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Zn in the +III Oxidation State

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S *Supporting Information*

ABSTRACT: The possibility that the group 12 elements Zn, Cd, and Hg can exist in an oxidation state of +III or higher has fascinated chemists for decades. It took nearly 20 years before experiments could confirm the theoretical prediction that Hg indeed can exist in the +IV oxidation state. While this unusual property of Hg is attributed to relativistic effects, Zn, which is much less massive than Hg, has not been expected to have an oxidation state higher than +II. Using density functional theory, we have shown that an oxidation state of +III for Zn can be realized by choosing specific ligands with large electron affinities. We demonstrate this by a systematic study of the interaction of Zn with the ligands F, BO_2, and AuF_6, whose electron affinities are progressively higher (3.4, 4.5, and 8.4 eV, respectively). The discovery of higher oxidation states of elements can help in the formulation of new reactions and hence in the development of new chemistry.

The oxidation state is a "measure of the degree of oxidation of an atom in a substance"[1] and it is the fundamental key to understanding redox reactions, reaction mechanisms, catalysis, etc. It is the charge an atom in a compound would have *if* the bonding were completely *ionic*. This description makes the determination of oxidation states in covalent systems less transparent, since charges are shared between atoms and not completely transferred. In such systems, the oxidation state is determined by assigning the bonding electron pair to the more electronegative atom. For example, the charge on the C atom in CH_4 is −0.797, but its oxidation number is −IV. Explicit rules for assigning oxidation states are available in the IUPAC Gold Book.[1] Transition metals, because of their incomplete d shells, exhibit variable oxidation states and hence form a large domain of complexes. The possibility of transforming group 12 elements such as Zn into transition metals has fascinated chemists for decades. Because of Zn's $3d^{10}4s^2$ ground state configuration and highly stable filled d orbitals, its inner d electrons seldom take part in bonding, and oxidation states of Zn beyond +II are difficult to achieve. Needless to say, the discovery of new oxidation states of Zn would enable us to formulate new reactions and develop new chemistry. This is particularly important as zinc has many applications in the pure metallic state (in alloys), as salts (used as white pigments), as biocomplexes (metalloenzymes), and as organometallic reagents (used in organic synthesis).

We realize that the major challenge in achieving oxidation states of +III and higher for group 12 elements is to involve their inner d orbitals. This is particularly difficult to accomplish for Zn, since its third ionization potential is the largest among its congeners (39.7, 37.5, and 34.2 eV for Zn, Cd, and Hg, respectively).[2] Since this decreases as we go down the periodic table, significant effort has been made in the past to achieve higher oxidation states for the heavier element mercury. In 1976, a short-lived $[Hg^{III}(cyclam)]^{3+}$ species generated through electrochemical oxidation was reported.[3]

The +IV state of Hg is expected to be more stable than the +III state since it has the same electronic configuration ($5d^8$) as the very stable Au^{3+} cation.[4] Consequently, HgF_4, where Hg is in the +IV oxidation state, was theoretically predicted[4−6] about 20 years ago. However, experimental observation eluded scientists until very recently, when it was prepared by a matrix isolation method.[7] Also, Riedel et al.[8] studied weakly coordinating anions as ligands that can stabilize the +IV oxidation state of Hg. Unlike HgF_4, in all cases they found that Hg^{IV} complexes have at least one exothermic fragmentation pathway. Zn has not yet been shown to exist in an oxidation state of +III or higher.

