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Vertical Electron Detachment Energies for Octahedral Closed-Shell Multiply-Charged Anions

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Abstract: The local stability of several octahedral species AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, TlF_6^{3-}, TaF_6^-, ZrF_6^{2-}, LaF_6^{3-}, and $LaCl_6^{3-}$ was studied by using ab initio methods. All systems were found to have minima at octahedral geometries. The electronic stability of these species was considered by using electron propagator theory (EPT) and the Møller–Plesset (MP) perturbation scheme. The results indicate that triply-charged molecular species may be electronically stable in the gas phase. Due to the slow convergence of the EPT and MP series and limitation in our one-electron basis set, the final conclusion requires a more advanced theoretical treatment. The doubly- (ZrF_6^{2-}) and singly-charged (TaF_6^-) species were found to possess very high electronic detachment energies of 5.0 and 10.6 eV, respectively. TaF_6^- is predicted to be thermodynamically stable and ZrF_6^{2-} slightly unstable with respect to the unimolecular decomposition $ML_6^{n-} \rightarrow ML_5^{(n-1)-} + L^-$.

I. Introduction

Multiply-charged anions are challenging species from the point of view of electronic structure theory. Coulomb repulsion between excess negative charges has to be counterbalanced by an advantageous distribution of the total charge to make the system electronically and geometrically stable. The multiply-charged systems are usually thermodynamically unstable, but if their lifetimes are long enough, they may be considered as promising candidates for high energy density materials.[1]

The discovery of the dianion of benzol[*cd*]pyrene-6-one by Dougherty[2] opened the field of doubly-charged molecular species in the gas phase. An excellent review of the subject from both an experimental and theoretical prespective has recently been published by Compton.[3] Briefly, Leiter et al. found doubly-charged anions of the oxygen clusters $(O_2)_n^{2-}$.[4] Schauer et al. reported on the long-lived C_n^{2-} ($n = 7$ to 28) species,[5] and dianions of fullerenes were found as well.[6] Korobov et al. estimated the electron affinity of PtF_6^- to be positive,[7] and Maas and Nibbering have produced doubly-charged decarboxylate negative ions.[8]

The challenge to supersede the Coulomb repulsion between two extra electrons provoked theoretical studies as well. Gutsev and Boldyrev estimated the maximal value of the second EA of hexafluorides MF_6 in the region of 1–2 eV on the basis of the electronic properties of the F_6 frame.[9] They also calculated the second EAs (SEA) of PtF_6 by the DV-Xα method and found SEA = 0.7 eV.[9] Miyoshi and Sakai predicted positive electron affinities for CrF_6^- and MoF_6^-.[10] Recently, Ewig and van Waser found CF_6^{2-} to be geometrically metastable at O_h symmetry.[11] Smaller tetrahedral (BeF_4^{2-}) and triangular (LiF_3^{2-}, NaF_3^{2-}, KF_3^{2-}, $LiCl_3^{2-}$, $NaCl_3^{2-}$, and KCl_3^{2-}) dianions consisting of halogen-type ligands and a metal atom have recently been carefully studied by Cederbaum and collaborators.[12–14] They presented convincing evidence for the stability of these species with respect to fragmentation and electron ejection as well as a kinetic stability of these anions. Although these dianions are not stable thermochemically with respect to dissociation into two singly charged anions, all these species have a high barrier and therefore have a long lifetime. The ionic nature of these systems was recognized as a key factor in compensating Coulomb repulsion between two extra electrons.[13,14] Boldyrev and Simons suggested that TeF_8^{2-} could be the MX_n^{2-} species with the largest electron detachment energy,[15] because of delocalization of two extra electrons through eight electronegative fluorines. The same authors also searched for linear doubly-charged anions and suggested $Mg_2S_3^{2-}$ as the smallest linear or quasilinear electronically stable species.[16] Second electron affinities of large linear[17] and of trigonal planar[17c] carbon clusters have been found theoretically. However, some free doubly-charged anions, such as CO_3^{2-},[13] SO_4^{2-}, SeO_4^{2-}, and TeO_4^{2-},[18] have been predicted to be electronically unstable notwithstanding that these anions are postulated in solid state, in solution, and in molten substances.

As far as the existence of more than doubly-charged anions is concerned, neither theory nor experiment has delivered a definite answer yet, although calculations reported in ref 14b indicate that $K_2F_5^{3-}$ should be stable. Early reports[19] on FeF_6^{3-} were interpreted as harmonic artifacts.[3] Miyoshi and Sakai con-

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cluded from their ab initio CI calculations that AuF_6^{3-} is electronically unstable at octahedral geometries,[10b] and Boldyrev and Simons have shown that PO_4^{3-}, AsO_4^{3-}, and SbO_4^{3-} are not electronically stable.[18]

In this work we explore the local stability of singly-, doubly-, and triply-charged closed-shell octahedral anions ML_6. By local stability we mean the existence of an O_h-symmetry geometrical minimum at which the value of the vertical electron detachment energy (VDE) is positive. Of course, these two features are necessary but not sufficient for long-lived (meta)stability. The latter requires that the closed-shell anion remain electronically stable for a range of molecular geometries which are probed in the zero-point vibrational motion and that the barrier height for unimolecular decomposition of these species be sufficiently high and wide. These topics are beyond the scope of the present paper. They will be addressed in the future for the most promising candidates selected on the basis of their local stability at octahedral geometries.

