

## Mass Spectrometric and Quantum Chemical Studies of the Thermodynamics and Bonding of Neutral and Ionized LnCl, LnCl<sub>2</sub>, and LnCl<sub>3</sub> Species (Ln = Ce, Lu)

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The mass spectral patterns of CeCl<sub>3</sub>(g) and LuCl<sub>3</sub>(g) and appearance energies for the identified ions were measured using a Nier-type mass spectrometer coupled with a Knudsen cell. The molecular ion CeCl<sub>3</sub><sup>+</sup> was found to be considerably less stable in comparison to LuCl<sub>3</sub><sup>+</sup>. Partial pressures and sublimation enthalpies of LnCl<sub>3</sub>(s) to monomeric LnCl<sub>3</sub>(g) and dimeric Ln<sub>2</sub>Cl<sub>6</sub>(g) species were obtained in the ranges of 882–1028 (Ln = Ce) and 850–1004 K (Ln = Lu). The contribution of dimeric Ce<sub>2</sub>Cl<sub>6</sub>(g) species to equilibrium vapors of CeCl<sub>3</sub>(s) is considerably smaller than the Lu<sub>2</sub>Cl<sub>6</sub>(g) contribution in LuCl<sub>3</sub>(s) vapors. The measurements were supplemented by quantum chemical ab initio studies of structures, energetics, and vibrational frequencies of neutral and singly ionized LnCl, LnCl<sub>2</sub>, and LnCl<sub>3</sub> species (Ln = Ce, Lu). The theoretical appearance energies of different ions, calculated from the energies of the gaseous species, are in good agreement with experimental data. The fragmentation energies of LnCl, LnCl<sub>2</sub>, and LnCl<sub>3</sub> were also computed and compared with the mass spectral patterns of respective vapor species. The Mulliken and natural bond orbital electron population methods were applied for the systematic analysis of the bonding scheme in molecules and cations.

### Introduction

Mass spectrometric studies of molecular fragmentation are an important source of systematic data of consecutive reactions leading to the decomposition or formation of molecules. The experiments record an equilibrium molecular composition of vapors and provide thermodynamic data for observed processes. Appearance energies and energetics of bonding in neutral, as well as in cationic, species are

available from these measurements. The experimental findings provide the grounds for the calibration of theoretical methods at every step of the reactions in the decomposition sequence. Theoretical studies supplement the measurements with structures, energetics, and vibrational frequencies and allow analyses of the electronic density distribution to be performed. The systematic data regarding the variation of molecular properties are important to provide an insight into the still poorly understood bonding in lanthanide compounds.

Knudsen effusion mass spectrometric studies of metal halide systems provide evidence for significant fragmentation of gaseous species present in vapors upon electron bombardment. The mechanism of the ionization and fragmentation processes leading to the formation of particular ions is still not clear. Experimental mass spectra of metal halides

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published in the literature depend on the energy of ionizing electrons and, to some extent, on the type of ion source of the mass spectrometer. In most magnetic field mass spectrometers used for high-temperature thermodynamic studies, the discrimination at magnet slit takes place depending on the focusing property of the magnet. To correlate theoretical predictions of mass spectrum patterns with measured values, the corrected mass spectra, obtained by the integration of peak areas, instead of recording intensities, should be taken into account.<sup>1,2</sup> Mass spectra of vapor species should, to some extent, correlate with the structures, bonding, and charge distribution of ions formed upon ionization/fragmentation. Recent developments in quantum chemistry have resulted in support of the theory of mass spectra in organic chemistry.<sup>3</sup> To our knowledge, only limited studies are available for the mechanism and nature of mass spectra formation for inorganic vapors (e.g., refs 4–7). The few available combined experimental and theoretical studies allow a discussion of the energetic considerations and a quantitative analysis of fragmentation data.<sup>8–10</sup> To understand the processes related to the ionization and fragmentation of species of the general formula DyX<sub>3</sub> and to rationalize the relative stability of different ions in their mass spectra, the electronic structure and thermodynamic properties were studied for dysprosium halides DyX<sub>n</sub> (X = F, Cl, Br, I; n = 0–3).<sup>11</sup> The role of f electrons in the bonding of Dy-containing moieties was also discussed. In the present work, we study the vaporization and mass spectra of CeCl<sub>3</sub> and LuCl<sub>3</sub> systems. To clarify the role of f electrons in the ionization and fragmentation processes of LnCl<sub>3</sub>(g) species, the first and the last elements of the lanthanide group were selected for this study.

The vaporization of cerium and lutetium chlorides was studied by applying different experimental approaches. The discussion and critical assessment of data for CeCl<sub>3</sub> was given previously.<sup>12–14</sup> Pogrebnoi et al.<sup>15</sup> have studied the vaporization of LuCl<sub>3</sub> by the Knudsen effusion mass spectrometry technique, and they have also supplied a

comparison with previously published results. The vapors of CeCl<sub>3</sub> and LuCl<sub>3</sub> are predominantly monomeric, although mass spectrometric studies show evidence for dimeric species of cerium chloride<sup>12,13</sup> and oligomers, up to tetramers, for lutetium chloride.<sup>15</sup> The ionic–molecular equilibria were investigated in cerium chloride and lutetium chloride vapors as well.<sup>13,15</sup> Several experimental and quantum chemical studies were carried out on the molecular structure of monomeric LnCl<sub>3</sub> species and are discussed in the recent reviews of Hargittai<sup>16</sup> and Kovacs and Konings.<sup>17</sup>

In the present work, we report the results of our experimental and theoretical studies of the vaporization of CeCl<sub>3</sub> and LuCl<sub>3</sub>. The ionization and fragmentation of gaseous species were investigated experimentally by recording mass spectra and ionization efficiency curves. In addition, the vapor composition and enthalpies of sublimation of the gaseous species were obtained and compared with previous studies. Experimental mass spectra, ionization and fragmentation energies, and thermodynamic data for gaseous species were obtained in two groups using different equipment. The aim of the experimental part of the present work was to get more reliable data in a systematic manner and to compare them with previous results, as well as with the theoretical predictions performed in the present study. The molecular structures and vibrational frequencies of LnCl<sub>3</sub><sup>+</sup> molecular ions and their fragments LnCl<sub>2</sub><sup>+</sup>, LnCl<sup>+</sup>, and Ln<sup>+</sup> were determined theoretically. Ionization and appearance energies were also calculated and compared with experimental values. The theoretical information regarding structures, stabilities, and dissociation energies constitutes a significant step toward the understanding of ionization and fragmentation processes in metal halide vapors and should therefore allow for the prediction of their mass spectra. The nature of chemical bonding was studied using the Mulliken and natural bond orbital (NBO) electron population analysis. The analysis of the electronic density distribution allows difficulties present in the common interpretation of bonding in lanthanide complexes to be removed and provides a model for an adequate representation of the experimental findings.