We wondered whether highly oxidizing ligands could enable Zn to exhibit the +III oxidation state. Armed with the knowledge that a class of molecules called superhalogens[9] can have electron affinities (EAs) far exceeding those of halogen atoms, we embarked on a systematic study of the interaction of zinc with a variety of atoms and molecules with progressively increasing EAs. The high EAs of these ligands could be expected to compensate for the large third ionization potential of Zn. In this work, we addressed two fundamental questions: (1) Can superhalogens stabilize the +III oxidation state of zinc? (2) Must d orbitals be involved to achieve this? We approached the problem in two ways. First, we performed a methodical study of the equilibrium geometries and total energies of neutral and anionic ZnX_3 clusters for X = F, BO_2, and AuF_6 using density functional theory. It should be noted that the EAs of F, BO_2, and AuF_6 are 3.4,[10] 4.5,[11] and 8.4[12] eV, respectively. In the case of ZnX_3, for zinc to be in the +III oxidation state, it would be necessary for zinc to be bound to three individual monovalent ligands (X) that are more electronegative than zinc. Second, we studied the simple ZnF_4^- system and its corresponding ionic salt, $KZnF_4$. Here also, the oxidation state of Zn would have to be +III to satisfy the net charge of −1 for the ZnF_4^- anion.

We performed all of the calculations using the Gaussian 03 and Gaussian 09 packages. We used the B3LYP hybrid functional for the exchange−correlation potential along with

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the 6-311+G* basis set for Zn, F, B, and O and the Stuttgart SDD pseudopotential for Au. To test the sensitivity of our results to the choice of basis sets and exchange−correlation functional, we repeated the calculations for selected cases using the aug-cc-pVTZ basis set and the M06 functional, which incorporates weak dispersive forces. We optimized all of the geometries without any symmetry constraints and removed any imaginary frequencies.

The optimized structures of neutral and anionic ZnX_3 are given in Figure 1. ZnX_3^- anions are expected to be very stable negative ions with large vertical detachment energies (VDEs). Table 1 shows the adiabatic detachment energies (ADEs) and VDEs of ZnX_3^- clusters. The ADE was determined by calculating the energy difference between the ground states of the anionic cluster and the corresponding neutral cluster. The VDE, on the other hand, was calculated by taking the energy difference between the anionic and neutral clusters, both at the ground-state geometry of the anion.[13] Our calculations showed that ZnF_3 is indeed a superhalogen, $KZnF_3$ being a well-known perovskite salt.[14,15] Similarly, we found $Zn(BO_2)_3$ and $Zn(AuF_6)_3$ to be hyperhalogens.[16] The oxidation state of Zn is +II in these anions. To achieve the +III oxidation state, ZnX_3 molecules must also be stable as neutrals. The structure, bonding, and stability of neutral ZnX_3 are discussed below.

