Theoretical Studies on the Structure, Thermochemistry, Vibrational Spectroscopy, and Other Features of HfX_6^{2-} (X = F, Cl, Br, I). Electrostatic Energy in Hexahalogenohafnates

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Bond lengths in octahedral HfX_6^{2-} (X = F, Cl, Br, I) were optimized at the ab initio Hartree−Fock SCF level using all-electron MIDI (X = Cl) and effective core potential valence basis sets of double-ζ quality, supplemented with diffuse functions. Energies resulting from these calculations were combined with energies of X_2 (at optimal geometries) and Hf in order to obtain energies of formation of HfX_6^{2-}. The effects of electron correlation were taken into account at the second-order Møller−Plesset level of theory. Vibrational frequencies were determined in the harmonic approximation and compared with available experimental data. Common routines were employed to evaluate entropies, heat capacities, heats of formation, and free enthalpies of formation of gaseous HfX_6^{2-} in the standard state. Electrostatic cohesive energies for hexahalogenohafnates were evaluated by the Ewald method adapted to complex ions. It was assumed for this purpose that the formal charge of each ion is a whole multiple of *e*. Net atomic charges in complex anions were found either from various population analyses or by fits to the ab initio quantum mechanical electrostatic potential. The Coulombic energies are inversely dependent on the volume of the simplest structural unit and distance between interacting centers (Hf−cation). Theoretically determined properties are in good agreement with available data, mostly of experimental origin.

Introduction

Continuous progress in the development of theoretical methods and capabilities of computational devices enables prediction of the structure, energetics, reactivity, and physicochemical features of various chemical entities existing in the gaseous phase.[1−3] This theoretical approach is not easily transferable to condensed phases, where numerous weak pairwise and nonadditive interactions occur for which it is difficult to formulate a quantitive model.[4−7] The problem is relatively simple in the case of crystalline ionic solids, which attain perfect constitution. In such phases, the crystal lattice (cohesive) energy is dominated by the electrostatic contribution, which is amenable to theoretical calculations.[8−11] This paper touches on the problem of the evaluation of the electrostatic part of the lattice energy in the case of ionic substances containing HfX_6^{2-} ions.

Crystal lattice energy is generally described as the amount of energy which has to be supplied to transfer ions (or other entities) from the lattice to the gaseous phase, where they do not interact with each other.[11,12] Knowledge of the enthalpies of formation of gaseous ions and crystalline substances therefore enables determination of their lattice energies following Hess's law. Similarly, the combination of lattice energies with enthalpies of formation of ions affords the enthalpies of formation of solid phases. Heats of formation of solid substances have so far been determined only experimentally.[13,14] For solid hexahalogenohafnates such thermochemical data are rather scattered and fragmentary.[15] Heats of formation of numerous monoatomic or complex organic base cations have been determined experimentally and are commonly available.[16,17] In the case of the latter species, heats of formation can also be obtained by employing quantum chemistry methods.[1,18,19] Unfortunately, only heats of formation of simple anions can be measured and are available in the literature.[13] There are also known heats of formation of several MX_6^{2-} ions (M = metal(IV)). Values of these quantities have, however, been assessed on the basis of the thermochemical cycle and lattice energies obtained theoretically for salts containing the aforementioned ions.[9] To our knowledge, except for our recent report on ZrX_6^{2-},[20] no advanced theoretical studies on these complex octahedral species have so far been undertaken. We therefore employed ab initio quantum chemistry methods to obtain information on the structure, thermodynamics, vibrational transitions, and net charges of atoms in HfX_6^{2-} ions.

Hafnium tetrahalides and hexahalogenohafnates are two of the simplest and best known derivatives of hafnium.[21] They play an important role in purifying and separating this element

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from others.[22] Owing to the high symmetry (T_d for MX_4 and O_h for MX_6^{2-}) and the closed-shell electronic structure of these species, they are frequently considered as models of coordinated compounds. These reasons prompted us to undertake studies on hexahalogenohafnates. Moreover, solid phase structures of several salts containing these dianions are known; therefore, relations between lattice energy and constitution, as well as structural parameters of the salts, can be revealed.

To determine the lattice energy, we explored several approaches to obtain charges localized on atoms. Particular attention has been given to charges which reproduce the ab initio electrostatic potential,[23,24] since certain physical meanings can be ascribed to them. This constitutes progress in comparison with our earlier studies, in which net atomic charges were obtained from the population analysis of semiempirical wave functions.[25–27] We believe that the approach adopted in this work constitutes a more reliable basis for examination of the interionic interactions in complex ionic substances.

