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Article

Quantum Chemical Study of Trivalent Group 12 Fluorides

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In view of the recent experimental observation of the existence of tetravalent Hg^{IV} in HgF_4, a quantum chemical study of various trivalent group 12 M^{III} fluoride complexes has been carried out. The M−F bonds in neutral MF_3 are relatively weak, making these species unlikely targets. Some additional stability can be obtained by dimerizing HgF_3 to Hg_2F_6, which has a doubly fluorine-bridged triplet ground state. Anionic $[MF_4]^-$ and $[MF_5]^{2-}$ species are found to be more stable toward F_2 elimination and M−F bond breaking than neutral MF_3.

1. Introduction

The recent identification of HgF_4 by IR spectroscopy under cryogenic conditions in either an argon or a neon matrix[1] has been the first experimental confirmation of a new oxidation state since that of neutral Ni(+IV) in NiF_4 almost two decades ago.[2] Neon was found to be superior to argon by providing larger amounts of HgF_4. The experiments indicated also that HgF_4 is a photosensitive species which decomposes under the irradiation used to generate the reacting fluorine atoms in the matrix.[1] These experiments confirmed the long-standing quantum chemical predictions of the existence of HgF_4[3–7] and thus establish Hg as a d-block element for the first time. This special character of mercury is due to relativistic effects, which are predicted to be even more pronounced for eka-mercury, element 112.[8,9] That is, these two heavier members of group 12 are thought to be distinct from Zn and Cd, for which so far no indications exist for compounds in which they use their inner d-orbitals for bonding.

In view of the existence of Hg(+IV), does oxidation state +III exist in group 12? An early report[10] about an electrochemically generated short-lived Hg^{+III}(cyclam) species has never been confirmed. Only a few calculations on group 12 M(III) species have been performed.[11,12] Here we evaluate by systematic state-of-the-art quantum chemical calculations the structures and stabilities of a variety of neutral and anionic trivalent Zn, Cd, and Hg fluoride complexes. Stabilities will be compared to those of the respective M^{II} and M^{IV} fluorides.

2. Computational Methods

Neutral MF_2, MF_3, and MF_4 have been optimized at DFT (B3LYP)[13–16] and CCSD(T) levels, using the programs Gaussian03[13] for the DFT and Molpro 2006.1[17] for the CCSD(T) calculations. CCSD(T) optimization of HgF_3 were not possible due to technical reasons. Instead single-point CCSD(T) calculations were performed at the B3LYP-optimized structure. The same was done for the dimeric mercury species Hg_2F_6 and Hg_2F_4. The anionic species were only studied at the DFT (B3LYP) level. Quasirelativistic energy-adjusted, small-core pseudopotentials (effective-core

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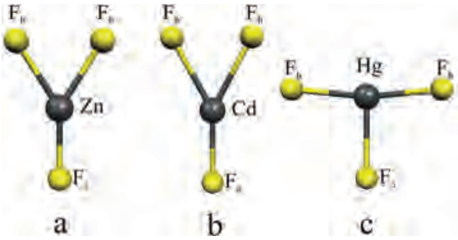

Figure 1. B3LYP-optimized structures of the trifluorides in C_{2v} symmetry.

potentials, ECP) of the Stuttgart group were used for the transition metals Zn,[18] Cd,[19] and Hg.[20] The corresponding (8s7p6d)/[6s5p3d] valence basis sets were used, augmented by two f-type and one g-type polarization functions (Zn $\alpha_f = 5.871$, 1.498, $\alpha_g = 4.365$; Cd $\alpha_f = 2.853$, 0.834, $\alpha_g = 1.795$; Hg $\alpha_f = 1.58$, 0.545, $\alpha_g = 1.384$),[21] together with a triple-ζ (aug-cc-pVTZ) fluorine basis set by Dunning.[22] Stationary points on the potential energy surface were characterized by harmonic vibrational frequency analyses at this level (providing also zero-point energy corrections to the thermochemistry). Contributions of basis-set superposition errors (BSSE) to the energetics were estimated by the counterpoise (CP)[23,24] procedure. We do not consider spin–orbit corrections in this work. Our previous studies indicated spin–orbit effects to have only a minor influence on the relevant thermochemical data or activation barriers, even when open-shell 5d species were involved.[25]

Table 1. Optimized B3LYP (CCSD(T)) Structures of Neutral Fluoride Complexes[a]