## Experimental Section

The mass spectra of equilibrium vapors over CeCl<sub>3</sub>(s,l) and LuCl<sub>3</sub>(s) were measured in two laboratories: Research Centre Jülich (RCJ) and Jozef Stefan Institute (JSI). Experiments were performed for the temperature ranges of 882–1103 (for CeCl<sub>3</sub>) and 850–1013 K (for LuCl<sub>3</sub>). The 60° magnetic high-resolution instrument of the MAT 271 type supplied by Finnigan MAT, Bremen, Germany, was used in RCJ.<sup>18</sup> Vapor species were ionized with electrons with an emission current of 1 mA and energy of 70 eV. The employed Knudsen cells are made of iridium with knife-edged effusion orifices of 0.3 mm diameter. Temperatures were measured with an automatic pyrometer of the ETSO-U type supplied by Dr. Georg Maurer GmbH, Kohlberg, Germany, and calibrated using the melting points of nickel, silver, and gold. The 60° magnetic low-resolution mass spectrometer with a modified Nier-type ion

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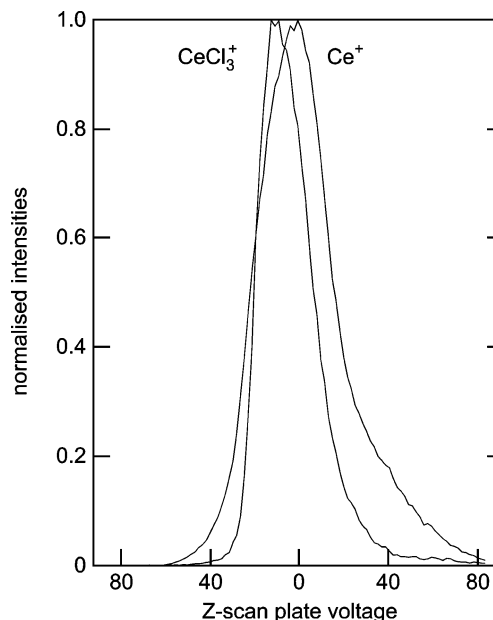
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source was used at JSI. Details of the ion source are given in ref 2. The samples were evaporated from a graphite cell with an effusion orifice of 0.5 mm. The Clausing factor was estimated to be 0.9 from the effusion orifice geometry (conical orifice of 0.5 mm diameter, length of 1 mm with a half angle of 40°). The temperature was measured by a Pt/PtRh (10%) thermocouple. The vapors were ionized with electrons of a total emission current of 20  $\mu\text{A}$  ( $10 \pm 0.1 \mu\text{A}$  trap current) and energy from the threshold up to 100 eV, depending on the type of measurement. To compensate for the discrimination effects for fragments at the magnet slit, Z scan distribution curves were measured using two semielectrodes<sup>2</sup> (45 mm of length, 14.5 mm apart), mounted immediately after the ion exit slit. The respective correction factors were measured at 35 eV. It was proven that they do not depend on the electron energy substantially. The calibration of the Knudsen cell–mass spectrometer system was performed by quantitative evaporation experiments. In addition, ionization efficiency curves were recorded from the threshold up to 100 V using the automatic scanning of electron energy and the simultaneous acquisition of the ion abundance at a rate of 10 points per second using the ATP discrete multiplier in the counting mode. The electron energy was scaled in situ with the ionization energy of H<sub>2</sub>O and O<sub>2</sub>. CeCl<sub>3</sub>(s) (99.9% purity) and LuCl<sub>3</sub>(s) (99.9% purity) were supplied by Aldrich Chem. Co., Poland.

## Theoretical Methods

The quantum-chemical calculations were carried out using the density functional theory (DFT) approach which utilized Becke's three-parameter functional<sup>19</sup> with the local correlation part<sup>20</sup> of Vosko et al. and the nonlocal part of Lee et al.<sup>21</sup> (abbreviated as B3LYP). The DFT performance was compared with the second-order Møller–Plesset perturbation method (MP2)<sup>22</sup> and the coupled-cluster approach with single and double excitations, as well as a perturbative treatment of triple excitations (CCSD(T)).<sup>23,24</sup> The calculations were carried out using the energy-consistent small-core (28 electrons) relativistic lanthanide pseudopotentials for Ce<sup>25</sup> and Lu<sup>26</sup> and the corresponding Gaussian (14s13p10d8f)/[10s8p5d4f] valence basis set.<sup>27</sup> The core electrons of Cl were also replaced by the pseudopotential, and the valence basis set represents 3s<sup>2</sup>p<sup>5</sup>.<sup>28</sup> The basis set of Cl was additionally supplemented by two d polarizations and a set of s and p diffuse functions proposed originally as a part of the aug-cc-PVTZ basis sets.<sup>29</sup> For all calculations, the eigenvalue of  $S^2$  was within 5% of an expected uncontaminated value indicating the applicability of the unrestricted Hartree–Fock wave function also for high-spin electronic states. For the MP2 calculations, projected values are reported.<sup>30</sup> Because of the ionic nature of the chemical bonds in the studied complexes, the applicability of the basis sets was validated by the computation of the ionization energies of Ce and Lu and the electron affinity of the Cl atoms. The agreement between the calculated ionization energy of



**Figure 1.** The Z scan curves for the Ce<sup>+</sup> and CeCl<sub>3</sub><sup>+</sup> ions observed in the mass spectrum of CeCl<sub>3</sub>(g) at a temperature of 1073 K and an electron energy of 35 eV.

Ce and Lu (5.46 and 5.55 eV, DFT results) and the experimental data (5.466, 5.426 eV<sup>31</sup>) indicates the reasonable treatment of the electronic states in neutral and cationic species. The theoretical electron affinity of Cl (3.72 eV) agrees satisfactorily with the respective experimental value of 3.61 eV.<sup>32</sup> The presence of unpaired electrons on the f orbitals of lanthanides allows for the rich manifold of electronic states in studied compounds. The calculations were performed for different electronic states, allowed by electronic configurations of participating atoms, to ensure the location of proper electronic ground states. All geometrical structures were optimized at the DFT level, and the location of the true minima was confirmed by vibrational analysis. Vibrational frequencies and thermodynamic properties were calculated by applying the ideal gas, rigid rotor, and harmonic oscillator approximations.<sup>33</sup> The electronic density distribution study, based on the MP2 calculated density, was performed within the Mulliken and natural bond orbital (NBO) population analysis approaches.<sup>34</sup> The calculations were carried out using the Gaussian98 package of programs.<sup>35</sup>

## Results and Discussion

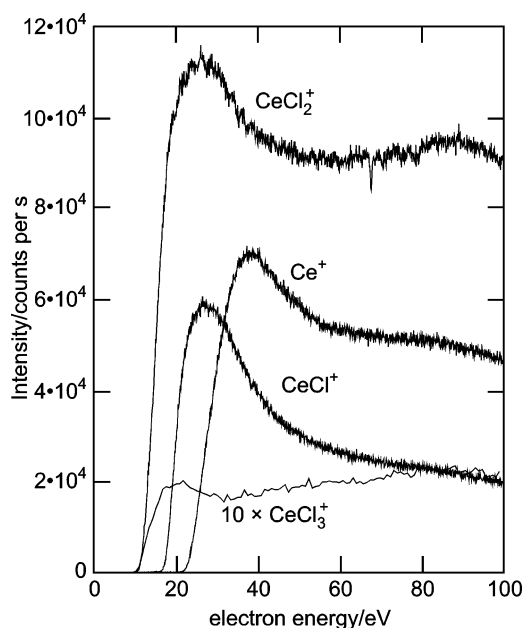
### Fragmentation Patterns of CeCl<sub>3</sub>(g) and LuCl<sub>3</sub>(g) and Appearance Energies (AE) of Ions. Figure 1 presents an

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**Table 1.** Experimental Mass Spectra of CeCl<sub>3</sub>(g) and LuCl<sub>3</sub>(g) Relative to the LnCl<sub>2</sub><sup>+</sup> Ion Intensity and in a Percentage (italic) of the Total Ion Intensity

LnCl <sub>3</sub>	E <sub>el</sub> (eV)	T (K)	LnCl <sub>3</sub> <sup>+</sup>	LnCl <sub>2</sub> <sup>+</sup>	LnCl <sup>+</sup>	Ln <sup>+</sup>	ref
CeCl <sub>3</sub> (g)	70	1070	2.3, 1.2	100, 53.9	26.6, 14.3	56.8, 30.6	this work, JSI (not corrected)
	70	1070	2.0, 0.96	100, 47.2	33.7, 15.9	76.1, 35.9	this work, JSI (corrected)
	70	882–1028	2.6, 1.2	100, 46.2	39.0, 18.0	74.9, 34.6	this work, RCJ
	50	1063	5.0, 3.9	100, 78.3	10.6, 8.3	12.1, 9.5	13
LuCl <sub>3</sub> (g)	70	900	20.3, 8.3	100, 41.0	48.6, 19.9	75.0, 30.7	this work, JSI (not corrected)
	70	900	18.8, 6.6	100, 34.9	59.9, 20.9	108, 37.6	this work, JSI (corrected)
	70	850–1004	23.0, 8.0	100, 34.8	39.1, 13.6	125, 43.6	this work, RCJ
	90	1056	38.1, 23.0	100, 60.4	13.6, 8.2	13.9, 8.4	15

