Inorg. Chem. **2003**, *42*, 851–858

Inorganic Chemistry
Article

Theoretical Study of Mixed $MLaX_4$ (M = Na, K, Cs; X = F, Cl, Br, I) Rare Earth/Alkali Metal Halide Complexes

Cornelis Petrus Groen[†] **and Ad Oskam**

Institute for Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands

Attila Kovács*

Research Group for Technical Analytical Chemistry of the Hungarian Academy of Sciences at the
Institute of General and Analytical Chemistry of the Budapest University of Technology and
Economics, H-1111 Budapest, Szt. Gellért tér 4, Hungary

Received October 9, 2002

The structure, bonding, and vibrational properties of the mixed $MLaX_4$ (M = Na, K, Cs; X = F, Cl, Br, I) rare earth/alkali metal halide complexes have been studied using the MP2 method in conjunction with polarized triple-ζ valence basis sets and quasi-relativistic effective core potentials for the heavy atoms. From the three characteristic structures, possessing 1- (C_{3v}), 2- (C_{2v}), or 3-fold coordination (C_{3v}) between the alkali metal and the bridging halide atoms, the bi- and tridentate forms are stable isomers with close dissociation energies. In general, for the complexes existing of lighter alkali metals and halogens, the bidentate structure corresponds to the global minimum of the potential energy surface, while the heavier analogues favor the tridentate structure. At experimentally relevant temperatures ($T > 800$ K), however, the isomerization entropy leads to a domination of the bidentate structures over the tridentate forms for all complexes. An important effect of the size of the alkali metal is manifested in the larger stabilities of the K and Cs complexes. The natural atomic charges are in agreement with strong electrostatic interactions in the title complexes. The marginal covalent contributions show a slight increasing trend in the heavier analogues. The calculated vibrational data indicate that infrared spectroscopy may be an effective tool for experimental investigation and characterization of $MLaX_4$ molecules.

Introduction

Complexes of general stoichiometry $MLnX_4$ (M = alkali metal, Ln = rare earth, X = halogen) are important constituents of the vapors of quasi-binary systems of lanthanide halides with alkali halides. Their existence has been evidenced and thermodynamic characteristics of the dissociation process have been determined by numerous experimental studies, the majority applying Knudsen effusion mass spectrometry.[1-7] Other techniques such as gas-phase spectrophotometry, torsion mass effusion, chemical analysis of the condensed equilibrium vapors, vapor transpiration techniques, and vapor pressure measurements by the boiling point technique have been applied as well (see ref 1 and references therein).

In several high-temperature applications, the $MLnX_4$ halogen-bridged vapor complexes are of fundamental importance.[8-11] A variety of bromide and iodide complexes are important vapor species in high-intensity metal halide

---

* To whom correspondence should be addressed. E-mail: akovacs@mail.bme.hu.

[†] Present address: Urenco Nederland BV, P.O. Box 158, 7600 AD Almelo, The Netherlands.

(1) Boghosian, S.; Papatheodorou, G. N. Halide Vapors and Vapor Complexes. In *Handbook on the Physics and Chemistry of Rare Earths*; Genschneider, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, 1996; Vol. 23; p 435.
(2) Hilpert, K.; Niemann, U. *Thermochim. Acta* **1997**, *299*, 49.
(3) Hilpert, K. *J. Electrochem. Soc.* **1989**, *136*, 2099.
(4) Metallinou, M. M.; Herstad, O.; Ostvold, T.; Papatheodorou, G. N. *Acta Chem. Scand.* **1990**, *44*, 683.
(5) Hilpert, K. Chemistry of Inorganic Vapors. In *Structure and Bonding*; Clarke, M. J., Goodenough, J. B., Ibers, J. A., Jorgensen, C. K., Mingos, D. M. P., Neilands, J. B., Palmer, G. A., Reinen, D., Sadler, P. J., Weiss, R., Williams, R. J. P., Eds.; Springer: Berlin, 1990; Vol. 73; p 97.
(6) Kapala, J.; Roszak, S.; Lisek, I.; Miller, M. *Chem. Phys.* **1998**, *238*, 221.
(7) Lisek, I.; Kapala, J.; Miller, M. *J. Alloys Compd.* **1998**, *280*, 77.
(8) Schäfer, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 713.

10.1021/ic0260973 CCC: $25.00

lamps as they are responsible for the vapor transport of rare earth elements from the cooler regions in these lamps to the emitting arc (see e.g. ref 2). The chloride complexes, on the other hand, were suggested for high-temperature extraction and separation of rare earths.[12,13]

In the process of optimizing the above-mentioned applications, thermodynamic modeling is often applied as valuable tool. This implies, however, the prerequisite of having a database with accurate thermodynamic functions of all chemical species involved. Thermodynamic functions are generally calculated from accurate data on the molecular structure and vibrational frequencies, but the experimental determination of these parameters in case of $MLnX_4$ species has several difficulties originating from the required high experimental temperatures and complex vapor compositions. Therefore, it is not surprising that the experimental information reported on the molecular properties of $MLnX_4$ compounds is rather limited.

