Ab Initio Studies of Molecular Structures and Energetics. 4. Hexacoordinated NF_6^- and CF_6^{2-} Anions

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Abstract: Quantum theoretical computations predicted the structural stabilities of two unique hexacoordinated species, NF_6^- and CF_6^{2-}. Both were found to be of O_h symmetry with six distinct linkages to the central atom. The energies, equilibrium molecular structures, and vibrational frequencies of both species were computed employing the second-order perturbation approximation (MP2) for the energy. These properties were also determined for F_2, F_3^-, CF_3^-, NF_3, CF_4, NF_4^+, and NF_5 in order to ascertain the thermodynamic stabilities of the hexacoordinate anions and to compare their geometric and electronic structures. CF_6^{2-} exhibits a free energy about 150 kcal/mol higher than $CF_4 + 2F^-$ but essentially the same as $CF_3^- + F_2 + F^-$. NF_6^- is of lower free energy than $NF_5 + F^-$, although nearly the same as $NF_3 + F_2 + F^-$. Analyses of the distributions of energy and charge in all CF_n and NF_n species showed them to be quite similar. The results were contrasted to the neutral hexalithium compound CLi_6, which was shown to exhibit an electronic structure much different from that of NF_6^- and CF_6^{2-}.

Although the development of quantum theoretical techniques has now made possible the accurate prediction of a wide range of molecular properties, among the more challenging both theoretically and computationally are those needed to assess molecular stabilities. Determining the degree of stability is clearly of primary importance in treating postulated species that have not yet been detected experimentally, in order for any computed properties to be ascribed more than limited value. The ability to predict with certainty whether or not a species is stable permits quantum theoretical techniques to predict the complete chemistries of unknown families of species, rather than being limited to a few specific properties of those that are already identified experimentally.

There are several distinct types of molecular stability, which may be categorized as electronic, structural, kinetic, and thermodynamic. The electronic stability, an important criterion that has often been overlooked in theoretical studies, is a measure of (a) whether the species will emit an electron either spontaneously or over a relatively short period of time or (b) whether there is another electronic structure of lower energy with the same number of electrons (i.e., a wave function dominated by a different electron configuration such as a differing electronic eigenstate). Structural stability implies that any change in the coordinates of the nuclei can only increase the total energy. Kinetic stability is the type quite commonly employed in the context of experimental chemical studies and means that the species will not undergo chemical changes in a reasonable period of time even in the presence of small external perturbations. Finally, by thermodynamic stability we mean that the free energy of a species is sufficiently low compared to all reasonable decomposition products such that detectable amounts of the former may exist at equilibrium. In practice of course, the energy barriers separating the various species often permit those of relatively high free energy to exist indefinitely. Each of these four categories may be assayed by quantum theoretical techniques.[1]

With the ability to test whether a species may exist according to these criteria, it is possible to attempt to predict on sheerly theoretical grounds whether a given assemblage of atoms and electrons may ultimately be amenable to preparation in the laboratory. In two previous papers[2,3] we have found systems of novel species that, although unknown experimentally, nonetheless appeared to be quite stable electronically and structurally. Both these studies have focused on the specific problem of determining how many atoms can be connected to a common central atom, that is, the maximum n for species with the formula XY_n. These are not only simple families of species with greatly varying energies and geometries but also present a test of modern qualitative models of molecular structure. In the first paper[2] we studied the second-row hydrides, particularly the chlorine hydrides ClH_3 and ClH_5. In the second[3] we examined a series of pentacoordinated nitrogen compounds NF_nH_{5-n} for which our computations indicated that structures corresponding to $n = 3$–5 are electronically and structurally stable.

An interesting result from our studies of this type is that, contrary to what might be expected intuitively, an increasing degree of coordination about a central atom often leads to *increased* rather than decreased stability of each linkage. This suggested that nitrogen species with even higher degrees of coordination might exist, and we have noted[3] that in fact SCF calculations predict the hexafluoronitrate anion, NF_6^-, to be structurally quite stable.

In this paper we describe a detailed study of NF_6^-. As part of this work we also examined the stabilities of several other first-row fluorides that are isoelectronic with NF_6^-. Of these species only the hexafluorocarbonate anion, CF_6^{2-}, was found to be electronically and structurally stable. BF_6^{3-} on the other hand was found to be unstable with respect to electron autodetachment. We were unable to find a stable molecular structure (exhibiting only real harmonic vibrational frequencies) for NeF_6^{2+}. F_7^+ (FF_6^+) was found to be structurally stable only in the SCF approximation but not when electron correlation was included in the energy. We were also not able to find structurally stable species with formulas NF_5H^- or CF_5H^{2-}.

OF_6 is different from the other species we have studied in that although it was found to be structurally stable similar to NF_6^- and CF_6^{2-}, its wave function was strongly spin-contaminated, leading to much lower energies when the electron spins were allowed to become unpaired (as in the unrestricted Hartree–Fock method), with concomitant unrealistic values of the total spin. This was not the case with NF_6^- and CF_6^{2-}, which were free of spin contamination. Therefore, OF_6 was not examined further at this stage but will be the subject of a later study.

