Theoretical Thermodynamics and the Nature of Interactions of the Quasi-Binary NaCl−SnCl₂ System

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The formation of $NaSnX_3$ (X = halogen) influences the sodium concentration in metal halide lamps making the thermodynamics of such reactions critical for technological developments. Theoretical predictions of the structure and vibrational properties of the quasi-binary NaCl−SnCl₂ system lead to thermodynamical data determined through the third law evaluation. Ab initio enthalpy and entropy of dissociation of $NaSnCl_3$ also is reported. Additionally, insight into the nature of chemical bonding is provided by electron population analysis and the interaction energy decomposition scheme.

1. Introduction

The sodium concentration in the gas phase can be increased by chemical vapor transport due to the formation of $NaSnX_3$(g) (X= Cl, Br, I).[1−4] This property is an important factor in the modeling of metal halide lamps. Such lamps are widespread because of their luminous efficiency and excellent color quality.[5] The study of gaseous metal halide complexes is also of fundamental interest for coordination chemistry because even structures of $(SnX_2)_2$ dimers are unusual and difficult to predict without advanced calculations.[6,7] The experimental data on $NaSnX_3$ heterocomplexes are restricted to their direct (by use of mass spectrometry)[1−4] or indirect[8] identification in the gas phase and to their thermochemistry studied in quasi-binary systems.[1−4] In ref 1, we reported thermodynamic studies of the NaCl−SnCl₂ system by Knudsen effusion mass spectrometry. The thermochemistry of the $NaSnCl_3$(g) heterocomplex was derived from the gaseous equilibria involving these species determined over a wide temperature range. Only the second law evaluation was applied in the study because of the lack of structural and spectroscopic data on the $NaSnCl_3$(g) complex. The strong fragmentation of AMX_n(g) gaseous complexes (A = alkali, M = multivalent metal, X = halogen) upon electron bombardment is well-known[9]. For this reason, most of the ions recorded in a mass spectrum have two or more neutral precursors. Therefore, the quantitative apportionment of their ion intensities has to be performed prior to the partial pressures and the equilibrium constant evaluation for the studied chemical reaction. Uncertainties of the mass spectrum interpretation can lead to serious errors in the second law enthalpies obtained by use of the estimated pressures. It is therefore of significant importance to apply the third law evaluation of the reaction enthalpies and to compare them with the second law values.

The present theoretical studies supplement experimental findings with the structures and vibrational properties of neutral $NaSnCl_3$ complexes and cations resulting from its fragmentation.[1] The electron population analysis and the interaction energy decomposition that were performed provide insight into the nature of bonding characterizing the $NaSnCl_3$ complex. Structural and spectroscopic data obtained for $NaSnCl_3$(g) species were applied to calculations of its thermodynamic functions. The functions, which supplemented the experimental data reported in ref 1, were later used for the third law evaluation of enthalpies for the gaseous reaction of formation of the $NaSnCl_3$(g) species. The third law data are compared with the second law values reported in the previous study[1] as well as with values obtained ab initio in the present work.

2. Computational Details

The ground-state geometries of the studied species were obtained by applying the second-order Møller−Plesset perturbation theory (MP2)[10] and the density functional theory (DFT)[11] methods. The DFT approach utilizes Becke's three parameter functional[12] with the Vosko et al. local correlation part[13] and the Lee et al.[14] nonlocal part, abbreviated as B3LYP. Geometry searches were performed for a number of possible isomers to ensure the location of the global minimum on the potential energy surface. No symmetry constraints were imposed during the optimization process. The location of true minima was confirmed by the vibrational analysis performed at the MP2 and the DFT levels of theory. The single point calculations at the coupled cluster method with single and double substitutions and noniterative triple excitations CCSD(T)[15,16] was further applied to enhance the quality of the theoretical thermodynamics. The calculations were performed using the relativistic effective core potential that retains the outer $4d^{10}5s^25p^2$ shells and the corresponding basis set of LaJohn et al. for tin.[17] Chlorine and sodium atoms were represented by the all-electron cc-pVTZ basis set.[18,19] Additionally, the chlorine basis set was augmented by a set of spdf diffuse functions.[19] Because of the ionic nature of the bonding in the studied species, the applicability of the basis sets was verified by evaluation of the ionization energies of Na and Sn and the electron affinity of the chlorine atom. The theoretical ionization energies (CCSD(T) level) of sodium (5.426 eV) and tin (6.956 eV) agree satisfactorily with the