The IR spectra of $MCl-NdCl_3$ (M = Li, Na, Cs) and $LiBr-DyBr_3$ systems, recorded by matrix-isolation infrared spectroscopy,[14] have been reported in which one IR-active stretching mode of the LnX_4 tetrahedron of $MLnX_4$ (from the altogether 12 fundamentals) could be identified. In a vapor Raman study of $CsI-ScI_3$[4] also only one signal, which could be attributed to the $CsScI_4$ complex, was observed. Evidently, the small pieces of information from both vibrational spectroscopic studies are insufficient to draw an unambiguous conclusion regarding the structure of the species and moreover do not allow the evaluation of the vibrational partition function. The only experimental information regarding the molecular structure of $MLnX_4$ species available to date is limited to the electron diffraction investigation of $KYCl_4$.[15] From the three possible structures (mono-, bi-, and tridentate), the bidentate model fitted best to the experimental data. It has to be noted that in the electron diffraction analysis a pure $KYCl_4$ vapor was assumed, while mass-spectrometric studies on $MLnX_4$ complexes resulted generally in a complex vapor composition containing also substantial amounts of MX, M_2X_2, and LnX_3.[5]

An efficient alternative for structural and vibrational analysis of $MLnX_4$ compounds is offered by quantum chemical calculations, which has found an increasing application in structural chemistry.[16] Theoretical studies of $MLnX_4$ complexes are nevertheless scarce. Published data include less sophisticated Hartree−Fock calculations on the bidentate structures of $NaCeCl_4$ and $NaNdCl_4$[6,17] as well as our recent systematic studies of $LiLnX_4$ complexes (Ln = La, Ce, Dy; X = F, Cl, Br, I).[18,19] The latter works revealed the superiority of MP2 theory[20] over the Hartree−Fock method and the Becke3−Lee−Yang−Parr[21,22] DFT method as well as the importance of extended basis sets for reliable energetics of the structural isomers. In general, the bidentate structure was found to be the global minimum for the complexes with X = F, Cl, and Br whereas the relative order was reversed in the case of the iodides. Trends in the energetic, structural, and bonding properties have been established within the lanthanide row and halogen group.

In this study we have extended the investigations to complexes formed by heavier alkali metals (M), focusing on the effect of the size of M on the molecular properties. Using the previously successfully applied MP2 theory in conjunction with extended basis sets, we have determined the energetic and structural properties of $MLaX_4$ (M = Na, K, Cs; X = F, Cl, Br, I) compounds. We report here the trends found for the above-mentioned properties. Additionally, we investigated the capabilities of IR and Raman spectroscopy to distinguish between the structural isomers of the complexes.

Computational Details

The calculations were carried out using the second-order Møller−Plesset perturbation theory in the frozen core approximation (MP2).[20] Initial geometry optimizations and the frequency calculations were performed with the following basis set (denoted as A): F, 6-311+G(d); Na, 6-311G(d);[23] La, quasi-relativistic effective core potential (ECP) with a (31111/3111/311) valence basis;[24] Cl, Br, and I, ECPs with (31/311/1) valence bases[25] and d polarization functions from ref 26; K and Cs, ECPs with (31111/3111/1) valence bases[27] and d functions obtained in this study according to ref 28 (exponents: $\alpha_{dK} = 1.024$; $\alpha_{dCs} = 0.353$). The ECP of lanthanum includes the f electrons in the core because of their insignificance for accurately predicting molecular geometries due to the relatively small 4f orbital radii.[29]

The final energetic and structural characterization of the complexes was carried out with the valence basis of La extended with 2fg and those of the other atoms with 2df polarization functions (denoted in the following as set B). The two-parameter set of f functions for La was taken from ref 24, while the 2d functions for the halides originate from ref 26. The g polarization function for

---

(9) Papatheodorou, G. N. Spectroscopy, structure, and bonding of high-temperature metal halide vapor complexes. In *Current Topics in Materials Science*; Kaldis, E., Ed.; North-Holland: Amsterdam, 1982; Vol. 10.

(10) Schäfer, H. *Adv. Inorg. Chem.* **1983**, *26*, 201.

(11) Hastie, J. W. *High-Temperature Vapors*; Academic Press: New York, 1975.

(12) Murase, K.; Machida, K.; Adachi, G. *J. Alloys Compd.* **1995**, *217*, 218.

(13) Murase, K.; Adachi, G.; Hashimoto, M.; Kudo, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 353.

(14) Feltrin, A.; Cesaro, S. N. *High Temp. Mater. Sci.* **1996**, *35*, 203.

(15) Spiridonov, V. P.; Brezgin, Y. A.; Shakhparonov, M. I. *Zh. Strukt. Khim.* **1971**, *12*, 1080.

(16) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233.

(17) Kapala, J.; Lisek, I.; Roszak, S.; Miller, M. *Polyhedron* **1999**, *18*, 2845.

(18) Groen, P.; Oskam, A.; Kovács, A. *J. Mol. Struct. (THEOCHEM)* **2000**, *531*, 23.

(19) Groen, P.; Oskam, A.; Kovács, A. *Inorg. Chem.* **2000**, *39*, 6001−6008.

(20) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(22) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(23) This keyword refers to the contracted (631111/42111/1) basis for Na in Gaussian 98.

(24) Dolg, M. Ph.D. Thesis, University of Stuttgart, 1989.

(25) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(26) Andzelm, J.; Huzinaga, S.; Klobukowski, M.; Radzio, E.; Sakai, Y.; Tatekawi, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(27) Leininger, T.; Nicklass, A.; Küchle, W.; Stoll, H.; Dolg, M.; Bergner, A. *Chem. Phys. Lett.* **1996**, *255*, 274.