This paper presents several computed properties of the stable anions NF_6^- and CF_6^{2-} that are related to their electronic, structural, and thermodynamic stabilities. For comparison we have carried out parallel studies of five carbon and nitrogen fluorides of lower coordination: CF_3^-, NF_3, CF_4, NF_4^+, and NF_5.

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(1) Each type of stability is not, of course, absolute but rather based on a theoretical model. In particular structural stability, which is a major focus of this paper, can be approached in many different ways, depending on how the energy surface is described. Here we follow the common practice of associating structural stability with harmonic energy minima—a criterion that follows naturally from the Born–Oppenheimer separation: Born, M.; Oppenheimer, R. *Ann. Phys.* (Leipzig) **1927**, *84*, 457–484. In very weakly bound species, such as van der Waals molecules, this would not necessarily suffice. Cf.: Hutson, J. M.; Howard, B. J. *Mol. Phys.* **1980**, *41*, 1113–1122.

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We focus here particularly on comparisons of their equilibrium molecular structures, relative energies, energy partitioning, and electron distributions.

These results for NF_6^- and CF_6^{2-} are to our knowledge the first indications, on either experimental or theoretical grounds, of the possible existence of species exhibiting six strong and distinct linkages to a first-row element. They are thus much different in electronic structure from Li compounds[4] such as CLi_6. In a subsequent section of this paper an analysis of CLi_6 is presented that demonstrates this difference.

Computational Details

All computations reported herein employed ab initio quantum theoretical methods. Since our experience has been that the energy surfaces, particularly the curvatures in terms of the presence of real vibrational frequencies at extrema, may be sensitive to the presence of electron correlation energy, all molecular structures, vibrational frequencies, and total energies were found with both the self-consistent field (SCF) and second-order many-body perturbation (MP2) approximations.[5] Their comparison gives an approximate measure of the magnitude of electron correlation effects. The computer program was CADPAC Issue 4.0.[6] It has the very useful feature of giving both the energy gradients and the force constant matrices analytically in the MP2 approximation.[7] However NF_6^- and CF_6^{2-} were found to be structurally stable whether or not electron correlation was included.

For comparison and to test for basis set superposition errors in the computed energies, two different basis sets were employed. The first was a split-valence set augmented by d polarization functions on the central atom and on each fluorine. This has been designated as the 6-31G* set.[8] We will refer to it hereinafter as basis I. Basis sets of this type have been shown to give accurate geometric structures for anions.[9,10] However, in order to compute realistic reaction energies involving anions it is necessary to add diffuse functions[11,12] in order to account for the anions' greater radial electron distributions. With a diffuse sp set on each atom this is termed the 6-31+G* basis. We will refer to it simply as basis II. All energies were computed at three levels: SCF/basis I, MP2/basis I, and MP2/basis II.

In searching for equilibrium structures of the title species, we began with a number of low-symmetry geometries deformed by up to 0.2 Å from the equilibrium arrangement. We verified that for each such distortion (a) the spin-paired wave function in basis I yielded the lowest SCF energy and (b) subsequent geometry optimization returned the structure to a unique equilibrium geometry. Thus, the symmetry of the equilibrium geometry was computed rather than being imposed. We searched for but were unable to find either a more stable geometry or electronic state within the range of deformations examined.

With the computed equilibrium structures in basis II we tested the electronic stability of the wave function of each species with respect to (a) electron autodetachment, (b) transitions to restricted Hartree–Fock (RHF) wave functions with lower energy (including those of lower symmetry), and (c) transitions breaking the spin pairing (such as result from unrestricted Hartree–Fock or UHF procedures[13]). The latter two types of electronic stability have been referred to as "external".[14] These all employed the algorithms embodied in the GAUSSIAN86 computer program.[14,15] The electronic stability is clearly essential to obtaining a qualitatively correct description of the electronic structure and also is a mathematical requirement for the correct computation of the electron correlation and the force constant matrices employing the coupled Hartree–Fock algorithms.[7]

Table I. Computed Total Energies[a]

	RHF/6-31G*	MP2/6-31G*	MP2/6-31+G*
F^-	−99.350482	−99.528509	−99.626071
F_2	−198.677757	−199.038824	−199.057788
F_3^-	*b*	−298.641403	−298.728200
CF_3^-	−336.117581	−336.770771	−336.844525
NF_3	−352.540057	−353.236611	−353.271130
CF_4	−435.645207	−436.462231	−436.494266
NF_4^+	−451.519393	−452.390626	−452.413098
NF_5	−551.103856	−552.228780	−552.283155
CF_6^{2-}	−634.142039	−635.386980	−635.541266
NF_6^-	−650.492323	−651.866987	−651.972908

[a] In hartrees, not including nuclear motion corrections, at the commensurate equilibrium molecular structures. [b] F_3^- not structurally stable at this level of approximation.