II. Systems of Interest

Octahedral hexafluorides represent a good choice for electronically-stable multiply-charged anions, because extra charges are distributed through the large number of electronegative ligands and repulsive ligand–ligand interactions are not very high.[20] Full delocalization of extra electrons is expected for MF_{k+1}^{-}, MF_{k+2}^{2-}, MF_{k+3}^{3-}, and MF_{k+n}^{n-} in general cases, where k is the maximal formal valence of the central atom M and n is the negative charge of the multiply charged anion. The central atom M should be from group V of the Periodic Table (P–Bi, V–Ta) for singly-charged anions ($k + 1 = 6$), from group IV (C–Pb, Ti–Hf) for doubly-charged anions, and from group III (B–Tl, Sc–La) for triply-charged anions. For all such systems, octahedral closed-shell structures are expected.

Quantum chemical calculations (DVM-X_α) of the nonmetallic hexafluorides MF_6^- and hexachlorides MCl_6^- have shown high vertical electron detachment energies (VEDE) for these species: PF_6^- (6.8 eV), AsF_6^- (7.2 eV), SbF_6^- (7.0 eV), PCl_6^- (4.3 eV), $AsCl_6^-$ (5.4 eV), and $SbCl_6^-$ (5.6 eV).[21] While experimental electron detachment energies for these anions are not known, theoretical results agree well with the thermochemical stabilities of noble gas compounds such as $KrF^+[SbF_6]^-$,[22] $Xe_2F_3^+[AsF_6]^-$,[23] and others (see refs 24 and 25).

The doubly negative nonmetallic hexafluoride anion CF_6^{2-} is geometrically stable.[11] However, the electronic stability has been studied only for SiF_6^{2-},[26] which was found to be electronically stable, with a vertical electron detachment energy equal to 0.2 eV. No experimental data are available for the stability of free, doubly-charged MF_6^{2-} anions, where M = C–Sn.

Unusually high first electron affinities of hexafluoride molecules containing transition metal atoms were recognized long ago.[27-29] For instance, the electron affinity of AuF_6 is believed to be ca. 10 eV.[27,29] Theoretical calculations of Gutsev and Boldyrev[20] confirm a high electron affinity of all 3d, 4d, and 5d metal hexafluoride species but also provide a theoretical explanation for the unusual electron affinities of VF_6, NbF_6, and TaF_6 as well as for hexafluorides of the metals from the end of the transition period (CuF_6, AgF_6, AuF_6, see ref 20 for details). Miyoshi and Sakai predicted the CrF_6^{2-} and MoF_6^{2-} dianions to be electronically stable at octahedral geometries.[10]

Table 1. Symmetry-Adapted Orbitals (SAO) That Can Be Formed from the Ligand (L) and Metal (M) Atomic Orbitals (AO) for Octahedral Complexes ML_6^{n-} [a]

atom	AO	SAO	orbital energy (au)
L	*n*s	$a_{1g} + e_g + t_{1u}$	−1.58 (F); −1.07 (Cl)
L	*n*p(‖ML)	$a_{1g} + e_g + t_{1u}$	−0.73 (F); −0.51 (Cl)
L	*n*p(⊥ML)	$t_{1g} + t_{1u} + t_{2g} + t_{2u}$	−0.73 (F); −0.51 (Cl)
M	(*m* − 1) s	a_{1g}	−3.20 (Ta); −2.51 (Zr) −1.82 (La)
M	(*m* − 1) p	t_{1u}	−1.78 (Ta); −1.50 (Zr) −1.05 (La)
M	(*m* − 1) d	$e_g + t_{2g}$	−0.31 (Ta); −0.30 (Zr) −0.23 (La)
M	*m*s	a_{1g}	−0.25 (Ta); −0.21 (Zr) −0.18 (La)
M	*m*p	t_{1u}	−0.08 (Ta); −0.13 (Zr) −0.16 (La)

[a] Orbital energies of L and M in au are calculated with the SBKJ+diff basis set. Symbols np‖ and np⊥ denote the ligands' np orbitals parallel and perpendicular to the ML bond, respectively.

We believe that electronic stability could be further increased by arranging a closed-shell, ionicity-enhancing structure for multiply-charged anions. This can be achieved by a proper choice of the central atom. Indeed, recent theoretical studies on thermochemical properties of doubly-charged hexahalogenometallates involving Ti, Zr, and Hf demonstrated their significant stability with respect to the metal atom plus three halogen molecules.[30] These promising results were obtained, however, at low theoretical levels, motivating us to extend the investigations to (a) higher levels of theory and (b) analogous closed-shell singly- and triply-charged systems.

We choose highly electropositive, bulky transition metals such as Ta, Zr, and La for the singly-, doubly-, and triply-charged anions, respectively, to ensure highly ionic character in the coordinated complex and to make the distance between the negatively charged ligands as large as possible. Hf would be more consistent with the choice of Ta and La, but it is well-known that chemical properties and bond distances are practically the same for the hafnium and zirconium atoms.[31]

Symmetry properties and orbital energies of the metal M and ligand L allow us to make an educated guess about the properties of the molecular orbitals in ML_6^{n-}. In Table 1 we show the symmetry-adapted orbitals (SAO) resulting from the valence atomic orbitals (AO), as well as orbital energies in M and L. The orbital energies permit prediction of the ordering and nature of the molecular orbitals in the ML_6^{n-} complexes. In particular, it is clear that high-energy, occupied molecular orbitals will be dominated by the ligands' np-type AO's. Mixing with the M orbitals will be largest for Ta and smallest for La. The ligands' np orbitals may be separated into two groups: parallel (np‖) and perpendicular (np⊥) to the ML bond. The np‖ group contains orbitals of the same symmetry as the valence orbitals of the M center, hence bonding interaction can develop. On the other hand, in the np⊥ group only the t_{1u} orbital can interact, presumably in an antibonding manner, with the M valence counterpart. All of the other ligand orbitals are nonbonding. We conclude that a few highest occupied orbitals of the closed-shell MX_6^{n-} complex will possess either a nonbonding (t_{1g}, t_{2u}, t_{2g}) or an antibonding (t_{1u}) character and that the doublet ground state of the $ML_6^{(n-1)-}$ system will be triply degenerate at the O_h geometry.