(28) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

(29) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.

La and the f polarization functions for Cl, Br, and I have been optimized in our previous study (exponents: $\alpha_{gLa} = 0.731$; $\alpha_{fCl} = 0.720$; $\alpha_{fBr} = 0.581$; $\alpha_{fI} = 0.426$).[19] The 2d and f functions for potassium and cesium were obtained in this study according to the procedure described in ref 28 (exponents: $\alpha_{dK} = 2.048, 0.512$; $\alpha_{fK} = 1.174$; $\alpha_{dCs} = 0.706, 0.1765$; $\alpha_{fCs} = 0.610$). For F the 6-311+G-(2df) and for Na the 6-311G(2df) basis sets were applied. The above basis set is consistent with that of our previous study on the $LiLaX_4$ derivatives.[19] All the quantum chemical calculations were performed using the Gaussian 98 program package[30] extended with the NBO 5.0 code.[31]

The thermodynamic functions were calculated by employing the usual statistical mechanical formulas (rigid rotator, harmonic oscillator approximation; see e.g. ref 32). The molecular constants were taken from the MP2/B, whereas the vibrational frequencies were from the MP2/A calculations. The vibrational frequencies were left unscaled, since recent computational studies on rare earth trihalides[33−35] have indicated that this level can reproduce the experimental vibrational data for such compounds quite well.

Results and Discussion

1. Structures and Energetics. According to previous results on $MLnX_4$ rare earth/alkali metal halide complexes, three structures have relevance as minima on the potential energy surface (PES). In the individual isomers one (structure 1), two (structure 2), or three (structure 3) halogen atoms act as a bridge between the alkali metal atom and the rare earth atom (cf. Figure 1). Structures 1 and 3 have C_{3v} while structure 2 possesses C_{2v} symmetry. In agreement with previous studies on $LiLnX_4$ complexes[18,19] structures 2 and 3 of the $MLaX_4$ compounds were found to be low-energy minima on the PES. Structure 1 is a high-lying local minimum in the case of the $MLaF_4$ complexes, whereas it is a second-order saddle point when X = Cl, Br, and I. The different character of structure 1 in the case of the fluoride derivatives may be explained by the high anionic character of F as compared to the other halogens, resulting in stronger M···X electrostatic interactions.

The stability of the individual structures can best be assessed from the dissociation energies compiled in Table 1. They include both zero-point vibrational energy (ZPE) and basis set superposition error (BSSE) corrections. We note the importance of especially the latter (ranging from 16 kJ/mol in structures 1 up to 35 kJ/mol in structures 3) despite the large basis sets used. Although the counterpoise method[36]

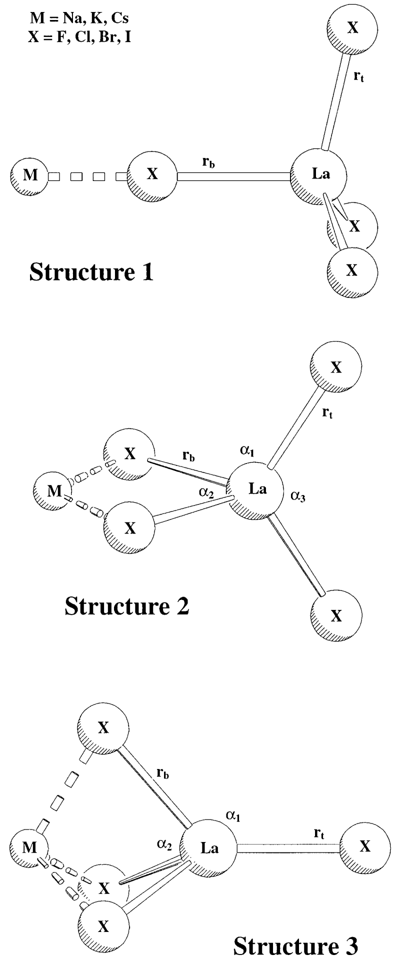

Figure 1. Characteristic structures and labeling of the geometrical parameters of the $MLaX_4$ (M = Na, K, Cs; X = F, Cl, Br, I) coordination complexes.

Table 1. Calculated Dissociation Energies[a] (kJ/mol) at 0 K of the $MLaX_4$ Complexes

	X			
structure	F	Cl	Br	I
		$LiLaX_4$[b]		
1	162.9	(126.2)	(112.8)	(99.0)
2	245.1	209.7	203.5	192.7
3	201.6	189.7	191.4	186.4
		$NaLaX_4$		
1	117.3	(72.6)	(53.5)	(35.6)
2	179.6	138.8	127.4	112.5
3	159.3	135.5	127.8	116.3
		$KLaX_4$		
1	221.5	(199.9)	(177.4)	(160.4)
2	272.8	234.7	222.6	206.8
3	262.0	240.0	231.0	217.8
		$CsLaX_4$		
1	219.2	(184.9)	(169.2)	(153.1)
2	260.8	232.8	222.2	207.3
3	253.0	240.3	232.6	220.1

[a] For the reaction $MLaX_4 = LaX_3 + MX$ calculated at the MP2/B level. The absolute energies were corrected for BSSE (MP2/B) and zero-point vibrational energy (MP2/A). The dissociation energies of the saddle-point structures 1 are given in parentheses. [b] From ref 19.