Table II. Computed Bond Lengths (Å)

	symmetry	RHF/ 6-31G*	MP2/ 6-31G*	MP2/ 6-31+G*
F_2	$D_{\infty h}$	1.3449	1.4206	1.4332
F_3^-	$D_{\infty h}$	*a*	1.7229	1.7376
CF_3^-[b]	C_{3v}	1.4107	1.4449	1.4457
NF_3[c]	C_{3v}	1.3279	1.3834	1.3897
CF_4	T_d	1.3018	1.3292	1.3335
NF_4^+	T_d	1.2798	1.3188	1.3222
NF_5(ax)	D_{3h}	1.5312	1.5472	1.5718
NF_5(eq)		1.3267	1.4098	1.4073
CF_6^{2-}	O_h	1.5300	1.5687	1.5825
NF_6^-	O_h	1.4945	1.5683	1.5848

[a] F_3^- not structurally stable at this level of approximation. [b] Bond angles 99.49, 99.16, and 99.56°, respectively. [c] Bond angles 102.68, 101.65, and 101.54°, respectively.

Since the paired-spin wave function gave the lowest energy in each case, this electronic description was employed in all subsequent computations. Thus, the ground electronic states of both NF_6^- and CF_6^{2-} exhibit A_{1g} symmetry.

In order to study the electron distributions we employed the PROAIM program package.[16] All other computed properties, such as the multicenter analysis to compute interaction energies among atomic centers, were obtained with specialized programs written in our laboratories.

The computed total energies (not including nuclear motion corrections) of the 10 species at the three levels of approximation employed in this study are listed in Table I.

Results

Comparison of Equilibrium Molecular Structures. In Table II we list the optimized molecular structures and symmetries of the 10 fluorine, nitrogen–fluorine, and carbon–fluorine species. The symmetry was the same in each case for each of the three levels of approximation.

The structures of F_2 and the nitrogen fluorides as computed at this level have been discussed previously.[3] For comparison we also list here the trifluoride ion[17] F_3^-. Note that this is another example of a species that is not structurally stable in the RHF approximation but appears stable when electron correlation is included in computations of its vibrational frequencies. It has apparently been observed experimentally in solid matrices at temperatures below 40 K.[18] We also include in this comparison the trifluoromethide ion, CF_3^-, which although its physical properties are not well-known experimentally, is becoming increasingly important as a synthetic reagent.[19]

NF_6^- and CF_6^{2-} are precisely octahedral. Their bond lengths increase upon including the MP2 electron correlation and also upon adding diffuse functions to their basis sets (denoted by the plus) by approximately the same amounts as for the other species. The bond length in NF_6^- is markedly increased upon going from the RHF to the MP2 approximation, but this difference is essentially the same as for the equatorial N–F bond in NF_5. The C–F bond length in CF_6^{2-} is fairly constant among all three approximations.

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Table III. Computed Vibrational Frequencies[a] (cm^{-1})

	CF_6^{2-}		NF_6^-	
	frequency	symmetry	frequency	symmetry
ν_1	321.03	E_g	328.66	F_{2u}
ν_2	335.69	F_{2u}	428.95	E_g
ν_3	451.91	F_{1u}	456.42	F_{1u}
ν_4	507.77	F_{2g}	484.56	F_{2g}
ν_5	631.13	A_{1g}	582.20	A_{1g}
ν_6	847.54	F_{1u}	846.89	F_{1u}

[a] Harmonic frequencies in the MP2/6-31G* approximation.

Table IV. Nuclear Motion Corrections to the Molecular Energies[a]

	$\Delta H°_{298}$	$\Delta G°_{298}$		$\Delta H°_{298}$	$\Delta G°_{298}$
F^-	1.48	-8.88	CF_4	14.05	-4.59
F_2	3.54	-10.89	NF_4^+	13.41	-5.28
F_3^-	5.38	-11.65	NF_5	14.32	-6.99
CF_3^-	8.98	-9.74	CF_6^{2-}	15.70	-6.00
NF_3	9.43	-9.13	NF_6^-	15.75	-5.80

[a] The sum of the rotation, translation, and vibration terms and PV at 298.15 K computed in the MP2/6-31G* approximation in kilocalories per mole.

Experimental bond lengths in F_3^- and CF_3^- have apparently not been determined. The experimental[20] C–F distance in CF_4 is $r_0 = 1.317$ Å, which is in fair agreement with our MP2/basis II computed equilibrium bond length of 1.3335 Å. For the nitrogen fluorides the agreement is roughly comparable; the experimental[21] bond length in NF_3 is $r_e = 1.365$ Å. For NF_4^+ in the solid phase it has recently been estimated[22] as lying between 1.265 and 1.321 Å.

Thus, the bond lengths in NF_6^- and CF_6^{2-} are somewhat larger than in the analogous smaller species. This might be expected on the basis of the negative charges of the anions. For example the experimental C–F distance in the trifluoromethyl radical[23] CF_3 is $r_0 = 1.318$ Å, which is almost exactly the same as in CF_4 but much less than our computed value for CF_3^-. There is a similar regular increase in N–F distances on going from our computed[3] value of 1.2336 Å in NF_3^{2+} to the more negatively charged species.