MF_2 (D_{4h})	ZnF_2	CdF_2	HgF_2[b]
M−F	172.8 (171.6)	192.8 (192.2)	193.4(192.2)
MF_3[c](C_{2v})	ZnF_3	CdF_3	HgF_3[d]
$M-F_a$	174.0(172.8)	194.2(193.5)	214.3
$M-F_b$	190.3(188.8)	212.9(210.9)	193.5
F_b-F_b	202.6(195.3)	201.0(195.0)	385.8
F_a-M-F_b	147.8(148.9)	151.3(152.9)	94.4
F_b-M-F_b	64.3(62.3)	56.4(55.0)	171.2
MF_4[e](D_{4h})	ZnF_4	CdF_4	HgF_4
M−F	174.8(174.1)	189.9(190.1)	190.7(189.3)

[a] Bond lengths in pm and angles in degrees. CCSD(T) values in parentheses. All CCSD T_1-diagnostics are below 0.020. [b] Compare refs 35 and 36 for previous calculations on HgF_2. [c] Optimized HgF_3 structure at nonrelativistic level: $Hg-F_a$ 214.5 pm, $Hg-F_b$ 205.5 pm, F_b-Hg-F_b 158.3 deg, F_a-Hg-F_b 100.9 deg. [d] The CCSD(T) optimization was not possible due to technical reasons. [e] QCISD M-F bond lengths of ref 4 were ZnF_4 172.7 pm, CdF_4 192.0 pm, and HgF_4 192.4 pm.

3. Results

Neutral Monomers, MF_3 and MF_4. Figure 1 shows that all three neutral trifluorides exhibit Jahn–Teller-distorted structures in their $^2A'$ ground states. Yet the T-shaped structure of HgF_3 differs notably from those of its lighter homologues. The latter exhibit Y-shaped structures with relatively short F_b-F_b distances (electron correlation is important here: at HF level, a Y-shaped structure is obtained also for HgF_3). Notably, except for the $Zn-F_a$ distance, which resembles the Zn−F distances in ZnF_2 and ZnF_4, all M−F distances are longer than in either the di- or the tetrafluorides (Table 1; results for MF_4 and MF_2 agree well with earlier studies[1,4]). Nonrelativistic calculations for HgF_3 provide yet another structure (cf. footnote b to Table 1).

Table 2 provides reaction energies for F_2 elimination and homolytical M−F bond breaking for tri- and tetrafluoride complexes. As has been shown previously[3–5,7] among the tetrafluorides only HgF_4 exhibits endothermic F_2 elimination, consistent with its experimental characterization under low-temperature matrix-isolation conditions.[1] The less relativistic ZnF_4 and CdF_4 eliminate F_2 with strong exothermicity.[3,4] Note that entropic contributions will destabilize the tetrafluorides further at increased temperatures.[1] Homolytic breaking of one M−F bond in MF_4 is also most endothermic for HgF_4, already appreciably less so for CdF_4, and weakly exothermic for ZnF_4. Note that the larger discrepancies between CCSD(T) and B3LYP results for CdF_4 and particularly ZnF_4 indicate significant nondynamical correlation effects for the more weakly bound lighter tetrafluorides.[4]

Turning to the trifluorides (Table 2), we note strongly endothermic F_2elimination, partly due to relatively weak M−F bonds[26] in the monofluorides. However, the homolytic bond breaking in the trifluorides is also very easy, with even a negative energy at the CCSD(T) level for HgF_3 (at B3LYP structure, as CCSD(T) optimizations did not converge). Considering the detrimental effects of entropy contributions (see above), this will render preparation and characterization of the neutral trifluorides very unlikely,

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Table 2. Calculated Reaction Energies in kJ mol^{-1} [a]