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On the basis of such an analysis, we selected the following triply-charged anions for our calculations—AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, TlF_6^{3-}, LaF_6^{3-}, and $LaCl_6^{3-}$—as well as the doubly-charged ZrF_6^{2-} and singly-charged TaF_6^-. All of the systems satisfy the MF_{k+3}^{3-}, MF_{k+2}^{2-}, and MF_{k+1}^- rules (see above).

III. Computational Aspects

A. Transition Metal Anions. For LaF_6^{3-}, $LaCl_6^{3-}$, ZrF_6^{2-}, TaF_6^-, LaF_5^{2-}, $LaCl_5^{2-}$, ZrF_5^-, TaF_5, LaF_4^-, $LaCl_4^-$, ZrF_4, and TaF_4^+ species, we used the relativistic, compact effective potentials of Stevens et al. together with their valence, energy-optimized, shared-exponent, contracted Gaussian basis sets, which we label SBKJ.[32] For the M atoms, the $(n-1)$s, $(n-1)$p, ns, np, and $(n-1)$d orbitals are chemically active and take advantage of the double-ζ sp and triple-ζ d basis sets. For the L atoms, only the valence ns and np orbitals are chemically active, and they are described within a double-ζ quality basis set.

Next, the SBKJ basis sets were supplemented with different sets of diffuse functions. The resulting differences in molecular geometries and Koopmans' theorem predictions of electron detachment energies were carefully monitored. For each M we tested one-term and for each L one- and two-term sets of diffuse functions. The exponents of the one-term diffuse basis sets were taken to be equal to $^1/_3$ of the lowest exponent in the original basis. For the two-term diffuse sets, a geometrical progression was assumed with the progression constant equal to 2.4. Numerical tests described in the next section suggested use of the original SBKJ basis set supplemented with one set of diffuse functions on the L's only. The resulting basis set for ML_6^{n-} complexes, labeled SBKJ+diff, consists of 106 contracted Gaussian basis functions. It should be stressed that due to the absence of polarization functions, our electron detachment energies are expected to be underestimated.

We performed geometry optimization for the octahedral ML_6^{n-} complexes with the SBKJ and SBKJ+diff basis sets using the GAMESS program package.[33] Gradient geometry optimization[34] was followed by calculation of the numerical Hessian matrix. Normal mode analyses were performed and IR intensities were then calculated.

We calculated two quantities that characterize the charge distribution in the multiply-charged anions. First, the radial extent of the distribution is characterized by the mean value of R^2 ($\langle R^2 \rangle$). Second, the effective charges assigned to the M and L atoms were determined from the fit to the electrostatic potential at points selected according to the Merz–Singh–Kollman scheme.[35] For atomic radii, we used 1.34, 1.45, and 1.69 Å for Ta, Zr, and La, respectively;[31] for the halogens we used the default values (1.35 Å (F) and 1.70 Å (Cl)).[36] These calculations were performed using the Gaussian 92 package[36] with the SBKJ+diff basis.

Vertical detachment energies were calculated directly, using the electron propagator theory (EPT) approach,[37–42] and indirectly, i.e., calculating the energy of the n-electron closed-shell anion and $(n-1)$-electron open-shell species using commonly available Hartree–Fock (HF) and the Møller-Plesset perturbation theory (MP) methods.[33,36]

In the EPT approach, two types of self-energy approximations are employed. In the first, second-order poles are calculated; these results, designated by the abbreviation EPT2, typically exaggerate electron correlation effects. The second method includes all third-order terms and many infinite order terms as well. Energy-independent terms through third order are added to an energy-independent self-energy that includes all ring and ladder diagrams through all orders in the fluctuation potential.[43] This method is therefore identified by the abbreviation EPT3+. Third-order methods have been thoroughly examined for electron affinities.[40,44] While the fluoride anion requires additional terms in order to obtain an accurate detachment energy,[44] third-order methods are generally reliable for fluorine-containing compounds.[38] The usual pole-search algorithms for second order have been used.[39] For EPT3+ calculations, a new algorithm, based on eigenvalue procedures used in configuration interaction calculations, has been employed.[45] A modified version of the EPT90 code[46] was used to perform these calculations.

Indirect calculations of VDE's were restricted to the electronic state of $ML_6^{(n-1)-}$ obtained by the removal of an electron from the highest occupied molecular orbital (HOMO) of ML_6^{n-}. The results discussed in the next section demonstrate that the ordering of the electronic states of $ML_6^{(n-1)-}$ predicted on the basis of the Koopmans' theorem remains the same in the EPT calculations.

We started from one-configuration calculations to determine the relaxation correction to the Koopmans' theorem prediction. Calculations for the triply-degenerate doublet state of the neutral were performed in two ways. First, a symmetry-unbroken solution was obtained with the hole delocalized over six ligands. This was achieved in the state-averaged (SA) SCF calculation[47] with three configuration state functions involved. It has been reported, however, that single-configuration calculations with a core[48] or valence[49] hole delocalized over equivalent atoms may produce unphysical electron binding energies. More reliable results were obtained when the hole was localized in a one-configuration calculation, i.e., when a symmetry broken solution was produced.[48,49] Hence, we reinforced the SA SCF calculation with UHF calculations in which we allowed for localization of the hole on one ligand. Of course, after inclusion of correlation effects, both single-configuration approaches should lead to the same final result. Our correlated MPn (n = 2, 3, 4) calculations were performed with the UHF reference function.[36]