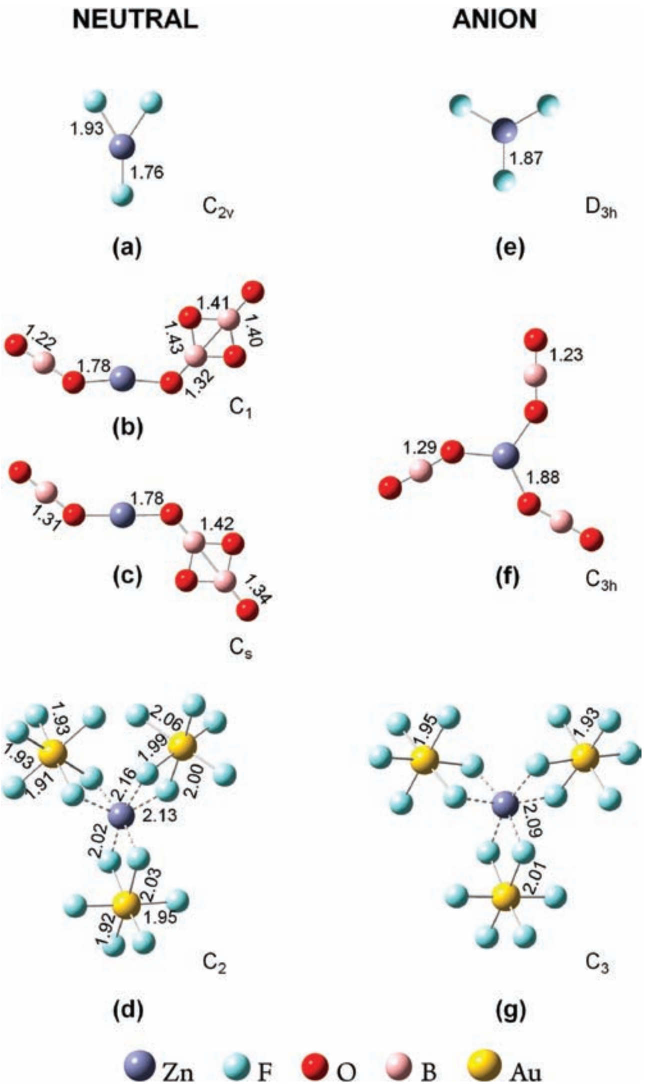


Figure 1. Optimized structures of (a−d) neutral and (e−g) anionic ZnX_3 (X = F, BO_2, AuF_6) clusters. Bond lengths are in Å.

Table 1. Adiabatic Detachment Energies (ADEs) and Vertical Detachment Energies (VDEs) of ZnX_3^- clusters (X = F, BO_2, AuF_6)

cluster	ADE	VDE
ZnF_3^-	6.20	6.59
$Zn(BO_2)_3^-$	5.63	6.78
$Zn(AuF_6)_3^-$	9.38	9.82

ZnF_3 is planar with C_{2v} symmetry and has two Zn−F bond lengths (1.93 Å and 1.76 Å) signifying two different bond strengths. These results are in good agreement with earlier work on ZnF_3 performed at the B3LYP and CCSD(T) levels using the effective core potentials (ECPs) of the Stuttgart group for Zn and the aug-cc-pVTZ basis set for F.[17] The F−F bond distance between the two nearest F atoms is 2.04 Å. It is worthwhile to point out that this distance is only slightly longer than the F−F bond distance in F_2^- (2.01 Å). This suggests that the two close F atoms in ZnF_3 are quasi-molecular. The quasi-molecular nature of two of the F atoms in ZnF_3 is further demonstrated in Figure 2, where we compare the charge density contours around the two closest F atoms in ZnF_3 with those around the F atoms in F_2^-. The presence of a quasi-molecular F−F interaction indicates that Zn should be in the +II oxidation state, not +III. This can be understood by comparing the molecule with BaO_2. Conventionally, O is assigned an oxidation state of −II in most compounds. However, as there is a peroxo linkage between the two O atoms in BaO_2, the oxidation state of O is assigned to be −I, and that of Ba is +II rather than +IV. Similarly, in ZnF_3, the two F atoms in the quasi-molecular F−F moiety should each be assigned an oxidation state of $-^1/_2$, thereby making the formal oxidation state of zinc +II. It is important to note that the fragmentation of ZnF_3 into ZnF_2 + $^1/_2$ F_2 is favorable [Table S2 in the Supporting Information (SI)]. The reaction is slightly exothermic (by 0.06 eV), which confirms earlier work[17] that ZnF_3 is not a stable compound of Zn in the +III oxidation state.

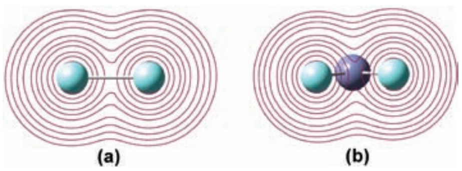
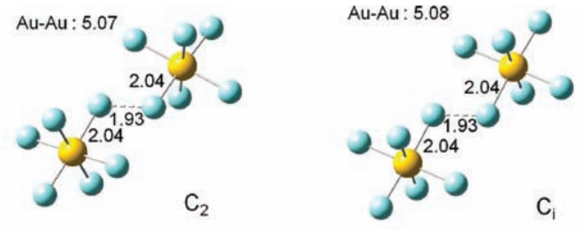


Figure 2. Contour diagrams of (a) isolated F_2^- and (b) the two closest F atoms in ZnF_3. The contour diagrams were plotted using default isovalues in Gaussview 5.0. Identical isovalues were used for both molecules.