**Figure 2.** Relative ionization efficiency curves for ions from mass spectrum of CeCl<sub>3</sub>(g).

example of normalized Z-scan curves for CeCl<sub>3</sub><sup>+</sup> and Ce<sup>+</sup> ion intensities detected in the mass spectrum of CeCl<sub>3</sub>. These curves show the distribution of the kinetic energy of different ions resulting from fragmentation<sup>2,36</sup> which leads to a considerably larger width for the Ce<sup>+</sup> fragment in comparison to the molecular CeCl<sub>3</sub><sup>+</sup> ion. The area below the respective Z scans of the ion intensities yields corresponding correction factors used for the recalculation of ion intensities to corrected mass spectra. The mass spectra of CeCl<sub>3</sub>(g) and LuCl<sub>3</sub>(g) (as measured in JSI) together with corrected values are summarized in Table 1. Additionally, uncorrected mass spectra obtained in RCJ, as well as those obtained by other authors, are also reported. It should be noted here that the loss of fragments also occurs at the ion source extraction slit, and further correction should be performed to improve the “true” spectra. Thus, the abundance of fragment ions in the corrected spectra should be considered as their lower limit.

Figure 2 presents ionization efficiency curves (IEC) for ions originating in the CeCl<sub>3</sub> system at 1023 K and a total pressure of ca. 0.1 Pa. Because of the broad energy distribution of the ionizing electrons of 0.8 eV, the appearance energies were obtained by deconvolution of measured curves according to the Vogt method using a Maxwell–Boltzmann distribution function.<sup>37</sup> The appearance energies

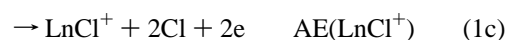
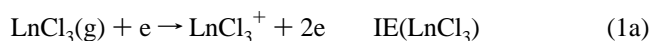
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	CeCl <sub>3</sub>				
	IE LnCl <sub>3</sub> <sup>+</sup> / LnCl <sub>3</sub>	AE LnCl <sub>2</sub> <sup>+</sup> / LnCl <sub>3</sub>	AE LnCl <sup>+</sup> / LnCl <sub>3</sub>	AE Ln <sup>+</sup> / LnCl <sub>3</sub>	IE Ln <sup>+</sup> /Ln
	experiment				
this work	9.5 ± 0.2	11.0 ± 0.2	16.3 ± 0.2	21.0 ± 0.2	5.466 <sup>a</sup>
ref 13	10.6 ± 0.5	12.4 ± 0.5	15.8 ± 0.5	21.4 ± 0.5	
ref 38	10.22 ± 0.07	12.30 ± 0.05	15.92 ± 0.07	21.17 ± 0.06	
	theory (this work)				
B3LYP	10.10	11.30	17.36	20.64	5.46
MP2		11.18	18.23	22.90	5.26
CCSD(T)					5.33
	LuCl <sub>3</sub>				
	experiment				
this work	11.15 ± 0.2	11.70 ± 0.2	17.3 ± 0.5	22.2 ± 0.5	5.4256 <sup>a</sup>
ref 15	11.4 ± 0.5	12.5 ± 0.5	16.6 ± 0.5	23.4 ± 0.5	
ref 39	11.5 ± 0.5	12.5 ± 0.3	16.0 ± 0.5	20.5 ± 0.5	
	theory (this work)				
B3LYP	10.67	12.19	16.52	20.39	5.55
MP2	10.84	12.15	16.68	20.54	5.15
CCSD(T)	10.74	12.01	16.34	19.91	4.99

<sup>a</sup> Ref 31.

obtained for ions observed in mass spectra of CeCl<sub>3</sub> and LuCl<sub>3</sub> are presented in Table 2. The respective values of the appearance energies available in the literature<sup>13,15,38,39</sup> are provided for comparison. Taking into account the accuracy of experimental values of about ±0.5 eV, the theoretical ionization/fragmentation energies generally agree with the respective energies derived from IEC (Table 2). The thermodynamic agreement indicates that the electronic ground states of the studied species were properly determined.

The thermodynamic meaning of the appearance energy (AE) is the energy associated with the dissociation of the metal–halide bond of the neutral molecule because of its interaction with an electron. The electron impact ionization processes of the LnCl<sub>3</sub> molecule are accompanied by the following fragmentation pathways:

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**Table 3.** Experimental and Theoretical (B3LYP) Dissociation Energies of Metal–Chlorine Bonds in CeCl<sub>3</sub>, LuCl<sub>3</sub>, and Their Derivatives<sup>a</sup>

origin of the system			dissociating species		
			<i>D</i> (LnCl <sub>2</sub> –Cl)	<i>D</i> (LnCl–Cl)	<i>D</i> (Ln–Cl)
CeCl <sub>3</sub>	molecule	theor	5.11	5.06	4.99
		cation	1.5 ± 0.3	5.3 ± 0.3	4.7 ± 0.3
		theor	1.2	6.05	3.28
LuCl <sub>3</sub>	molecule	theor	4.98	4.38	5.48
		cation	0.55 ± 0.28	5.6 ± 0.5	4.9 ± 0.7
		theor	1.50	4.34	3.87

<sup>a</sup> Energies in eV. Averaged dissociation energies of Ln–Cl bond in neutral LnCl<sub>3</sub>(g) were obtained as 5.2 ± 0.1 (exptl) and 5.05 eV (theor) for CeCl<sub>3</sub>(g), as well as 5.6 ± 0.2 (exptl) and 4.95 eV (theor) for LuCl<sub>3</sub>(g).

The combination of appearance energies yields the dissociation energies of lanthanide–chlorine bonds in ions. The difference AE(LnCl<sub>2</sub><sup>+</sup>) – IE(LnCl<sub>3</sub><sup>+</sup>), AE(LnCl<sup>+</sup>) – AE(LnCl<sub>2</sub><sup>+</sup>), and AE(Ln<sup>+</sup>) – AE(LnCl<sup>+</sup>) correlates with the energy of the LnCl<sub>3</sub><sup>+</sup> = LnCl<sub>2</sub><sup>+</sup> + Cl, LnCl<sub>2</sub><sup>+</sup> = LnCl<sup>+</sup> + Cl, and LnCl<sup>+</sup> = Ln<sup>+</sup> + Cl dissociation process, respectively. The averaged dissociation energy of the LnCl<sub>2</sub>–Cl bond in neutral species was calculated as 1/3 of the AE(Ln<sup>+</sup>) – IE(Ln) difference. The IE(Ln) values were adopted from literature as given in Table 2. Experimental appearance energies yield, in fact, the upper limits of the adiabatic values because of the additional kinetic energy of the fragment ions.<sup>2,36</sup> Therefore the determination of the energies of the dissociation and fragmentation processes by the use of experimental appearance energies is limited. The sequential dissociation energies of LnCl<sub>3</sub> and LnCl<sub>3</sub><sup>+</sup> are presented in Table 3. Averaged dissociation energy of the LnCl<sub>2</sub>–Cl bond in the neutral species was calculated from theoretical data as 1/3{*D*(LnCl<sub>2</sub>–Cl) + *D*(LnCl–Cl) + *D*(Ln–Cl)}. Although the precision of data is not high, the qualitative conclusions resulting from the experimental and theoretical data are similar. The dissociation energy for LnCl<sub>3</sub> molecules is higher than that of their ionized form, LnCl<sub>3</sub><sup>+</sup>. The LnCl<sub>3</sub><sup>+</sup> cation is shown to be significantly less stable than any other fragment studied. The above observation is consistent with its low abundance in the LnCl<sub>3</sub>(g) mass spectra.

