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Thermodynamic Studies of Bromine−Iodine Competition in the Formation of NaSnXYZ (X, Y, Z, = Br or I) Complexes

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The thermodynamic studies of NaSnXYZ (X, Y, Z = Br or I) are presented. The determined theoretical structures and vibrational properties lead to improved experimental values of dissociation enthalpies and entropies. The *ab initio* thermodynamic data is also reported. The nature of bonding of binary SnXY-NaZ complexes is discussed with the emphasis on differences between bromine and iodine.

1. Introduction

The development of metal halide lamps[1,2] requires systematic data on the vaporization processes involving metal halides and their complex systems.[3] In general the arc tube of lamps contains metal bromides and iodides which vaporize. Particularly important are quasibinary systems composed of NaI and a second metal iodide (MI_n).[4] The sodium concentration in the arc tube can be enhanced by the formation of $NaMI_n$ complex.[5] Low wattage metal halide lamps containing $SnBr_2$ and SnI_2 were developed for applications with the high luminous efficiency, good color rendering, and a low color temperature.[6] Besides the practical importance, such complexes are of fundamental interest for the chemistry of coordination compounds. The properties of recently studied complexes $(SnXY)_2$ (X = Br or I) are somehow unusual and escape the intuition even for the prediction of basic structures.[7,8] The addition of the reactive element to the environment is expected to complicate chemistry of vapors of interest.

In the presented work complexes of the general formula NaSnXYZ (X, Y, Z = Br or I) and corresponding molecular and fragment cations were studied with the emphasis on the bromine and iodine competition. The structures and thermodynamic properties were determined and compared with available experimental results. The theoretical geometries and vibrational frequencies were used to calculate Gibbs energy functions (GEF) which were applied for the recalculation of thermodynamic properties. The differences in bonding due to bromine substitution by iodine were studied applying the electron population analysis and the interaction energy decomposition scheme.

2. Theoretical Methods and Computational Details

The neutral and cationic species were optimized applying the density functional theory (DFT)[9] and the second-order Møller−Plesset perturbation (MP2)[10] approaches. The applied DFT version utilized Becke's three-parameter functional[11] with the Vosko et al. local part[12] and the Lee et al.[13] nonlocal part (abbreviated as B3LYP). No symmetry constraints were applied during the optimization processes. To ensure a location of the global minimum, geometry searches were carried out for a variety of possible configurations. All molecular geometries were verified to be minimum energy species by vibrational frequency calculations performed at both DFT and MP2 levels of theory. Additionally, the single point calculations were carried out utilizing the coupled cluster method with single and double substitutions and including triple excitations noniteratively [CCSD(T)].[14,15] Presented calculations were carried out using the relativistic effective core potentials (RECPs) developed by the Stuttgart group.[16] The cc-pVTZ basis set was applied for sodium,[17] CRENBL ECP for tin,[18] and the SDB-aug-cc-pVTZ basis set for bromine and iodine.[19] The ionization potentials of Na and Sn, and the electron affinity of halogen atoms, were calculated to verify the applicability of the basis sets for studied species. Theoretical ionization potentials of sodium (5.426 eV) and tin (7.17 eV) calculated at CCSD(T) agree satisfactorily with experimental values of 5.139 and 7.344 eV, respectively.[20] The calculated electron affinities of bromine (3.459 eV) and iodine (3.292 eV) also agree reasonably with complementary data of 3.364[21] and 3.059 eV.[22] The Mulliken and natural bond orbital (NBO)[23] population analyses calculations were carried out using the electron density obtained from MP2 calculation. Vibrational frequencies and thermodynamic properties of studied complexes were calculated applying the ideal gas, rigid rotor, and harmonic oscillator approximations.[24]

The low dissociation energy of complexes into monomers allows the bonding properties in moieties of interest to be studied within the interaction energy decomposition scheme developed for intermolecular interactions. The applied variation-perturbation scheme was originally proposed by Sokalski et al.[25] In this approach the total interaction energy ΔE_{MP2} is decomposed

$$\Delta E_{\mathrm{MP2}} = \Delta E_{\mathrm{HF}} + \epsilon_{\mathrm{MP}}^{(2)}$$

into the Hartree−Fock (HF) and the correlation components ($\epsilon_{\mathrm{MP}}^{(2)}$). The Hartree−Fock interaction energy is partitioned further into the first-order electrostatic ($\epsilon_{\mathrm{el}}^{(10)}$), Heitler−London exchange ($\epsilon_{\mathrm{ex}}^{\mathrm{HL}}$), and higher order delocalization ($\Delta E_{\mathrm{del}}^{\mathrm{HF}}$) terms.

