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Structure and Thermodynamics of the Tin Dichloride Dimer—A Computational Study

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The molecular structures of $SnCl_2$ and Sn_2Cl_4 have been calculated by high-level quantum chemical methods. The global minimum structure found for the tin dichloride dimer is of C_s symmetry and has two halogen bridges. This structure is very different from the one suggested earlier by Fields et al. based on their gas-phase Raman spectroscopic measurements. Thermodynamic functions for gaseous $SnCl_2$ and Sn_2Cl_4 have also been calculated. The minimum-energy geometry of the trimeric molecule, Sn_3Cl_6, has a six-membered ring with alternating Sn and Cl atoms in the highly puckered ring. The possible structural changes during evaporation are discussed in some detail.

I. Introduction

A recent paper on a spectroscopic study of the vapor over $SnCl_2$ melts prompted us to probe into the question of the dimer structure for this molecule.[1] This paper reports the laser Raman spectroscopic study of gaseous tin dichloride over the temperature range 666−1047 K and at three different argon laser lines. While the high-temperature spectra corresponded to the monomer molecule, the low-temperature spectra were interpreted as originating partly from the dimer with a one-chlorine bridged C_s symmetry structure (see structure **G** in Figure 1). The authors suggest that the newly formed bond between the two monomer units is a double bond and, accordingly, stronger than either of the monomer bonds. Various thermodynamic functions have also been calculated for this new structure.

Tin dichloride has been studied earlier by spectroscopic techniques: by gas-phase Raman spectroscopy,[2,3] matrix isolation infrared[4] and Raman spectroscopy,[5] and electron spectroscopy.[6] In these works only passing mention is given to possible higher aggregates, and they were not investigated. Its molecular structure was also determined by gas-phase electron diffraction,[7] but in this case there was no mention of dimers in the vapor.

The paper by Fields et al.,[1] on the other hand, focuses on the study of the dimeric species. The structure they suggest for the Sn_2Cl_4 molecule is, however, a surprising one. From the different possible structures, some of them shown in Figure 1, the authors found structure **G** as the most probable. When trying to validate their suggestion of a one-bridged dimer, they argue that while in the usual dimer structures two chlorine bridges are formed between two monomeric units, "it is also possible that this process could occur only once, to give a structure with one bridging chlorine atom". We think that in the vapors over molten tin dichloride the process is the opposite one: the dimers form when the crystal, or the melt, is heated and the substance evaporates first as dimers. Then, on further heating, at higher temperatures, these dimeric units break into monomers. This process is also supported by the fact that at higher temperatures (>700 K) only monomers are found in the vapor.[8]

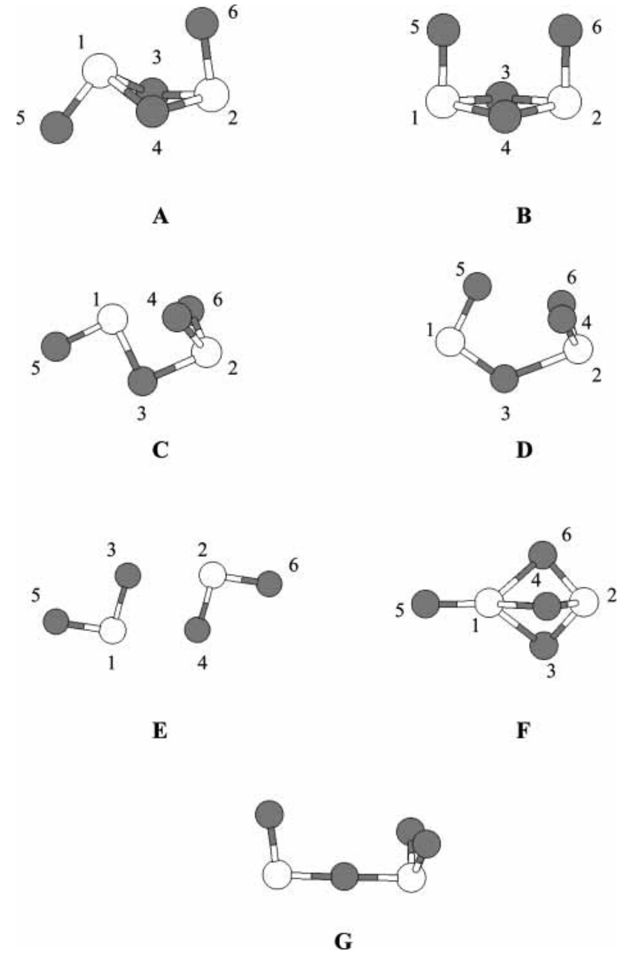

Figure 1. Different geometrical arrangements for the Sn_2Cl_4 molecule. The numbering of atoms for the tables is also indicated.