Methods

Geometry and Force Field Calculations. Bond lengths in HfX_6^{2-} at constrained O_h symmetry were determined at the Hartree–Fock level of the theory (HF) by employing Baker's optimization procedure[28] together with the relativistic compact effective core potentials of Stevens et al.[29,30] and their valence, energy-optimized, shared-exponents, contracted-Gaussian basis sets, which we labeled SBKJ. For the Hf atom, 60 electrons were incorporated into pseudopotential and the double-ζ quality s, p basis sets and triple-ζ quality d basis sets were used to model the chemically active 5s, 5p, 6s, 6p, and 5d orbitals. For X atoms, the valence *n*s and *n*p orbitals with the double-ζ quality basis sets were considered. Calculations with the all-electron MIDI basis set[31] were restricted to the $HfCl_6^{2-}$ ion only due to the fact that the GAMESS program package used[32] did not enable gradient optimization in the case of basis sets involving f symmetry functions (for Hf) and nongradient optimization followed by Hessian evaluation was very time consuming.

Validity of the geometry optimization procedure was tested in the subsequent Hessian (second derivatives of the energy as a function of nuclear coordinates) calculations followed by the normal-mode analyses. In the HF/SBKJ calculations all positive curvatures were found at the O_h symmetry stationary points, which confirms that minima on the potential energy surfaces were actually located. At this level of theory, vibrational frequencies in the harmonic approximation were also determined.[33]

To improve the quality of ab initio calculations, the SBKJ basis sets were augmented with diffuse functions.[1] For X, one extra set of L(sp) functions was added whereas, for Hf, two, one L(sp) and one d, diffuse sets were used. For every symmetry, the exponent of the diffuse basis function was equal to one-third of the lowest exponent in the original basis. The influence of the diffuse functions on the results of ab initio calculations was thoroughly tested in the case of $HfCl_6^{2-}$. It was found that augmenting the SBKJ basis sets with diffuse functions on (i) X only (SBKJ+d), and (ii) X and Hf (SBKJ+dd), leaves the geometry unaffected and influences only slightly the energy and the free enthalpy of formation of this species. To unify the results, mostly single-point HF calculations were performed with the SBKJ+dd basis sets at the geometries optimal for the SBKJ basis sets (relevant information is referred to as HF/SBKJ+dd||HF/SBKJ, where "||" means "at the geometry of").

All the quantum mechanical calculations were carried out on a Hewlett-Packard 730 Apollo workstation employing the GAMESS (General Atomic and Molecular Electronic Structure System) program package.[32]

Thermodynamic Quantities. The energies of formation of HfX_6^{2-} (ΔE_f) were determined by following Hess's law, i.e., by subtracting from the energy of gaseous HfX_6^{2-} the energies of gaseous X_2 (three times) and Hf in the lowest electronic state (RHF energy at the SCF level or UHF+MP2 energy at the MP2 level). Values of ΔE_f were not corrected for the zero-point vibrational energy. As thermodynamic properties may be markedly affected by the electron correlation effects,[1] the HF results were supplemented with the second-order Møller–Plesset (MP2) electron correlation correction[34] calculated for the SBKJ basis set (relevant values are referred to as e.g. MP2/SBKJ+dd||HF/SBKJ).

The enthalpies ($\Delta H_{f,298}$) and free enthalpies ($\Delta G_{f,298}$) of formation of HfX_6^{2-} were evaluated analogously to ΔE_f.[35] For this purpose routines incorporated in GAMESS,[32] employing statistical thermodynamics, were used to determine entropies (S_{298}) and heat capacities ($C_{p,298}$), as well as enthalpies and free enthalpies of species relative to their ab initio energies. Such values correspond to the gaseous state of all entities at a pressure of 1 atm. To bring $\Delta H_{f,298}$ values to the standard conditions in the usual sense (relevant information is referred to as e.g. $\Delta H^\circ_{f,298}$), the ab initio energies of Hf, Br_2, and I_2 were lowered by (in kJ/mol) 611 (enthalpy of atomization[36]), 31 (enthalpy of vaporization[16]), and 62 (enthalpy of sublimation[16]), respectively. To obtain free enthalpies of formation under the standard conditions, the theoretically determined entropies of Hf, Br_2, and I_2 were lowered by (in J/(mol K)) 143.3, 93.1 and 144.5, i.e., the differences in entropy of the species in gaseous and standard states, respectively.[16]

Net Atomic Charges. Net atomic charges in HfX_6^{2-} were initially evaluated on the basis of the Mulliken,[37] Löwdin,[38] and Stone[39] population schemes. Data thus obtained demonstrated strong dependence on the choice of the basis sets used. Therefore, we determined charges fitted so as to reproduce the ab initio molecular electrostatic potential (MEP charges).[24] For this purpose, the procedure incorporated in MOPAC 6.0 was employed.[40] First, the optimal HfX_6^{2-} (at the HF/SBKJ level) geometries were introduced into MOPAC in order to generate a grid of about 500 points, which results from the conventional-space-filling model (CPK).[40] The CPK surfaces were obtained by scaling the atomic van der Waals radii[41] with the factor ranging from 1 to 7. The grid for each shell was then transferred to GAMESS[32] to calculate MEP with the SBKJ+dd wave functions. Thus-determined electrostatic potentials were again transferred to MOPAC to fit the charges.