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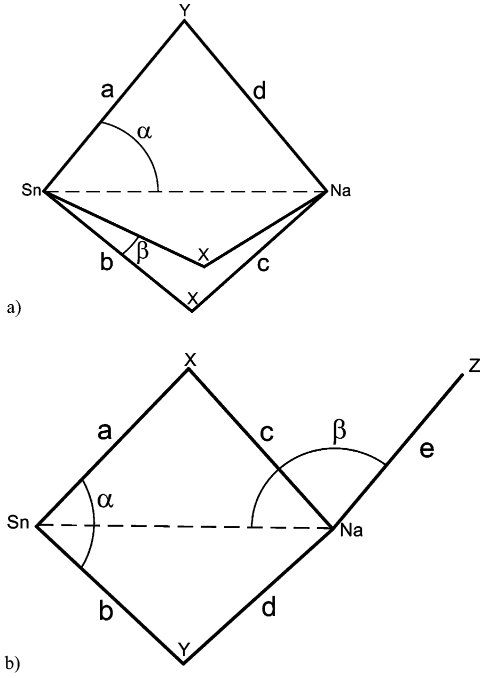

Figure 1. Molecular structures of (a) pyramidal and (b) planar isomers of NaSnXYZ. X, Y, and Z represent Br and I in particular complexes.

The $\Delta E_{\mathrm{del}}^{\mathrm{HF}}$ energy includes the charge transfer and induction interactions. The total interaction energy and all of its components are corrected for the basis set superposition error (BSSE) according to the "full" correction procedure proposed by Boys and Bernardi.[26] The calculations were performed using the Gaussian 03 suite of programs.[27] The interaction energy decomposition was carried out applying the modified version[28] of the Gamess code.[29]

3. Neutral and Cationic Structures

Two isomers were located for studied "pure" $SnBr_3Na$ and SnI_3Na, and "mixed" $NaSnBr_2I$ and $NaSnBrI_2$ complexes. The energetically preferred isomer is characterized by three Sn−X−Na bridges leading to the spatial C_{3v} structure in the case of "pure" species or to the deformed trigonal bipyramid in the case of "mixed" moieties (Figure 1a). The Sn−X bonds are about 0.22 and 0.15 Å longer from corresponding bond distances in $SnBr_2$ and SnI_2, respectively (Table 1). The X−Na distance is approximately longer by 0.31 Å from corresponding values in NaBr and NaI. Such an increase of bonds is expected in view of bond changes observed previously in other complexes characterized by halogen bridges.[30] The $NaSnBrI_2$ complex is more distorted compared to $NaSnBr_2I$. The second isomer is planar and possesses noticeably longer bonds compared to the special structure and consequently is less stable. The higher energy isomer (Figure 1b) is formed due to dipole−dipole interactions of parent molecules. The planar complex, although a minimum energy structure, as confirmed by frequency calculations, is energetically 147.5 kJ mol^{-1} above the pyramidal conformer and because of that will be difficult to detect in vapors. The weaker interactions within the quasibinary system are well visible, causing only small variations in geometries of parent monomers (Table 1).

The ionization of studied systems leads to structural changes manifested as breaking the weakest Na−I bond (Na−Br in the case of the "pure" $NaSnBr_3$ complex) (Figure 2a). As expected, the newly formed Sn−X terminal bond is shorter compared to that in the Sn−X−Na bridge (Table 2). Interestingly, all Sn−halogen bonds in molecular cations are much shorter compared to neutral complexes and are close to those characterizing noninteracting monomers. The length of sodium−halogen bond has increased as an effect of the ionization. The mass spectrum of vapors also indicated the presence of the planar $NaSnXY^+$ cation (Figure 2b). Its bond distances (Table 2) are different from that observed for the $NaSnXYZ^+$ cation, suggesting deep differences in the nature of bonding between observed cation.