The crystal structure of $SnCl_2$ is known; it is a polymeric chain containing bent $SnCl_2$ molecules joined together by single chlorine bridges and with three coordination of tin.[9] The Raman spectra of both crystalline anhydrous tin dichloride and its melt have been studied.[10] Due to their strong similarity, it was concluded that the melt very likely contains $(SnCl_2)_n$ units with different chain lengths; the rather broad stretching region of the spectrum also suggests that there are both terminal and

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bridging Sn−Cl bonds in the melt with different bond lengths. The position of the band attributed to the stretching region moved slightly toward larger values as the temperature of the melt increased, suggesting that the lengths of the $(SnCl_2)_n$ chains decrease with temperature and, thus, the proportion of terminal vs bridging bonds increases.

The mass spectra of $SnCl_2$ have also been studied repeatedly, mostly because of its importance in high-pressure discharge lamps.[8,11−13] Although the conclusions of these studies are not the same, it seems that there is only a very small fraction of dimeric molecules in the vapor over solid and molten $SnCl_2$ and that the mole fraction of the dimer decreases with temperature, at least in the measured temperature range of about 600−900 K.

It is rather common to have a certain amount of dimeric molecules in the vapors of metal dihalides.[14−17] Their structures have been studied before by both experimental and computational methods.[15] These molecules usually appear in very small amounts in the vapors of metal halides; therefore, their structure determination from experiments poses difficulties. Nonetheless, there are many cases where dimers were detected in the vapor (for references see ref 15). Earlier it was usually assumed that they have a D_{2h} symmetry structure with double halogen bridges, irrespective of the type of the metal atom—as, for example, was supposed in the mass spectrometric study of dimeric $SnBr_2$ as well.[18] Later computations, however, have shown that, while the D_{2h} symmetry structure is, indeed, the minimum-energy structure for many metal dihalide dimers,[19] this is only so if the monomer is a linear molecule.[20] Most transition metal dihalides and the dihalides of the lighter alkaline earth metals are examples.[21] On the other hand, a recent computational study of the heavier alkaline earth dihalide dimers has shown that bent monomers form a dimer that has a different minimum-energy geometry; namely one with C_{3v} symmetry and with three halogen bridges (see structure **F** in Figure 1).[20] This structure can be considered as a complex ion consisting of an MX^{3-} unit and an MX^+ unit.

The above example suggests that the D_{2h} symmetry geometry for metal dihalide dimers is not as obvious as presumed earlier. Considering the lone electron pair on the central atom in group 14 dihalides, common structural considerations suggest that their dihalides should not have a D_{2h} symmetry geometry either, but rather a lower symmetry one, in which the stereochemical requirements of the lone electron pair are taken into consideration.[22] Several such structures can be drawn, and many have been checked by Fields et al. for Sn_2Cl_4.[1]

The structure they suggested for the Sn_2Cl_4 molecule has C_s symmetry, with only one bridging chlorine atom and one two-coordinated tin atom and one three-coordinated tin atom (structure **G** in Figure 1). As mentioned earlier, this structure is rather unusual, and that is why we decided to investigate the structure of tin dichloride dimers by high-level computational methods. By using the results of the calculations, various thermodynamic functions for the monomer and dimer were also computed, and then the dimer formation in the vapor phase above molten $SnCl_2$ was discussed from both the thermodynamic and the structural points of view.

II. Computational Details

To check the reliability of our calculations, first we performed extensive computations on the monomeric $SnCl_2$ molecule, for which both geometrical and vibrational data are available in the literature from experiment.