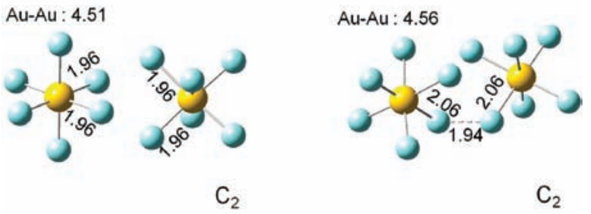
Unlike ZnF_3, the ground state of $Zn(BO_2)_3$ is stable with respect to fragmentation (Table S3). However, here Zn is attached to one BO_2 ligand and one B_2O_4 ligand. This is the case because two molecules of BO_2 dimerize exothermically (−1.70 eV) to form B_2O_4. The BO_2 and B_2O_4 ligands can be either trans or cis to each other, giving rise to two degenerate structures. The significance of this result is that Zn is not in the +III oxidation state even though there are three BO_2 units in the molecule. We were able to determine a local minimum geometry where all the BO_2 moieties are attached individually to Zn, corresponding to a structure where Zn is in +III oxidation state. However, this structure is 1.07 eV higher in energy than the ground state. Some energetically low-lying structures of neutral and anionic $Zn(BO_2)_3$ are given in Figures S1 and S2 in the SI.

$Zn(AuF_6)_3$ has C_2 symmetry. Zn is surrounded by three AuF_6 units. The three Au atoms form the vertices of an isosceles triangle with the Au−Au distance being 5.92 Å for the equal sides of the triangle and the remaining Au−Au distance being 4.56 Å. The Zn atom is at a distance of 3.15 Å from one Au atom and 3.26 Å from the other two Au atoms. Zn is hexacoordinated with six F atoms. We note that as in the case of ZnF_3, here also two AuF_6 moieties are close to each other. However, in contrast to ZnF_3, $Zn(AuF_6)_3$ is stable with respect to all of the fragmentation channels studied (Table S4). Therefore, $Zn(AuF_6)_3$ is a *stable* molecule of Zn in the +III oxidation state.