	Zn		Cd		Hg	
reaction	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP	CCSD(T)
$MF_4 \rightarrow MF_2 + F_2$	−102.4 (−110.6)	−152.1	−48.6 (−54.5)	−109.0	42.3 (35.5)	9.5[b,c]
$MF_4 \rightarrow MF_3 + F$	−1.4 (−13.5)	−16.5	50.6 (40.5)	17.9	170.1 (158.9)	178.4[c]
$MF_3 \rightarrow MF + F_2$	383.3 (379.8)	376.2	320.8 (319.9)	311.5	247.7 (245.3)	225.0[c]
$MF_3 \rightarrow MF_2 + F$	54.3 (51.3)	17.6	56.0 (53.5)	26.3	27.4 (25.0)	−16.3[c]
$2MF_3 \rightarrow 2MF_2 + F_2$	−46.7	−118.0	−43.3	−100.5	−100.4	−185.1[c]
$2MF_3 \rightarrow MF_2 + MF_4$	55.7	34.1	5.4	8.5	−142.7	−194.7[c]
$2MF_4 \rightarrow 2MF_3 + F_2$	−158.1	−186.2	−54.0	−117.4	185.0	204.3[c]

[a] Results with counterpoise and zero-point vibrational corrections in parentheses. No thermal contributions were included. [b] With an aug-cc-pVQZ basis set for fluorine, +27.4 kJ mol^{-1} are obtained. [c] CCSD(T) single-point calculations using the B3LYP optimized structure.

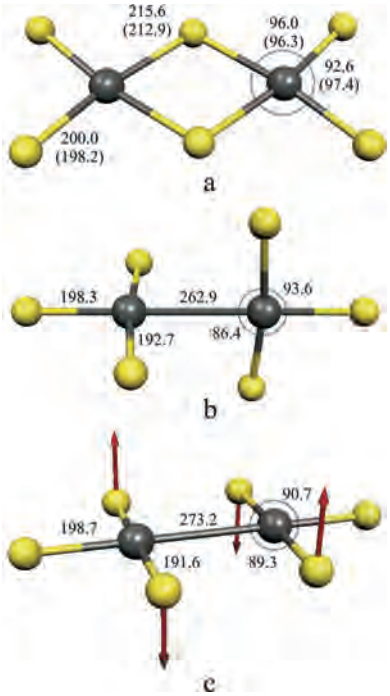

Figure 2. B3LYP optimized structures for Hg_2F_6. Distances in pm, angles in degrees. (a) Triplet ground-state with D_{2h} symmetry. Values in parentheses are for the corresponding D_{2h} minimum on the singlet surface (see text). (b) Lowest singlet minimum with D_{2d} symmetry. (c) D_{2h} singlet transition state on singlet surface; indication of the imaginary normal vibrational mode by arrows.

except maybe at the very lowest temperatures. We note that the matrix isolation experiments that allowed the identification of HgF_4 provided no indications for HgF_3 (nor for ZnF_3 or ZnF_4 when carried out with zinc).[1] Bimolecular F_2 elimination reactions of the tetra- and trifluorides (Table 2) turn out to be also strongly exothermic, except for HgF_4. An interesting further observation is that the strong exothermicity of a disproportionation of HgF_3, which is due to the relative stability of HgF_4, is not paralleled for ZnF_3 or CdF_3 (Table 2).

A possible preparation of HgF_3 via the cationic precursor species $[HgF_3]^+$ and electron attachment in a gas-phase experiment, as suggested by a referee, is unlikely: While HgF_3^+ has indeed a large adiabatic electron affinity (13.3 eV at B3LYP//B3LYP and 13.0 eV at CCSD(T)//B3LYP level), it appears unclear how to access the cationic precursor $[HgF_3]^+$. For example, fluoride abstraction from HgF_4 costs appreciable 11.4 eV.

Table 3. Reaction Energies for Hg_2F_6 in kJ mol^{-1}

reaction	B3LYP	CCSD(T)[a]
$2HgF_3 \rightarrow Hg_2F_6$	−78.8	−109.4
$2HgF_2 \rightarrow Hg_2F_4$[b]	−33.3	−55.7
$Hg_2F_6 \rightarrow 2HgF_2 + F_2$	−21.6	−75.7
$Hg_2F_6 \rightarrow Hg_2F_4 + F_2$	−54.9	−131.4
$Hg_2F_6 \rightarrow HgF_4 + HgF_2$	−63.9	−85.3

[a] Single-point calculations at B3LYP-optimized structures. T_1-diagnostic of the triplet Hg_2F_6 species: 0.020. [b] Previous counterpoise-corrected MP2 calculations provided −61.9 kJ mol^{-1}.[32]