Computations have been carried out with the Gaussian 98 program package.[23] Geometries were optimized and vibrational frequencies calculated using standard methods available in Gaussian 98: HF, MP2, CCSD(T), and DFT with the B3LYP and B3PW91 hybrid functionals. For Sn a Stuttgart quasirelativistic pseudopotential (ECP) covering 46 electrons[24] was used. Two different types of associated valence basis sets were used; one of them was of the type (14s10p2d1f)/[3s3p2d1f],[25] and this is referred to as ECP1. A second set of calculations was carried out with a larger valence basis set of the type (15s11p4d3f2g)/[5s5p4d3f2g] (ECP2).[25] For chlorine Dunning's correlation consistent basis sets were applied, the triple-ζ cc-pVTZ, (15s9p2d1f)/[5s4p2d1f],[26,27] and the quadruple-ζ cc-pVQZ, (16s11p3d2f1g)/[6s5p3d2f1g],[27,28] both with and without polarization functions. Wiberg bond orders and natural atomic charges were calculated by the method of Reed, Weinstock, and Weinhold from the MP2 electron density.[29]

Computations of the dimeric molecules have been carried out at the HF and MP2 levels of theory. For the tin atom both the smaller and the larger basis sets were checked, while for chlorine only the cc-pVTZ-type triple-ζ basis was used, based on the good performance of these basis set combinations for the monomeric molecule. Several geometrical arrangements have been checked, as indicated in Figure 1. Vibrational frequencies were also calculated for all species.

Since we were interested in the possible structural changes during evaporation, we also checked several geometrical arrangements for the possible trimeric molecules. These latter calculations have only been carried out at the HF level, with the ECP1 basis on Sn and the triple-ζ cc-pVTZ on Cl. Frequencies were calculated for the two lowest energy trimer structures.

III. Results and Discussion

Monomer. Table 1 lists the geometrical parameters and vibrational frequencies of $SnCl_2$. The experimental bond length, r_g, from electron diffraction, is a thermal average distance and as such has a different physical meaning from the computed equilibrium bond length and thus cannot reliably be compared with it. The comparison should be made with the estimated experimental equilibrium bond length, 2.335(3) Å.[7] Interestingly, most computed values are larger, by about 0.04 Å, even with relatively large basis sets and with high-level computations. The two density functional computations resulted in the longest bond lengths with the worse agreement with experiment; therefore, these values are not given in the table. These results were consistent with the earlier quasirelativistic B3LYP calculation.[30] It is only the MP2 computation with the large Sn basis (ECP2) and the quadruple-ζ aug-cc-pVQZ basis set of Dunning that gives a good agreement with the experiment as far as the bond length is concerned. The nonrelativistic SCF result of Escalante et al.[30] is similar, probably only by a fortuitous agreement. On the other hand, the computed bond angle agrees very well with the experimental one for most computations.

As for the frequencies, there are several experimental determinations by different techniques. It seems that the frequencies are rather well determined around 351, 120, and 330 cm^{-1} for the symmetric stretching, bending, and asymmetric stretching vibrational modes, respectively. It should be noted, however, that the frequencies determined for the monomer by Fields et al.[1] are conspicuously about 10 cm^{-1} higher for the two stretching modes than the ones observed in the other studies. This fact, by itself, puts some doubt on the reliability of these data, concerning not only assignment but even the recording of the spectra. From among the computed frequencies, the best agreement with experiment comes from our MP2 calculation

TABLE 1: Geometrical Parameters and Vibrational Frequencies of $SnCl_2$ from Computation and Experiment[a]

	r, Å	∠, deg	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ref
		Computed				
MP2:[b] Sn, ECP1; Cl, cc-pVTZ	2.389	97.7	352	121	334	this work
MP2: Sn, ECP1; Cl, aug-cc-pVTZ	2.390	97.2	347	121	328	this work
HF: Sn, ECP2; Cl, cc-pVTZ	2.377	97.8	356	134	335	this work
MP2: Sn, ECP2; Cl, cc-pVTZ	2.376	98.1	358	123	341	this work
CCSD(T): Sn, ECP2; Cl, aug-cc-pVTZ	2.384	98.1				this work
MP2: Sn, ECP2; Cl, aug-cc-pVTZ	2.379	97.8	354	122	337	this work
MP2: Sn, ECP2; Cl, cc-pVQZ	2.357	101.4				this work
MP2:[c] Sn, ECP2; Cl, aug-cc-pVQZ	2.334	98.4				this work
MRSDCI	2.363	98.4				35
HF, NR	2.331	98.2				30
HF, QR	2.393	97.7				30
B3LYP, NR	2.353	99.3				30
B3LYP, QR	2.417	98.9				30
CCSD(T), ECP, Ch	2.357	98.4				36
CCSD(T), ECP, St	2.380	98.4				36
		Experimental				
ED, r_g[d]	2.345(3)	98.5(20)				7
ED, r_e[e]	2.335(3)	98.1				7
Ra (g)			352	120		3
Ra (g)			350	120		6
Ra (Ar)			353		332	5
IR (Ar)			354		334	4
Ra, (g)			362	127	344	1
			355	121	347	1
			358	121	340	1