Now the question arises whether the inner 3d electrons are involved in the bonding of the ZnX_3 clusters. To understand the nature of the bonding involved, we computed the natural bond orbital (NBO) charge distributions (Table S6). The natural population analysis indicates that the d orbitals of Zn are completely filled in ZnF_3. The NBO charge on Zn is 1.682. The charge on one of the F atoms is −0.821 and that on each of the other two quasi-molecular F atoms is about −0.430. In both the cis and trans isomers of $Zn(BO_2)_3$, the charge on Zn is 1.655, while those on the BO_2 and B_2O_4 units are −0.844 and −0.811, respectively. As before, the d orbitals in Zn are completely occupied. In $Zn(AuF_6)_3$, one AuF_6 moiety has a charge of −0.893, whereas each of the two AuF_6 groups closer to each other has a charge of −0.428. This is similar to the case of ZnF_3. Again, the natural population analysis suggests that the d orbitals of Zn are completely occupied in $Zn(AuF_6)_3$. To understand why Zn should be in the +III oxidation state in $Zn(AuF_6)_3$ while it is in the +II oxidation state in ZnF_3, we point out a major difference between the bonding modes in ZnF_3 and $Zn(AuF_6)_3$. As stated before, the two closest F atoms in ZnF_3 appear to form a quasi-molecular F_2^- unit. Hence, even if ZnF_3 were stable with respect to fragmentation, the oxidation state of Zn would still be +II. This possibility is negated in case of $Zn(AuF_6)_3$. Though two of the AuF_6 moieties are close to each other, they do *not* form a quasi-molecular $(AuF_6)_2^-$ unit. This is because unlike F_2^-, $(AuF_6)_2^-$ itself is *not* a stable molecule; it fragments into $Au_2F_{11}^-$ + $^1/_2F_2$, releasing 0.42 eV of energy. Similarly, neutral $(AuF_6)_2$ is also unstable by 2.02 eV (Table S1). Also, comparison of the optimized geometries of $(AuF_6)_2$ and $(AuF_6)_2^-$ with the geometry of the two close AuF_6 moieties in $Zn(AuF_6)_3$ (Figure 3) shows stark differences in the structures that further reduce the possibility of a quasi-molecular interaction between the two close AuF_6 moieties in $Zn(AuF_6)_3$. Therefore, $Zn(AuF_6)_3$ is a genuine and stable compound of Zn in the +III oxidation state. As far as the direct participation of d orbitals in bonding is concerned, we note that the NBO charge of +3 in Zn is only possible if the bonding is purely *ionic*. In neutral $Zn(AuF_6)_3$, the bonding is not purely ionic; rather, a combination of covalent and ionic bonding is featured. We want to emphasize that here the focus is on Zn in the +III oxidation state and *not* in the +3 cationic state. Zn does not *have to* give up a d electron to be in the +III oxidation state, although this is a requirement for Zn to be in the +3 cationic state. In this connection, we note that while in AuF_5, a d^6 system, Au exists in the +V oxidation state, the NBO charge on Au is +2.116, not +5. Also, the natural electron configuration is $[core]6s^{0.38}5d^{8.46}$ as opposed to $[core]5d^6$. Moreover, in case of $Hg^{IV}F_4$ (which has been experimentally confirmed[7]), Hg does not give up two d electrons to become a "true" +4 cation according to natural population analysis. As a matter of fact, the NBO charge on Hg is +2.019, and its electron configuration is $[core]6s^{0.56}5d^{9.37}$, whereas for a true Hg^{4+} cation it would be $[core]5d^8$. Therefore, the formal oxidation state and partial atomic charges are two fundamentally different concepts, as has been pointed out earlier by Kaupp and von Schnering.[18] Our results imply that to attain the +III oxidation state of Zn, two criteria should be simultaneously satisfied: the ligands must have a high EA and must not preferentially dimerize. The success of AuF_6 as a ligand is attributed to the fulfillment of these two requirements.



(a) Degenerate $(AuF_6)_2$ anions



(b) $(AuF_6)_2$ neutral

(c) Two close AuF_6 moieties in $Zn(AuF_6)_3$

Figure 3. Structures of (a) two degenerate $(AuF_6)_2^-$ anions, (b) isolated $(AuF_6)_2$, and (c) the two close AuF_6 moieties in $Zn(AuF_6)_3$. Bond lengths are in Å.

An alternate approach for stabilizing Zn(III) is in the form of an anionic molecule. We studied ZnF_4^- and $KZnF_4$ as potential candidates. Optimized structures and fragmentation energies are given the in Figure S4 and Table S5. We note that an earlier gas-phase study had shown that ZnF_4^- is stable with respect to atomic or molecular fluorine ejection.[17] It was suggested that the stability could be increased further by building salts with a counterion. Our calculations indicate that ZnF_4^- is indeed stable in the gas phase. However, it is likely that the formation of the energetically more favorable salt K_2ZnF_4, where zinc is in the +II oxidation state, would be preferred over that of $KZnF_4$, especially in the condensed phase. The energies corresponding to the lowest-energy fragmentation pathways of all the clusters studied are given in Table 2. To verify the magnitudes of these energies, the structures were reoptimized at the M06 level using the SDD basis set for Au; the aug-cc-pVTZ basis set for Zn, B, O, and F; and the 6-311+G* basis set for K. We note that in ZnF_4^- and $KZnF_4$, the electron configurations of Zn are $[core]4s^{0.28}3d^{9.82}$ and $[core]4s^{0.27}3d^{9.86}$, respectively, indicating that the d electrons of Zn are somewhat involved in the bonding.