Hg_2F_6 Dimer. Given the appreciable stability of the d^8 Au_2F_6 dimer, identified by gas-phase electron diffraction,[27] we have also considered Hg_2F_6, that is, the dimerization of HgF_3. At the B3LYP level, a triplet ground-state with a planar D_{2h} structure is found (Figure 2a). The Hg−Hg distance is computed as 341.2 pm slightly longer than the known Au−Au distance of 308.2 ± 0.6 pm[27,28] in Au_2F_6. The corresponding doubly bridged structure is also a minimum on the closed-shell singlet surface of Hg_2F_6, 40.7 kJ mol^{-1} above the triplet. We find a second singlet minimum of D_{2d} symmetry (Figure 2b), 99.1 kJ mol^{-1} above the triplet minimum. This structure exhibits a direct Hg−Hg bond between two perpendicular HgF_3 fragments. Previously, only a planar D_{2h} structure on the singlet surface with a Hg−Hg bond had been considered by Hartree–Fock calculations.[12] At B3LYP level we find this now to be a transition state with an imaginary frequency of −55.3 cm^{-1} for rotation around the Hg−Hg axis, 35.8 kJ mol^{-1} above the D_{2d} singlet minimum (Figure 2c). Optimizations on the triplet surface starting from directly Hg−Hg bonded structures led to dissociation into two HgF_3 fragments.

Table 3 summarizes the relevant thermochemical energies for Hg_2F_6 (computed for the triplet ground state). Interestingly, dimerization of HgF_3 is computed to be more exothermic than that of HgF_2 and may thus be considered to stabilize Hg(+III) relative to Hg(II) (in contrast to Hg(IV) vs Hg(II)[4]). Nevertheless, the key decomposition reactions, that is, F_2 elimination and disproportionation, remain appreciably exothermic. The magnitude of the relevant activation barriers for these reactions will be of interest in our ongoing work (which will consider also oligomeric Zn(III) and Cd(III) species).

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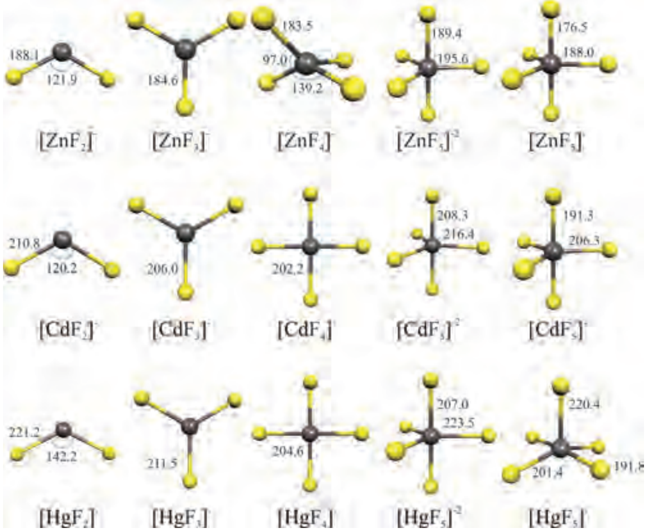

Figure 3. B3LYP optimized structures for anionic species. Distances in pm, angles in degrees. Symmetries: $[MF_2]^-$ C_{2v}; $[MF_3]^-$ D_{3h}; $[ZnF_4]^-$ C_2; $[CdF_4]^-$, $[HgF_4]^-$ D_{4h}; $[MF_5]^{2-}$ D_{3h} $[ZnF_5]^-$, $[CdF_5]^-$ D_{3h}; $[HgF_5]^-$ C_{2v}.

Table 4. B3LYP Reaction Energies of Anionic Species in kJ mol^{-1}

reaction	M = Zn	M = Cd	M = Hg
a. $[MF_4]^- \rightarrow [MF_2]^- + F_2$	527.2	424.1	386.8
b. $[MF_4]^- \rightarrow [MF_3]^- + F$	88.3	106.0	169.0
c. $2[MF_4]^- \rightarrow 2[MF_3]^- + F_2$	21.3	56.7	182.7
d. $2[MF_4]^- \rightarrow [MF_3]^- + [MF_5]^-$	110.8	100.3	111.1
e. $[MF_5]^{2-} \rightarrow [MF_3]^{2-} + F_2$	358.0	450.7	418.7
f. $[MF_5]^{2-} \rightarrow [MF_4]^{2-} + F$	73.1	90.9	145.1
g. $2[MF_5]^{2-} \rightarrow 2[MF_4]^{2-} + F_2$	−9.0	26.6	134.9
h. $2[MF_5]^{2-} \rightarrow [MF_4]^{2-} + [MF_6]^{2-}$	118.3	89.7	62.9
i. $MF_2 + F^- \rightarrow [MF_3]^-$	−302.1	−279.3	−196.9
j. $MF_3 + F^- \rightarrow [MF_4]^-$	−336.0	−329.3	−338.4
k. $[MF_3]^- + F^- \rightarrow [MF_4]^{-2}$	188.2	155.6	184.4
l. $[MF_4]^- + F^- \rightarrow [MF_5]^{-2}$	203.4	170.6	208.3