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experimental values of 5.139 and 7.344 eV,[20] respectively. The calculated electron affinity of chlorine (3.678 eV) also agrees well with the corresponding experimental value of 3.614 eV.[21,22] The thermodynamic properties of the studied complexes were calculated applying the ideal gas, rigid rotor, and harmonic oscillator approximations.[23] The electron distribution was studied using the natural bond orbital (NBO)[24] electronic population analysis approach and the MP2 electron densities.

The total interaction energy was calculated at the MP2 level of theory, as

$$\Delta E_{\mathrm{MP2}} = E_{AB} - E_A - E_B$$

and ΔE_{MP2} has been further partitioned into Hartree−Fock (ΔE_{HF}) and correlation ($\epsilon_{\mathrm{MP}}^{(2)}$) components according to the equation

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

The Hartree−Fock (HF) interaction energy decomposition was performed within the variational-perturbational scheme corrected for the basis set superposition error (BSSE).[25] In this scheme, ΔE_{HF} is partitioned into electrostatic ($\epsilon_{\mathrm{el}}^{(10)}$) and Heitler−London exchange ($\epsilon_{\mathrm{ex}}^{\mathrm{HL}}$) first-order components and the higher order delocalization ($\Delta E_{\mathrm{del}}^{\mathrm{HF}}$) term. The delocalization energy represents the charge transfer, induction, and other higher order Hartree−Fock terms.[26] The $\epsilon_{\mathrm{MP}}^{(2)}$ correlation correction includes the intermolecular dispersion contribution term ($\epsilon_{\mathrm{disp}}^{(20)}$) and the higher order correlation energy components.[27] The calculations of energy of monomers were performed in the dimer basis set according to the "full" correction scheme proposed by Boys and Bernardi.[28] The computations were carried out using the Gaussian 03 suite of programs.[29] The interaction energy decomposition was performed applying the modified version[30] of the Gamess code.[31]

3. Results and Discussion

3.1. Structures. The calculations reveal two isomers of the NaSnCl₃ molecule with an energy separation of 133.5 kJ mol⁻¹. The energetically preferred structure for NaSnCl₃ is represented by the trigonal bipyramid where the tin atom is separated from sodium via three equivalent chlorine bridges (Figure 1a). The equilibrium structure of NaSnCl₃ is confirmed by calculations of vibrational frequencies leading to the series: 110.4, 153.9, 156.7, 224.7, 264.9, and 291.2 cm⁻¹. All distances in the ground state pyramidal isomer indicate the single molecule character of the moiety. The formation of chemical bonds is confirmed by changes in bond distances in parent monomers and the formed molecule that is mainly SnCl (from 2.375 to 2.511 Å in the complex) and NaCl (2.414 to 2.719 Å). The second isomer possesses the C_{2v} planar geometry (Figure 1b). It is characterized by two chlorine atoms involved in the Sn−Cl−Na bridged bonds and a single terminal Na−Cl bond. A comparison of the bond distances reveals significant differences in the bonding that governs the structure of the complexes. The bond distances in the planar isomer are comparable to that observed in the corresponding monomers, allowing the two independent interacting molecules SnCl₂ and NaCl to be distinguished.

The ionization of the NaSnCl₃ isomer leads to a significantly distorted structure with only two Na−Cl bonds (Figure 2a). The NaSnCl₂⁺ cation also is detected as a fragmentation product. Its structure is characterized by a planar ring with two bridged chlorines connecting tin and sodium (Figure 2b). The theoretical
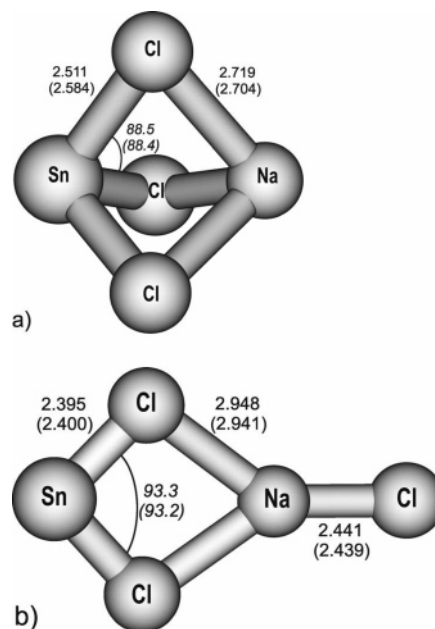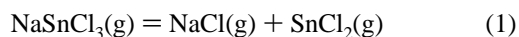