[a] Abbreviations: MRSDCI, multireference singles and doubles configurational interaction; NR, nonrelativistic; QR, quasirelativistic; ECP, effective core potential; Ch, from Christiansen; St, from the Stuttgart group; ECP1, Stuttgart ECP for Sn, with smaller valence basis set, see text for details; ECP2, Stuttgart ECP for Sn, with larger valence basis set, see text for details; ED, electron diffraction; Ra, Raman spectroscopy; IR, infrared spectroscopy. [b] Best agreement with experimental gas-phase frequencies. [c] Best agreement with estimated experimental equilibrium bond length. [d] r_g: electron diffraction thermal average distance at 683 K. [e] Equilibrium distance, estimated by vibrational corrections from r_g.

TABLE 2: Some Geometrical Parameters of the Sn_2Cl_4 Dimers[a]

	dimer structure					
parameter	**A**	**B**	**C**[b]	**D**[b]	**E**[c]	**F**[c]
symmetry	C_s	C_{2v}	C_s	C_s	C_{2h}	C_{3v}
Sn1−Cl5	2.395	2.383	2.409	2.351	2.396	2.449
Sn2−Cl6	2.422	2.383	2.483	2.414	2.396	2.549
Sn1−Cl3	2.684	2.662	2.595	2.467	2.427	2.987[d]
Sn1−Cl4	2.684	2.662			3.590	2.987[d]
Sn2−Cl3	2.626	2.662	2.688	3.023	3.590	2.549
Sn2−Cl4	2.626	2.662	2.483	2.414	2.427	2.549
Cl5−Sn1−Cl3	92.6	93.9	89.0	99.3	95.4	136.8
Sn1−Cl3−Sn2	91.3	97.7	92.1	123.6	105.2	83.4
Cl3−Sn1−Cl4	79.9	81.9			74.8	72.7
Cl3−Sn2−Cl6	90.0	93.9	84.4[e]	89.6[e]	170.3	88.1
Cl3−Sn1−Cl4−Cl5	−92.2	93.4			0.0	141.6
Cl3−Sn2−Cl4−Cl6	−90.0	−93.4			180.0	88.1
Sn1−Cl3−Sn2−Cl4			46.2	49.0	0.0	−44.1
Sn1−Cl3−Sn2−Cl6			−46.2	−49.0	0.0	44.1
rel energy, (kJ mol^{-1})	0	8.8	28.7	71.5	77.2	72.7

[a] MP2 calculations with the ECP1 basis on Sn and cc-pVTZ on Cl (for details see text). The numbering of atoms is shown in Figure 1. [b] One negative frequency. [c] Two negative frequencies. [d] Sn1−Cl3,4,6. [e] Cl3−Sn2−Cl6 and Cl3−Sn2−Cl4.

with the smaller, ECP1, basis on Sn and the triple-ζ Dunning basis set, cc-pVTZ, on Cl.

Dimer. Our major goal with this paper is the study of the tin dichloride dimer. Since the bond angle and the experimental frequencies of the monomer are best reproduced by the MP2 level computations with the triple-ζ basis on Cl and the ECP1 basis on Sn, we decided to adopt this method/basis set combination for the study of the Sn_2Cl_4 molecule. To check the relative energies of the different geometries, the same structures have also been calculated at the same level with the ECP2 basis on Sn.

Different geometrical arrangements were studied for the dimer, as indicated in Figure 1. Their geometrical parameters are given in Table 2, together with their relative energies. The numbering of atoms is shown in Figure 1.