**Partial Pressures and Vaporization Thermodynamics of CeCl<sub>3</sub> and LuCl<sub>3</sub>.** Mass spectra of CeCl<sub>3</sub> and LuCl<sub>3</sub> vapors were recorded in JSI and RCJ over the temperature ranges reported in Table 4. Ion intensities, *I*(*i*), of the respective gaseous species, *i*, recorded at temperature *T* are related to the partial pressure, *p*(*i*), via the expression<sup>40</sup>

$$p(i) = kT(\sum I(i))/\sigma(i) \quad (2)$$

where *k*,  $\sum I(i)$ , and  $\sigma(i)$  denote the pressure calibration factor, the sum of intensities of ions originating from the same neutral precursor *i*, and the relative ionization cross section of species *i*, respectively. Ion intensity of Ln<sub>2</sub>Cl<sub>6</sub><sup>+</sup> was considered in each case as  $\sum I(\text{Ln}_2\text{Cl}_6)$ . The relative pressure calibration factors, *k*/σ(LnCl<sub>3</sub>), were obtained by using the mass-loss Knudsen effusion technique combined with the mass spectrometry. By combining eq 2 with the Hertz–Knudsen expression<sup>41</sup>

$$p(i) = \frac{\Delta m}{\Delta t CA} \sqrt{\frac{2\pi RT}{M}} \quad (3)$$

the estimation of the calibration factor is given as

$$\frac{k}{\sigma(\text{LnCl}_3)} = \sqrt{\frac{2\pi R}{MT}} \frac{\Delta m}{\Delta t CA} \left( \sum I(\text{LnCl}_3) + \sqrt{2} \sum I(\text{Ln}_2\text{Cl}_6) \frac{\sigma(\text{LnCl}_3)}{\sigma(\text{Ln}_2\text{Cl}_6)} \right) \quad (4)$$

where *R* denotes the gas constant, *M* represents the molecular mass of LnCl<sub>3</sub>, *C* is the Clausing factor, and Δ*m* is the mass loss of the sample from evaporation during time Δ*t* from the effusion area, *A*, of the Knudsen cell. The relative ionization cross section σ(Ln<sub>2</sub>Cl<sub>6</sub>)/σ(LnCl<sub>3</sub>) was assumed to be 1.5.<sup>18</sup> Mass losses of 3.01 mg of CeCl<sub>3</sub> (after 1130 min at 1023 K) and 9.60 mg of LuCl<sub>3</sub> (after 582 min at 1003 K) were obtained in experiments with the isothermal evaporation of both studied substances. In every run, the mass spectrum used for the calibration in eq 4 was interpolated to the respective temperature of the isothermal vaporization experiment. Partial pressures were evaluated by eq 2 for each temperature of the measurement. Figure 3a and b show the partial pressures determined over CeCl<sub>3</sub>(s,l) and LuCl<sub>3</sub>(s). Expressions for partial pressures of LnCl<sub>3</sub>(g) and Ln<sub>2</sub>Cl<sub>6</sub>(g) as functions of temperature are a result of the least-squares method (Table 4). For CeCl<sub>3</sub>(g) and Ce<sub>2</sub>Cl<sub>6</sub>(g) species, the point recorded in JSI above the melting temperature of CeCl<sub>3</sub>(s), *T*<sub>m</sub> = 1095 K,<sup>42</sup> was not considered in this calculation. The second law sublimation enthalpies of CeCl<sub>3</sub>(g), LuCl<sub>3</sub>(g), and Lu<sub>2</sub>Cl<sub>6</sub>(g) at 298 K (standard pressure *p*<sup>o</sup> = 101 325 Pa) were computed from the slopes, *a*, of the pressure equations given in Table 4. Recalculation to the standard temperature was performed using the thermodynamic functions for CeCl<sub>3</sub>(s),<sup>42–44</sup> LuCl<sub>3</sub>(s),<sup>42</sup> and Ce<sub>2</sub>Cl<sub>6</sub>(g)<sup>12</sup> reported in the literature. Thermodynamic functions for CeCl<sub>3</sub>(g), LuCl<sub>3</sub>(g), and Lu<sub>2</sub>Cl<sub>6</sub>(g) were estimated on the basis of molecular parameters obtained in the present study. The results of the calculations are summarized in Table 5. The second law sublimation enthalpies of LnCl<sub>3</sub>(g) are represented by the arithmetical mean values obtained in RCJ and JSI. The second law treatment of data was not performed for Ce<sub>2</sub>Cl<sub>6</sub>(g) because only four experimental points were recorded for this species.

Sublimation enthalpies of the LnCl<sub>3</sub>(g) and Ln<sub>2</sub>Cl<sub>6</sub>(g) species were additionally obtained according to the third-law method by applying the equation

$$\Delta_r H^\circ(298 \text{ K}) = -T\{R \ln K_p^\circ + \Delta_r [G^\circ(T) - H^\circ(298)]/T\} \quad (5)$$

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**Table 4.** Partial Pressures of LnCl<sub>3</sub>(g) and Ln<sub>2</sub>Cl<sub>6</sub>(g) (Ln = Ce, Lu) over LnCl<sub>3</sub>(s)<sup>a</sup>

species	N	ΔT	ln p(i) = -a/T + b			ref
			a	b	p(i) at 1000 K	
CeCl <sub>3</sub> (g)	15	882–1028	37197 ± 437	34.215 ± 0.457	5.1 × 10 <sup>-2</sup>	this work, RCJ
	18	923–1093	38 695 ± 126	35.675 ± 0.125	4.9 × 10 <sup>-2</sup>	this work, JSI
					7.5 × 10 <sup>-2</sup>	12
					0.12	13
					5.8 × 10 <sup>-2</sup>	14
3.7 × 10 <sup>-2</sup>	43					
Ce <sub>2</sub> Cl <sub>6</sub> (g)	4	1063–1093	43378 ± 975	33.767 ± 0.905	6.8 × 10 <sup>-5</sup>	this work, JSI
LuCl <sub>3</sub> (g)	25	850–1004	36 427 ± 318	35.862 ± 0.344	4.3 × 10 <sup>-6</sup>	13
					8.0 × 10 <sup>-5</sup>	12 <sup>b</sup>
					0.57	this work, RCJ
Lu <sub>2</sub> Cl <sub>6</sub> (g)	12	903–1013	42594 ± 357	39.162 ± 0.374	0.57	this work, JSI
					0.34	15
					3.2 × 10 <sup>-2</sup>	this work, JSI
					0.10	15

<sup>a</sup> The measurement included *N* experimental points in the Δ*T* temperature range. Partial pressures at 1000 K are given for the comparison. Pressure in Pa, temperature in K. <sup>b</sup> Extrapolated from the temperature range of study of 1037–1091 K.

where Δ<sub>r</sub>[*G*<sup>o</sup>(*T*) – *H*<sup>o</sup>(298)]/*T* is the variation of the Gibbs energy function for the respective sublimation reaction. *K*<sub>p</sub><sup>o</sup> is the equilibrium constant for the respective sublimation reaction



Computations were carried out for each temperature of the measurement. Mean values of sublimation enthalpies obtained for all experimental points are given in Table 5. Statistical uncertainties equal to 2σ are given for individual second and third law values in Table 5. Selected sublimation enthalpies obtained in the present study are a result of the computation of weighted averages from the second- and third-law values. In the case of Ce<sub>2</sub>Cl<sub>6</sub>(g), the third-law sublimation enthalpy is given as the selected value. Reciprocal probable overall errors given in Table 5 were taken as a weight of each value. The probable overall errors of the selected enthalpies of the sublimation reactions reported in Table 5 were estimated by considering statistical errors and probable uncertainties of the data used in the calculations. The following probable uncertainties were assumed for the computation of the overall errors: *p*(LnCl<sub>3</sub>), ±20%; *p*(Ln<sub>2</sub>Cl<sub>6</sub>), ±50%; *T*, ±5 K; [*G*<sup>o</sup>(*T*) – *H*<sup>o</sup>(298)]/*T*, ±2 (for LnCl<sub>3</sub>(s)), ±5 (for LnCl<sub>3</sub>(g)), and ±10 J mol<sup>-1</sup> K<sup>-1</sup> (for Ln<sub>2</sub>Cl<sub>6</sub>(g)).