B. Nontransition Element Hexafluorides. Bond lengths and harmonic frequencis for the isoelectronic AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, and TlF_6^{3-} as well as for AlF_3, GaF_3, InF_3, TlF_3, AlF_4^-, GaF_4^-, InF_4^-, and TlF_4^- have been obtained by using RHF approximation and the Los Alamos pseudopotentials,[50] which we label LAP. We used Dunning's valence double-ζ basis set (9s5p/3s2p) for the fluorine atoms[51] and a valence 2s2p basis sets for the aluminum, gallium, indium, and tallium,[50] extended by polarization d-functions on all atoms (LAP/DZ+d) and diffuse s- and p-functions on the fluorine atoms (LAP/DZ+d+diff). Exponents for the polarization d-functions 0.198 (Al), 0.207 (Ga), 0.160 (In), and 0.146 (Tl) were taken from ref 52 and exponents of the diffuse s- and p-functions 0.074 were taken from ref 53. All calculations with Los Alamos pseudopotential were performed using the Gaussian 92 package.[36]

IV. Results

A. Nontransition Metal Hexafluorides. The results of SCF (at LAP/DZ+d and LAP/DZ+d+diff) geometry optimization and frequency calculations are presented for AlF_3, GaF_3, InF_3, and TlF_3 in Table 2A, for AlF_4^-, GaF_4^-, InF_4^-, and TlF_4^- in Table 2B, and for AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, and TlF_6^{3-} in Table 2C. Experimental data are available for AlF_3, GaF_3, AlF_4^-, and all triply-charged hexafluorides. Our optimized bond lengths and frequencies are nearly the same for the LAP/DZ+d and LAP/

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Table 2. SCF Optimized Central Atom–Ligand Distances (R_{ML} in Å), Vibrational Frequencies (cm^{-1}), and IR Intensities [D^2/(Å^2 amu), in parentheses] for the Octahedral Closed-Shell Anions[a]

A. AlF_3, GaF_3, InF_3, and TlF_3

species	method	R_{ML}	$\langle R^2 \rangle$	Q_L	frequencies			
					a_1'	a_2''	e′	e′
AlF_3	LAP/DZ+d	1.645	320	–0.53	690	315 (4.6)	958 (4.8)	254 (1.2)
	LAP/DZ+d+diff	1.644			687	311 (4.6)	945 (5.1)	252 (1.2)
	EXPT	1.626^b			672^b	284^c	960^c	252^c
GaF_3	LAP/DZ+d	1.659	325	–0.57	683	242 (2.6)	757 (2.3)	234 (1.1)
	LAP/DZ+d+diff	1.663	327		674	238 (2.5)	759 (2.6)	229 (1.2)
	EXPT	1.713^b			643^b	202^d	759^d	193^d
InF_3	LAP/DZ+d	1.794	377	–0.68	600	187 (2.5)	623 (1.9)	181 (1.2)
	LAP/DZ+d+diff	1.799	379	–0.57	591	185 (2.5)	619 (2.0)	177 (1.3)
TlF_3	LAP/DZ+d	1.991	474	–0.60	609	138 (1.4)	612 (2.3)	104 (1.0)
	LAP/DZ+d+diff	1.993	475	–0.52	607	137 (1.5)	607 (2.7)	99 (1.1)

B. AlF_4^-, GaF_4^-, InF_4^-, and TlF_4^-

species	method	R_{ML}	$\langle R^2 \rangle$	Q_L	frequencies			
					a_1	e	t_2	t_2
AlF_4^-	LAP/DZ+d	1.702			615	200	803 (5.4)	312 (1.5)
	LAP/DZ+d+diff	1.702			609	201	782 (5.7)	312 (1.4)
	EXPT				622^e	210^e	760^e	322^e
GaF_4^-	LAP/DZ+d	1.725	468	–0.67	608	195	629 (3.0)	274 (1.7)
	LAP/DZ+d+diff	1.729	472	–0.61	600	192	623 (3.1)	269 (1.2)
InF_4^-	LAP/DZ+d	1.861	540	–0.75	544	159	532 (2.1)	218 (2.0)
	LAP/DZ+d+diff	1.867	544	–0.69	534	156	524 (2.4)	214 (2.0)
TlF_4^-	LAP/DZ+d	2.054	666	–0.69	553	111	526 (2.6)	146 (1.6)
	LAP/DZ+d+diff	2.060	671	–0.67	545	108	512 (3.1)	143 (1.7)

C. AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, and TlF_6^{3-}

species	method	R_{ML}	HOMO	$\langle R^2 \rangle$	Q_L	frequencies					
						t_{2u}	t_{2g}	t_{1u}	e_g	t_{1u}	a_{1g}
AlF_6^{3-}	LAP/DZ+d	1.893	+1.28	840	–0.75	180	292	354 (0.02)	293	544 (9.1)	455
	LAP/DZ+d+diff	1.900	+0.46	853	–0.85	176	283	343 (0.01)	267	508 (10.6)	443
	SBKJ	1.900	+0.73			182	292	353 (0.2)	335	571 (9.2)	442
	SBKJ+diff.	1.914	+0.26			177	282	341 (0.04)	284	516 (10.2)	430
	EXPT	1.81^f				228^g	322^g	387^g	400^g	568^g	541^g 515^h
GaF_6^{3-}	LAP/DZ+d	1.924	+1.09		–0.78	170	262	330 (1.1)	262	374 (5.8)	442
	LAP/DZ+d+diff	1.932	+0.24	880	–0.85	165	270	318 (1.2)	237	349 (6.7)	434
	EXPT	1.89^i				198^g	281^g	298^g	398^g	481^g	535^g
InF_6^{3-}	LAP/DZ+d	2.049	+0.38	973	–0.83	140	238	269 (3.4)	270	345 (3.5)	411
	LAP/DZ+d+diff.	2.060	–0.41	990	–0.84	135	229	260 (3.0)	243	323 (4.0)	399
	EXPT	2.04^i				162^g	229^g	226^g	395^g	447^g	497^g
TlF_6^{3-}	LAP/DZ+d	2.218	+0.69	1145	–0.80	108	190	203 (2.3)	267	341 (4.4)	415
	LAP/DZ+d+diff	2.229	–0.20	1164	–0.84	106	184	198 (4.7)	232	316 (5.2)	401
	EXPT	1.96^j				148^g	209^g	202^g	387^g	412^g	478^g