The global minimum structure turns out to be rather different from the one suggested by Fields et al.[1] It is a structure with two halogen bridges and C_s symmetry and a puckered four-membered ring, as shown as structure **A** in Figure 1. The next structure in energy is also a stable minimum, about 9 kJ mol^{-1} higher than the global minimum structure. This is a C_{2v} structure, again with two halogen bridges and two terminal Sn−Cl bonds strongly bent toward each other (structure **B** in Figure 1). The difference in energy between these two structures is rather small, so it is a possibility that their order might be somewhat method or basis set dependent. Our calculations, however, with a better ECP on Sn gave the same order. Moreover, our separate electron diffraction and quantum chemical study of $SnBr_2$ resulted in the same two dimeric structures as the lowest energy ones with many more basis set combinations.[31] The Wiberg (covalent) bond orders in the two structures are similar, about 0.6 for the terminal Sn−Cl bonds and 0.3 for the bridging bonds. The difference in energy between the C_s and C_{2v} structures appears to be electrostatic rather than covalent in nature, as suggested by Coulomb's law calculations based on the computed natural charges (about −0.6 on Cl and 1.2 on Sn). The electrostatic effect is understandable in view of the proximity of the two terminal chlorines in the C_{2v} structure.

The structure by Fields et al.[1] does not appear to be a minimum-energy structure. Full geometry optimizations starting out from this arrangement produced two somewhat different structures, both with one negative frequency and thus representing a transition state on the potential energy surface. These structures are **C** and **D** in Figure 1, and they are higher in energy

TABLE 3: Comparison of the Vibrational Frequencies (in cm^{-1}) of the Most Stable Dimer Structures (A and B) Obtained from ab Initio Calculations with Those Observed and Calculated by Fields et al. (Ref 1)[a]

symmetry species	dimer **A**	dimer **B**	calc (obs) by Fields et al.[1]
A′	341, 326, 250, 219, 129, 122, 72, 37		470.2 (470), 351.8, 347.6, 263.3 (263), 196.9 (197), 177.1, 143.0 (143), 80.4
A″	236, 137, 104, 66		347.5, 231.9, 100.4 (101), 58
A_1		351, 232, 133, 87, 27	
A_2		140, 62	
B_1		218, 99	
B_2		244, 225, 81	

[a] Computed frequencies from MP2 calculations with the ECP1 basis on Sn and cc-pVTZ on Cl (for details, see text).

than the global minimum geometry by 29 and 72 kJ mol^{-1}, respectively. Optimization of a C_{2h} symmetry structure results in two almost completely separated monomeric molecules in which the bridging Sn−Cl distance is 3.590 Å, no longer a bond (see structure **E** in Figure 1). The structure has two negative frequencies.

There is one more structure that may be worth mentioning. It has C_{3v} symmetry and is shown as structure **F** in Figure 1. This structure is about 73 kJ mol^{-1} higher in energy than the global minimum and has two negative frequencies, so it is not a stable structure. Considering the lone electron pair on the tin atom, the nonstability of this structure is not surprising, indeed. Why we wanted to mention it is that this structure was found as the global minimum for those heavy alkaline earth dihalide dimers whose monomers have a bent shape.[20] Of course, in the alkaline earth dihalide monomers it is not a lone electron pair but rather the polarizability of the central atom that makes them bent.

The vibrational frequencies of the two most stable dimer structures are given in Table 3. They do not match the frequencies measured by Fields et al.[1] The low temperature spectra shown in their paper are rather noisy, and the bands attributed to the dimeric molecules are hardly distinguishable from the noise. The difficulty in the experimental observation of the vibrational bands of the dimer is understandable if one takes into consideration that in the temperature range of their spectroscopic investigation (666−1047 K) the concentration of the dimers is expected to be less than 1 mol %.[8] The feature around 477 (470) cm^{-1} is especially difficult to see. It was basically this large-frequency band, 120 cm^{-1} higher than the symmetric stretching frequency of the monomer, that made the authors choose a structure in which one of the Sn−Cl bridging bonds has a much higher force constant (265 N m^{-1}) than the force constant of the monomer (193 N m^{-1}). We did not find any evidence for such a structure. The normal coordinate analysis carried out by Fields et al.[1] for different dimer structures does not prove in a convincing way the superiority of the dimer structure with one bridging chlorine atom, since the geometry used in the calculations is not based on experimental results and the number of independent force constants (eight) exceeds the number of input frequency data (five).

Structural Changes during Evaporation. We were also interested in what structural changes might occur during evaporation, and therefore, we calculated the structure of a possible trimeric molecule of tin dichloride, to see what way the breaking up of the individual long chain units of the crystal or the melt might happen. The trimers have only been calculated at the HF level, with the ECP1 basis on Sn and the cc-pVTZ on Cl. The most stable trimer structure has a six-membered ring and no apparent symmetry, as shown in structure **A** in Figure 2. Another structure, about 6 kJ mol^{-1} higher in energy, has two four-membered rings joined together (structure **B** in Figure 2). The geometrical parameters and vibrational frequencies of these molecules are given as Supporting Information.