The sublimation enthalpies of CeCl<sub>3</sub> and LuCl<sub>3</sub> measured in both laboratories (RCJ and JSI) agree well. The selected second- and third-law enthalpies differ less than the estimated uncertainty. Satisfactory agreement can also be seen with previous studies (Table 5). Partial pressures of monomeric species also agree well between laboratories and other studies. It is not the case, however, for the cerium chloride dimeric species, where the vapor pressure obtained in the present study is a factor of 17 higher than the results of Pogrebnoi et al.<sup>13</sup> The value of *p*(Ce<sub>2</sub>Cl<sub>6</sub>) measured in this work for 1000 K agrees, however, with the value of our former study<sup>12</sup> extrapolated from the temperature range of 1037–1091 K. Also if somewhat contradictory data concerning dimer contributions in CeCl<sub>3</sub> and LuCl<sub>3</sub> vapors are considered, Ce<sub>2</sub>Cl<sub>6</sub> seems to be considerably less stable

than Lu<sub>2</sub>Cl<sub>6</sub>. The vapor pressure of Ce<sub>2</sub>Cl<sub>6</sub>(g) at 1000 K is less than 0.2% of the total equilibrium pressure over cerium chloride. Vapors of LuCl<sub>3</sub> at the same temperature are over 5% dimeric molecules. A similar tendency regarding the dimerization in vapors for the sequence from Ce to Lu was previously stated by Gietmann<sup>45</sup> as a result of his studies of lanthanide bromides.

The [*G*<sup>o</sup>(*T*) – *H*<sup>o</sup>(298)]/*T* function estimated for gaseous species in the present study was compared with values previously obtained by other authors.<sup>13,15,42–44</sup> The accuracy of this function determines the validity of the third-law sublimation enthalpies calculated from experimental partial pressures. Maximal differences (in J mol<sup>-1</sup> K<sup>-1</sup>) of 5 (CeCl<sub>3</sub>(g)), 19 (LuCl<sub>3</sub>(g)), 27 (Ce<sub>2</sub>Cl<sub>6</sub>(g)), and 21 (Lu<sub>2</sub>Cl<sub>6</sub>(g)) exist between the individual [*G*<sup>o</sup>(*T*) – *H*<sup>o</sup>(298)]/*T* values reported in the cited sources for *T* = 1000 K. This agreement can be considered to be satisfactory if the fact that a difference of 1 J mol<sup>-1</sup> K<sup>-1</sup> in the [*G*<sup>o</sup>(1000) – *H*<sup>o</sup>(298)]/*T* function results in a 1 kJ mol<sup>-1</sup> difference in the third-law enthalpy of sublimation is taken into account.

**Structures and Nature of Bonding in CeCl<sub>3</sub>, LuCl<sub>3</sub>, and their Derivatives.** The available experimental structural and vibrational data are restricted to LnCl<sub>3</sub> species. However, the reasonable agreement between experimental<sup>46–50</sup> and theoretical structural parameters for trichlorides (Tables 6 and 7) gives us a confidence in the calculated values for other neutral and ionic LnCl<sub>*n*</sub> species. The interatomic distances in cerium chlorides are about 0.15 Å longer than bonds characterizing lutetium chlorides. This trend agrees well with the difference of the metallic radius of atoms of 0.10 Å.<sup>51</sup> Interatomic distances in CeCl<sub>*n*</sub> and LuCl<sub>*n*</sub> com-

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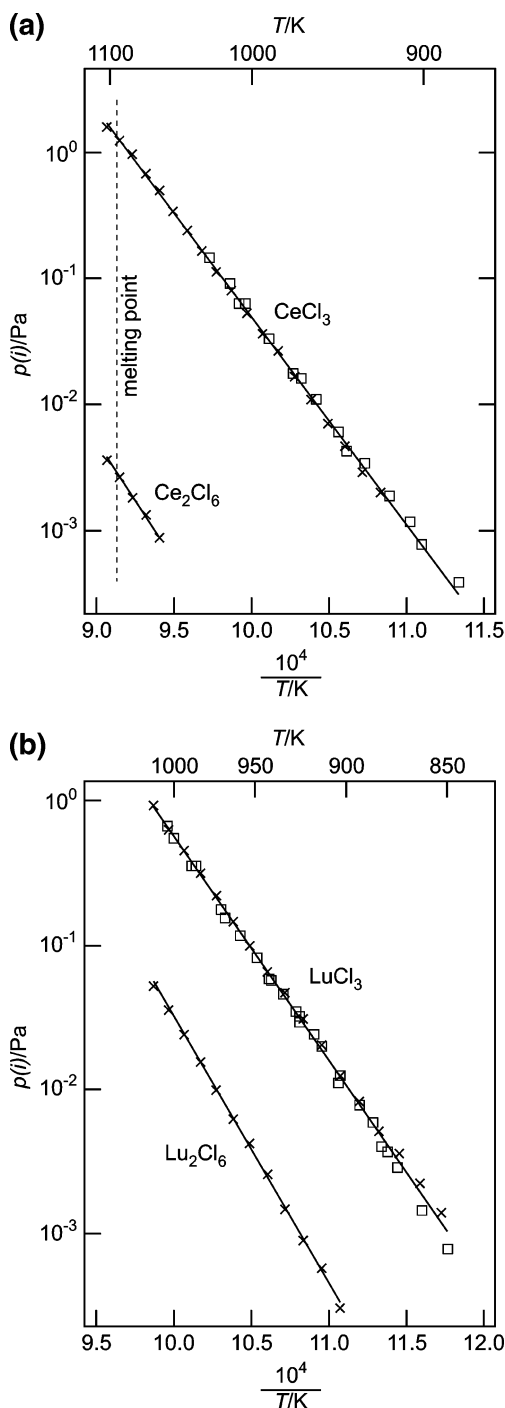
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**Figure 3.** Partial pressures of gaseous species over  $\text{CeCl}_3(\text{s.l})$  (a) and  $\text{LuCl}_3(\text{s})$  (b) at different temperatures obtained in JSI ( $\times$ ) and RCJ ( $\square$ ).

pounds follow the same pattern with the little increase in the bond length from  $\text{LnCl}$  to  $\text{LnCl}_3$ . The ionization of molecules leads to a shortening of bonds by as much as 0.1 Å and to the blue shifting of the vibrational stretching modes. The effect is well explained as a consequence of removing the nonbonding electrons of metals in  $\text{LnCl}$  and  $\text{LnCl}_2$  leading to an increase of electrostatic interactions (Tables 8 and 9). The ionization of  $\text{LnCl}_3$  involves the electrons of chlorine atoms, leading to a different bonding scheme in