D. TaF_6^-, ZrF_6^{2-}, LaF_6^{3-}, and $LaCl_6^{3-}$

species	method	R_{ML}	$\langle R^2 \rangle$	Q_L	frequencies					
					t_{2u}	t_{2g}	t_{1u}	e_g	t_{1u}	a_{1g}
TaF_6^-	SBKJ	1.921			129	282	238 (1.8)	586	590 (7.5)	690
	SBKJ+diff	1.922	707	–0.46	122	283	233 (1.7)	581	585 (7.6)	686
	EXPT					272^k	240^k	581^k	560^k	692^k
ZrF_6^{2-}	SBKJ[l]	2.065			123	230	240 (1.4)	456	512 (8.2)	545
	SBKJ+diff	2.067	818	–0.81	118	229	235 (1.3)	446	497 (8.9)	539
	EXPT	2.02^m				$249–258^n$	280^n	480^n	527^n	$555–577^n$
LaF_6^{3-}	SBKJ	2.462			83	163	163 (1.3)	276	295 (6.2)	351
	SBKJ+diff	2.475	1151	–0.97	82	161	161 (1.2)	258	276 (6.9)	338
	EXPT					171^o	$139–170^o$	334^o	362^o	443^o
$LaCl_6^{3-}$	SBKJ	2.998			52	93	102 (0.3)	151	181 (3.9)	193
	SBKJ+diff	3.004	1756	–0.90	51	91	99 (0.3)	145	172 (4.4)	190
	EXPT	2.95^p				106^p		193^p		242^o
					65^q	114^q	121^q	217^q	$130–170^q$	282^q

[a] Spatial extent of the SCF electronic charge distribution $\langle R^2 \rangle$ in au. Effective atomic charge (Mulliken) on the ligand atom (Q_L) in au. [b] Data from ref 65. [c] Data from ref 66. [d] Data from ref 67. [e] Data from ref 68. [f] Data from refs 55 and 56. [g] Data from ref 69. [h] Data from ref 70. [i] Data from ref 57. [j] Data from ref 58. [k] Data from ref 71. [l] Data from ref 30a. [m] Data from ref 60. [n] Data from ref 61. [o] Data from ref 72. [p] Data from ref 73. [q] Data from ref 74.

DZ+d+diff calculations and agree with available experimental data within 0.05 Å for bond lengths and 30 cm^{-1} for vibrational frequencies (Tables 2A and 2B).

The optimized bond lengths R(Al–F) = 1.89–1.91 Å of AlF_6^{3-}, R(Ga–F) = 1.92–1.96 Å of GaF_6^{3-}, R(In–F) = 2.05–2.06 Å of InF_6^{3-}, and R(Tl–F) = 2.22–2.24 Å of TlF_6^{3-} can be compared with the experimental data for these anions in crystal salts: R(Al–F) = 1.81 Å in Na_3AlF_6,[54] Cs_2NaAlF_6;[55] R(Ga–F) = 1.89 Å in $(NH_4)_3GaF_6$;[56] R(In–F) = 2.04 Å in $(NH_4)_3InF_6$,[57] and R(Tl–F) = 1.96 Å in Rb_3TlF_6.[57] From these data one can see that the difference between the calculated and corresponding experimental bond lengths is high for AlF_6^{3-} (0.1 Å), decreases in GaF_6^{3-} (0.03–0.07 Å) and further decreases for InF_6^{3-} (0.01–0.02 Å), but the difference is very large in TlF_6^{3-} (0.26–0.28 Å). Why our bond length is too high for TlF_6^{3-} is not clear at this time. The experimental bond lengths increase from AlF_3 to AlF_6^{3-} and from GaF_3 to GaF_6^{3-} by approximately 0.18 Å, and the same variation is found in our calculations. From this point of view, the calculated difference in bond lengths (0.24 Å) for TlF_3 and TlF_6^{3-} may not be unreasonable.

All of AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, and TlF_6^{3-} have local minima at the octahedral structure, and thus all of the computed vibrational frequencies are real (see Table 2C). Therefore, if we keep the number of electrons constant, these trianions are geometrically stable. However, the disagreement between our calculated and the corresponding vibrational frequencies of crystal salts is unexpectedly high (80–160 cm^{-1}). At the same level of theory the maximum difference between experimental and calculated frequencies for AlF_3, AlF_4^-, and GaF_3 is only 30 cm^{-1} (see Tables 2A and 2B). Moreover, when we improved the basis sets and included diffuse functions, the disagreement became even worse.

We suspect that these large differences may be related to the electronic instability of the anions. In particular, the MX_6 in the solid state would probably bear a smaller excessive charge than that assumed in our ab initio calculations. The smaller excess charge would make the species less floppy, in agreement with the experimental/theoretical difference. Moreover, electronic instability may enhance the coupling between the vibrations of MX_6 and the neighboring species. Therefore, some vibrations should not be assigned to the isolated anions, but rather to a collective motion also involving the cations and even the lattice as a whole. If so, the so called "experimental force fields"[58,59] for these anions should be revised.