Lattice Energetics. (1) General Problems. Crystal lattice energy (E_c) reflects the magnitude of intermolecular interactions (cohesive forces) keeping molecules in the rigid solid phase. In thermodynamics, the lattice energy of an ionic substance of a general formula K_mA_n

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Table 1. Structural Data for Hexahalogenohafnates

substance							
no.	formula	name of cation (amine)	space group	Z^a	V/Z (Å^3)^b	Hf−cation (N) dist (Å)	ref
1a	K_2HfF_6	potassium	$Cmcm$	4	129	3.76	45
1b			$C2/c$	4	131	3.80	46
2	Rb_2HfF_6	rubidium	$P\bar{3}m1$	1	157	3.84	45
3	Cs_2HfF_6	cesium	$P\bar{3}m1$	1	177	3.99	45
4a	$CuHfF_6$	cupric	$Fm3m$	4	124	3.96	47, 48
4b			$R\bar{3}$	3	121	3.92	47, 48
5	$CaHfF_6$	calcium	$Fm3m$	4	151	4.23	49
6	$ZnHfF_6$	zinc	$R\bar{3}$	3	121	3.93	47, 50
7a	$MnHfF_6$	manganous	$Fm3m$	4	136	4.08	47, 48, 50
7b			$R\bar{3}$	3	136	4.08	48, 50
8a	$FeHfF_6$	ferrous	$Fm3m$	4	132	4.04	47, 48, 50
8b			$R\bar{3}$	3	132	4.04	48, 50
9a	$CoHfF_6$	cobaltous	$Fm3m$	4	128	4.00	47, 48
9b			$R\bar{3}$	3	123	3.95	47, 48, 50
10a	$NiHfF_6$	nickel	$Fm3m$	4	124	3.96	47, 48
10b			$R\bar{3}$	3	117	3.89	47, 48, 50
11	K_2HfCl_6	potassium	$Fm3m$	4	255	4.36	9, 51
12	Cs_2HfCl_6	cesium	$Fm3m$	4	283	4.51	9, 52
13	$Bi_{10}(HfCl_6)_3{}^c$		$P6_3/m$	2	893^d		53
14	$[N(C_2H_5)_4]_2HfCl_6$	*N,N,N*-triethylethanaminium	$C2/c$	4	672	5.91; 5.99	54
15	K_2HfBr_6	potassium	$Fm3m$	4	296	5.29	55
16	Cs_2HfBr_6	cesium	$Fm3m$	4	325	5.46	55
17	Li_2HfI_6	lithium	$Fm3m$	4	303	4.78	56, 57
18	Cs_2HfI_6	cesium	$Fm3m$	4	391	5.81	57, 58

[a] Number of structural units in unit cell. [b] Ratio of volume of unit cell to number of structural units in the cell. [c] The constitution of the compound can be considered as $Bi^+Bi_9{}^{5+}(HfCl_6)_3$. [d] Value represents one-third of the volume of the $Bi_{10}(HfCl_6)_3$ stoichiometric unit.

expresses the energy change for the process[12]

$$K_mA_n(c) \rightarrow mK^{\alpha n+}(g) + nA^{\alpha m-}(g) \qquad (1)$$

where α is the multiplicator indicating the valence of both ions. It is generally recognized that four effects influence E_c,[11] namely

$$E_c = -E_{el} + E_r - E_d + E_0 \qquad (2)$$

where E_{el} represents the electrostatic (Coulombic) interactions between ions, E_r the repulsive interactions (occurring due to the intervention of the Pauli exclusion principle), E_d the dispersive interactions, and E_0 the zero-point energy of the crystal. $-E_{el}$ and $-E_d$ stabilize whereas E_r and E_0 destabilize the lattice. However, individual terms do not contribute to E_c equally. The data for several ionic systems revealed that E_r and E_d possessed similar values (usually not exceeding ${}^1/_{10}E_{el}$) and an opposite sign and that E_0 was negligible.[9,11,42] The conclusion is that $-E_{el}$ alone well approximates the crystal lattice energy of ionic substances. Therefore, in this study we have restricted calculations to this term.