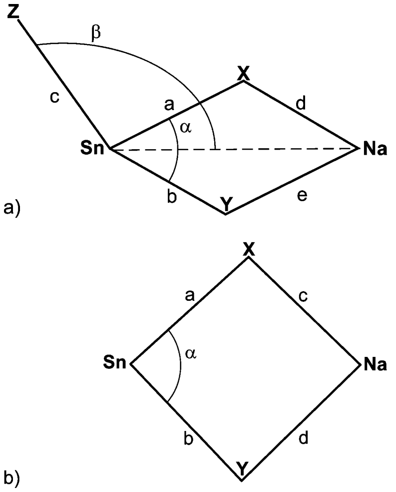

Figure 2. The $NaSnXYZ^+$ and $NaSnXY^+$ (X, Y, Z = Br or I) cations: products of the ionization/fragmentation processes.

4. Thermodynamics

4.1. The Third-Law Reevaluation of Experimental Data. Third-law enthalpies of the gaseous reactions of the dissociation of $NaSnXY_2$ (X, Y = Br or I) were reevaluated in the present study according to the third-law method by applying the equation

$$\Delta_r H^\circ(298\ \mathrm{K}) = -T\{R \ln K_p^\circ + \Delta_r[G^\circ(T) - H^\circ(298)]/T\}$$

for the experimental data reported in ref 4. The thermodynamic functions for gaseous $NaSnXY_2$ complexes used in the present evaluation were estimated on the basis of the molecular parameters obtained theoretically in this study and are available in Supporting Information (Table 1s). The calculations were performed applying thermodynamic functions available from literature for NaBr(g),[31] NaI(g),[31] $SnBr_2$,[32] and SnI_2(g)[33] monomers. The third-law enthalpies were calculated in each case for the maximal and minimal temperature of the experimental range given in ref 4. The results are summarized in Table 3. Enthalpies obtained for both temperatures agree in each case within less than 2 kJ/mol, thereby showing only a small variation of the third-law data with the temperature change. The arithmetic mean of two values obtained for each reaction is presented in Table 3 as the selected third law enthalpy. Second law enthalpies obtained in ref 4 were recalculated for 298 K by the use of the $H^\circ(T) - H^\circ(298)$ functions determined in this work for gaseous complexes. Required values for monomers were taken again from the respective sources cited above. The obtained results are also included in Table 3. The recommended reaction enthalpies result from the computation of the weighted average from second- and third-law values. The reciprocal probable overall errors given in Table 3 were assumed as a weight of each value. The further discussion of errors is given as Supporting Information.

The recommended entropies of dissociation reactions were calculated as follows. Gibbs energy for each reaction was

TABLE 1: Structural Parameters for Pyramidal and Planar Isomers of NaSnXYZ Complexes (for parameters definition, see Figure 1) and Corresponding Monomers Calculated at the MP2 Level of Theory. Distances in Angstroms, Angles in Degrees

molecule				bond distances					angles	
X	Y	Z	symmetry	*a*	*b*	*c*	*d*	*e*	α	*β*
				Pyramidal Isomer						
Bρ	Br		C_{3v}	2.741		2.856			54.9	90.2
Br	I		C_s	2.742	2.978	2.846	3.077		53.6	92.4
I	Br		C_s	2.906	2.666	3.091	2.865		57.6	90.3
I	I		C_{3v}	2.903		3.086			56.3	92.1
				Planar Isomer						
Br	Br	Br	C_s	2.607	2.604	3.075	3.083	2.557	96.1	142.5
Br	Br	I	C_s	2.608	2.605	3.070	3.078	2.770	96.0	142.5
Br	I	Br	C_s	2.591	2.727	2.992	3.367	2.593	96.3	164.2
I	Br	I	C_s	2.734	2.585	3.345	2.998	2.808	96.2	94.3
I	I	Br	C_s	2.773	2.771	3.302	3.305	2.579	97.7	142.5
I	I	I	C_s	2.832	2.829	3.304	3.312	2.769	98.5	141.2
				Parent Monomers						
NaBr			C_v	2.555 2.502[a]						
NaI			C_v	2.771 2.711[a]						
$SnBr_2$			C_{2v}	2.525 2.504[b]					98.6	
SnBrI			C_s	2.526	2.753				99.1	
SnI_2			C_{2v}	2.753 2.699[b]					99.4	

[a] Reference 34. [b] Reference 35.