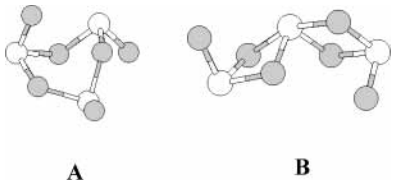

Figure 2. Two minimum-energy structures for the Sn_3Cl_6 trimeric molecule.

In the Raman spectra of molten $SnCl_2$, no frequency characteristic of the Sn−Cl stretching of the monomer (around 330−350 cm^{-1}) was observed and the authors concluded that “depolymerization does not appear to proceed to the formation of significant quantities of discrete $SnCl_2$ molecules” (page 1825).[10] Consequently, it may seem plausible that during the vaporization process it is the dimers and not the monomers that evaporate. This is supported by the fact that according to the thermodynamic measurements the heat of sublimation of dimers is about the same as that of monomers in the crystalline phase (see Table 3 of ref 11). It is reasonable to assume that the dissociation of the dimers into monomers takes place in the vapor phase and the monomer−dimer equilibrium is being established there. According to our earlier study of metal halide systems, dimers usually appear in the vapor phase only if the structural unit of the dimer can be recognized already in the crystal,[17] that is, there is no need for substantial reorganization. Looking at the chain structure of the $SnCl_2$ crystal,[9] the four-membered dimers can easily form from them. We can similarly easily visualize the formation of the six-membered ring trimers from these chains. On the basis of earlier thermodynamic considerations of dimer vaporization processes,[17] the possibility of the evaporation of trimers cannot be excluded; however, it is not possible to draw any definite conclusion as to what extent it may occur.

In the crystal of $SnCl_2$ each tin atom is attached to two bridging chlorines and one terminal chlorine. This is also true of the minimum structures that we found for the dimer (puckered four-membered rings with one terminal Cl atom attached to each tin atom) and the trimer (whose global minimum structure is a puckered six-membered ring with alternating Sn and Cl atoms and also with one terminal chlorine attached to each tin atom). Therefore, it is even possible that there are trimeric species present already in the melt of $SnCl_2$ besides the possible different-length polymers suggested by Clarke and Solomons.[10] On the other hand, if we consider the structure suggested by Fields et al.,[1] it is unlike the crystal, in that one Sn is attached to one terminal chlorine and only one bridging chlorine and the other Sn is attached to two terminal chlorines and one bridging chlorine.

TABLE 4: Molecular Parameters of $SnCl_2$ and Sn_2Cl_4 Used in the Calculation of Thermodynamic Functions in the Gaseous Phase

	$SnCl_2$	Sn_2Cl_4 structure **A**	Sn_2Cl_4 structure **B**
molecular mass, (g mol^{-1})	187.83951	375.67901	375.67901
vibrational frequencies (cm^{-1})	121, 334, 353	37, 66, 72, 104, 122, 129, 137, 219, 236, 250, 326, 341	27, 62, 81, 87, 99, 133, 140, 218, 225, 232, 244, 351
product of moments of inertia ($I_aI_bI_c \times 10^{117}$), ($g^3$ cm^{-6})	37662	5029170	5723214
symmetry (symmetry number)	C_{2v} (2)	C_s (1)	C_{2v} (2)

TABLE 5: Thermodynamic Functions of $SnCl_2$(g) and Sn_2Cl_4(g)