It is also useful to compare these results with those of the analogous anions of the second-row elements, PF_6^- and SiF_6^{2-}, for which experimental molecular structures and other data are available. Both these ions are of course octahedral. The bond lengths in PF_5 (1.576 Å axial and 1.530 Å equatorial[24]) increase[25] to 1.73 Å in PF_6^-. (We note however that the experimental internuclear distances in PF_6^-, and likely in SiF_6^{2-}, are extremely sensitive to the precise nature of the solid lattice in which they are measured.[26]) Similarly, the experimental[20] Si–F distance in SiF_4, 1.55 Å, increases[27] to about 1.7 Å in SiF_6^{2-}.

Vibrational Frequencies. The harmonic vibrational frequencies were computed for each species with both the RHF/basis I and MP2/basis I approximations. Each was found to be structurally stable, thus possessing no imaginary or exceptionally small real frequencies. As noted above, the exception is F_3^-, which exhibits an imaginary vibrational frequency in the RHF approximation. It has been shown to be stable, however, when electron correlation is included by means of a coupled-cluster method.[17] We have now found this to be the case with the MP2 approximation as well.

The frequency and symmetry of each normal mode of NF_6^- and CF_6^{2-} are listed in Table III. These frequencies bear marked similarities to those of PF_6^- and SiF_6^{2-}. For example, the experimental frequencies and symmetries[28] in PF_6^- are (cm^{-1}) 316 (F_{2u}), 475 (F_{2g}), 557 (F_{1u}), 561 (E_g), 746 (A_{1g}), and 817 (F_{1u}). The absence of any unusually small frequencies suggests that NF_6^- and CF_6^{2-} are structurally robust and hence that any barrier to their dissociation is likely to be appreciable. In other words this is an indirect measure of their kinetic stabilities.

Employing the computed harmonic frequencies of all species, as well as the molecular structures obtained at the same level of approximation, we obtained the nuclear motion corrections (due to rotation, translation, and vibration) to the energy, enthalpy ($H°_{298}$), and the Gibbs free energy ($G°_{298}$). The latter two properties, computed at 1 atm of pressure and at 298.15 K, are listed in Table IV.

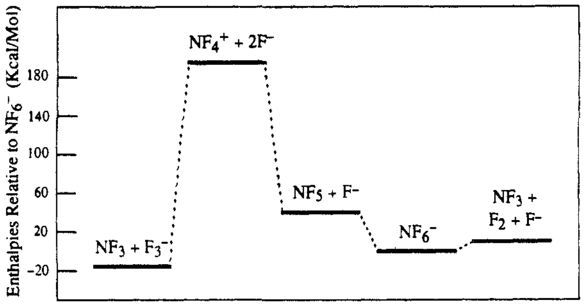

Figure 1. Computed relative energies of species relevant to the formation of NF_6^- as computed in the MP2/6-31+G* level of approximation.

Reaction Enthalpies and Free Energies. In Table V we list the enthalpies of seven reactions relevant to the formation of the highly coordinated carbon and nitrogen fluorides, each within the three types of energy approximations. The free energies are given in parentheses. The structures in each case were those commensurate with the energy. However the frequencies were obtained with the MP2/basis I approximation throughout.

Although there is only fair agreement among the three types of approximations, several qualitative results are unambiguous. The formation of F_3^- is clearly exothermic. We have shown previously that the formation of NF_5 is strongly favored (exhibiting a negative $\Delta G°_{298}$) by means of reaction ii but its decomposition is favored by iv. Reaction iii shows that NF_6^- should be appreciably more stable thermodynamically than $NF_5 + F^-$. However, the enthalpy and free energy of decomposition reaction v, $NF_6^- \rightarrow NF_3 + F_2 + F^-$, are essentially zero within the precision of these computations. The same is true for the reactions of the isoelectronic species $CF_6^{2-} \rightarrow CF_3^- + F_2 + F^-$. Unlike NF_6^-, CF_6^{2-} is seen to be thermodynamically quite unstable with respect to loss of two fluoride ions.

Figure 1 summarizes the enthalpies of the nitrogen–fluorine species involved in these possible unimolecular formation or decomposition reactions of NF_6^-. These values are given relative to the enthalpy of NF_6^-, and all were computed within the MP2/basis II approximation. Note that, except for NF_3 plus the postulated trifluoride ion, NF_6^- is the lowest in total enthalpy.

Multicenter Analysis. A useful technique for understanding the electronic structures of highly coordinated species such as NF_6^- and CF_6^{2-} is to expand their total energies in terms of the contributions of the individual atoms and sets of atoms.[2] The central principle is that the molecular energy may be written as a sum of terms each of which is identified only by the basis functions and nuclei on which it depends. Any criterion that is used to segregate basis functions into unique sets, such as the nuclei on which they are centered, will lead to an exact decomposition of the total energy. Thus,

$$E^{\text{total}} = \sum_{n} E_n^{(1)} + \sum_{mn} E_{mn}^{(2)} + \sum_{lmn} E_{lmn}^{(3)} + \sum_{klmn} E_{klmn}^{(4)}$$

where the sum in each case is over all sets to which each of basis functions belongs, such as all the nuclei on which the basis functions are centered in the species under study. This type of expansion not only resolves the total energy into terms that depend on the coordinates of individual nuclei but also reflects the "centeredness" of the energy in terms of two-, three-, and four-center interactions.