(2) Use of the Ewald Method. The electrostatic energy of 1 mol of an ionic substance composed of $(K^{\alpha n+})_m(A^{\alpha m-})_n$ units is given by the equation[12]

$$E_{el} = {}^1/_2N_A[m(\alpha n+)eV_p{}^{\alpha n+} + n(\alpha m-)eV_p{}^{\alpha m-}] \qquad (3)$$

where N_A is the Avogadro number, e the elementary charge, and V_p the potential created at the site of location of a given ion by all other ions in the lattice, while the factor ${}^1/_2$ eliminates the duplication of electrostatic interactions. The problem of evaluating the electrostatic energy boils down, therefore, to the determination of lattice potentials. We used the Ewald method for this purpose,[43] the details of which are given, among others, in refs 8 and 11.

Compounds examined in this work always contain molecular ions, while the Ewald method was originally developed to calculate the electrostatic potential in crystals made up of monoatomic ions. The application of the Ewald method to systems examined in this work requires, therefore, certain assumptions:[20] (i) in the lattice, species constituting the simplest stoichiometric unit to which energy is referred are distinguished; (ii) in each such unit, positive and negative fragments (ions) are distinguished; (iii) to each fragment are ascribed charges which are whole multiples of *e;* (iv) within each such fragment, a charge is distributed between all atoms forming the fragment or is placed on certain chosen atoms; (v) each partial charge contributes to the electrostatic potential (i.e., is considered independently in calculations); (vi) the electrostatic potential is determined at the sites of the location of each partial charge (atom) of a given fragment and partial charges ascribed to the remaining atoms forming this fragment are neglected.

Crystal lattice energies were calculated by using a computer program based on the principles of the Ewald method which included the above mentioned assumptions.

(3) Structural Information. Electrostatic energy calculations can be carried out if location of charges in the lattice is known, i.e. for systems whose crystal structures are established. A search of *Chemical Abstracts* and the *Cambridge Structural Database*[44] revealed that actually structures of 17 hexahalogenohafnates were sufficiently refined to be considered in the lattice energy calculations (Table 1). For several cubic salts (*Fm3m* space group), only the locations of Hf and metal cations have been established. In such cases, halogen atoms were placed at distances predicted theoretically (Table 2), preserving the symmetry typical for this type of structure. The structure of *N,N,N*-triethylethanaminium hexachlorohafnate appeared incomplete, since two

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Table 2. Thermochemical and Structural Characteristics of HfX_6^{2-}

		thermochemical data[a]					Hf−X bond length[a]	
species	basis set‖geometry	ΔE_f	$\Delta H^\circ_{f,298}$[b,c]	$\Delta G^\circ_{f,298}$[b]	S°_{298}	$C_p{}^\circ_{298}$	this work	lit. (ref)
HfF_6^{2-}	HF/SBKJ‖HF/SBKJ	−3054	−2441	−2372	402.0	134.9	2.035	2.04 (46)
	MP2/SBKJ‖HF/SBKJ	−3170	−2557	−2488				
	MP2/SBKJ+dd‖HF/SBKJ	−3184	*−2571*	*−2502*				
$HfCl_6^{2-}$	HF/SBKJ‖HF/SBKJ	−2144	−1527	−1459	474.9	149.6	2.547	2.574 (52)
	MP2/SBKJ‖HF/SBKJ	−2198	−1581	−1513				
	MP2/SBKJ+d‖HF/SBKJ	−2209	−1592	−1524				
	MP2/SBKJ+d‖HF/SBKJ+d	−2209	−1592	−1524			2.548	
	MP2/SBKJ+dd‖HF/SBKJ	−2210	*−1593*	*−1525*				
	MP2/SBKJ+dd‖HF/SBKJ+dd	−2210	−1593	−1525			2.548	
	HF/MIDI‖HF/MIDI	−2016					2.526	
$HfBr_6^{2-}$	HF/SBKJ‖HF/SBKJ	−1819	−1108	−1124	544.6	154.3	2.715	
	MP2/SBKJ‖HF/SBKJ	−1907	−1196	−1212				
	MP2/SBKJ+dd‖HF/SBKJ	−1921	*−1210*	*−1226*				
HfI_6^{2-}	HF/SBKJ‖HF/SBKJ	−1510	−706	−769	592.1	155.8	2.961	2.829 (58)
	MP2/SBKJ‖HF/SBKJ	−1664	−860	−923				
	MP2/SBKJ+dd‖HF/SBKJ	−1676	*−872*	*−935*				

[a] ΔE_f, $\Delta H^\circ_{f,298}$, and $\Delta G^\circ_{f,298}$ in kJ/mol; S°_{298} and $C_p{}^\circ_{298}$ in J/(mol K); bond lengths in Å. [b] Italic values can be considered to be the most reliable. [c] Literature values of the enthalpy of formation (in kJ/mol): $HfCl_6^{2-}$, −1626[15] and −1640;[9] $HfBr_6^{2-}$, −1275;[15] HfI_6^{2-}, −878.[15]

ethyl substituents were disordered.[54] In the latter case, the lattice energy calculations could be carried out by considering the location of the N atom only.