The orbital energies of the t_{1g}-HOMO are positive for AlF_6^{3-} and GaF_6^{3-} and therefore both these anions are certainly electronically unstable, because according to our experience, when electron relaxation and electron correlation are taken into account the electronic stability of multiply-charged anions decreases. InF_6^{3-} and TlF_6^{3-} both have negative orbital energies of the t_{1g}-HOMO: –0.41 and –0.20 eV, respectively. Therefore, both the anions are electronically stable at the Koopmans level of theory. However, previous ab initio calculation for BeF_4^{2-},[12] MX_3^{2-} (where M = Li–K and X = F–Cl,[13,14] SeO_4^{2-}, and TeO_4^{2-} [18] have shown that electron correlation and electron relaxation corrections decrease electronic stability by 1–2 eV. Therefore we conclude that all free AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, and TlF_6^{3-} species are not electronically stable.

B. Transition Metal Hexafluorides. The results of SCF geometry optimization for TaF_6^-, ZrF_6^{2-}, LaF_6^{3-}, and $LaCl_6^{3-}$ closed-shell anions with the SBKJ basis set are presented in Table 2D. We also report vibrational frequencies (all real) and IR intensities for these species. We have demonstrated that augmenting the SBKJ set with diffuse functions on X and/or M affects the M–L equilibrium distance by less than 0.01 Å. Results of Cederbaum and collaborators indicate that correlation effects barely affect equilibrium geometries of tetrahedral and triangular doubly-charged anions.[12–14] Hence, our further calculations were performed at the SBKJ equilibrium geometries.

Table 3. Electron Vertical Detachment Energies (in eV) from the Highest Occupied Molecular Orbital of the Closed-Shell Anion

final state	KT	SA SCF	UHF	MP2	MP3	MP4	EPT2	EPT3+
$F(^2P)$	4.85	1.37	1.31	3.11	2.77	3.12	0.86	4.60
$Cl(^2P)$	4.04	2.59	2.56	3.06	3.07	3.12	2.53	3.41
$TaF_6(^2T_{1g})$	12.34	11.82	9.08	9.91	10.01	9.47	7.79	10.61
$ZrF_6^{2-}(^2T_{1g})$	6.31	5.75	3.01	4.22	4.14	3.99	2.01	4.99
$LaF_6^{2-}(^2T_{1u})$	1.64	1.01	–1.87	–0.29	–0.53	–0.35	–2.40	0.78
$LaCl_6^{2-}(^2T_{1g})$	0.98	0.70	–0.49	–0.13	–0.10	–0.12	–0.77	–0.03

Calculated geometries and vibrational frequencies for isolated TaF_6^- and ZrF_6^{2-} anions are in good agreement with available experimental data from the solid phase.[60,61,71] The discrepancies in frequencies are less than 25 cm^{-1} for TaF_6^-. For ZrF_6^{2-}, the SCF/SBKJ+diff frequencies are systematically lower than the solid state data, but the discrepancies do not exceed 45 cm^{-1}. For the triply-charged LaF_6^{3-} and $LaCl_6^{3-}$ species, however, the discrepancies are more significant (108 cm^{-1} for the valent symmetrical vibration, Table 2D). These triply-charged anions are electronically barely stable or even unstable (see below). This may cause larger disagreement with experimental data (see above discussion for nontransition metal hexafluorides).

The values of $\langle R^2 \rangle$ presented in Table 2 demonstrate how the spatial extent of the electronic charge distribution changes in the sequence of multiply-charged but otherwise similar anions. For comparison, the values of $\langle R^2 \rangle$ for F^- and Cl^- are 15.8 and 36.9 au, respectively. As expected, the spatial extent is particularly large in the case of three excess electrons. Interestingly, inspection of the orbitals in the HOMO region indicates that they *are not* dominated by the most diffuse functions which are available in the basis set. We interpret this feature as the first indication that the triply-charged anion may be electronically stable. Effective atomic charge, presented in the fourth column of Table 2, reflects the increasing ionic character in the Ta, Zr, La sequence. Replacing F's by Cl's substantially increases the spatial extent of the electronic charge distribution and slightly decreases the ionicity of the complex. The reported values of effective atomic charges allow consideration of ZrF_6^{2-}, LaF_6^{3-}, and $LaCl_6^{3-}$ as ionic complexes with six singly charged ligands coordinated to the $M^{(6-n)+}$ core, consistent with the ionic model of Cederbaum and collaborators.[13,14]

Vertical detachment energies from the HOMO orbital of the closed-shell species are reported in Table 3. All the species are electronically stable at the Koopmans theorem level. Augmenting the SBKJ basis set with one set of L(sp) diffuse functions centered on L's may change the HOMO orbital energy even by 0.4 eV (LaF_6^{3-} case). However, further extensions of the basis set with two sets of ligand diffuse functions or one set of M diffuse functions changes the HOMO orbital energy by, at most, a few hundredths of an electronvolt. This further supports our choice of SBKJ+diff as the basis set for the production runs.

The SCF relaxation energies for F^- and Cl^- calculated within the SA SCF and UHF procedures are very large but quite similar. For MF_6^{n-}, however, the SA SCF relaxation energies do not exceed 0.65 eV. At the same time the UHF relaxation energies may be as large as 3.51 eV and the triply-charged anions are predicted to be unstable at this level of theory. Interestingly, the relaxation effects are much smaller for $LaCl_6^{3-}$, as they are for Cl^- compared to F^-.

In contradiction to conclusions of other authors,[48,49] we do not observe advantageous properties of the single configuration scheme based on a symmetry-broken solution leading to the localized

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hole. In all fluoride-containing species studied here, the UHF based VDE is further from the correlated result than the SA SCF prediction; the latter, however, systematically overestimates the magnitude of the electron binding energy in all ML_6^{n-} systems. We think that the relative performance of the UHF vs the SA SCF scheme is system dependent and the recommended approach is to include enough correlation effects so that the difference at the level of the reference function becomes irrelevant.