In Table VI we list the individual one-, two-, and three-center energies and the total four-center energy of NF_6^- as computed in basis I at the MP2/basis II molecular structure. The N–F two-center interactions, totaling -5.1162 hartrees, are of course strongly stabilizing and readily overcome the "through-space" crowding between adjacent fluorines, +0.7560. The three-center terms are predominantly positive and hence destabilizing. As is often the case, they are dominated by the bond angle between adjacent fluorines, labeled $(F–N–F)_{adj}$ in the table.

The analogous analysis of CF_6^{2-} is given in Table VII. The total energy of the two-center C–F interactions, -8.0154 hartrees, is considerably more negative than in NF_6^-, but all the other terms are also larger including the positive contributions. The two-center repulsions between adjacent fluorines are nearly doubled. The result is that the sum of two-, three-, and four-center energies is only moderately lower than in NF_6^-.

In Table VIII the two-center and total in energies are compared for all of the carbon and nitrogen fluorides included in this study. Both the strongest two-center interaction with fluorine and the largest stabilization

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Table V. Computed Enthalpies and Free Energies[a] at 298.15 K for Reactions Relevant to the Formation of CF_6^{2-} and NF_6^- (kcal/mol)

	SCF/6-31G*	MP2/6-31G*	MP2/6-31+G*
(i) $F^- + F_2 \rightarrow F_3^-$	*b*	-46.1 (-38.4)	-27.5 (-19.7)
(ii) $NF_4^+ + F^- \rightarrow NF_5$	-147.4 (-139.7)	-194.9 (-187.1)	-153.7 (-145.9)
(iii) $NF_5 + F^- \rightarrow NF_6^-$	-23.9 (-13.8)	-68.9 (-58.8)	-40.0 (-29.9)
(iv) $NF_3 + F_2 \rightarrow NF_5$	72.9 (84.5)	30.6 (42.3)	30.1 (41.7)
(v) $NF_3 + F_2 + F^- \rightarrow NF_6^-$	49.0 (70.8)	-38.3 (-16.5)	-9.9 (11.9)
(vi) $CF_4 + 2F^- \rightarrow CF_6^{2-}$	126.8 (144.4)	81.7 (99.4)	127.4 (145.1)
(vii) $CF_3^- + F_2 + F^- \rightarrow CF_6^{2-}$	4.1 (25.9)	-29.0 (-7.2)	-6.4 (15.4)

[a] ΔH°_{298} and ΔG°_{298} computed at the commensurate equilibrium molecular structures and including nuclear motion corrections computed in the MP2/6-31G* approximation. ΔG°_{298} values given in parentheses. [b] F_3^- structurally unstable in the SCF approximation.

Table VI. Multicenter Resolution of the Total RHF Energy[a] of NF_6^- (Hartrees)

	individual energy	sum of energies
One-Center		
N	-51.9915	-51.9915
F	-99.3000	-595.8000
total one-center		-647.7915
Two-Center		
N-F	-0.8527	-5.1162
$(F-F)_{adj}$	0.0630	0.7560
$(F-F)_{opp}$	0.0093	0.0279
total two-center		-4.3323
Three-Center		
$(F-N-F)_{adj}$	0.1593	1.9116
$(F-N-F)_{opp}$	0.0541	0.1623
$F-(F-F)_{adj}$	-0.0138	-0.1104
$F-(F-F)_{opp}$	-0.0057	-0.0684
total three-center		1.8937
total four-center		-0.2341
total stabilization energy[b]		-2.6713

[a] Computed in the 6-31G* basis at the MP2/6-31+G* optimized molecular structure. [b] The sum of two-, three-, and four-center energies.

Table VII. Multicenter Resolution of the Total RHF Energy[a] of CF_6^{2-} (Hartrees)

	individual energy	sum of energies
One-Center		
C	-34.4883	-34.4883
F	-99.2914	-595.7484
total one-center		-630.2367
Two-Center		
C-F	-1.3359	-8.0154
$(F-F)_{adj}$	0.1143	1.3716
$(F-F)_{opp}$	0.0517	0.1551
total two-center		-6.4887
Three-Center		
$(F-C-F)_{adj}$	0.2380	2.8560
$(F-C-F)_{opp}$	0.1289	0.3867
$F-(F-F)_{adj}$	-0.0240	-0.1920
$F-(F-F)_{opp}$	-0.0131	-0.1572
total three-center		2.8935
total four-center		-0.3007
total stabilization energy[b]		-3.8959

[a] Computed in the 6-31G* basis at the MP2/6-31+G* optimized molecular structure. [b] The sum of two-, three-, and four-center energies.

Table VIII. Computed[a] Individual Two-Center X-F Energies and Total Bonding Energies[b] in XF_n Compounds

	individual X-F	total bonding
CF_3^-	-0.6889	-1.4135
NF_3	-0.7008	-1.6254
CF_4	-1.5929	-4.5197
NF_4^+	-1.3282	-3.9583
NF_5(ax)	-1.1199	-3.2348
NF_5(eq)	-1.0479	
CF_6^{2-}	-1.3359	-3.8959
NF_6^-	-0.8527	-2.6731

[a] In the 6-31+G* basis at the MP2/6-31+G* equilibrium structures, in hartrees. [b] The sum of all two-, three-, and four-center energies.