TABLE 2: Structural Parameters for the Most Stable $NaSnXYZ^+$ and $NaSnXY^+$ (X, Y, Z = Br or I) Cations (for the parameters definition, see Figure 2). Distances in Angstroms, Angles in Degrees

cation				bond distances					angles	
X	Y	Z	symmetry	*a*	*b*	*c*	*d*	*e*	α	*β*
				$NaSnXYZ^+$						
Br	Br	Br	C_{2v}	2.533		2.446	2.955		98.4	117.6
Br	Br	I	C_{2v}	2.543		2.670	2.937		97.4	120.4
Br	I	I	C_s	2.553	2.761	2.672	2.909	3.192	99.3	120.9
I	I	I	C_{2v}	2.770		2.674	3.156		101.3	122.3
				$NaSnXY^+$						
Br	Br		C_{2v}	2.585		2.856			94.0	
Br	I		C_s	2.586	2.801	2.892	3.132		94.4	
I	I		C_{2v}	2.808		3.067			97.2	

TABLE 3: Second- and Third-Law Enthalpies and Their Recommended Values (in kJ/ mol) of Gaseous Reactions in the SnXY-NaZ (X, Y, Z = Br or I) System. Values T_1, T_2 Are Minimal and Maximal Temperatures of Experiment. Uncertainties Are Represented by Probable Overall Errors. Temperatures in K, Enthalpies in kJ/mol

no.	reaction	T_1	T_2	$K_p(T_1)$	$K_p(T_2)$	$\Delta H°_1$(III law, 298)	$\Delta H°_2$(III law, 298)	$\Delta H°$ (III law, 298) selected
(1)	$NaSnBr_3 = NaBr + SnBr_2$	723	805	2.24×10^{-6}	4.83×10^{-5}	175.7	174.5	175.1 ± 5.6
							$\Delta H°$(II law, 298)[a]	186.5 ± 8.2
							$\Delta H°$(298 K), recommended	178.7 ± 9.2
(2)	$NaSnBr_2I = NaI + SnBr_2$	683	805	9.33×10^{-7}	8.17×10^{-5}	170.5	170.0	170.2 ± 5.6
							$\Delta H°$(II law, 298)[a]	172.9 ± 6.4
							$\Delta H°$(298 K), recommended	171.4 ± 4.6
(3)	$NaSnBrI_2 = NaBr + SnI_2$	663	823	1.08×10^{-7}	5.41×10^{-5}	178.3	177.5	177.9 ± 5.6
							$\Delta H°$(II law, 298)[a]	181.6 ± 5.8
							$\Delta H°$(298 K), recommended	179.8 ± 4.9
(4)	$NaSnI_3 = NaI + SnI_2$	623	823	5.11×10^{-7}	9.54×10^{-4}	159.1	157.1	158.1 ± 5.5
							$\Delta H°$(II law, 298)[a]	165.9 ± 5.3
							$\Delta H°$(298 K), recommended	162.0 ± 6.6

[a] Reference 4.

calculated at mean experimental temperature, T_m, from $K_p(T_m)$ given in ref 4. These values were combined with the respective selected enthalpies recalculated to the mean temperature T_m in order to obtain $\Delta_r S°(T_m)$. The entropies were recalculated to 298 K by the use of the $S°(T_m - 298)$ functions taken for each gaseous species from thermochemical tables cited above.