Figure 1. MP2 and B3LYP (in parentheses) structures of (a) trigonal bipyramid C_{3v} (low energy) and (b) planar C_{2v} (high energy) isomers of NaSnCl₃. Distances in angstroms, angles in degrees.
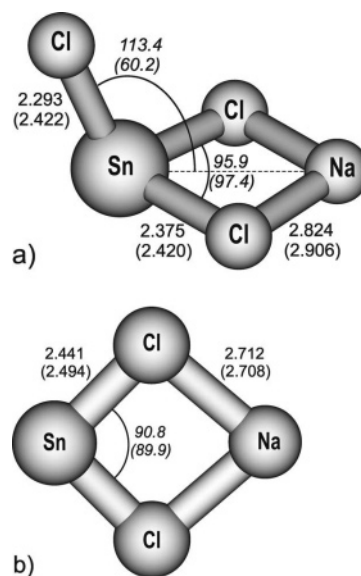
Figure 2. MP2 and B3LYP (in parentheses) structures of (a) NaSnCl₃⁺ and (b) NaSnCl₂⁺ cationic products of NaSnCl₃ fragmentation. Distances in angstroms, angles in degrees.

prediction of the stable NaSnCl₃⁺ and NaSnCl₂⁺ species is consistent with the observed mass spectra of the parent NaSnCl₃ complex.[1]

3.2. Thermodynamics. Enthalpies of the gaseous reactions

$$\mathrm{NaSnCl_3(g)} = \mathrm{NaCl(g)} + \mathrm{SnCl_2(g)} \tag{1}$$

$$\mathrm{SnCl_2(g)} + \mathrm{Na_2Cl_2(g)} = \mathrm{NaSnCl_3(g)} + \mathrm{NaCl(g)} \tag{2}$$

were calculated from the experimental data reported in ref 1 according to the third law method applying the equation

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

The calculations were performed applying thermodynamic functions for NaCl(g), Na₂Cl₂(g),[32] and SnCl₂(g)[6] reported in the cited literature. The thermodynamic functions for NaSnCl₃(g)

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TABLE 1: Thermochemical Functions for the High (C_{3v}) Energy Isomer of NaSnCl$_3$ Calculated from Theoretical Structure and Vibrations Determined at the MP2 Level of Theory

		NaSnCl$_3$(g)		
		$H°(298\ \text{K}) - H°(0\ \text{K}) = 23.61\ \text{kJ mol}^{-1}$		
T/K	$C_p°$ J mol^{-1} K^{-1}	$S°$ J mol^{-1} K^{-1}	$H°(T) - H°(298\ \text{K})$ J mol^{-1} K^{-1}	$-[G°(T) - H°(298)]/T$ J mol^{-1} K^{-1}
298.15	102.41	390.13	0	390.13
300	102.48	390.76	0.19	390.13
400	104.84	420.61	10.57	394.19
500	105.98	444.14	21.12	401.90
600	106.61	463.53	31.75	410.61
700	106.99	479.99	42.44	419.37
800	107.24	494.30	53.15	427.86
900	107.42	506.94	63.88	435.96
1000	107.54	518.26	74.63	443.64
1100	107.64	528.52	85.39	450.9
1200	107.70	537.89	96.15	457.76
1300	107.76	546.51	106.92	464.26
1400	107.80	554.50	117.70	470.42
1500	107.84	561.94	128.48	476.28

TABLE 2: The Third Law Evaluation of the Enthalpy Changes for Different Reactions Obtained in Run 1[a]