Table IX. Population Analyses[a] for XF_n Compounds

	charge on X	charge on F
CF_3^-	0.5680 (-0.0271)	-0.5227 (-0.3243)
NF_3	0.6816 (0.1654)	-0.2272 (-0.0551)
CF_4	1.6474 (0.6079)	-0.4118 (-0.1520)
NF_4^+	1.1233 (0.4741)	-0.0308 (0.1315)
NF_5(ax)		-0.3346 (-0.1730)
NF_5(eq)	0.9003 (0.3730)	-0.0771 (-0.0090)
CF_6^{2-}	1.8661 (0.4991)	-0.6443 (-0.4165)
NF_6^-	0.8472 (0.3434)	-0.3079 (-0.2239)

[a] Mulliken gross RHF populations, in numbers of electrons, computed at the MP2/6-31+G* optimized molecular structures. Basis 6-31+G* except for the values in parentheses, which are STO-3G.

energy are found for CF_4. The weakest interactions according to this analysis occur in CF_3^-, while NF_3 is the least stabilized nitrogen species. Note that the two hexacoordinate anions assume intermediate values.

Analysis of Charge Distributions. An alternative and complementary procedure for examining these electronic structures is analysis of the overall charge distributions. In Table IX we list the Mulliken gross atomic populations[29] for each of the three carbon-fluorine and four nitrogen-fluorine species. The first column of data gives the charge on the central atom, while the second gives the charge on the fluorine. The molecular structure in each case corresponded to the MP2/basis II approximation. Two basis sets were employed: basis II (6-31+G*) and a minimal STO-3G basis.[30] Values obtained with the second basis are given in parentheses. The Mulliken analysis with the STO-3G set often gives more physically reasonable values than larger basis sets, especially for overlap populations, but tends to give smaller atomic charges than do other sets.[31]

As is often seen in practice, there are considerable differences between the results obtained with the two basis sets. They disagree even on the sign of the charge on the carbon atom in CF_3^- and on the fluorine in NF_4^+. Nonetheless several qualitative trends are apparent. The charge on the carbon changes by only 0.1-0.2 electron on going from CF_4 to CF_6^-, indicating that the polarizations of the molecular charges in the two species are about the same according to this analysis. The same is seen in comparing NF_3 with NF_6^-. The charge on nitrogen is about the same in NF_5 as in NF_6^-. Thus, from the charges on the central atoms, it is clear that the excess negative charge in the NF_6^- and CF_6^{2-} anions resides predominantly on the fluorines, whereas in CF_3^- and NF_4^+ the extra negative and positive charges are more evenly distributed.

Another way of viewing the molecular electronic distributions has been proposed by Bader.[32] Whereas the Mulliken populations are based on the expansion of the wave function in terms of analytic basis functions, Bader's approach examines the electron density in a pointwise fashion,

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(31) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 1919-1921. CLi_6 is an extreme example of the vicissitudes of the Mulliken population analysis with changes in basis set. For example at the MP2/6-31+G* optimized structure, the gross charge on the carbon is -0.7 in the 6-31G* basis but +5.6 in the 6-31+G* basis. Hence, any analysis of the electronic structures of these lithium compounds based solely on Mulliken populations is unlikely to be very meaningful.

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Table X. Computed[a] Distances, r_{min}, from the Central Atom to the Point of Minimal Electron Density, ρ_{min}, along the X–F Axis and along the F–F Axis

	r_{min}[b]	ρ_{mio}(XF)[c]	ρ_{min}(FF)[c,d]
CF_3^-	0.8712 (60.26)	0.1969	0.0043
NF_3	1.1469 (82.53)	0.3188	0.0039
CF_4	0.8121 (60.90)	0.2879	0.0038
NF_4^+	1.1541 (87.29)	0.4021	0.0014
NF_5(ax)	1.3857 (88.16)	0.2134	0.0010[e]
NF_5(eq)	1.2391 (88.05)	0.3220	0.0022[f]
CF_6^{2-}	1.1731 (74.13)	0.1637	0.0044
NF_6^-	1.4058 (88.71)	0.2022	0.0040

[a] Computed in the 6-31+G* basis at the MP2/6-31+G* optimized structures. [b] Distance in angstroms of the point of minimal electron density, ρ_{min}, from the central atom X. Values in parentheses percentages of the total bond lengths. [c] Minimal electron density in electrons per cubic bohr. [d] The position of ρ_{min} in each of these cases fixed by symmetry. [e] Minimal electron density between axial and equatorial fluorines. [f] Minimal electron density between two equatorial fluorines.

regardless of the contributions of individual functions. The fundamental step in this procedure is the partitioning of the overall electron distribution into regions about each atom separated by "zero-flux" surfaces, that is points specified by the position vector **r** such that if $\rho(\mathbf{r})$ is the electron density and n is vector normal to the surface, $\nabla\rho(\mathbf{r})\cdot n = 0$. A line connecting nuclei is defined as a bond when the value of $\rho(\mathbf{r})$ for points on it are maximal with respect to all lateral displacements. The point at which the zero-flux surface crosses a bond is a "critical point" at which $\nabla\rho(\mathbf{r}) = 0$, the null vector. At such critical points the electron density is generally a minimum of all values along the bond.