---

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Jr, J. A. M.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5 ed.; Gaussian Inc.: Pittsburgh, PA, 1998.

(31) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.

(32) Knox, J. H. *Molecular Thermodynamics*, 2nd ed.; John Wiley & Sons: New York, 1978.

(33) Kovács, A.; Konings, R. J. M.; Booij, A. S. *Chem. Phys. Lett.* **1997**, *268*, 207.

(34) Kovács, A.; Konings, R. J. M. *Vib. Spectrosc.* **1997**, *15*, 131.

(35) Kovács, A. *Chem. Phys. Lett.* **2000**, *319*, 238.

applied usually for the estimation of BSSE is known to make a slight overestimation of the BSSE,[37] the large values obtained indicate that our very large basis set B is not yet converged to saturation. The unsaturated character of an analogous extended basis set for $LaCl_3$ in conjunction with MP2 theory was reported recently.[35]

Three trends for the minimum structures on the PES are clear from Table 1:

(i) Within the Alkali Metal Group. The energies of dissociation to MX and LaX_3 are the largest in the $CsLaX_4$ and $KLaX_4$ complexes, having values between 200 and 270 kJ/mol. The dissociation energies of $LiLaX_4$ are somewhat, while those of the $NaLaX_4$ complexes are considerably, lower. Thus, the first effect of the alkali metal size that can be established from the computations is an increased stability of the heavy (K, Cs) complexes with respect to the lighter (Li, Na) derivatives. The increasing stability toward the heavier analogues is in agreement with experimental[38] and computational results[39] on the structurally related $MAlX_4$ complexes as well as with recently reported dissociation energies at 298.15 K for $NaCeCl_4$,[6] $CsCeCl_4$,[7] $NaNdCl_4$,[17] and $CsNdCl_4$.[40] A comparison with earlier experimental dissociation energies of $MLnX_4$ compounds is less straightforward. In fact, on the basis of the diverse early results, Boghosian and Papatheodorou suggested a probable decreasing stability upon going to the heavier alkali metals.[1] On the other hand, the lower stability of $NaLaX_4$ complexes is in agreement with the smaller bond enthalpies of NaX halides with respect to those of LiX, KX, and CsX.[41] Additional effects come from the more strained structures of the $NaLaX_4$ complexes, which will be analyzed in the next section.

(ii) Within the Halogen Group. The relative stability of the different halides is in agreement with expectations on the basis of their anionic character. Most stable are the fluoride complexes with the strongest ionic bonding. The considerable drop in ionic character between the fluorides and chlorides is accompanied by a drop in the dissociation energy, while the decrease becomes gentle from the chlorides to the iodides.

(iii) Structure 2 versus Structure 3. The dissociation energies in Table 1 indicate a close stability of the two structures of an $MLaX_4$ complex. In general, the lighter alkali metals and halogens favor structure 2, whereas the heavier analogues have an energetic preference for structure 3. Consequently, structure 2 is definitely the most stable for the $MLnX_4$ complexes with M = Li or X = F. The order of stability is reversed for $NaLaI_4$ and for the $KLaX_4$ and $CsLaX_4$ complexes with X = Cl, Br, and I. The largest energy difference in favor of structure 3 can be observed for $CsLaI_4$.

The situation regarding the relative stabilities of the two structures changes somewhat when we go from 0 K to the experimentally relevant higher temperatures (800−1500 K). Under these conditions the thermal and entropy effects also have to be taken into account. To ascertain how the latter effects influence the basic energetics of $MLaX_4$ systems, the equilibrium constants of the isomerization processes have been derived from the relative Gibbs free energies of both isomers by evaluating $-RT \ln K_p = \Delta H°(T) - T\Delta S°(T)$. The derived relative amounts of structures 2 and 3 in the temperature range $T = 0$ K to $T = 3000$ K for $KLaX_4$ (X = F, Cl, Br, I) and $MLaI_4$ (M = Li, Na, K, Cs) are presented in Figure 2. It should be noted that small deviations in the computed relative energies of the two structures can affect seriously the (steeply changing) concentrations at low temperatures (<1000 K). On the other hand, at higher temperatures the $-T\Delta S°$ term dominates the equilibrium constant; therefore, the relative contributions are practically independent of the uncertainty of the computed energies.

