.*, an increase in the ν^s(MCl) frequencies in the spectrum of solution by ~40 cm^{-1} compared to the spectrum of crystalline sample indicates an increase in the M—Cl bond order in solution owing to breakdown of intermolecular coordination M...Cl. Thus, the M^{II} atoms in the crystals of compounds **4** and **5** are in essence hexacoordinate, being located at the centers of pseudooctahedra (Fig. 3).

It should be noted that similarly to the spectra of the complexes with PPh_3 the spectra of the complexes with dioxane also exhibit frequency inversion (ν^s(MHal) > > ν^{as}(MHal)), which is reproduced in quantum-chemical calculations. Analysis of the published data[10] shows that frequency inversion is also observed in the spectra of a large number of $M^{II}Hal_2$ complexes with other Lewis bases. Therefore, spectral data confirm the conclusion,[13] according to which the divalent state of the M atom in the complexes under study is retained. This conclusion was drawn based on consideration of the geometric parameters and reactivities of the complexes.

Thus, inversion of the metal—halogen stretching frequencies ($\nu^s(M^{II}Hal) > \nu^{as}(M^{II}Hal)$), which was found in our studies of the spectra of dihalosilylenes, -germylenes, and -stannylenes reflects specific features of the divalent state and can be used for analytical purposes to distinguish between the M^{II} and M^{IV} halides. Observation of this inversion in the vibrational spectra of the $M^{II}Hal_2$ (M = Ge, Sn; Hal = Cl, Br) complexes with triphenylphosphine, 1,4-dioxane, and other Lewis bases[10] indicates that the $MHal_2$ species in these complexes preserve their "identity" as carbene analogs.

Experimental

Complexes **1**—**5** were synthesized following the known procedures.[7,12,18,19] All experiments with complexes **1**—**5** were carried out either in an inert atmosphere or *in vacuo* (10^{-5} Torr). 1,4-Dioxane necessary for the preparation of solutions of the complexes **1** and **2** was dried over sodium in the presence of benzophenone and used immediately after distillation.

In order to obtain Raman spectra, polycrystalline samples of complexes **1—5** and solutions of complexes **1** and **2** were sealed in capillaries. The Raman spectra were recorded using U-1000 and T-64000 laser Raman spectrometers (Jobin—Yvon, France) with excitation by the line λ = 514.5 nm of an SP-2020 Ar^+ laser. The depolarization ratios of the Raman lines in the solution spectra were estimated qualitatively.

The IR spectra of the Nujol and hexachlorobutadiene mulls were recorded on a Carl Zeiss M-82 spectrophotometer and a Bruker IFS 113V Fourier spectrometer.

Density functional quantum-chemical calculations (geometry optimization and normal coordinate analysis) of the $GeCl_4$ and $GeCl_2$ molecules, complexes **1** and **2**, and a simplified model of complex **4** [11] were carried out using the GAUSSIAN-98 program package[20] with the MPW1PW91 functional and the 6-311++G(d,p) extended basis set.

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