4.2. Theoretical Thermodynamics. The calculated enthalpies of dissociation of binary systems (Table 4) are within the error bars of measured values. Calculated values of entropy of dissociation reactions also closely reproduce measured results. The corresponding standard atomization enthalpies are reasonably reproduced by theoretical values (Table 2s). Assuming the

TABLE 4: Calculated and Experimental Dissociation Energies, Enthalpies, and Entropies of Dissociation Reactions of $NaSnXY_2$ (X, Y = Br or I) Complexes. Enthalpies and Energies in kJ/mol, Entropies in kJ/ mol

		method				
no.	reaction	theor	expmtl	$D_\circ$	ΔH°_{298}	ΔS°_{298}
(1)	$NaSnBr_3 = NaBr + SnBr_2$		ref 6		193.3 ± 4.9	159.7 ± 7.5
			ref 36		190 ± 6	160 ± 7
			ref 4		186.5 ± 8.2	153.1 ± 11.7
			ref 37		188.4 ± 6.4	158.5 ± 8.4
			this work		178.7 ± 9.2	144.4 ± 12.6
		DFT		161.7	160.4	144.6
		MP2		192.3	191.1	149.3
		CCSD(T)		184.1	183.0	
(2)	$NaSnBr_2I = NaI + SnBr_2$		ref 4		172.9 ± 6.4	140.5 ± 9.9
			this work		171.4 ± 4.6	139.7 ± 7.7
		DFT		149.9	148.4	145.9
		MP2		180.7	179.4	148.2
		CCSD(T)		171.6	170.3	
(2a)	$NaSnBr_2I = NaBr + SnBrI$					
		DFT		159.0	157.6	146.1
		MP2		192.2	190.9	148.6
		CCSD(T)		183.4	182.1	
(3)	$NaSnBrI_2 = NaBr + SnI_2$		ref 4		181.6 ± 5.8	143.1 ± 9.3
			this work		179.8 ± 4.9	142.0 ± 8.1
		DFT		155.9	154.4	145.3
		MP2		191.7	190.3	147.8
		CCSD(T)		182.3	181.0	
(3a)	$NaSnBrI_2 = NaI + SnBrI$					
		DFT		147.3	145.7	145.1
		MP2		181.2	179.7	147.6
		CCSD(T)		171.3	169.9	
(4)	$NaSnI_3 = NaI + SnI_2$		ref 4		165.9 ± 5.3	147.8 ± 8.7
			ref 38		166.3 ± 4.5	144.2 ± 6.5
			this work		162.0 ± 6.6	144.2 ± 10.1
		DFT		144.4	142.7	144.2
		MP2		181.3	179.7	146.9
		CCSD(T)		170.7	169.1	

additivity of bonding, the contributions to the atomization energy representing single Sn−Br−Na and Sn−I−Na bridges amount to 412 kJ/mol for $NaSnBr_3$ and 356 kJ/mol for $NaSnI_3$ complexes. The total atomization enthalpies of mixed $NaSnBr_2I$ and $NaSnBrI_2$ complexes calculated from the above single bridge enthalpies amount to 1180 and 1124 kJ/mol and very closely match *ab initio* results of 1179.7 and 1123.9 kJ/mol, respectively. The same procedure applied to experimental data leads to estimated values of 1116 and 1053 kJ/mol for mixed $NaSnBr_2I$ and $NaSnBrI_2$ complexes which are close to the measured atomization enthalpies of 1101.7 ± 10.2 and 1065.8 ± 8.0 kJ/mol,[4] respectively. The above results indicate the additive character of bonding in studied complexes, with three and higher body interactions constituting the contribution comparable to error bars. The comparison of DFT and higher level of theory results indicates the lack of the proper accounting for the correlation energy in the case of the B3LYP functional, leading to the conclusion that DFT results cannot be trusted.

The difference between energies characterizing Sn−Br and Sn−I bonds calculated from the atomization enthalpy according to the partition formula

$$\Delta E_{\text{atom}} = E(\text{Na}-\text{X}) + E(\text{Na}-\text{Y}) + E(\text{Na}-\text{Z}) + E(\text{Sn}-\text{X}) + E(\text{Sn}-\text{Y}) + E(\text{Sn}-\text{Z})$$

amounts to 12 kJ/mol (average). The energetical advantage of the Na−Br bond over Na−I amounts to only 0.8 kJ/mol (average). Hence, the number of Sn−Br bonds present in the complex governs the stability of complexes, and obviously $NaSnBr_3$ is the most stable moiety.