It should be mentioned here that Riedel, Straka, and Kaupp tried to utilize "weakly coordinating anions" such as AlF_4^-, $Al_2F_7^-$, AsF_6^-, etc. to stabilize the +IV oxidation state of Hg.[8] In their work, they also stated that aggregation of the ligands is a

Table 2. Fragmentation Energies of Neutral ZnX_3 Clusters, ZnF_4^-, and $KZnF_4$ for the Lowest-Energy Pathways (B3LYP Zero-Point-Corrected Energies Are Given in Parentheses)

		fragmentation energy (eV)	
cluster	fragmentation pathway	B3LYP[a]	M06[b]
ZnF_3	$ZnF_2 + {}^1/_2F_2$	−0.06 (−0.05)	−0.23
$Zn(BO_2)_3$	$Zn(BO_2)_2 + {}^1/_2B_2O_4$	1.07 (1.03)	1.32
$Zn(AuF_6)_3$	$Zn(AuF_6)_2 + {}^1/_2Au_2F_{10} + {}^1/_2F_2$	0.26 (0.23)	0.17
ZnF_4^-	$ZnF_3^- + {}^1/_2F_2$	0.11 (0.11)	0.01
$KZnF_4$	${}^1/_2K_2ZnF_4 + {}^1/_2ZnF_2 + {}^1/_2F_2$	−0.07 (−0.06)	−0.16

[a] Basis sets: SDD for Au; 6-311+G* for Zn, B, O, F, and K. [b] Basis sets: SDD for Au; aug-cc-pVTZ for Zn, B, O, and F; 6-311+G* for K.

major obstacle to achieving higher oxidation states. Furthermore, it is interesting to note that the weakly coordinating ligands tested were all superhalogens, that is, they all have high EAs. In fact, we believe that most weakly coordinating ligands are superhalogens, from which they derive their ability to stabilize high oxidation states of metals. Our results open the door for the synthesis of new compounds containing metals in unusual oxidation states with the potential for applications. It has already been demonstrated that unusually high oxidation states of elements have important consequences. For example, high-valent iron species such as Fe^{IV} (in oxoferryl porphyrins) and Fe^{V} (in nitridoirons) are important in biochemistry,[19] whereas Fe^{VI} (in FeO_4^{2-}) has been used for wastewater management.[20]

In summary, we have shown that higher and unusual oxidation states of metals can be achieved using ligands with large electron affinities such as superhalogens. We have demonstrated this in the particular case of $Zn(AuF_6)_3$, in which zinc is in the hitherto unknown +III oxidation state. In addition to bearing large EAs, it is also important that these ligands have no tendency to dimerize, since the contrary would favor fragmentation of the metal−ligand complex. Equally important, we have shown that ZnF_3 is a superhalogen with a vertical detachment energy of 6.59 eV, while $Zn(AuF_6)_3$ is a hyperhalogen with a VDE of 9.82 eV. Consequently, these molecules are predicted to form very stable negative ions. However, in the neutral form, whereas ZnF_3 is *not* stable with respect to fragmentation, $Zn(AuF_6)_3$ *is* by 0.26 eV. Though the oxidation state of zinc in the latter molecule is +III, it seems from the NBO charge distribution and natural population analysis that the d orbitals of zinc are not strongly involved in the bonding. We emphasize that the NBO charge alone can be used to determine the oxidation state *if* the bonding is purely ionic, that is, if there is complete charge transfer between the metal and the ligand. However, the situation is less clear when the bonding is partly ionic and partly covalent. Nonetheless, our results show that even in the absence of significant direct involvement of the d electrons, it is still possible to increase the degree of oxidation of a species and hence form new compounds by using specific ligands. This finding not only demonstrates a way to enhance the chemistry of zinc but also opens the door for the synthesis of unusual compounds by using the strong oxidizing properties of superhalogens.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Isomers of $Zn(BO_2)_3$, optimized structures of ZnF_4^- and $KZnF_4$, fragmentation energies and NBO charge distributions of all clusters investigated, and references for the theoretical methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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