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Can Zinc Really Exist in Its Oxidation State +III?

Tobias Schlöder,[†] Martin Kaupp,[‡] and Sebastian Riedel*,[†]

[†]Institut für Anorganische und Analytische Chemie, *Albert-Ludwigs Universität Freiburg*, Albertstrasse 21, D-79104 Freiburg im Breisgau, Germany

[‡]Fakultät II, Institut für Chemie, Theoretische Chemie, Technische Universität Berlin, Sekr. C7, Straße des 17. Juni 135, 10623 Berlin, Germany

Supporting Information

ABSTRACT: Very recently, a thermochemically stable Zn^{III} complex has been predicted by Samanta and Jena (*J. Am. Chem. Soc.* **2012**, *134*, 8400−8403). In contrast to their conclusions we show here by quantum chemical calculations that (a) $Zn(AuF_6)_3$ is not a thermochemically feasible compound, and (b) even if it could be made, it would not represent a Zn^{III} oxidation state by any valid definition.

The elements of group 12, Zn, Cd, and Hg, usually use only their s orbitals for bonding. That is why these elements are not commonly considered as transition metal elements,[1] because their $(n - 1)$d orbitals remain fully occupied in their usually highest oxidation state +II. The only experimentally verified exception from this rule is the HgF_4 molecule, which has been identified under cryogenic conditions in rare gas matrices,[2] and which indeed contains mercury in its +IV oxidation state, as a square-planar low-spin d^8 complex.[3−6] A much earlier report[7] on a complex $[Hg^{III}(cyclam)](BF_4)_2$ has later been shown by calculations to correspond to a Hg(II) system with an oxidized cyclam ligand.[8] Oxidation state +III is thus still missing in group 12. For mercury, oxidation states beyond +II are favored by the relativistic destabilization of the corresponding Hg^{II} complexes with electronegative ligands (this holds even more so for element 112, röntgenium[9]). No such stabilization is possible for zinc. In the case of the trifluorides, CCSD(T) calculations showed neither of the group 12 elements to exhibit favorable thermochemistry. Indeed, the MF_3 complexes ZnF_3 and CdF_3 exhibit partial F−F bonding between the ligands and thus do not contain M^{III}.[10] This is in line with previous matrix-isolation experiments of laser-ablated zinc atoms codeposited with fluorine under excess of rare gases to form matrices at cryogenic conditions (see Supporting Information of ref 2). Only ZnF_2 was produced, and no absorptions corresponding to higher fluorides occurred in the spectra.

In a very recent communication in this journal, Samanta and Jena[11] (SJ) reported DFT calculations (B3LYP/6-311+G* level with quasi-relativistic pseudopotentials for the metals) on a number of Zn model complexes. They claimed that the complex $Zn(AuF_6)_3$ is a thermodynamically stable Zn^{III} system. In contrast to the conclusions of ref 11, we show here by quantum chemical calculations that (a) $Zn(AuF_6)_3$ is not a thermochemically feasible compound, and (b) even if it could be made, it would not represent a Zn^{III} oxidation state by any valid definition.

SJ used the B3LYP functional to compute structures and energetics and cross-checked this by a few single-point calculations with the M06 functional, which features slightly larger exact-exchange admixture (27% instead of 20% for B3LYP). While we have found previously that B3LYP-based calculations reproduce well large-basis-set CCSD(T) benchmark calculations on the thermochemical stability of HgF_4,[1] and on other closed-shell fluorides in high oxidation states, this does not hold for open-shell systems such as ZnF_3, as was shown in ref 10. The comparison of B3LYP and CCSD(T) data in Table 1 demonstrates our previous observation that stability with respect to F_2-elimination is appreciably overestimated at B3LYP level (reaction a).

No CCSD(T) benchmark calculations are feasible for the $Zn(AuF_6)_3$ target system due to its extended size. Simple extrapolation of the B3LYP performance for ZnF_3 to the larger complex suggests that reaction (c) will not be endothermic but exothermic at higher computational levels. As an additional confirmation for this conclusion, Table 1 also provides spin-component-scaled MP2 (SCS-MP2) and scaled opposite-spin MP2 (SOS-MP2) results (for the C_2 minimum structure of $Zn(AuF_6)_3$, see below). These levels perform relatively well for Hg^{IV} complexes.[1] For ZnF_3, they provide a much more exothermic decomposition reaction (a) than B3LYP, thus *underestimating* the CCSD(T) data by a similar amount as B3LYP *overestimates* them. Indeed, for the relevant reaction (c), both SCS-MP2 and SOS-MP2 suggest dramatically exothermic values, in stark contrast to the B3LYP data, on which the conclusions of SJ were based. Even if we take into account the possibility that the SCS-MP2 and SOS-MP2 data might be still less reliable[12] here than for the ZnF_3 case, it is obvious that B3LYP calculations are also unreliable for the energetics of reaction (a) and are expected to be even more unreliable for reaction (c). We note in passing that our def2-TZVPP basis sets differ slightly from the 6-311+G* basis used by SJ, but the B3LYP energetics are altered very little by this difference. Note that due to entropic contributions, the Gibbs standard free reaction enthalpies for reactions (c) and (d) are even already exergonic at B3LYP level. For ZnF_3, breaking one Zn−F bond homolytically is endothermic, but the bimolecular elimination of F_2 is already exothermic.[10] While the unimolecular process of