The calculated vibrational frequencies reasonably reproduce experimental values of $SnBr_2$ and SnI_2, indicating that predicted values for complexes should allow for a reliable interpretation of spectra[7] and more important would provide the proper base for calculations of thermodynamical parameters. The analysis of vibrational spectra (Table 3s) confirms the decreasing bonding strength, as bromine atoms are replaced by iodine in molecule. The systematic shift to the red is observed in all bonds after the increase of iodine presence. The ionization energy decreases systematically as a number of iodine atoms increase, namely 8.40, 8.13, 8.09, and 8.08 eV for $NaSnBr_3$, $NaSnBr_2I$, $NaSnBrI_2$, and $NaSnI_3$, respectively. The similar order (9.56, 9.57, 8.99, and 9.01 eV) is observed for the appearance potentials of $NaSnXY^+$ moieties.

5. Nature of Bonding

Both population analyses applied (NBO and Mulliken) lead to the qualitatively same picture of the electron density distribution although the differences between Br and I displayed by the NBO approach are slightly higher (Table 5). Sn and Na atoms donate approximately one electron each to halogens of bridges. In molecules rich in Br the transfer of electron to halogens is higher compared to that dominated by I. The ionization of molecular complexes removes an electron from halogen atoms. Interestingly, according to NBO analysis, as an effect of the ionization the sodium atom is subject to the significant back-donation of electron density. Bromine atoms absorb more electron density than iodine and in the effect form the stronger bond. Based on population analyses, the distribution of charge leads to the neutral $(SnXY_2)$-(Na^+) complex and the isomerization removes an excess electron from the $SnXY_2$ part. The $NaSnXY^+$ ion is characterized by the distinct singly charged sodium cation. This confirms the geometrical observation indicating the $(SnXY)(Na^+)$ structure of the complex.

TABLE 5: Atomic Charges (in Electron) Calculated within NBO and Mulliken (in Parentheses) Electron Population Schemes for Pyramidal and Planar Isomers of $NaSnXY_2$ and $NaSnXYZ^+$ and $NaSnXY^+$ (X, Y, Z = Br or I) Cations. Structures Correspond to Figures 1 and 2

			bridged halogens				terminal		
complex	symmetry	Sn	X	charge	Y	charge	Z	charge	Na
				Pyramidal					
$NaSnBr_3$	C_{3v}	1.024 (1.043)	Br	−0.646 (−0.540)					0.913 (0.578)
$NaSnBr_2I$	C_{2v}	0.943 (1.105)	Br	−0.639 (−0.579)	I	−0.564 (−0.584)			0.899 (0.638)
$NaSnBrI_2$	C_{2v}	0.879 (0.978)	Br	−0.637 (−0.528)	I	−0.562 (−0.528)			0.883 (0.606)
$NaSnI_3$	C_{3v}	0.763 (1.046)	I	−0.545 (−0.572)					0.872 (0.671)
				Planar					
$NaSnBr_3$	C_s	1.172 (1.115)	Br	−0.565 (−0.484)			Br	−0.933 (−0.652)	0.894 (0.503)
				$NaSnXYZ^+$					
$NaSnBr_3^+$	C_s	0.958 (1.502)	Br	−0.186 (−0.437)			Br	−0.069 (−0.402)	0.483 (0.773)
$NaSnBr_2I^+$	C_s	0.861 (1.401)	Br	−0.197 (−0.453)			I	0.052 (−0.259)	0.482 (0.763)
$NaSnBr_2^+$	C_1	0.790 (1.356)	Br	−0.208 (−0.461)	I	−0.099 (−0.382)	I	0.038 (−0.282)	0.478 (0.769)
$NaSnI_3^+$	C_s	0.722 (1.315)	I	−0.111 (−0.394)	I	−0.111 (−0.394)	I	0.028 (−0.299)	0.472 (0.773)
				$NaSnXY^+$					
$NaSnBr_2^+$	C_{2v}	1.269 (1.196)	Br	−0.614 (−0.455)					0.960 (0.715)
$NaSnBrI^+$	C_s	1.166 (1.143)	Br	−0.611 (−0.451)	I	−0.504 (−0.416)			0.950 (0.724)
$NaSnI_2^+$	C_{2v}	1.058 (1.092)	I	−0.498 (−0.410)					0.939 (0.729)