Inclusion of correlation effects at the Møller–Plesset level of theory increases the detachment energy in comparison with the UHF predictions. The convergence in consecutive orders of the perturbation theory is, however, not uniform, with the MP2 and MP4 results being usually close to each other. The similarity between the MP2 and MP4 VDE's should not be considered as a firm argument that the converged result has been reached. For instance, for CN^-, the MP2 and MP4 results are quite similar but inaccurate.[45] The experimental electron detachment energies for F^- and Cl^- are 3.40 and 3.62 eV, respectively.[62] Therefore, our MP4 results for these species are off by 0.28 and 0.50 eV, respectively. Hence, the electronic instability of LaF_6^{3-} and $LaCl_6^{3-}$ predicted at the MP4 level is probably misleading.

Vertical detachment energies calculated within the EPT method also exhibit a non-uniform convergence. The EPT2 correction to the Koopmans theorem result is destabilizing and overshoots. Triply-charged anions are unstable at this level of theory. The EPT3+ results are, however, much more positive, predicting LaF_6^{3-} to be electronically stable and $LaCl_6^{3-}$ marginally unstable. Since the EPT3+ result for Cl^- is underestimated by 0.21 eV, we think that $LaCl_6^{3-}$ may be electronically stable. Contrariwise, the EPT3+ result for F^- puts the electronic stability of LaF_6^{3-} in question. The slow convergence of EPT methods in the case of F^- is well documented.[44] An encouraging observation is that EPT VDE's of the fluorine-containing compounds are usually reliable.[38]

Our MP4 and EPT3+ results demonstrate that TaF_6^- is a striking example of a superhalogen, i.e., an anion with the electron binding energy exceeding that of Cl^- ion.[21,63,64] Its EPT3+ value of VDE (10.61 eV) is at least as large as the experimental result of 10 ± 0.5 eV for the "unusual" AuF_6^- species.[27,28] The previously calculated VDE(TaF_6^-) = 8.4 eV by the DV-X_α method[20a] is somewhat underestimated.

Interestingly, in the doubly-charged molecular anion ZrF_6^{2-}, the second excess electron is bound more strongly than the first excess electron in the leading monoatomic anion Cl^-. This conclusion is valid both at the MP4 and the EPT3+ level. The value of 4.99 eV (EPT3+ result) is comparable with the estimation (4.9–5.1 eV) of VDE in TeF_8^{2-}, claimed to be the MX_n^{2-} dianion with the largest VDE.[15] Since many ionic solids containing the ZrF_6^{2-} dianion are known,[30a] one could try to produce this unusual species in sputtering experiments.

Table 4. EPT Electron Vertical Detachment Energies (in eV) from the Closed-Shell $^1A_{1g}$ Octahedral Anion to Different Doublet States[a]

transition to	KT	EPT2	EPT3$^+$
$TaF_6(^2T_{1g})$	12.34	7.79	10.61 (0.906)
$TaF_6(^2T_{1u})$	12.56	8.28	10.85 (0.909)
$TaF_6(^2T_{2u})$	12.87	8.38	11.12 (0.908)
$ZrF_6^-(^2T_{1g})$	6.31	2.01	4.99 (0.910)
$ZrF_6^-(^2T_{1u})$	6.55	2.42	5.22 (0.910)
$ZrF_6^-(^2T_{2u})$	6.70	2.46	5.39 (0.912)
$LaF_6^{2-}(^2T_{1u})$	1.64	−2.40	0.78 (0.912)
$LaF_6^{2-}(^2T_{1g})$	1.66	−2.52	0.80 (0.913)
$LaF_6^{2-}(^2T_{2u})$	1.83	−2.31	1.01 (0.919)

[a] Values of the EPT3$^+$ pole strengths are in parentheses.

As expected from the symmetry analysis and orbital energies presented in Table 1, for all MX_6^{n-} species the three highest occupied molecular orbitals are of t_{1u}, t_{1g}, and t_{2u} symmetry. In Table 4, VDE's for the transitions to the doublet T_{1u}, T_{1g}, and T_{2u} states are reported for all fluoride-containing complexes. The ordering of these states depends on the system, but for every species it remains the same at the KT and EPT3+ level. More interestingly, the separation between the first and third state predicted at the KT level remains within 0.04 eV of the separation at the EPT3+ level. Moreover, the pole strengths in the EPT3+ calculations, which are reported in Table 4, never drop below 0.91. These two factors support our claim that not only doubly- but also triply-charged octahedral anions may be electronically stable.

Finally, we briefly discuss thermodynamic stability of the ML_6^{n-} species with respect to two dissociation steps:

$$ML_6^{n-} \rightarrow ML_5^{(n-1)-} + L^- \tag{1a}$$

$$ML_6^{n-} \rightarrow ML_4^{(n-2)-} + 2L^- \tag{1b}$$

Equilibrium geometries, vibrational frequencies, and IR intensities for the product molecules $ML_5^{(n-1)-}$ (D_{3h}) and $ML_4^{(n-2)-}$ (T_d) were determined at the SCF/SBKJ level and are reported in Table 5.

Energy changes for reactions 1a and 1b were determined at the MP2 level with the SBKJ+diff basis sets and are reported in Table 6. In these MP2 calculations, the four lowest occupied orbitals were not correlated. The results demonstrate that the decomposition of ML_6^{3-} will be exothermic in both reaction steps. The amount of energy released, 533 and 475 kJ/mol for LaF_6^{3-} and $LaCl_6^{3-}$, respectively, is significant and the entropy factor would increase exothermicity. Our results also indicate that LaF_5^{2-} and $LaCl_5^{2-}$ species are promising candidates for electronically and geometrically stable pentacoordinate dianions. Their KT values of VDE are 5.4 and 4.2 eV, respectively.