Anionic Complexes. Formation of anionic complexes is a frequently used method to stabilize high oxidation states.[4,29] While this has been considered a less favorable route for Hg(IV), due to the low-spin d^8 configuration,[4] anionic d^9 complexes (e.g., of Cu(II)) are more common. We have therefore investigated computationally the group 12 $[MF_4]^-$ and $[MF_5]^{2-}$ complexes (the $[MF_6]^{3-}$ anions exhibited too large negative charge for successful optimization as isolated gas-phase species). Figure 3 shows that $[CdF_4]^-$ and $[HgF_4]^-$ exhibit square planar D_{4h} minima, whereas $[ZnF_4]^-$ is distorted with C_2 symmetry. $[ZnF_5]^{2-}$ and $[CdF_5]^{2-}$ exhibit trigonal bipyramidal (D_{3h}) structures, whereas $[HgF_5]^{2-}$ stands out by featuring a distorted square pyramidal arrangement (C_{2v} symmetry).

Monomolecular F_2 elimination and homolytical M−F bond breaking are appreciably endothermic for all three $[MF_4]^-$ monoanions and for all three $[MF_5]^{2-}$ dianions (Table 4, reactions a, b, e, and f). The homolytic bond breaking is most endothermic with M = Hg, as one might have expected for a $5d^9$ complex. The trends for F_2 elimination are less clear-cut, likely due to the relative stability of the product anions (for example, $[MF_2]^-$ or $[MF_3]^{2-}$ with a monovalent group 12 center are not very stable species and thus of limited meaningfulness). Inclusion of counterions is likely to increase the stability of the smaller anions relative to the larger ones and to thereby destabilize the M^{III} anions relative to loss of F_2 or F. However, the computed gas-phase reaction energies are sufficiently positive to let us expect this to leave the overall endothermicity valid. Dinuclear F_2 elimination is also mostly endothermic, and disproportionation into M^{II} and M^{IV} anions (reactions d and h) is also computed to be endothermic.

The question of how such M^{III} mono- and dianionic fluoride complexes may be made is partly answered by the fluoride attachment energies (reactions j and l): The first fluoride ion is in all cases bound rather exothermically, whereas Coulomb repulsion renders the second attachment endothermic. Interaction with counterions would likely stabilize in particular the dianions and thus render even the latter reaction exothermic (calculations on ion pair complexes are outside the scope of this paper).

Given that we will need to include environmental effects to judge the stability of $[MF_5]^{2-}$, we may consider here in particular the possible routes to $[MF_4]^-$: The oxidation of $2[MF_3]^-$ by F_2 is predicted to be exothermic (reverse of reaction c), increasingly so with increasing atomic number of M. The same holds for reaction of $[MF_3]^-$ with a fluorine atom (reverse of reaction b). The difficulty will thus be in the initial preparation of species comparable to $[MF_3]^-$ in a condensed-phase environment, where aggregation of neutral MF_2 is expected to be a competing reaction.[1,4,30–32] Note that the ion-pair complex $M[HgF_3]$ (M = Cs, Rb, K) is known,[33,34] and we might envision an electrochemical oxidation as a possible access pathway.

Conclusions

This initial quantum chemical study of group 12 M(III) fluoride complexes indicates the following. (a) The neutral monomeric trifluorides are rather unstable and unlikely to be observable under currently available reaction conditions. (b) Stabilization of HgF_3 by dimerization to Hg_2F_6 is appreciable, but exothermic decomposition pathways

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remain. It will be interesting to further scrutinize oligomeric group 12 M(III) species. (c) Anionic stabilization is also of interest, and the present calculations suggest that a route to trivalent group 12 complexes will have to seriously consider anionic fluoride species. This would involve molecular beam or matrix isolation conditions that tolerate anionic species.

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