TABLE 6: Interaction Energy Components for the Lower Energy Isomer of $NaSnBr_xI_{3-x}$ ($x = 0-3$) Systems. Energies in kJ/mol

n	molecule/ assumed monomers	$\epsilon_{el}^{(10)}$	ϵ_{ex}^{HL}	ΔE_{del}^{HF}	ΔE_{HF}	$\epsilon_{MP}^{(2)}$	ΔE_{MP2}	D_e
1	$NaSnBr_3$/NaBr-SnBr)	−195.2	309.7	−306.0	−191.5	−24.9	−216.4	−194.8
2	$NaSnBr_2I$/NaI-$SnBr_2$	−166.7	294.7	−301.5	−173.5	−30.8	−204.2	−183.1
3	$NaSnBr_2I$/NaBr-SnBrI	−188.6	312.1	−311.1	−187.6	−26.4	−214.0	−194.7
4	$NaSnBrI_2$/NaBr-SnI_2	−181.8	314.2	−315.7	−183.3	−28.0	−211.2	−194.1
5	$NaSnBrI_2$/NaI-SnBrI	−159.4	297.3	−307.6	−169.8	−32.7	−202.5	−167.7
6	$NaSnI_3$/NaI-SnI_2	−152.1	299.6	−313.2	165.7	−34.6	−200.3	−183.5

TABLE 7: The Difference between Metal−Br and Metal−I Contributions to the Total Interaction Energy Calculated for Interaction Energy Decomposition Components. Energy Differences in kJ/mol

reference complexes[a]	complementary interactions	$\epsilon_{el}^{(10)}$	ϵ_{ex}^{HL}	ΔE_{del}^{HF}	ΔE_{HF}	$\epsilon_{MP}^{(2)}$	ΔE_{MP2}
			E^X(Sn-Br)−E^X(Sn-I)				
(1)−(2)	NaBr/ NaBr	−28.2	15.0	−4.5	−18.0	5.9	−12.2
(3)−(5)	NaBr/NaI	−29.2	14.8	−3.5	−17.8	6.3	−11.5
(4)−(6)	NaI/NaI	−29.7	14.6	−2.5	−17.6	6.6	−10.9
			E^X(Na-Br)−E^X(Na-I)				
(1)−(3)	SnBr	−6.6	−2.4	5.1	−3.9	1.5	−2.4
(3)−(4)	SnBr	−6.8	−2.1	4.6	−4.3	1.6	−2.8
(2)−(5)	SnI	−7.3	−2.6	6.1	−3.7	1.9	−1.7
(5)−(6)	SnI	−7.3	−2.3	6.6	−4.1	1.9	−2.2

[a] The definition of complexes (n) is provided in Table 6.

The more adequate picture of bonding characterizing the $NaSnXY_2$ molecule is provided by application of the interaction energy decomposition scheme to the complex of parent SnXY and NaZ monomers. The interactions involve three atom−atom contacts (bonds). The largest dissociation energy considered ($SnBr_2$−NaBr) leads to the single atom−atom contribution of 65 kJ/mol, the amount which can be reliably explored within the perturbation theory. The decomposition analysis indicates (Table 6) that the bonding energy is dominated by the delocalization energy (ΔE_{del}^{HF}) resulting from the electronic charge transfer. Electrostatic interactions ($\epsilon_{el}^{(10)}$) constitute large part of interaction energy, while the correlation contribution ($\epsilon_{MP}^{(2)}$) is one order smaller. The total interaction energy is reduced by the significant repulsive exchange energy (ϵ_{ex}^{HL}) contribution resulting from short distances of formed bonds. The exchange energy is almost exactly balanced by the delocalization term. The stabilization of complexes due to the correlation energy (dispersion) is proportional to the number of iodine atoms. In the agreement with an electron population picture, an increasing number of Br atoms leads to the higher electrostatic interactions. As expected, the planar isomer is bound due to the domination of electrostatic forces (dipole−dipole complex). The replacement of Br by I enhances covalent components (delocalization and correlation) and reduces the ionic character of bonding. The formation of bonds leads to the significant structural relaxation that covers 10% of the overall interaction energy.