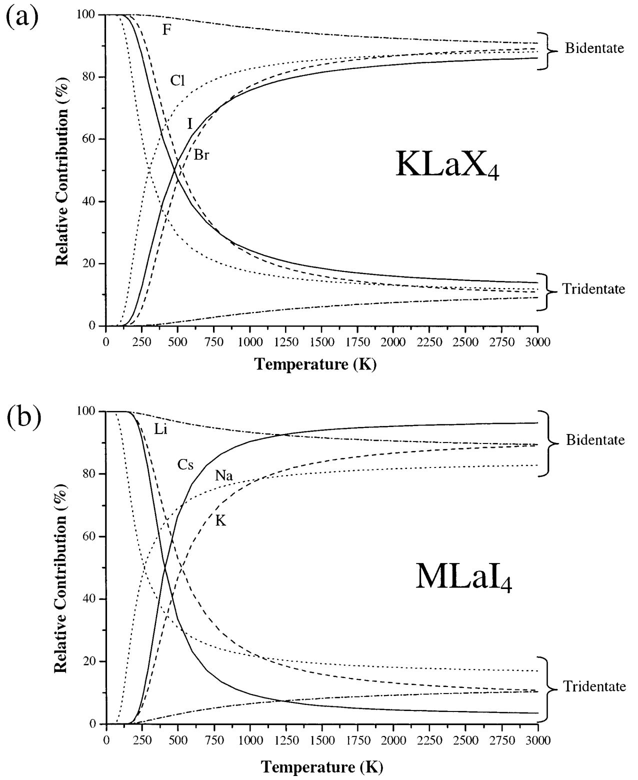

Figure 2. Temperature dependence of the relative content of structures 2 and 3 under the following equilibrium conditions: (a) $KLaX_4$ (X = F(− • −), Cl (•••), Br (---), I (EmDash)); (b) $MLaI_4$ (M = Li (− • −), Na (•••), K (---), Cs (EmDash)).

According to the above-discussed relative stabilities at 0 K the $KLaF_4$ and $LiLaI_4$ systems are characterized by a positive enthalpy change ($\Delta H°$) of the isomerization process structure 2 ↔ structure 3, whereas for all the other compounds in Figure 2 this enthalpy change is negative. On the other hand, the entropy change of the isomerization ($\Delta S°$) is negative for all the complexes as determined by the change in symmetry upon going from structure 2 to structure 3. Consequently, for $KLaF_4$ and $LiLaI_4$ the bidentate structure is the most abundant over the complete temperature range. Only at elevated temperatures, the relative amount of structure 2 is slightly decreased due to the thermal population

---

(36) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(37) Johnson, A.; Kollman, P.; Rothenberg, S. *Theor. Chim. Acta* **1973**, *29*, 49.

(38) Sholtz, V. B.; Sidorov, L. N. *Vestn. Moskovsk. Univ.* **1972**, *4*, 371.

(39) Solomonik, V. G.; Sliznev, V. V. *J. Struct. Chem.* **1999**, *40*, 368.

(40) Lisek, I.; Kapala, J.; Miller, M. *J. Alloys Compd.* **1998**, *278*, 113.

(41) *CRC Handbook of Chemistry and Physics 1999−2000*, 81st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2000.

Table 2. Calculated Geometrical Parameters[a] of the MLaX$_4$ Complexes and the Respective Simple Halides

	NaLaX$_4$				KLaX$_4$				CsLaX$_4$			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
Structure 2												
r_b	2.311	2.741	2.902	3.121	2.283	2.716	2.870	3.090	2.276	2.707	2.859	3.081
r_t	2.166	2.605	2.758	2.975	2.169	2.608	2.765	2.979	2.172	2.614	2.766	2.984
M−X	2.208	2.577	2.749	2.967	2.457	2.954	3.118	3.377	2.749	3.269	3.429	3.680
α_1	114.0	112.6	112.0	111.0	113.5	112.1	111.4	110.5	113.1	111.7	111.1	110.3
α_2	81.7	85.3	89.7	94.2	79.0	88.0	91.5	96.3	81.2	89.5	92.9	97.0
α_3	117.3	117.1	116.4	116.5	117.6	117.1	117.0	110.5	117.6	117.2	117.0	116.9
X−M−X	81.7	92.3	96.2	100.8	72.5	79.4	82.5	86.0	65.2	71.3	74.3	77.7
La−X−M	100.5	91.2	87.1	82.5	104.1	96.3	93.0	88.9	106.8	99.6	96.4	92.6
Structure 3												
r_b	2.251	2.684	2.841	3.061	2.236	2.672	2.826	3.048	2.233	2.669	2.824	3.044
r_t	2.187	2.624	2.775	2.991	2.185	2.623	2.776	2.990	2.184	2.624	2.777	2.990
M−X	2.380	2.741	2.929	3.148	2.626	3.112	3.279	3.540	2.935	3.422	3.576	3.828
α_1	130.3	127.3	125.6	123.8	128.4	124.7	123.3	121.4	126.3	123.2	121.9	120.2
α_2	82.6	87.0	89.5	92.1	85.5	90.7	92.7	95.4	88.5	92.9	94.7	96.9
X−M−X	77.3	84.8	86.2	88.8	70.6	75.3	77.2	79.1	64.1	68.8	71.0	73.1
La−X−M	84.2	76.2	73.5	69.9	86.5	79.9	77.2	74.1	88.5	82.4	79.8	76.8
MX												
M−X	1.986	2.378	2.540	2.754	2.204	2.697	2.857	3.096	2.415	2.946	3.117	3.363
exptl[b]	1.926	2.361	2.502	2.711	2.171	2.667	2.821	3.048	2.345	2.906	3.072	3.315
LaX$_4^-$												
La−X	2.221	2.658	2.813	3.0 30								

[a] Calculated at the MP2/B level. Bond lengths are given in Å, and bond angles, in deg. For abbreviation of the geometrical parameters see Figure 1. [b] Equilibrium bond distances from MW experiments. The seven figures after the decimal point (as given in ref 44) were reduced here to accommodate the table columns. The data have an experimental error of ca. 10^{-6} Å.

of structure 3. The other complexes prefer the tridentate coordination at low temperatures, whereas the positive entropy term ($-T\Delta S°$) results in an increase of the relative amount of structure 2 with increasing temperature. At temperatures where the complexes exhibit sufficiently high vapor pressures to be studied experimentally (T > 800 K), also for these species the bidentate structures dominate over the tridentate ones. The effect is most pronounced in the case of the heavy analogues where the change in molecular structure has the largest impact on the rotational partition function (cf. e.g. CsLaI$_4$ in Figure 2b).