Results and Discussion

Structure, Features, and Thermochemistry of HfX_6^{2-}. Because ab initio methods require time-consuming calculations, we chose the $HfCl_6^{2-}$ ion as a model system for (i) examining the effect of the one-electron basis set saturation and (ii) determining the extent to which the geometry of this entity changes at various levels of the theoretical approach. This is the reason for presenting the most detailed information regarding this ion in Table 2.

The length of the Hf−Cl bond in $HfCl_6^{2-}$ predicted at the HF/MIDI level is slightly shorter than that obtained at the HF/SBKJ level (Table 2), although the latter compares better with that of the crystal phase. In general, the theoretically predicted Hf−X bond lengths agree quite well with the experimental results, which confirms the soundness of the approach applied.

Supplementing the SBKJ basis sets with diffuse functions on either Cl or Hf changes the Hf−Cl bond length by less than 0.001 Å (Table 2). It thus seemed justifiable to carry out only single-point calculations for all HfX_6^{2-} complexes, at the optimal HF/SBKJ geometry. Some improvement of geometry and energy predictions would undoubtedly be achieved by inclusion of d diffuse functions on chlorine or halogens in general. Calculations with basis sets so extended were, however, beyond our capability.

The length of the Hf−X bond increases on moving from species containing F to those containing I. This should be accompanied by a decrease in bonding power between constituents, which is, indeed, reflected in the energy, enthalpy, and free enthalpy of formation; the thermodynamic stability decreases on moving from HfF_6^{2-} to HfI_6^{2-}.

In all HfX_6^{2-} ions (X = F, Cl, Br, I), the lowest occupied valence orbitals are of a_{1g} and t_{1u} symmetries. Singly degenerated a_{1g} orbitals are dominated by 5s orbitals, while triply degenerated t_{1u} orbitals are dominated by 5p orbitals of Hf. The highest occupied molecular orbitals (HOMOs) are of t_{1g} symmetry and are dominated by *n*p orbitals of halogens. On the other hand, 5p and 6p orbitals of Hf, as well as *n*p orbitals of the halogens, contribute to the triply degenerated t_{1u} HOMO-1 molecular orbitals. The LUMO orbital of HfF_6^{2-} is singly degenerated (a_{1g}), with the major contribution from 6*s* of Hf, while LUMO orbitals of HfX_6^{2-} (X = Cl, Br, I) are triply degenerated (t_{2g}) and dominated by 5d orbitals of Hf and *n*p orbitals of the halogens. In general, unoccupied orbitals are dominated by atomic orbitals of Hf.

The usefulness of the ab initio approach is revealed by the fact that it predicts correctly the heats of formation of gaseous HfX_6^{2-} (Table 2). The value of $\Delta H^\circ_{f,298}[HfCl_6^{2-}(g)]$ obtained in this work, equal to −1593 kJ/mol, is only 47 kJ/mol higher than that available in the literature, which can be considered to be of experimental origin.[9] Supplementing the SBKJ basis set with diffuse functions has almost no effect on the ΔE_f values, while adding MP2 corrections substantially improves the values of heats of formation, bringing them closer to those evaluated with the use of experimentally derived data.[15] On the other hand, comparison of ΔE_f values indicates that MIDI seems less adequate than the SBKJ basis set when the thermodynamics of complex HfX_6^{2-} ions are examined.

Entropies, free enthalpies, and heat capacities of HfX_6^{2-} (Table 2) were, to our knowledge, determined for the first time. The entropies and heat capacities increase on moving from HfF_6^{2-} to HfI_6^{2-}, which is predominantly caused by the increase in the density of vibrational states (Table 3).

Vibrational Spectroscopy of HfX_6^{2-}. Vibrational analysis of HfX_6^{2-} afforded six normal modes, namely four triply (t), one doubly (e), and one singly (a) degenerate (Table 3), of which ν_1, ν_2, and ν_5 are Raman active, ν_3 and ν_4 are infrared active, and ν_6 is inactive.[59,61,62] The ν_1 and ν_2 vibrations are predicted to be almost completely stretching modes and ν_5 and ν_6 are completely or essentially bending modes, whereas ν_3 and ν_4 exhibit a complex nature. The latter information does not agree with that reported in the literature.[62]

Frequencies predicted compare quite well with those found in condensed phases (Table 3). Differences may arise as the result of the influence of the countercations. Moreover, in