The formation of complexes from SnXY and NaZ monomers leads to three new one tin−halogen and two sodium−halogen bonds. The new tin−halogen bond is formed because of the donation of an electron pair from halogen to tin. Ionic Na^+−$(X_3)^-$ bonds may be considered as three mesomers characterized by ionic Na^+−X^- interactions. Assuming the additivity of atom−atom interactions, the total interaction energy characterizing the (SnXY)(NaZ) complex may be expressed as the sum

$$\Delta E = E(\mathrm{Sn-Z}) + E(\mathrm{Na-X}) + E(\mathrm{Na-Y})$$

were X, Y, Z = Br or I. The formal complex of $SnBr_2$···NaBr associated with the $NaSnBr_3$ molecule (Table 3, reaction (1)) is represented by Sn−Br and two Na−Br interacting contacts.

Similarly, $SnBr_2\cdots NaI$ complex of $NaSnBr_2I$ (reaction (2)) moiety is represented by Sn−I and two Na−Br interactions. Such a representation leads to the expression

$$E(\mathrm{Sn{-}Br}) - E(\mathrm{Sn{-}I}) = \Delta E(1) - \Delta E(2)$$

describing the energetical difference between Sn−Br and Sn−I contributions to the total interactions. The above procedure may be easily extended to interaction energy decomposition components (Table 7). The results of calculations indicate that differences between Br and I, regarding stabilization of studied complexes, is governed by Sn−halogen interactions. The energy partitioning emphasizes the fact that the differences result from larger electrostatic interactions in the case of Br. The decomposition reveals the differences between Sn and Na regarding the nature of interactions with halogens. The replacement of Br for I has the reverse effect in the case of exchange and delocalization terms (Table 7). The correlation contributions always favor iodine atoms; however, since total interactions are dominated by electrostatics the overall stability is driven by Br atoms. The differences between atom−atom interactions are only weakly influenced by complementary interactions imposed by other bonds present in complexes, again confirming the additivity of studied bonds.

6. Conclusions

The theoretical studies of structural and vibrational properties of quasibinary complexes SnXY-NaZ (X, Y, Z = Br or I) allowed for the reevaluation of experimental thermodynamic properties and provide enhanced values of recommended dissociation enthalpies and entropies. The *ab initio* calculated enthalpies of dissociation of binding systems are within error bars of measured values. The number of Sn−Br bonds present in the complex governs the stability of moieties, with $NaSnBr_3$ being the most stable. As expected, the studies indicate that in the series $NaSnCl_3$, $NaSnBr_3$, and $NaSnI_3$ the most stable is the chlorine complex. The $NaSnCl_3$ is also characterized by the highest entropy of dissociation[39] indicating its highest rigidity.

The results of population analysis indicate that neutral complexes possess the $(SnXY_2)^-Na^+$ form. The ionization of the complex removes an electron from the $SnXY_2$ fragment. The decomposition of interaction energy indicates that the binding energy is dominated by the electron charge-transfer energy represented in applied scheme by the $\Delta E_{\mathrm{del}}^{\mathrm{HF}}$ term. The decomposition indicates that the presence of iodine atoms enhances the covalent interactions ($\Delta E_{\mathrm{del}}^{\mathrm{HF}}$ and $\epsilon_{\mathrm{MP}}^{(2)}$) while Br atoms lead to the increase of electrostatic interactions. The differences between atom−atom interactions, representing single Br−Br, Br−I, or I−I bonds, are only weakly influenced by interactions of other pairs present in the complex, indicating the additive nature of interactions in studied moieties.

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Supporting Information Available: The discussion of error evaluation, tables of theoretical thermochemical functions, and a table of standard atomization enthalpies. This material is available free of charge via the Internet at http://pubs.acs.org.

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