**Table 5.** Second- and Third-Law Standard Enthalpies ( $T = 298 \text{ K}$ ) of Sublimation of  $\text{LnCl}_3(\text{s})$  to  $\text{LnCl}_3(\text{g})$  and  $\text{Ln}_2\text{Cl}_6(\text{g})$ ,  $\text{Ln} = \text{Ce}, \text{Lu}^a$

species	second law	third law	selected	ref
$\text{CeCl}_3(\text{g})$	$331.7 \pm 7.2$	$331.6 \pm 1.2$		this study, RCJ
	$344.1 \pm 2.0$	$331.8 \pm 1.4$		this study, JSI
			$333.2 \pm 6.3$	this study, selected
			$331.0 \pm 5.3$	12 <sup>b</sup>
			$334.8 \pm 7.2$	12 <sup>c</sup>
$\text{Ce}_2\text{Cl}_6(\text{g})$			$329 \pm 10$	13
			$331 \pm 5$	14
			330.5	43
		$439.6 \pm 10.6$	$439.6 \pm 10.6$	this study, JSI
			$443.2 \pm 12.0$	12
$\text{LuCl}_3(\text{g})$			$451 \pm 25$	14
	$318.6 \pm 5.4$	$296.1 \pm 2.2$		this study, RCJ
	$307.4 \pm 2.4$	$295.2 \pm 1.2$		this study, JSI
	$313.0 \pm 7.9$	$295.7 \pm 5.2$	$300.9 \pm 12.9$	this study, selected
			$285 \pm 5$	15
$\text{Lu}_2\text{Cl}_6(\text{g})$	$373.7 \pm 11.2$	$358.0 \pm 10.6$	$365.4 \pm 13.5$	this study, JSI
			$370 \pm 10$	15

<sup>a</sup> Enthalpies in kJ/mol <sup>b</sup> Original value. <sup>c</sup> Recommended value.

$\text{LnCl}_3^+$  than that observed in  $\text{LnCl}^+$  and  $\text{LnCl}_2^+$ . As a consequence, the structure of  $\text{LnCl}_3^+$  cations is significantly perturbed from that of neutral trichlorides, and their  $C_3$  symmetry is destroyed. The  $\text{Lu}_2\text{Cl}_6$  dimer possesses a  $D_{2h}$  structure similar to other  $\text{Ln}_2\text{Cl}_6$  compounds studied before.<sup>12</sup> The planar four-membered  $\text{Lu}(\text{Cl}_2)\text{Lu}$  ring is formed by equivalent  $\text{Lu}-\text{Cl}$  bridged bonds (2.570 Å) with a  $\text{Cl}-\text{Lu}-\text{Cl}$  angle of  $82.7^\circ$ . Terminal  $\text{Lu}-\text{Cl}$  bonds (of 2.403 Å) define the plane perpendicular to the central ring. The  $\text{Cl}_{\text{term}}-\text{Lu}-\text{Cl}_{\text{term}}$  angle is  $116.1^\circ$ .

An electronic population analysis allows electronic density changes resulting from the formation of new bonds or from ionization processes to be tracked. Despite the differences in absolute values, both methods lead to a similar pattern of variations in the density distribution. Mulliken values are presented in the following text along with NBO values given in parentheses. The chemical bond in  $\text{CeCl}$  possesses an ionic nature with  $\sim 0.40$  ( $\sim 0.77$ ) electron transferred from Ce to Cl (Table 8). The electronic density is donated almost exclusively to the p orbitals of Cl. The density distribution in the  $\text{Ce}-\text{Cl}$  bonds of  $\text{CeCl}_2$  and  $\text{CeCl}_3$  may be considered additive since a similar amount of electron is transferred, when each bond is considered separately. Orbitals s, d, and f of cerium are involved in the bonding, while the p orbitals are totally inactive. The total  $\sigma$  donations from Ce (s and f electrons) to Cl are 0.993 (1.070), 1.904 (2.010), and 2.571 (2.751) electrons in  $\text{CeCl}$ ,  $\text{CeCl}_2$ , and  $\text{CeCl}_3$ , respectively. The overall electron transfer is reduced by the  $\pi$  back-donation to the d orbitals of Ce amounting to 0.561, 0.924, and 1.080 according to Mulliken analysis or 0.300, 0.485, and 0.490 electron for  $\text{CeCl}$ ,  $\text{CeCl}_2$ , and  $\text{CeCl}_3$ , respectively, when the NBO scheme is applied. Although the NBO analysis generally leads to a smaller amount of electron back-donation than the Mulliken approach, the trends of the changes remain similar. The smaller  $\sigma$  donation per single  $\text{Ce}-\text{Cl}$  bond in  $\text{CeCl}_3$  of 0.857 (0.917) electron is compensated by the lower electron back-donation per bond of 0.360 (0.163) electron. In the case of  $\text{CeCl}_3$ , the total electronic density withdrawn from Ce, as predicted by the Mulliken population analysis, amounts to 1.438 electrons. The NBO approach gives a picture that is qualitatively similar, although

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## Neutral and Ionized LnCl, LnCl<sub>2</sub>, and LnCl<sub>3</sub> Species

**Table 6.** Theoretical (B3LYP) and Experimental (in square brackets) Bond Lengths (*R*), Bond Angles (Cl–Ce–Cl), and Vibrational Frequencies ( $\tilde{\nu}$ ) for Neutral and Charged Fragments of the Parent Molecule CeCl<sub>3</sub>

	multiplicity	<i>R</i> (Å)	Cl–Ce–Cl (deg)	$\tilde{\nu}$ (Cm <sup>-1</sup> )			
Ce	3						
Ce <sup>+</sup>	4						
CeCl	2	2.530		301.8			
CeCl <sup>+</sup>	1	2.433		364.9			
CeCl <sub>2</sub>	3	2.559	125.7	299.7 ( $\nu_1$ )	62.8 ( $\nu_2$ )	311.3 ( $\nu_3$ )	
CeCl <sub>2</sub> <sup>+</sup>	2	2.462	110.1	377.7 ( $\nu_1$ )	55.5 ( $\nu_2$ )	381.6 ( $\nu_3$ )	
CeCl <sub>3</sub>	2	2.571	119.0	311.3 ( $\nu_1$ )	45.0 ( $\nu_2$ )	324.9 ( $\nu_3$ )	69.0 ( $\nu_4$ )
		[2.577] <sup>a</sup>		[320] <sup>c</sup>	[58] <sup>b</sup>	[321] <sup>b</sup>	[85] <sup>c</sup>
CeCl <sub>3</sub> <sup>+</sup>	3	2.459	109.3 (×2)	381.1 ( $\nu_1$ )	209.1 ( $\nu_2$ )	181.1 ( $\nu_3$ )	46.7 ( $\nu_4$ )
		2.656 (×2)	61.1	307.7 ( $\nu_5$ )	61.6 ( $\nu_6$ )		

<sup>a</sup> Ref 46 (estimated). <sup>b</sup> Ref 47. <sup>c</sup> Ref 17 (recommended values).