The decomposition of ZrF_6^{2-} shown in reaction 1a is predicted to be slightly exothermic. The product ZrF_5^- is thermodynamically stable. In addition, ZrF_5^- displays properties of a remarkable pentacoordinate superhalogen. Its VDE at the KT level is 11.4 eV.

Finally, TaF_6^-, which was recognized above as a remarkable hexacoordinated superhalogen, is thermodynamically stable with respect to decompositions 1a and 1b.

V. Summary

We have studied the local geometric and electronic stability of closed-shell octahedral species AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, TlF_6^{3-}, TaF_6^-, ZrF_6^{2-}, LaF_6^{3-}, and $LaCl_6^{3-}$ using ab initio methods. We have found that local minima exist for these species at octahedral geometries.

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Table 5. SCF/SBKJ Optimized Metal–Ligand Axial (R_{ax}) and Equatorial (R_{eq}) Distances (in Å), Vibrational Frequencies (cm^{-1}), and IR Intensities [D^2/(Å^2 amu), in parentheses]

A. D_{3h} Closed-Shell Complexes ML_5

				frequencies							
species	method	R_{ax}	R_{eq}	e′	e′	a$_2$″	e″	a$_1$′	a$_2$″	a$_1$′	e′
TaF_5	SBKJ	1.888	1.855	99 (0.1)	210 (1.3)	253 (1.2)	290	648	652 (7.4)	748	718 (4.6)
	EXPT			213[a]	245[a]			690[a]		756[a]	713[a]
ZrF_5^-	SBKJ	2.020	1.984	91 (0.0)	209 (1.6)	229 (1.3)	232	515	571 (8.3)	600	609 (6.3)
LaF_5^{2-}	SBKJ	2.384	2.347	62 (0.0)	145 (1.7)	156 (1.3)	162	342	359 (6.0)	409	388 (4.7)
$LaCl_5^{2-}$	SBKJ	2.906	2.866	52 (0.0)	139 (0.4)	158 (0.3)	154	263	342 (6.5)	330	364 (4.2)

B. T_d Closed-Shell Complexes ML_4

			frequencies			
species	method	R	e	t$_2$	a$_1$	t$_2$
TaF_4^+	SBKJ	1.811	196	183 (0.8)	808	791 (3.7)
ZrF_4	SBKJ	1.930	155	176 (1.4)	659	679 (5.7)
	EXPT	1.902[b]		190 ± 20[c]		668[c]
LaF_4^-	SBKJ	2.273	114	128 (1.5)	464	453 (4.3)
$LaCl_4^-$	SBKJ	2.773	62	76 (0.6)	256	269 (2.7)

[a] Data from ref 75. [b] Data from ref 76. [c] Data from ref 77.

Table 6. MP2 Electronic Energy Changes (in kJ/mol) for Reactions 1a and 1b[a]

reaction	TaF_6^-	ZrF_6^{2-}	LaF_6^{3-}	$LaCl_6^{3-}$
1a	454.8	–56.6	–453.0	–387.0
1b	1439.1	337.3	–533.3	–475.0

[a] The zero point vibrational corrections are not included.

The AlF_6^{3-} and GaF_6^{3-} ions have positive HOMO energies and therefore are not electronically stable even at the Koopmans theorem level. The InF_6^{3-} and TlF_6^{3-} species have negative orbital energies of –0.41 and –0.21 eV. Because both energies are low and because corrections from electron correlation and electron relaxation should destabilize both anions by 1–2 eV, we conclude that all four of these triply-charged anions are probably not electronically stable species.

Calculated vibration frequencies for the electronically unstable AlF_6^{3-}, GaF_6^{3-}, InF_6^{3-}, and TlF_6^{3-} species are underestimated by 100–160 cm^{-1}, while for the electronically stable species (AlF_3, AlF_4^-, GaF_3, ZrF_4, and ZrF_6^{2-}), these numbers differ from experimental data by no more than 45 cm^{-1}. We consider these larger disagreements for triply-charged anions to be a result of (a) different excess negative charges operative in the solid state and (b) interactions between vibrational modes of the isolated anions and the lattice (cations) for electronically unstable anions. Therefore, experimental vibrational spectra for solids containing multiply-charged electronically unstable anions should be treated by taking the collective modes, including cations and anions, into account.

The electronic stability of TaF_6^-, ZrF_6^{2-}, LaF_6^{3-}, and $LaCl_6^{3-}$ was investigated using the electron propagator and the Møller–Plesset perturbation approaches. Our results indicate that triply-charged molecular anions may be electronically stable as isolated species. The convergence of the EPT and MP series was found to be slow but the error analysis for isolated F^- and Cl^- supports the hypothesis of electronic stability of ML_6^{3-} species studied here.

Both of the triply-charged species studied here were found to be thermodynamically unstable with respect to two consecutive unimolecular decompositions. The energy released would be 533 and 475 kJ/mol for LaF_6^{3-} and $LaCl_6^{3-}$, respectively.

More advanced ab initio calculations as well as exploration of geometries probed in the zero-point vibrational motion of ML_6^{3-} species are required to make conclusions about the metastability of these interesting species.

The ZrF_6^{2-} species was found to be a promising candidate as an extremely stable molecular dianion. Its VDE value amounts to 4.99 eV at the EPT3+ level of theory, and it has a relatively low thermodynamic instability with respect to $ZrF_5^- + F^-$.

Finally, TaF_6^- was recognized as a thermodynamically stable superhalogen with the VDE value of 10.6 eV at the EPT3+ level of theory.

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