Worth mentioning is the observation that NaLaI$_4$ has the largest relative content of tridentate species at experimental temperatures of all MLaI$_4$ considered in Figure 2b. The reason for this can be found in the somewhat peculiar geometrical properties of the NaLaX$_4$ complexes (vide infra) resulting in a relatively small change in the rotational partition function upon isomerization as compared to the other MLaX$_4$ species.

2. Molecular Geometry and Atomic Charges. The calculated geometrical parameters of the MLaX$_4$ complexes as well as those of the simple reference halides (MX and the tetrahedral LaX$_4^-$ anions) are compiled in Table 2. For comparison, available experimental data on the MX diatomics are also included. The data show an overestimation of the M−X bond length by a few hundredths of an angstrom by the computations, found generally for heavy atom compounds.[35,42]

In this discussion we focus on the effect of alkali metal size on the geometrical properties. The trends in the halogen row have been investigated in detail in our previous study,[19] hence, they will be commented here only briefly. The molecular geometries are assessed from the point of view of the M$^+$···LaX$_4^-$ interaction. The consequences of this interaction appear in the M−X distances as well as in the geometrical parameters of the LaX$_4^-$ moieties.

The efficiency of M···X bonding in the title complexes is reflected by their M−X distances with respect to those in the simple MX halides. Longer M−X bonds in MLaX$_4$ indicate weaker interatomic interactions and vice versa. The following trends on M−X are clear from Table 2:

(i) Type of Coordination. The M···X bond weakens with increasing coordination number of M. It should be kept in mind that although the M···X bonds in structures 2 and 3 are individually weaker than that in the respective structure 1, however, their double/triple occurrence results in an altogether much larger enthalpy of formation.

(ii) Within the Halogen Group. In agreement with previous results on the Li derivatives,[19] the M−F distances have the largest (relative) deviation from the bond length in MX whereas the deviation decreases with increasing halogen size.

(iii) Within the Alkali Metal Group. The M−X bond distances imply a slight weakening trend with the size of the alkali metal: e.g. they are longer by ca. 8% and 15% in structures 2 and 3 of NaLaX$_4$ as compared to the respective MX whereas the relation amounts to ca. 10% and 16% lengthening in the structures of CsLaX$_4$, respectively. We note that the stronger effect in structures 2 parallels their decreasing stability with respect to structures 3 (vide supra). On the other hand, the variation in the M−X distances with different M does not follow the trend outlined above for the stability of the complexes. This indicates the importance of other factors besides the M···X interaction.

---

(42) Kovács, A.; Szabó, A. *Chem. Phys. Lett.* **1999**, *305*, 458.

Table 3. Natural Atomic Charges of the $MLaX_4$ Complexes and the Respective Simple Halides[a]

	$NaLaX_4$				$KLaX_4$				$CsLaX_4$			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
Structure 2												
M	0.920	0.951	0.933	0.900	0.989	0.978	0.970	0.957	0.987	0.978	0.977	0.965
La	2.600	2.373	2.283	2.075	2.606	2.366	2.276	2.067	2.604	2.365	2.269	2.069
X_b	−0.888	−0.854	−0.828	−0.769	−0.919	−0.860	−0.838	0.787	−0.915	−0.857	−0.835	−0.788
X_t	−0.872	−0.808	−0.780	−0.719	−0.879	−0.812	−0.785	0.725	−0.880	−0.814	−0.787	−0.729
Structure 3												
M	0.908	0.931	0.912	0.874	0.986	0.968	0.955	0.937	0.987	0.972	0.965	0.950
La	2.602	2.375	2.288	2.082	2.601	2.362	2.273	2.064	2.596	2.358	2.269	2.062
X_b	−0.880	−0.827	−0.801	−0.739	−0.901	−0.835	−0.810	0.755	−0.900	−0.836	−0.812	−0.758
X_t	−0.870	−0.825	−0.798	−0.738	−0.884	−0.824	−0.798	0.737	−0.884	−0.824	−0.798	−0.738
MX												
M	0.965	0.951	0.934	0.905	0.980	0.976	0.967	0.953	0.960	0.959	0.957	0.949
X	−0.965	−0.951	−0.934	−0.905	−0.980	−0.976	−0.967	0.953	−0.960	−0.959	−0.957	−0.949
LaX_4^-												
La	2.765	2.534	2.473	2.317								
X	−0.941	−0.884	−0.868	−0.829								

[a] Calculated at the MP2/B level. The subscripts "b" and "t" mean bridged and terminal, respectively (cf. Figure 1).

Other significant geometrical consequences of the M···X interaction are the lengthening of the bridging La−X bonds (r_b) with respect to those in the free LnX_4^- ions as well as the deformation from the tetrahedral LnX_4^- geometry (cf. Table 2). The lengthening of the La−X bonds is considerably more in the $NaLaX_4$ complexes than in the $KLaX_4$ and $CsLaX_4$ structures. This weakening of the La−X bonds in the $NaLaX_4$ species (increasing the absolute energy of the complexes with respect to $MX + LnX_3$) may be a significant reason for their much lower stability than the complexes with M = Li, K, and Cs.