T, K	$-[G^\circ_m(T) - H^\circ_m(0)]/T$, J K^{-1} mol^{-1}	$H^\circ_m(T) - H^\circ_m(0)$, kJ mol^{-1}	$S^\circ_m(T)$, J K^{-1} mol^{-1}
	$SnCl_2$(g)		
100	215.13	3.69	252.06
200	242.44	8.45	284.70
298.15	260.04	13.68	305.91
300	260.32	13.78	306.25
400	273.88	19.33	322.20
500	284.85	24.98	334.80
600	294.07	30.68	345.20
700	302.03	36.42	354.04
800	309.01	42.17	361.73
900	315.26	47.95	368.53
1000	320.89	53.73	374.62
1100	326.03	59.51	380.14
1200	330.75	65.31	385.18
	Sn_2Cl_4(g) **A**		
100	270.59	6.51	335.67
200	323.48	17.52	411.07
298.15	360.86	29.62	460.21
300	361.48	29.85	460.99
400	391.16	42.64	497.76
500	415.48	55.63	526.73
600	436.07	68.71	550.59
700	453.91	81.86	570.86
800	469.65	95.05	588.47
900	483.74	108.26	604.03
1000	496.47	121.49	617.97
1100	508.10	134.74	630.59
1200	518.80	147.99	642.12
	Sn_2Cl_4(g) **B**		
100	268.76	6.73	336.09
200	323.26	17.97	413.10
298.15	361.48	30.18	462.71
300	362.10	30.42	463.49
400	392.28	43.27	500.45
500	416.92	56.29	529.51
600	437.74	69.41	553.42
700	455.75	82.58	573.72
800	471.62	95.78	591.35
900	485.81	109.00	606.92
1000	498.63	122.24	620.87
1100	510.32	135.49	633.50
1200	521.07	148.75	645.04

Thermodynamic Calculations. Detailed thermodynamic calculations have been carried out by Fields et al.[1] based on their, what we believe, erroneous dimer structure. Since tin dichloride may have potential importance in the lamp industry, these thermodynamic data might be of importance. This is why we decided to recalculate them on the basis of our minimum-energy structure (**A**) and also of the structure with the next lowest relative energy (**B**).

Thermodynamic functions for the gaseous monomers and dimers have been calculated in the rigid rotator harmonic oscillator approximation by using the equations given in ref 32. Naturally, the anharmonicity of vibrations at these high temperature conditions cannot be excluded. However, the correction due to anharmonicity would possibly be smaller than the effect of the uncertainty of the computed frequencies at the applied computational methods and basis sets. The values of the molecular parameters (vibrational frequencies, moments of inertia) used in the computations were obtained by our ab initio calculations and are collected in Table 4. The thermodynamic functions (Gibbs energy function, enthalpy increment, and entropy) for the monomer and the two dimer structures (**A** and **B**) are listed for different temperatures in Table 5. In the case of the monomer there is a fairly good agreement between the calculated Gibbs energy function and enthalpy values and those given in Table VI of the review paper of Brewer et al.[33] For example, at 298.15 K our values and those of Brewer et al. are 13.7 and 13.5 kJ mol^{-1} for $H^\circ_m(T) - H^\circ_m(0)$ and 260.0 and 260.7 J K^{-1} mol^{-1} for $-[G^\circ_m(T) - H^\circ_m(0)]/T$, respectively. The differences can be accounted for by the different molecular parameters used in the calculations. The calculated entropy value for the monomer at 298.15 K agrees perfectly with the value of 305 J K^{-1} mol^{-1} used by Mucklejohn and O'Brien in the thermodynamic evaluation of vapor pressure data for tin dichloride.[8] As far as the thermodynamic functions of Sn_2Cl_4 are concerned, the enthalpy and entropy values calculated by Fields et al.[1] for their suggested dimer structure with one bridging chlorine atom are lower than the values obtained for the dimer structures of the present work (e.g. at 298.15 K by about 11% and 6.5%, for structures **A** and **B**, respectively). Unfortunately, in their paper no thermodynamic quantities are given for the monomer.

The Gibbs energy functions and the enthalpy increments of $SnCl_2$(g) and Sn_2Cl_4(g) can be used in the calculation of the enthalpy of dimerization:

$$2SnCl_2 = Sn_2Cl_4$$

The enthalpy change of the dimerization reaction at 298 K ($\Delta_r H^\circ_m(298.15)$) can be obtained by the third-law method[32] from the experimentally determined equilibrium constant of the dimerization (K_p) using the equation

$$\Delta_r H^\circ_m(298.15) = -T\{R \ln K_p + \Delta_r[G^\circ_m(T) - H^\circ_m(298.15)]/T\}$$

where K_p is the equilibrium constant and Δ_r on the right-hand side of the equation denotes the change of the Gibbs energy function in the dimerization process.