**Table 7.** Theoretical (B3LYP) and Experimental (in square brackets) Bond Lengths (*R*), Bond Angles (Cl–Lu–Cl), and Vibrational Frequencies ( $\tilde{\nu}$ ) for Neutral and Charged Species of the Parent Molecule LuCl<sub>3</sub>

	multiplicity	<i>R</i> (Å)	Cl–Lu–Cl (deg)	$\tilde{\nu}$ (cm <sup>-1</sup> )			
Lu	2						
Lu <sup>+</sup>	1						
LuCl	1	2.391		330.5			
LuCl <sup>+</sup>	2	2.292		406.9			
LuCl <sub>2</sub>	2	2.400	129.7	335.3 ( $\nu_1$ )	62.1 ( $\nu_2$ )	343.2 ( $\nu_3$ )	
LuCl <sub>2</sub> <sup>+</sup>	1	2.314	113.1	401.5 ( $\nu_1$ )	87.1 ( $\nu_2$ )	403.9 ( $\nu_3$ )	
		2.403		335.2 ( $\nu_1$ )	37.4 ( $\nu_2$ )	354.5 ( $\nu_3$ )	82.6 ( $\nu_4$ )
LuCl <sub>3</sub>	1	[2.417(6)] <sup>a</sup>	120.0	[342] <sup>b</sup>	[60] <sup>c</sup>	[331] <sup>c</sup>	[88] <sup>c</sup>
		[2.403(5)] <sup>d</sup>		[345] <sup>e</sup>	[69] <sup>e</sup>	[351] <sup>e</sup>	[98] <sup>e</sup>
LuCl <sub>3</sub> <sup>+</sup>	2	2.467 (×2)	115.1 (×2)	397.4 ( $\nu_1$ )	255.3 ( $\nu_2$ )	148.6 ( $\nu_3$ )	66.7 ( $\nu_4$ )
		2.322	68.8	328.1 ( $\nu_5$ )	67.1 ( $\nu_6$ )		

<sup>a</sup> Ref 49 (thermal average). <sup>b</sup> Ref 50 (estimated). <sup>c</sup> Ref 52. <sup>d</sup> Ref 17 (recommended values). <sup>e</sup> Ref 53 (thermal average).

**Table 8.** Orbital Occupancies (in electron) from Mulliken and NBO (in parentheses) Population Analysis in CeCl<sub>3</sub> Molecule and Related Fragments<sup>a</sup>

	Ce					Cl				Cl			
	s	p	d	f	total	s	p	d	total	s	p	d	total
Ce	6.000	12.000	10.000	2.000	30.000								
	(6.000)	(12.000)	(10.000)	(2.000)	(30.000)								
Ce <sup>+</sup>	5.000	12.000	10.000	2.000	29.000								
	(5.000)	(12.000)	(10.000)	(2.000)	(29.000)								
Cl						2.000	5.000	0.000	7.000				
						(2.000)	(5.000)	(0.000)	(7.000)				
Cl <sup>-</sup>						2.000	6.000	0.000	8.000				
						(2.000)	(6.000)	(0.000)	(8.000)				
CeCl	5.548	12.021	10.561	1.459	29.589	1.966	5.427	0.018	7.411				
	(5.512)	(11.997)	(10.300)	(1.418)	(29.227)	(2.010)	(5.754)	(0.009)	(7.773)				
CeCl <sup>+</sup>	4.569	11.999	10.550	1.576	28.694	2.036	5.242	0.028	7.306				
	(4.535)	(11.997)	(10.277)	(1.534)	(28.343)	(1.982)	(5.653)	(0.021)	(7.656)				
CeCl <sub>2</sub>	4.765	12.039	10.924	1.331	29.059	1.998	5.455	0.018	7.471				
	(4.724)	(11.999)	(10.485)	(1.266)	(28.474)	(1.988)	(5.767)	(0.008)	(7.763)				
CeCl <sub>2</sub> <sup>+</sup>	4.100	12.000	11.052	1.249	28.401	2.043	5.230	0.027	7.300				
	(4.038)	(11.986)	(10.542)	(1.182)	(27.748)	(1.987)	(5.622)	(0.019)	(7.628)				
CeCl <sub>3</sub>	4.176	12.053	11.080	1.253	28.562	2.014	5.447	0.018	7.479				
	(4.061)	(11.996)	(10.490)	(1.188)	(27.735)	(1.985)	(5.763)	(0.008)	(7.756)				
CeCl <sub>3</sub> <sup>+</sup>	4.155	12.047	11.051	1.252	28.505	2.010	5.058	0.029	7.097 <sup>b</sup>	2.043	5.233	0.026	7.302
	(4.082)	(11.988)	(10.498)	(1.191)	(27.759)	(1.985)	(5.313)	(0.012)	(7.310)	(1.981)	(5.617)	(0.019)	(7.617)

<sup>a</sup> Populations are given for valence configurations defined in the text. Cl (core)3s<sup>2</sup>3p<sup>5</sup>; Ce (core)4s<sup>2</sup>4p<sup>6</sup>4d<sup>10</sup>4f<sup>2</sup>5s<sup>2</sup>5p<sup>6</sup>6s<sup>2</sup>. <sup>b</sup> Populations for the symmetry equivalent atoms.

the amount of total density transferred out of Ce slightly exceeds two electrons (2.265 electrons). A rough estimation of the sharing of two electrons between the metal and chlorine atoms in CeCl<sub>3</sub> correlates with the consecutive ionization energies of the Ce atom of 5.446, 11.85, and 20.198 eV.<sup>28</sup> The transfer of the third electron out of Ce to the vicinity of chlorine atoms, as one corresponding to the third ionization energy, is not feasible. The common scheme of bonding in LnCl<sub>3</sub> postulated as [Ln<sup>3+</sup>][(Cl<sub>3</sub>)<sup>3-</sup>] is not adequate for the CeCl<sub>3</sub> case. The more appropriate electronic configuration representing the Ce center within the CeCl<sub>3</sub>

molecule is the double ionized atom with the 6s<sup>0</sup>4f<sup>1</sup>5d<sup>1</sup> electronic configuration corresponding to the lowest-excited electronic state of the Ce<sup>2+</sup> cation.

In the studied compounds, the ionization of the molecules competes with bond formation. The ionization of CeCl removes an electron exclusively from the 6s orbital of Ce leaving the original bonding electrons almost untouched (Table 8). In CeCl<sub>2</sub>, only ~0.76 (~0.72) electron occupies the valence 6s orbital with the rest of the s density being involved in the Ce–Cl bonding. The ionization of CeCl<sub>2</sub> proceeds mostly through 6s electrons. Part of the electronic



**Table 9.** Orbital Occupancies (in electron) from Mulliken and NBO (in parentheses) Population Analysis in LuCl<sub>3</sub> Molecule and Relative Fragments<sup>a</sup>

	Lu					Cl				Cl			
	s	p	d	j	total	s	p	d	total	s	p	d	total
Lu	6.000	12.000	11.000	14.000	43.000								
	(6.000)	(12.000)	(11.000)	(14.000)	(43.000)								
Lu <sup>+</sup>	6.000	12.000	10.000	14.000	42.000								
	(6.000)	(12.000)	(10.000)	(14.000)	(42.000)								
Cl						2.000	5.000	0.000	7.000				
						(2.000)	(5.000)	(0.000)	(7.000)				
Cl <sup>-</sup>						2.000	6.000	0.000	8.000				
						(2.000)	(6.000)	(0.000)	(8.000)				
LuCl	5.976	12.142	10.536	14.008	42.662	1.940	5.380	0.018	7.338				
	(5.886)	(12.031)	(10.363)	(14.000)	(42.280)	(1.986)	(5.716)	(0.017)	(7.719)				
LuCl <sup>+</sup>	5.016	12.099	10.702	14.009	41.826	1.998	5.145	0.030	7.173				
	(4.950)	(12.013)	(10.517)	(14.000)	(41.480)	(1.966)	(5.530)	(0.025)	(7.521)				
LuCl <sub>2</sub>	5.0027	12.21	10.912	14.015	42.146	1.990	5.418	0.020	7.428				
	(4.881)	(12.048)	(10.765)	(14.000)	(41.694)	(1.950)	(5.688)	(0.014)	(7.652)				
LuCl <sub>2</sub> <sup>+</sup>	4.417	12.172	10.989	14.018	41.595	1.999	5.173	0.029	7.201				
	(4.169)	(12.008)	(10.842)	(13.999)	(41.018)	(1.956)	(5.513)	(0.021)	(7.490)				
LuCl <sub>3</sub>	4.540	12.245	10.965	14.024	41.774	1.986	5.402	0.020	7.408				
	(4.203)	(12.020)	(10.972)	(14.001)	(41.196)	(1.940)	(5.647)	(0.014)	(7.601)				
LuCl <sub>3</sub> <sup>+</sup>	4.476	12.229	10.992	14.021	41.718	2.010	5.192	0.028	7.230 <sup>b</sup>	1.985	5.011	0.030	7.026
	(4.215)	(12.010)	(10.939)	(13.999)	(41.163)	(1.941)	(5.504)	(0.021)	(7.466)	(1.952)	(5.216)	(0.018)	(7.186)