The distorted X−La−X angles refer to a considerable strain in the $MLaX_4$ complexes. The larger ionic radii of the heavier alkali metals and halogens lead to some relaxation, but the α_2 angles are still well below the tetrahedral value even in $CsLaI_4$. The slightly more efficient relaxation in structures 3 of the heavier analogues may also contribute to their larger stability with respect to structures 2.

Information on the bonding interactions in the title molecules can be obtained from the computed natural atomic charges[43] using the simple MX and LaX_4^- halides as reference. The atomic charges of the MX diatomics show the expected (decreasing) trend downward in the halogen group, whereas there is a curve with a maximum at K for the alkali metals (cf. Table 3). The increase of the cationic character from Na to K is in agreement with the decreasing electronegativity in this direction. On the other hand, the larger size and the consequently larger polarizability may be responsible for the weaker ionic character of Cs.

The following characteristics observed upon complex formation should be noted:

(i) The atomic charge of Na is slightly decreased (similarly to that found previously for Li[19]), while that of K and Cs is increased with respect to MX.

(ii) The charge separation between M^+ and LaX_4^- is somewhat larger in structures 2 than in structures 3 implying slightly stronger M···X ionic interactions in the former.

(iii) The magnitudes of the atomic charges of La and the halogens are considerably decreased with respect to those in the reference LaX_4^-. This indicates an increased covalent contribution of bonding within the LaX_4 moieties in the complexes. Generally, the terminal halogens are less ionic than the bridging ones.

3. Vibrational Spectra. Our present computations can assist in the experimental identification of the complexes by vibrational spectroscopy. As pointed out previously, the LnX_3, MX, and M_2X_2 species might be present besides $MLnX_4$ in considerable amounts in equilibrium vapors over $MX-LnX_3$ systems.[5] Their vibrational bands appear in the same, and rather small (ca. 500 cm^{-1}), spectral region as those of the respective $MLnX_4$ molecules with possible overlaps of close lying fundamentals.[18,19] Moreover, both isomers of the $MLnX_4$ species are expected to be present in the vapor and their spectral features cannot be distinguished from experiments alone. The only straightforward interpretation of these spectra can be performed on the basis of a comparison with computed frequencies and intensities. In the following the main differences in the spectral properties of structures 2 and 3 of the title $MLnX_4$ compounds are summarized.

For visual presentation the calculated IR and Raman spectra of the $KLaX_4$ complexes were selected (Figure 3). The spectra of the sodium and cesium derivatives carry analogous features. Some differences include the stretching and bending vibrations involving the alkali metal: because of the different atomic weights, these vibrations of Na are shifted to higher and those of Cs to lower wavenumbers with respect to $KLaX_4$ and there are minor changes in the relative intensities. The calculated vibrational frequencies as well as IR and Raman activities of all the molecules are available in the Supporting Information.

From Figure 3 it is obvious that for distinguishing between structures 2 and 3 the high-wavenumber part of the vibra-

---

(43) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(44) *Landolt-Börnstein. Numerical Data and Functional Relationships in Science and Technology*; Hellwege, K.-H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin, 1974; Vol. II/6, pp 2−10.