There are two ways in which this type of analysis may be used to study the molecular charge distributions. Since the zero-flux surfaces partition the density into closed regions of space about each atom, the charges on the atoms may be found by integrating $\rho(\mathbf{r})$ over all r within each region. However, this is a computationally demanding task for larger molecules, since it requires setting up densities over extensive three-dimensional grids of points in space. A second approach, which is computationally straightforward and perhaps as meaningful, is to examine the position of the bond critical points and the electron density at these points. This is clearly a measure of the polarization of the bond (inferred from the position of the critical point) and the strength of the interaction (from the density). Note that the density at the critical point may be used to distinguish between covalent bonding and ionic bonding since in the latter case this density should be relatively small. The use of the second approach in this context has recently been extensively studied[33,34] for diatomic hydrides and also shown to be fairly insensitive to the choice of basis set for sets of the type employed here.[33]

In Table X we list the results of this type of analysis applied to the seven XF_n species. In this table r_{min} is the length of the vector **r** from the central atom to the critical point, the point of minimal electron density between the atoms. The electron density at this point, ρ_{min}, is given both for the line between the central atom and a fluorine and also between adjacent fluorines. We also verified that in each case the former ρ_{min} corresponds to a "bond" in the Bader sense, while the latter type of interaction does not. This is indirectly reflected by the values of ρ_{min} in the table, which show that nearly all of the concentration of charge is between the central atom and a fluorine rather than between adjacent fluorines.

Comparing the seven species, the effective size of the carbon as reflected by r_{min} is seen to be greater in CF_6^{2-} than in the other carbon species, and similarly the nitrogen in NF_6^- is larger than in the others containing nitrogen. This corresponds to the charge being ***higher*** on the central atom in the hexacoordinated anions, contrary to the prediction of the Mulliken analysis. However, these also exhibit lower values of ρ_{min} than the other species containing the same elements, implying a slightly lessened covalent bond type of interaction.

A general conclusion from inspection of the values in Tables VIII–X is that the seven species, including NF_6^- and CF_6^{2-}, are characterized by energies and electron distributions (in terms of both the Mulliken populations and Bader's approach) that are not greatly dissimilar.

Comparison with CLi_6. The possibility of stable hexacoordinate carbon species, with six strong and distinct bonds to the central atom, has long been debated.[35] Only one other species containing hexacoordinated carbon, CLi_6, has been reported[4] as being structurally stable on the basis of ab initio computations. Its structure was initially believed to be well described by six independent linkages to the carbon atom. However, a subsequent analysis of its charge distribution[31] has suggested that it is more accurately described as a C^{4-} ion surrounded by a cage of lithiums, with relatively little interaction with the central carbon.

Table XI. Multicenter Resolution of the Total RHF Energy[a] of CLi_6 (Hartrees)

	individual energy	sum of energies
One-Center		
C	−36.7873	−36.7873
Li	−7.2873	−43.7238
total one-center		−80.5111
Two-Center		
C–Li	−0.1575	−0.9450
$(Li-Li)_{adj}$	0.0392	0.4704
$(Li-Li)_{opp}$	0.0657	0.1971
total two-center		−0.2775
Three-Center		
$(Li-C-Li)_{adj}$	−0.1112	−1.3344
$(Li-C-Li)_{opp}$	−0.0825	−0.2475
$Li-(Li-Li)_{adj}$	−0.0551	−0.4408
$Li-(Li-Li)_{opp}$	−0.0342	−0.4104
total three-center		−2.4326
total four-center		0.7371
total stabilization energy[b]		−1.9726

[a] Computed in the 6-31G* basis at the MP2/6-31+G* optimized molecular structure. [b] The sum of two-, three-, and four-center energies.

Therefore, we have carried out an analysis of the electronic structure of CLi_6 in the same way as for the other species described herein, to determine whether the same types of interactions are involved. The equilibrium bond length computed with the MP2/basis I approximation is 2.0705 Å. The corresponding RHF energy is −82.483 808 hartrees, and the MP2 energy is −82.763 742 hartrees.

In Table XI we show the multicenter analysis of CLi_6. Each term in this table may be compared directly with the analogous term for CF_6^{2-} in Table VII. The differences are dramatic. The two-center energy between carbon and its substituents is only −0.9450 hartrees in CLi_6, compared to −8.0154 hartrees in CF_6^{2-}. CLi_6, unlike all other species we have analyzed in this way, is characterized by three-center terms that are all negative (stabilizing) and appreciably larger than the two-center contributions. This supports the interpretation that in CLi_6 the bonding interactions are primarily multicenter interactions among the lithiums, rather than two-center bonds between individual lithiums and the central atom.