	NaSnCl$_3$(s) = NaCl(g) + SnCl$_2$(g)[b]			SnCl$_2$(g) + Na$_2$Cl$_2$(g) = NaSnCl$_3$(g) + NaCl(g)[b]		
		$-\Delta_r[G°(T) - H°(298)]/T$			$-\Delta_r[G°(T) - H°(298)]/T$	
T/K	$K_p°$	J mol^{-1} K^{-1}	$\Delta H°(298\ \text{K})$/kJ mol^{-1}	$K_p°$	J mol^{-1} K^{-1}	$\Delta H°(298\ \text{K})$/kJ mol^{-1}
773	3.40E−06	139.536	188.8	8.09E−02	−10.109	8.3
723	4.21E−07	140.020	189.5	8.21E−02	−10.304	7.6
713	2.39E−07	140.118	190.3	9.06E−02	−10.344	6.9
733	6.46E−07	139.922	189.4	8.96E−02	−10.265	7.2
753	1.51E−06	139.728	189.1	8.36E−02	−10.186	7.9
743	1.01E−06	139.825	189.2	8.51E−02	−10.225	7.6
763	2.19E−06	139.632	189.2	8.25E−02	−10.148	8.1
783	4.64E−06	139.440	189.1	8.27E−02	−10.071	8.3
793	6.82E−06	139.345	188.9	8.11E−02	−10.033	8.6
803	9.76E−06	139.251	188.8	8.20E−02	−9.996	8.7
813	1.39E−05	139.156	188.7	8.07E−02	−9.958	8.9
823	1.79E−05	139.062	189.2	8.86E−02	−9.921	8.4
833	2.71E−05	138.969	188.6	8.31E−02	−9.884	9.0
843	3.60E−05	138.876	188.8	8.45E−02	−9.848	9.0
853	5.38E−05	138.783	188.1	7.90E−02	−9.811	9.6
863	7.06E−05	138.691	188.3	8.10E−02	−9.775	9.6
mean:			189.0 ± 0.5			8.4 ± 0.8

[a] See ref 1. [b] Errors are standard deviations.

TABLE 3: Second and Third Law Enthalpies of Gaseous Reactions in the NaCl−SnCl$_2$ System

reaction	run	$\Delta H°$(II law, 298 K) kJ mol^{-1a}	$\Delta H°$(III law, 298 K) kJ mol^{-1a}
NaSnCl$_3$(s) = NaCl(g) + SnCl$_2$(g)	1	195.2 ± 1.1	189.0 ± 0.5
	2	196.9 ± 0.9	188.1 ± 0.5
	3	199.1 ± 1.2	188.5 ± 0.5
	4	194.9 ± 1.2	188.6 ± 0.5
	5	199.4 ± 1.4	188.3 ± 0.5
	mean:	197.1 ± 5.7[b]	188.5 ± 6.0[b]
	selected:		$\Delta H°(298\ \text{K}) = 193.0 ± 7.4\ \text{kJ mol}^{-1b}$
SnCl$_2$(g) + Na$_2$Cl$_2$(g) = NaSnCl$_3$(g) + NaCl(g)	1	−3.2 ± 1.0	8.4 ± 0.8
	2	−3.3 ± 0.8	9.4 ± 0.8
	3	−4.2 ± 1.4	8.9 ± 0.8
	4	−2.3 ± 1.4	8.9 ± 0.8
	5	3.8 ± 2.8	8.6 ± 0.8
	mean:	−1.8 ± 3.2[b]	8.8 ± 6.4[b]
	selected:		$\Delta H°(298\ \text{K}) = 0.3 ± 8.0\ \text{kJ mol}^{-1b}$

[a] Standard deviation. [b] Probable overall error.