The equilibrium constants for the dimerization were taken from Table 6 of the paper of O'Brien and Mucklejohn,[11] who studied the vapor-phase equilibria over $SnCl_2$ by a combination of different experimental techniques. (Note that the equilibrium constant for the dimerization is the reciprocal of their value given for the dissociation reaction.) The calculations were carried out for each K_p point in the temperature range 570−640 K (where ln K_p is a linear function of $1/T$) by using the values of the thermodynamic functions for the monomer and dimer **A** calculated in the same way as the values given in Table 5. The average value for the enthalpy of dimerization ($\Delta_r H^\circ_m(298.15)$) was found to be -103.8 ± 3 kJ mol^{-1}. This is comparable with the values -106.8 ± 3.6 kJ mol^{-1} and -101.0 ± 4.4 kJ mol^{-1}

obtained for gaseous tin dibromide[18] and tin diiodide,[34] respectively. It should be noted that the second-law evaluation[32] based on the temperature dependence of the equilibrium constant (Figure 4 in ref 11) resulted in an average value of -145 ± 8 kJ mol^{-1} for the temperature range 570−640 K. From this value, by using the enthalpy increments given in Table 5, one obtains -150 ± 8 kJ mol^{-1} for the enthalpy of dimerization at 298.15 K. The disagreement between the values obtained by second- and third-law evaluation methods in the case of Sn_2Cl_4 was mentioned before.[18] A plausible reason for the discrepancy may be that the experimental determination of the temperature dependence of the vapor pressure of the dimer[11,8] is erroneous, thus leading to a lower enthalpy of vaporization of the dimer. According to a thermodynamic analysis of the vaporization of a number of metal dihalides, it is highly improbable that the enthalpy of vaporization of the dimer is significantly smaller than that of the monomer.[17]

The value of -69.6 ± 13 kJ mol^{-1} obtained for the enthalpy of formation of Sn_2Cl_4 from the Raman spectroscopic study of the vapor phase between 666 and 1047 K by Fields et al.[1] is significantly lower than the value obtained here. This should not be surprising, since the temperature dependence of K_p changes drastically with increasing temperature (see Figure 4 in ref 11). The dissociation enthalpy of Sn_2Cl_4 in the vapor in equilibrium with the crystalline phase below the melting point (518 K) was also determined by O'Brien and Mucklejohn,[11] and an average value of 82 ± 12 kJ mol^{-1} was obtained at 494 K, which is smaller than the value above the melting point of tin dichloride. Since individual K_p values are not given in the paper, it was not possible to calculate $\Delta_r H_m^\circ(298.15)$ by the third-law evaluation method.

The calculation carried out for the dimer structure **B** has given, within the error limit (± 3 kJ mol^{-1}), the same value for $\Delta_r H_m^\circ(298.15)$, as that obtained for dimer **A**; thus, on the basis of thermodynamic calculations, one cannot make any decision as far as the structure of the dimer is concerned. In other words, since the change of the Gibbs energy during dimerization is determined largely by the enthalpy change, the symmetry difference between dimer **A** (C_s) and **B** (C_{2v}) cannot be expected to play a decisive role in the thermodynamics of the dimerization of $SnCl_2$.

IV. Conclusions

Ab initio quantum chemical calculations, carried out at the HF and MP2 levels of theory, on Sn_2Cl_4 molecules have shown that its global minimum structure (**A** in Figure 1) has C_s symmetry and contains two halogen bridges and a puckered four-membered ring. The next structure with somewhat higher (9 kJ mol^{-1}) energy has C_{2v} symmetry and also contains two halogen bridges (**B** in Figure 1). The peculiar structure proposed by Fields et al.[1] for Sn_2Cl_4 (C_s symmetry, with one bridging chlorine atom and one two-coordinated tin atom and one three-coordinated tin atom; see **G** in Figure 1) on the basis of their Raman spectroscopic study of the vapor phase above molten $SnCl_2$ has not been found to be a stable structure. The value for the enthalpy of dimerization at 298.15 K (-103.8 ± 3 kJ mol^{-1}) obtained by the thermodynamic analysis of the vapor-phase equilibria over molten $SnCl_2$ is in accord with the observed values for gaseous tin dibromide[18] and tin diiodide.[34] The present study has definitely demonstrated that gaseous tin dichloride dimers have a structure with two halogen bridges between the two tin atoms, and the structure with one halogen bridge can be considered highly improbable.

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Supporting Information Available: Geometrical parameters and vibrational frequencies for the two lowest energy stable structures of the Sn_3Cl_6 trimer. This material is available free of charge via the Internet at http://pubs.acs.org.

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