Even greater differences are seen upon comparing charge distributions. The population analysis of CLi_6 gives the charge on lithium as ranging from approximately 0 to nearly −4 depending on how the analysis is carried out.[31] However, it is especially illuminating to examine the results of the analysis in terms of bond critical points as in Table X. r_{min} in this case is 1.1683 Å (56% of the C–Li distance). ρ_{min}(CLi), the minimal electron density between the carbon and lithium, is only 0.0058, while ρ_{min}(LiLi) is 0.0044. This is the same order of magnitude but slightly smaller than is found in Li clusters.[36] (The latter are exceptional in that the critical point is a density maximum and does not lie on a zero-flux surface.) Thus, the critical electron density between the central atom and a lithium in CLi_6 is only 3% of the value in CF_6^{2-} and essentially the same as that between lithiums. This further supports the view[37] that CLi_6 is essentially a carbon atom inside a cage of lithiums, the whole held together by primarily weak attractions.

Conclusions

These computed results for the hexafluoronitrate and hexafluorocarbonate anions NF_6^- and CF_6^{2-} are to our knowledge the first indications, either experimental or theoretical, of structurally stable species with truly 6-fold coordination to a first-row element. Their molecular structures, energy distributions, and electronic

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structures have been shown to be commensurate with simpler nitrogen–fluorine and carbon–fluorine species.

The tendency of first-row hexafluorides to form stable octahedral structures reflects the behavior of analogous second-row species such as PF_6^- and SiF_6^{2-}. The extremely large fluoride affinity of PF_5, i.e. the large negative enthalpy of the reaction $PF_5 + F^- \rightarrow PF_6^-$, has been well studied experimentally. One study[38] has reported a value of −85 ± 10 kcal/mol while another[39] found −101 ± 8 kcal/mol. These may be compared with our computed result for the nitrogen species, −40 kcal/mol. The fluoride affinity of SiF_4 is apparently less well-known, although it is certainly much smaller than that of PF_5. The double-fluoride affinity, i.e. the enthalpy of the reaction $SiF_4 + 2F^- \rightarrow SiF_6^{2-}$, has been reported as −33 kcal/mol from one experimental approach[40] and ranging between −1 and −33 kcal/mol depending on the way the data was interpreted according to another study.[41] We computed the enthalpy of the analogous reaction involving carbon, $CF_4 + 2F^- \rightarrow CF_6^{2-}$, to be +127 kcal/mol. A comprehensive theoretical study of the fluoride affinities of a number of species, on the basis of SCF calculations, has been reported by O'Keeffe.[42] His computed energy differences are in good agreement with the available experimental data and correspond to −97 kcal/mol for $PF_5 + F^- \rightarrow PF_6^-$ and −33 kcal/mol for $SiF_4 + 2F^- \rightarrow SiF_6^{2-}$.

The structure of "hypermetalated" species such as CLi_6 on the other hand appears to be more analogous to the octahedral environment often encountered in interstitial carbides.[43,44] Such solids frequently contain octahedral defects in their close-packed lattices in which a small atom such as hydrogen, boron, carbon, or nitrogen may reside if the spacing between the metal atoms is large enough.[43] A very similar situation occurs in metal–carbonyl clusters, compounds in which a carbon atom is frequently trapped in an octahedral or trigonal-prismatic arrangement of metal atoms.[45]

Our previous results[3] showed that increasing the number of fluorines attached to nitrogen increased the magnitude of stabilizing two-center energies of the resulting species and suggested the stability of NF_6^-. It is tempting to speculate that three-center, four-electron "hypervalent bonds"[46] account for the apparent stabilities of NF_6^- and CF_6^{2-}, which would be viewed as possessing three such linear three-center bonds at right angles to each other. However as shown by Tables VI and VII the multicenter analysis does not support this picture.

Clearly experimental tests (and/or computations employing much higher levels of approximation) will be required to establish conclusively whether these unique hexacoordinate anions are structurally unstable (or metastable) or whether they exhibit considerable structural stability, as the present study indicates. Our computed results for the thermodynamic properties, summarized in Figure 1, indicate that NF_6^- in particular might be readily prepared under experimental conditions favoring condensation into the larger species. These hexacoordinate ions should also present a useful test of current qualitative concepts of molecular electronic structures as applied to the first-row elements.

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The Syn Rotational Barrier in Butane

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Abstract: The syn barrier for rotation about the central bond in butane has been determined via ab initio theoretical techniques, with various basis sets up to and including triple-ζ with two sets of polarization functions of carbon, and with varying amounts of electron correlation up to and including the coupled cluster with single and double excitations (CCSD) level of theory. After including zero-point and thermal corrections, these studies give the best available $\Delta H^{\ddagger}_{298}$ value for this quantity at present as 4.89 kcal/mol. Previous theoretically determined syn–anti energy differences that disagreed with spectroscopically and molecular mechanics derived values are shown to be too large because of inadequate basis sets.

The butane molecule has long been regarded as the cornerstone of conformational analysis in organic chemistry.[1] Pitzer[2] in his classic work on the conformational properties of butane and alkanes in general, following his earlier work on the rotation barrier in ethane,[3] concluded that the rotational profile for rotation about the central bond in butane was characterized by three minima, two of which are an enantiomeric pair of gauche conformations, and the other of which is the anti conformation. He concluded from the thermodynamic and spectroscopic properties of butane and other alkanes that the gauche conformation was higher in energy than the anti by about 0.8 kcal/mol. He also concluded that there were rotational barriers separating these conformations, the lower of which separated the anti form from the gauche forms

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