(Table 1) were estimated on the basis of the molecular parameters obtained in the present study. Table 2 presents the results of the third law calculations for run 1 in ref 1. The mean values of the second law and the third law enthalpies obtained for both reactions are summarized in Table 3. The second law values reported in ref 1 were corrected by the $H°(T) - H°(298)$ function estimated in the present study for NaSnCl$_3$(g). The selected sublimation 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 taken as a weight of each value. The second and third law enthalpies of reaction, eq 1, agree within the estimated uncertainties whereas the respective values for reaction, eq 2, differ by 1 kJ mol^{-1} more comparing to estimated uncertainties. The probable overall errors of the second law enthalpies in Table 3 were taken from ref 1. The respective errors for the third law enthalpies were estimated by considering the statistical errors and probable uncertainties of the data used in the calculations. The following

TABLE 4: Calculated and Experimental Dissociation Energy, Enthalpy, Entropy, and Equilibrium Constants[a]

isomer	method	D_o kJ/mol	$\Delta H_{298}°$ kJ/mol	$\Delta S_{298}°$ J/mol^{-1} K^{-1}	K_p(819 K)
C_{3v}	B3LYP	176.7	176.2	149.8	
	MP2	204.6	204.2	151.2	1.15×10^{-5}
	CCSD(T)	198.3	198.0		
	Exper[b]		193.0 ± 7.4	148.8 ± 6.7	1.75×10^{-5} $\pm 49\%$
C_{2v}	B3LYP	44.7	42.6	102.9	
	MP2	47.7	45.5	95.4	

[a] Of the gaseous dissociation reaction NaSnCl$_3$ = NaCl + SnCl$_2$ for high (C_{3v}) and low (C_{2v}) energy isomers of NaSnCl$_3$. [b] Ref 1.

probable uncertainties were assumed for the computation of the overall errors: K_p (eq 1) $\pm 49\%$, K_p (eq 2) $\pm 46\%$, and $[G°(T) - H°(298)]/T \pm 1$ J mol^{-1} K^{-1} (for NaCl(g)), ± 3 J mol^{-1} K^{-1} (for Na$_2$Cl$_2$(g) and SnCl$_2$(g)), and ± 6 J mol^{-1} K^{-1} (for NaSnCl$_3$(g)). The probable uncertainties of K_p values were adopted from ref 1. Uncertainties of the thermochemical functions were estimated from the accuracy reported for the respective table in ref 32 (NaCl, Na$_2$Cl$_2$) and from uncertainties of calculated molecular parameters (SnCl$_2$, NaSnCl$_3$).

The calculated enthalpy of the NaSnCl$_3$(g) = NaCl(g) + SnCl$_2$(g) reaction is properly predicted by ab initio calculations (Table 4). The calculated data indicate the sensitivity of the theoretical results to the inclusion of the correlation energy. At least the MP2 level of theory has to be applied to accomplish the quantitative predictions. The calculated entropy of the reaction is also in excellent agreement with the corresponding measured value. The latter value was adopted from ref 1 and corrected according to the selected enthalpy of reaction 1 and thermodynamic functions of NaSnCl$_3$(g) obtained in the present study. The close agreement of the thermodynamic data leads to the reproduction of the equilibrium constant of the dissociation of NaSnCl$_3$ in the gas phase within the limit of the experimental error bar. As expected, the formation of the second isomer leads to the weakly bonded complex. More importantly, the close reproduction of the experimental data confirms the proper location of the NaSnCl$_3$ structure on the potential energy surface.

3.3. Nature of Bonding. The natural bond orbital population analysis indicates that the C_{3v} structure of NaSnCl$_3$ is formed with an almost perfect ionic Cl−Na bond characterized by an atomic charge out of Na close to one (Table 5). The electronic density corresponding to the electron transferred from Na is

equally distributed between the three chlorine atoms. The separation of Na$^+$ according to the formal equations NaCl = Na$^+$ + Cl$^-$ and NaSnCl$_3$ = SnCl$_3^-$ + Na$^+$ leads to dissociation energies of 537.4 and 529.1 kJ/mol, respectively. The close matching of these dissociation energies confirms the ionic character of the Cl−Na bonds due to the additivity of the electrostatic interactions. The Sn−Cl bonds are more covalent comparing to Na−Cl because two electrons of Sn involved in the bonding lead to an atomic charge on Sn of 1.21 electrons. For formally separated SnCl$_2$ and NaCl fragments of NaSnCl$_3$, the charge transfer from NaCl to SnCl$_2$ amounts to 0.03 electron only. As indicated by the NBO analysis, the ionization of the molecule removes an electron exclusively from the chlorine atoms. Interestingly, such a process enhances the back-donation of electronic density to Na. The loss of an electron as described by the Mulliken analysis leads, however, to a different conclusion indicating that the qualitative considerations should be treated with caution.