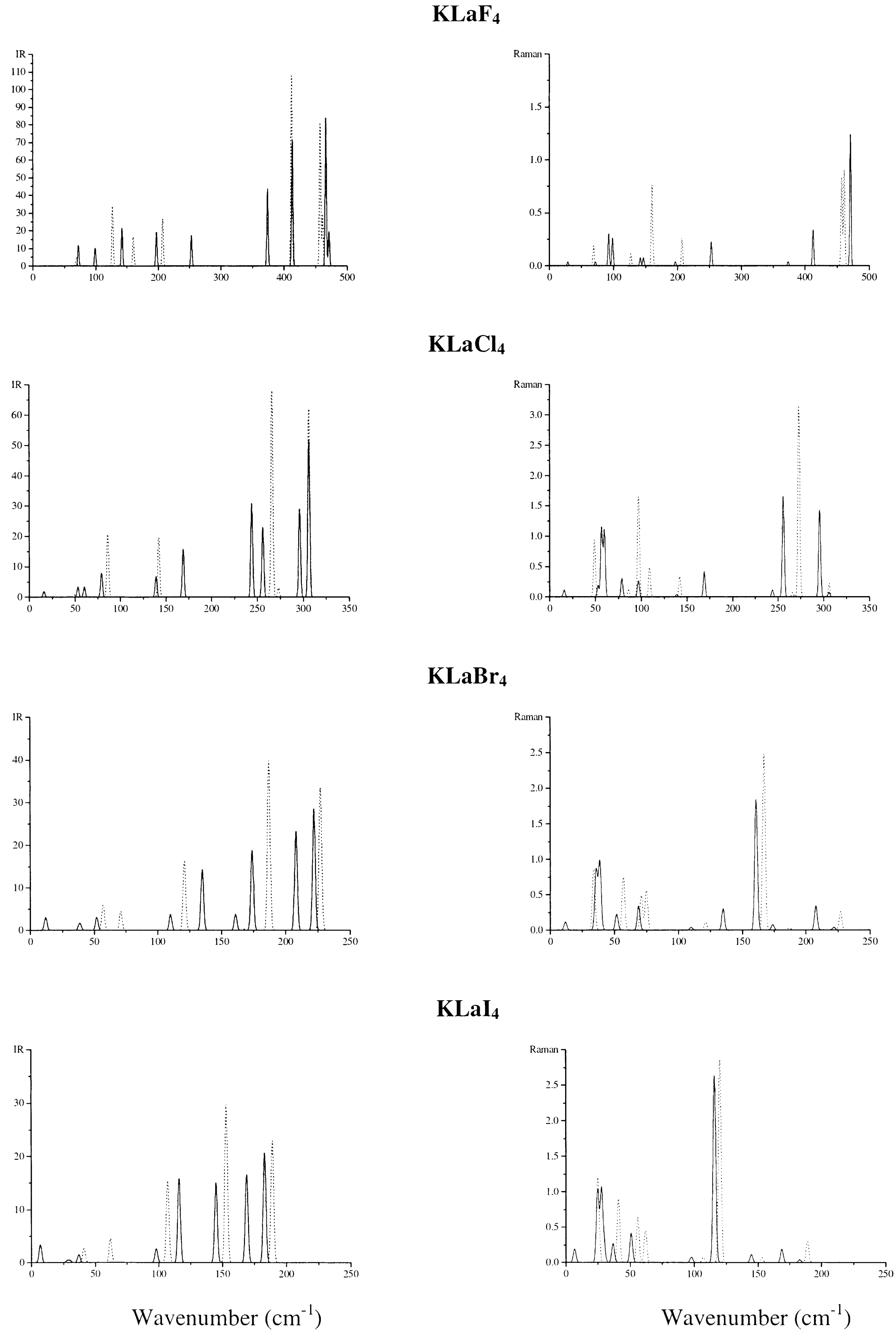

Figure 3. Calculated vibrational spectra of the bi- (solid line) and tridentate (dotted line) structures of KLaX$_4$ complexes. The curves were obtained by Gaussian fit of the calculated data. Units of the IR and Raman intensities are km/mol and Å^4/amu, respectively.

tional spectra, where the intense stretching bands (important under the low-concentration conditions of the vapor) appear, is the most suited. This region shows significant differences between the infrared spectral parameters of structures 2 and 3. As a result of the degeneracy in the C_{3v} point group, structure 3 has less vibrational bands compared to structure 2. Generally, 2−3 of the 8 fundamentals of structure 3 and 3−4 of the 12 fundamentals of structure 2 appear in the stretching region with considerable IR intensity. Although these features should, in principle, provide a possibility to distinguish between the two structures, we note that the vibrational fundamentals of both structures are found within a small frequency range. To observe relative amounts of 20% or less of structure 3 (vide supra), an experimental technique providing narrow signals is of highest importance.

The latter remark of course also applies to an experimental investigation by Raman spectroscopy. However, the computed Raman spectra indicate that a chance to distinguish between signals of the two structures only exists in the case of the fluorides and chlorides. The spectra of $MLaF_4$ have two close-lying intense bands around 450 cm^{-1} in the case of structure 3, whereas an intense band above 450 cm^{-1} and a less intense one around 400 cm^{-1} in the case of structure 2. The spectra of structure 3 of $MLaCl_4$ contain a single intense band around 270 cm^{-1}, while those of structure 2 have two intense bands around 250 and 300 cm^{-1}. On the other hand, the spectra of the bromide and iodide isomers have no significant differences, which limits the value of Raman investigations in trying to experimentally observe the structural isomerism of these species.

Conclusions

Our theoretical study has uncovered the energetic and structural characteristics of $MLaX_4$ ($M = Na, K, Cs$; $X = F, Cl, Br, I$) complexes. Most computed dissociation energies were above 200 kJ/mol, suggesting a stability sufficient for high-temperature gas-phase experiments. The effect of the alkali metal size is manifested in the larger stabilities of the K and Cs complexes. The stability of the $NaLaX_4$ complexes is much lower, which originates partly from a destabilization in the LaX_4 moiety of these molecules.

The computations confirmed the significance of the bi- (C_{2v}) and tridentate (C_{3v}) structures for $MLaX_4$ compounds. The bidentate structure is the most stable in the case of the fluoride complexes, but the heavier alkali metals and halogens prefer the tridentate arrangement at the temperature referring to the computations, 0 K. The contribution of the entropy at experimentally meaningful high temperatures supports the predominance of structure 2 in a thermodynamic equilibrium with structure 3 for all $MLaX_4$ complexes under study here.

In accordance with the observed trends in the relative potential energies, the geometrical parameters indicate a more favored coordination of M in structure 3 with increasing alkali metal and halogen size. The natural atomic charges are in agreement with strong ionic interactions in the title complexes. Minor covalent contributions appear in the complexes with heavier alkali metals and halogens.

The IR and Raman spectra of the chemically relevant structures 2 and 3 have characteristic features, on the basis of which the complexes can be identified in the vapor phase. In principle, the two structures could be distinguished unambiguously by their infrared spectra.

Acknowledgment. This research has been supported by the Hungarian Scientific Research Foundation (OTKA, Grant No. T038189) and the Ministry of Education of Hungary (FKFP 0364/1999). Prof. Dr. E. H. P. Cordfunke is gratefully acknowledged for critically reviewing the manuscript. The computations have partly been performed on the SUN E10000 supercomputer of the National Information Infrastructure Development Program of Hungary.

Supporting Information Available: Vibrational frequencies of structures 2 and 3 calculated at the MP2/A level as well as IR and Raman activities. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0260973