<sup>a</sup> Populations are given for valence configurations defined in the text. Cl (core)3s<sup>2</sup>3p<sup>5</sup>; Lu (core)4s<sup>2</sup>4p<sup>6</sup>4d<sup>10</sup>4f<sup>14</sup>5s<sup>2</sup>5p<sup>6</sup>5d<sup>1</sup>6s<sup>2</sup>. <sup>b</sup> Populations for the symmetry equivalent atoms.

density is supplemented from the 4f orbital. As discussed above, the electronic distribution in CeCl<sub>3</sub> indicates that the total loss of the electronic density of Ce, as an effect of the bond formation, amounts approximately to two electrons. The further removal of electrons from Ce would correspond to third (20.198 eV)<sup>31</sup> or higher ionization energies. The ionization energy of chlorine atoms is much lower (12.967 eV),<sup>32</sup> however. The electron population analysis indicates that the ionization of the CeCl<sub>3</sub> molecule leads to the CeCl<sub>3</sub><sup>+</sup> cation with an electronic configuration on Ce similar to the one found in the parent molecule. The ionization of CeCl<sub>3</sub> proceeds through the electron detachment almost exclusively from two chlorine atoms. The atomic charge on these atoms drops by 0.382 (0.446) electron compared to CeCl<sub>3</sub>. Such a mechanism leads to drastic energetical changes in the bonding in CeCl<sub>3</sub><sup>+</sup>, as was demonstrated above, and the properties of CeCl<sub>3</sub><sup>+</sup> do not continue the sequence of the CeCl<sup>+</sup> and CeCl<sub>2</sub><sup>+</sup> cations. In each studied system the electron loss from the metal atom was not significantly higher than two.

The  $\sigma$ -donation- $\pi$ -back-donation bonding scheme in lutetium chlorides is similar to the one observed in cerium moieties; however, the role of the metal orbitals is different. The Lu atom possesses the 4f<sup>14</sup> closed shell which is inactive in all species studied (Table 9). Orbitals s, p, and d are involved in the bonding. The formation of the bond is based on the  $\sigma$  donation of s and d (in-plane) valence electrons. This donation is balanced by the  $\pi$  back-donation to the p and d (out-of-plane) orbitals of Lu. Because d orbitals are involved in  $\sigma$ , as well as in  $\pi$ , electron transfers, the picture of bonding is more complex than that in the Ce compounds. The  $\sigma$  donations from the s and d orbitals to chlorine atoms are 0.488 (0.751), 0.860 (1.354), and 1.495 (1.825) for LuCl, LuCl<sub>2</sub>, and LuCl<sub>3</sub>, respectively, and they are balanced by the back-donation to the Lu p orbitals (0.142, 0.217, and 0.245 electron in the Mulliken approach and negligible when the NBO scheme is applied). Despite the involvement of an

orbital of a different nature (d), the overall picture of bonding is similar in Ce and Lu compounds. The bonding in LuCl<sub>3</sub> correlates with the central atom ionization series of 5.42, 13.9, and 20.95 eV.<sup>28</sup> The total electron sharing between the Lu and chlorine atoms amounts to 1.226 (1.804) electrons supporting the [Lu<sup>2+</sup>][Cl<sub>3</sub><sup>2-</sup>] bonding scheme.

The ionization of LuCl removes electrons from the 6s orbital with little influence on the Lu-Cl bond formed because of the electron transfer from the d valence orbital of Lu core (Table 9). Both population schemes provide the same picture of the ionization process. The ionization mechanism, with an electron being removed from the 6s orbital, also explains the ionization of LuCl<sub>2</sub>. The ionization of LuCl<sub>3</sub> does not change the electronic configuration of lutetium. The high value of the third ionization energy of the Lu atom (20.95 eV)<sup>31</sup> prevents Lu from being "ionized", and as is well illustrated by the spin-density distribution (Table 4), electrons are removed from the chlorine part of the molecule. Similar to the cerium chlorides, no more than two electrons are involved in bond formation or ionization. The qualitative bonding scheme of LuCl<sub>3</sub><sup>+</sup> can be described as [Lu<sup>2+</sup>][Cl<sub>3</sub><sup>-</sup>] with the 6s<sup>0</sup>d<sup>1</sup> configuration on the metal. The ionization of LuCl<sub>3</sub> involves the chlorine part.

## Conclusions

Mass spectra of CeCl<sub>3</sub>(g) and LuCl<sub>3</sub>(g) species, corrected for the kinetic energy distribution of fragment ions, consist of the parent ion LnCl<sub>3</sub><sup>+</sup> and LnCl<sub>2</sub><sup>+</sup>, LnCl<sup>+</sup>, and Ln<sup>+</sup> fragment ions. Results obtained in RCJ and JSI, for the same electron energy, are in an excellent agreement despite the difference in ion source construction. Data obtained by other authors are also in the satisfactory agreement with the corrected mass spectra determined in the present study (Table 1). The highest contribution to the mass spectra comes from the LnCl<sub>2</sub><sup>+</sup> fragment. This observation correlates well with the highest stability of LnCl<sub>2</sub><sup>+</sup> ions, as measured by the Ln-Cl bond dissociation energy. The LnCl<sub>3</sub><sup>+</sup> ions are character-

ized by the lowest abundance in the mass spectra, which is again in agreement with the lowest LnCl<sub>2</sub><sup>+</sup>–Cl dissociation energy (Table 3).

The mass spectrometry measurement of the molecular fragmentation is an important source of data concerning consecutive processes leading to the formation or decomposition of molecules. The measurement provides appearance energies which lead to averaged enthalpies of chemical bonds in molecules, LnCl<sub>3</sub>, and sequences of ions, LnCl<sup>+</sup>, LnCl<sub>2</sub><sup>+</sup>, and LnCl<sub>3</sub><sup>+</sup>. The theory, calibrated through the prediction of thermodynamics, supplements and supports the experiment with structural data and electron density population distribution. The ionization of LnCl<sub>*n*</sub> molecules leads to the significant (0.1 Å) shortening of bonds caused by the removal of nonbonding metal electrons. Electron density analysis indicates that the formation of bonds and the electron ionization compete since the same atomic orbitals are involved in both processes. The bonding in LnCl, LnCl<sub>2</sub>, and LnCl<sub>3</sub>, as well as that in LnCl<sup>+</sup> and LnCl<sub>2</sub><sup>+</sup>, is well explained within the  $\sigma$ -donation– $\pi$ -back-donation scheme. The electron transfer from metal to the chlorine part is restricted to less than two electrons which is in agreement with the increase of consecutive ionization energies of Ce and Lu. The electronic configuration of the metallic core in CeCl<sub>3</sub><sup>+</sup> and LuCl<sub>3</sub><sup>+</sup> cations is very similar to that observed in the parent molecules since the ionized electron originates from chlorine atoms. The simplified bonding scheme in

CeCl<sub>3</sub> and LuCl<sub>3</sub> may be best represented by the [Ln<sup>2+</sup>][Cl<sub>3</sub><sup>2-</sup>] scheme, with the Ln<sup>2+</sup> core cation being represented by the lowest-electronic excited state. None of studied complexes is well described, assuming the triple-ionized metal core is involved in the bonding.

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**Supporting Information Available:** The relative correction factors, *F*, thermochemical functions and their comparison estimated by different investigators, and the spin-energy distribution from Mulliken population analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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