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Table 3. Calculated Harmonic Frequencies (cm^{-1}) and Intensities ($D^2/(Å^2$ amu)) (in Parentheses) Together with Observed Vibrational Frequencies (cm^{-1}) for HfX_6^{2-}

		frequency	
species	mode	HF/SBKJ	obsd (ref[a])
HfF_6^{2-}	$t_{2u}(\nu_6)$	126	
	$t_{2g}(\nu_5)$	241	230−246 (59)
	$t_{1u}(\nu_4)$	227 (1.895)	184−220 (60)
	$e_g(\nu_2)$	462	467−471 (60)
	$t_{1u}(\nu_3)$	466 (6.292)	478−486 (60)
	$a_{1g}(\nu_1)$	554	586−595 (59, 60)
$HfCl_6^{2-}$	$t_{2u}(\nu_6)$	83	
	$t_{2g}(\nu_5)$	146	153−167 (61−63)
	$t_{1u}(\nu_4)$	145 (0.636)	138−150 (61−63)
	$e_g(\nu_2)$	236	237−264 (61−63)
	$t_{1u}(\nu_3)$	263 (4.361)	260−288 (61−64)
	$a_{1g}(\nu_1)$	297	326−333 (61−63)
$HfBr_6^{2-}$	$t_{2u}(\nu_6)$	54	
	$t_{2g}(\nu_5)$	92	101−116 (61−63)
	$t_{1u}(\nu_4)$	99 (0.095)	102−112 (61−63)
	$e_g(\nu_2)$	140	142−157 (61−63)
	$t_{1u}(\nu_3)$	183 (2.992)	189−193 (61−63)
	$a_{1g}(\nu_1)$	182	197−201 (61−63)
HfI_6^{2-}	$t_{2u}(\nu_6)$	41	
	$t_{2g}(\nu_5)$	68	
	$t_{1u}(\nu_4)$	76 (0.014)	80−85 (65)
	$e_g(\nu_2)$	97	
	$t_{1u}(\nu_3)$	146 (2.387)	145−165 (65)
	$a_{1g}(\nu_1)$	129	

[a] All values correspond to the species in condensed phases.

condensed phases, somewhat higher values of frequencies can be expected for HfX_6^{2-}, due to the possible contraction of their geometry (Table 2). Finally, our results were obtained in the harmonic approximation at the SCF level of theory.

In general, the conformity between calculated and observed vibrational frequencies is reasonably good (Table 3), which implies that the theory foresees the spectral features of octahedral hexahalogenohafnate anions fairly well.

Charge Distribution between Atoms. Distribution of the charge in HfX_6^{2-} depends greatly on the method of its evaluation (Table 4). MEP atomic charges are influenced by the choice of the CPK surface. Figure 1 demonstrates the dependence of the net MEP charge at Hf in HfX_6^{2-} on the factor scaling the van der Waals atomic radii. As can be noted, charges become stable for a scaling factor greater than 4. Such charges are given in Table 4 and are used in the lattice energy calculations.

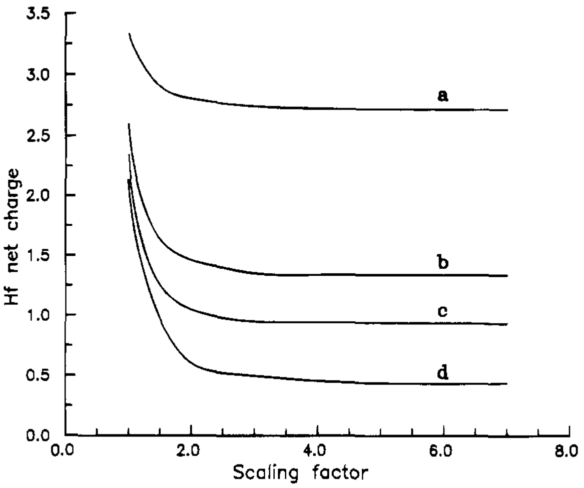

Figure 1. MEP net charge on Hf in HfF_6^{2-} (a), $HfCl_6^{2-}$ (b), $HfBr_6^{2-}$ (c), and HfI_6^{2-} (d) determined at the HF/SBKJ+dd‖HF/SBKJ level versus the scaling factor of the van der Waals atomic radii.

In general, the electronic charge is spread throughout the whole molecule (Table 4). The "MEP fit" always predicts the excess of a negative charge at more electronegative halogens and a net *positive* charge on a less electronegative hafnium atom, even though we are dealing with dianions. Unfortunately, results of the Mulliken, Löwdin, and Stone population analyses do not always follow this trend. In several cases, the net charge on Hf, obtained with the SBKJ basis sets, appeared to be negative (for HfI_6^{2-} a value as high as −17.708 was even found). We think, that these nonphysical results may be caused by the unbalanced nature of the basis sets supplemented with diffuse functions. On the other hand, the application of the MIDI basis set (balanced) in the case of $HfCl_6^{2-}$ (Table 4) and ZrX_6^{2-} (Table 4 in ref 20) always leads to positive net charges on the central atom, which seems to be realistic and consistent with our general knowledge of this problem. The values obtained with the latter basis set are also closer to the net charges reported in the literature. It might, therefore, be that the MIDI basis set better reflects this feature of complex dianions than SBKJ does.