The calculated dissociation energy of NaSnCl$_3$ into SnCl$_2$ and NaCl monomers of 204.6 kJ/mol (MP2) may be interpreted as the result from the breaking of one Sn−Cl and two Na−Cl contacts. Such energetics of the complex allow tools that have been developed to study intermolecular interactions to be applied. The total interaction energy in the SnCl$_2$−NaCl complex representing the C_{3v} symmetry molecule is dominated by delocalization and electrostatic terms (Table 6). The partitioning indicates mixed covalent−ionic bonding. The correlation energy gives only a small contribution to the attractive forces. Because of the densely packed complex, the repulsive contribution from the exchange interactions is significant on both the Hartree−Fock and the energy correlation levels. As expected, the C_{2v} isomer is stabilized mainly by electrostatic forces that almost match the total interaction energy, due to the cancellation of other terms. As indicated by studies of the electron density distribution, the separation of the interacting fragments in the ionized system is ambiguous; thus, the results of the (SnCl$_2^+$)-(NaCl) interaction energy decomposition should be treated with caution. The exchange energy is almost the same as in the parent molecule, and interestingly, the system is mostly stabilized by the covalent (delocalization energy component) forces.

4. Conclusions

Theoretical studies of the structure, vibrational properties, thermodynamics, and charge distribution properties are reported

TABLE 5: Total Atomic Charges for NaSnCl$_3$ Isomers and NaSnCl$_3^+$ and NaSnCl$_2^+$ Cations Calculated within NBO and Mulliken Population Analysis (in Parentheses) Schemes[a]

molecule/cation	symmetry	Sn	Cl (bridge)	Cl (terminal)	Na
NaSnCl$_3$	C_{3v}	1.209	−0.713		0.930
		(1.149)	(−0.644)		(0.783)
NaSnCl$_3$	C_{2v}	1.329	−0.649	−0.948	0.918
		(1.191)	(−0.572)	(−0.679)	(0.634)
NaSnCl$_3^+$	C_{3v}	1.136	−0.240	−0.144	0.488
		(1.659)	(−0.553)	(−0.464)	(0.912)
NaSnCl$_2^+$	C_{2v}	1.417	−0.693		0.969
		(1.275)	(−0.569)		(0.862)

[a] Population analysis is based on the MP2 electronic density. Charges in electrons.

TABLE 6: Interaction Energy Decomposition Terms Corresponding to (SnCl$_2$)(NaCl) Complexes Representing NaSnCl$_3$ Isomers and the NaSnCl$_3^+$ Cation[a]

complex/symmetry	$\epsilon_{el}^{(10)}$ [b]	ΔE_{ex}^{HL} [b]	ΔE_{del}^{HF} [b]	ΔE_{HF} [b]	$\epsilon_{MP}^{(2)}$ [b]	$\epsilon_{DS}^{(20)}$ [b]	ΔE_{MP2} [b]
NaSnCl$_3$/C_{3v}	−262.998	341.753	−294.897	−216.141	−16.050	−90.780	−232.191
NaSnCl$_3$/C_{2v}	−44.221	18.410	−19.681	−45.493	−0.134	−2.849	−45.622
NaSnCl$_3^+$/C_s	−243.063	934.678	−703.266	−11.662	−33.186		−44.843

[a] In the case of cation the charge is located on the SnCl$_2$ fragment. [b] Energies in kJ/mol^{-1}.

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to supplement mass spectrometric data for the binary NaCl−SnCl$_2$ system. The theoretical Gibbs energy functions (GEF) for the NaSnCl$_3$ complex allow for a third law evaluation of thermodynamics. The ab initio calculations of enthalpy and entropy of the dissociation reaction confirm the validity of the structural predictions. The electron population analysis and analysis of the interaction energy components indicate the differences between the natures of the Na−Cl and the Sn−Cl bonds with the latter being more covalent. The ionization of the molecule drastically changes the skeleton of the parent species.

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