Lattice Energy of Hexahalogenohafnates. Theoretically determined Coulombic energies of hexahalogenohafnates, together with data available from the literature, are listed in Table 5. Our results for potassium and cesium hexachlorohafnates conform quite well with those reported by others.[9] In addition, we recently evaluated lattice energies for these two and four other compounds following the thermochemical cycle and using (i) enthalpies of formation of gaseous HfX_6^{2-} determined here, (ii) literature values of heats of formation of relevant cations, and (iii) literature values of heats of formation or thermal decomposition of the salts.[15] The conformity between the explicitly calculated lattice energies (the second column in Table 5) and the results obtained from the thermochemical cycle (the last column in Table 5) strengthens the soundness of the approach applied. Due to the lack of reliable thermochemical data for hexafluorohafnates,[15] it is difficult to judge the quality of values of lattice energy determined here. Available data for numerous hexahalogenometalates containing monovalent cations

Table 4. Charge on Hf (q_M) in HfX_6^{2-} [a]

			from pop. anal.			
species	basis set‖geometry	fitted to MEP	Mulliken	Löwdin	Stone	lit. (ref)
HfF_6^{2-}	HF/SBKJ+dd‖HF/SBKJ	2.725	3.118	1.750	1.366	2.641 (66)
$HfCl_6^{2-}$	HF/SBKJ‖HF/SBKJ	1.253	0.281	−0.930	2.705	1.96 (9)
	HF/SBKJ+d‖HF/SBKJ+d	1.360	1.877	−0.210	−1.876	2.153 (66)
	HF/SBKJ+dd‖HF/SBKJ+dd	1.338	1.790	−0.299	−1.808	
	HF/SBKJ+dd‖HF/SBKJ	1.340	1.777	−0.303	−1.819	
	HF/MIDI‖HF/MIDI	1.857	1.931	1.596	2.130	
$HfBr_6^{2-}$	HF/SBKJ+dd‖HF/SBKJ	0.939	−2.303	−0.829	2.582	2.116 (66)
HfI_6^{2-}	HF/SBKJ+dd‖HF/SBKJ	0.452	−2.763	−1.592	−17.708	1.726 (66)

[a] Charge on X (q_X) equals $-(2 + q_M)/6$.

Table 5. Crystal Lattice Energies of Hexahalogenohafnates (kJ/mol)

compd no.[a]	this work ((−) electrostatic energy),[b] HF/SBKJ+dd‖HF/SBKJ[c] MEP fit	Mulliken	Löwdin	lit. value[d]	ref[e]
1a	2316	2437	2044		
1b	2089	2166	1974		
2	2071	2112	1968		
3	1925	1958	1841		
4a	3246	3298	3100		
4b	3261	3346	3045		
5	2838	2874	2734		
6	3249	3333	3034		
7a	3066	3111	2938		
7b	3075	3151	2880		
8a	3124	3171	2990		
8b	3127	3206	2925		
9a	3191	3240	3050		
9b	3228	3311	3016		
10a	3254	3306	3107		
10b	3301	3389	3081		
11	1347	1309	1484	1345	9
				1404	15
12	1334	1302	1447	1315 (1225)	9
				1333	15
13	2118	2121	2125		
14	1004	1297	551		
15	1309	1551	1446	1391	15
16	1293	1502	1410	1341	15
17	1475	1403	1435	1497	15
18	1233	1437	1368	1223	15

[a] For names and formulas of the compounds, see Table 1. [b] Atomic charges on monovalent and divalent metal cations were assumed to be +1 and +2, respectively. For $Bi^{+}Bi_{9}^{5+}(HfCl_{6})_{3}$,[53] we assumed a net charge equal to $+^{5}/_{9}$ on each of 9 Bi atoms and a net charge equal to +1 on 1 distinguished Bi atom. In compound **14** a net charge equal to +1 was assigned to the N atom. [c] Method of net atomic charge evaluation in HfX_6^{2-}. [d] Value in parentheses indicates the calculated energy of Coulombic interactions. [e] Values referring to ref 15 are the mean from those listed there for a given compound (Table 2 in ref 15, under D) and considered to be reliable.

Table 6. Electrostatic Lattice Energies of Hexachlorohafnates for Various Charge Distributions in Ions (kJ/mol)

compd	method of charge distribution and geometry determination: MEP fit	Mulliken	Löwdin	Stone
		HF/SBKJ		
K_2HfCl_6	1353	1436	1530	1219
Cs_2HfCl_6	1339	1407	1486	1228
		HF/SBKJ+d		
K_2HfCl_6	1344	1297	1475	1599
Cs_2HfCl_6	1331	1292	1440	1544
		HF/SBKJ+dd		
K_2HfCl_6	1345	1305	1482	1593
Cs_2HfCl_6	1332	1299	1446	1540
		HF/MIDI		
K_2HfCl_6	1299	1292	1323	1274
Cs_2HfCl_6	1294	1288	1313	1273

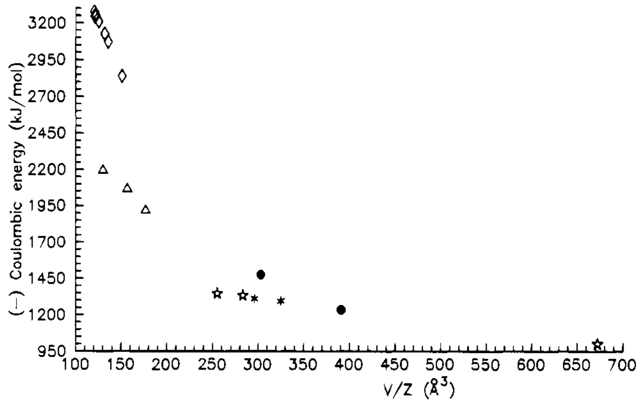

Figure 2. Coulombic energy versus volume of a basic stoichiometric unit (V/Z; for information see Table 1): (◊) values for hexafluorohafnates of divalent cations; (△) values for hexafluorohafnates of monovalent cations; (☆) values for hexachlorohafnates; (⁎) values for hexabromohafnates; (+) values for hexaiodohafnates. The electrostatic energies are those given in the first column of Table 5 under "MEP fit" (mean value was taken if more than one was evaluated for a given compound; omitted also was value for compound **13**).

reveal that differences in the lattice energy between fluoro and chloro salts do not usually exceed 300−400 kJ/mol.[9] Data in Table 5 demonstrate that differences in $-E_{el}$ between relevant hexahalogenohafnates are roughly twice as high. A similar effect has been noted in the case of hexahalogenozirconates,[67] and it is most probably due to the relatively high separation of the charge between Hf and F atoms in HfF_6^{2-} (Table 4), which causes an increase in the calculated energy of Coulombic interactions.

Data in Table 6 illustrate that the electrostatic part of the lattice energy depends markedly on the method of charge distribution evaluation. The most stable appear to be values based on the MEP net atomic charges. This is understandable, since the MEP net atomic charges are fitted so as to reproduce the electrostatic potential, which is the key quantity in the evaluation of the electrostatic part of the lattice energy.

Electrostatic lattice energies gradually decrease with the increase in size of the ionic fragments, which is in accordance with the well-known empirical rules.[68] This is clearly seen in Figure 2, where $-E_{el}$ values show a decreasing tendency as regards the volume of a basic stoichiometric unit. The Coulombic energies further decrease with the increase in distance between interacting fragments (Table 1).

Electrostatic lattice energies of hexahalogenohafnates with doubly charged cations are generally much higher than those of salts of monovalent cations. Analogous regularity, being the consequence of differences in net charges of interacting centers, has been noted for other systems.[20,25-27]

Concluding Remarks. The ab initio methods with effective core potentials and valence basis sets[29,30] appeared very useful in determining the geometry, thermochemical characteristics, and vibrational frequencies of gaseous hexahalogenohafnate ions. To reproduce the existing thermochemical data quantitatively, it was necessary, however, to include the electron correlation correction. To our knowledge, this is the first attempt to apply such an advanced approach to predict features of these complex species.

Heats of formation of HfX_6^{2-} (X = Cl, Br, I) (Table 2) and electrostatic lattice energies of hexahalogenohafnates determined theoretically (Table 5) are consistent, throughout the thermochemical cycle, with known heats of formation of gaseous cations and experimental heats of formation of crystalline salts.[15] This is an important finding which increases the reliability of our theoretical results.

The MEP net atomic charges determined in this work proved to be quite stable with respect to the choice of the one-electron basis set and seem adequate for the electrostatic lattice energy evaluations.[69] On the other hand, the net atomic charges resulting from various population analyses depend greatly on

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the basis sets used, are in some cases completely nonphysical, and may afford unrealistic lattice energy values.

Finally, the results obtained prove that the Ewald method is highly useful in examining lattice energetics of complex ionic substances. More advanced calculations would, undoubtedly, necessitate consideration of interactions other than electrostatic, namely repulsive and dispersive. This is not an easy task if one intends to approach it on a purely theoretical basis. However, even the simple method employed here affords quite a good description of energy of interactions in the solid phase. We hope that the combination of this approach with quantum chemistry methods will open new avenues for studying the reactivity of solids, and it is this problem which is currently the subject of our attention.

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