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Table 1. Computed Reaction Energies and Standard Free Reaction Enthalpies (in kJ mol^{-1}) of Zn^{III} Compounds at Different Levels of Theory[a]

reaction	CCSD(T)	SCS-MP2	SOS-MP2	B3LYP	
				ΔE	$\Delta G°$
$ZnF_3 \rightarrow ZnF_2 + \frac{1}{2}F_2$ (a)	−59.0[b]	−94.2	−99.5	−18.3 (−17.0)	−23.2
$Zn(AuF_6)_3 \rightarrow Zn(AuF_6)_2 + AuF_6$ (b)		−197.4	−191.9	81.7 (80.1)	27.8
$Zn(AuF_6)_3 \rightarrow Zn(AuF_6)_2 + \frac{1}{2}Au_2F_{10} + \frac{1}{2}F_2$ (c)		−306.1	−322.0	26.9 (24.1)	−26.4
$Zn(AuF_6)_3 \rightarrow Zn(AuF_6)_2 + \frac{1}{3}Au_3F_{15} + \frac{1}{2}F_2$ (d)		−313.8	−329.9	21.2 (18.5)	−23.4

[a] (SCS,SOS)MP2/def2-TZVPP//B3LYP/def2-TZVPP and B3LYP/def2-TZVPP data; values in parentheses are ZPE corrected. [b] CCSD(T)/aug-cc-pVTZ/SDD data taken from ref 10.

splitting off one AuF_6 unit from $Zn(AuF_6)_3$ (reaction (b) in Table 1) would be endothermic at B3LYP level (+80.1 kJ mol^{-1}), it is still appreciably exothermic at SCS-MP2 level (−197.4 kJ mol^{-1}). Note that AuF_6 itself is a very unlikely species, due to its enormous electron affinity.[13,14] Most likely, even reaction (b) is nevertheless still exothermic. Reaction (c) is expected to be even much more exothermic. Kinetic barriers for both reactions (b) and (c) are expected to be small, due to small reorganization energies involved (cf. similar bond lengths in $Zn(AuF_6)_2$ and $Zn(AuF_6)_3$ in Figure S1 in Supporting Information (SI), as well as preformation of a partial F−F bond in $Zn(AuF_6)_3$).

Notably, entropic contributions shift equilibrium (c) even more to the right side at finite temperatures. Corrections for basis-set superposition errors, for spin−orbit coupling, and for other aspects neglected in these calculations, will of course alter these data further to some extent, but none of these contributions is large enough to revert the conclusion that $Zn(AuF_6)_3$ is not stable with respect to reaction (c). In fact, AuF_5 is known to form trimers (reaction (d)), thereby shifting the decomposition reaction even more to the right side.[13,15]

Mazej found that the reactions of ZnF_2 and AuF_3 with both KrF_2 (reaction (e)) and UV-photolyzed F_2 (reaction (f)) as the oxidizer in anhydrous HF (aHF) only yielded $Zn(AuF_6)_2$.[16]

$$ZnF_2 + 2KrF_2 + 2AuF_3 \xrightarrow[\text{aHF},RT]{} Zn(AuF_6)_2 + 2Kr \quad (e)$$

$$ZnF_2 + F_2 + AuF_3 \xrightarrow[\text{aHF},h\nu]{} Zn(AuF_6)_2 \quad (f)$$

No oxidation of zinc was observed in either of the reactions. As an excess of KrF_2 was used in the first reaction and an excess of F_2 in the second, sufficient oxidation equivalents would have been available in both cases to achieve further oxidation in case this would have been feasible.

Even if $Zn(AuF_6)_3$ could be made, there is still the issue of the zinc oxidation state. The arguments in ref 11 based on NPA charges were not convincing. The minimum structure found by SJ is the C_2 complex depicted in Figure 1 B. Our calculations confirm that this is a local minimum on the B3LYP and SOS-MP2, and SCS-MP2 potential energy surfaces. We found a second minimum with D_3 symmetry (A) which, however, is higher in energy by 10 kJ mol^{-1} at B3LYP/def2-TZVPP level. In the lower-lying C_2 minimum (B), two fluorine atoms of two different AuF_6-groups approach each other to a distance of 197 pm (Figure 1). This is way below twice the fluorine van der Waals radius (280 pm) and also shorter than the distance between the two closest fluorine atoms (202.9 pm) in ZnF_3. In fact, the structure is closely related to the Y-shaped structure of ZnF_3, which may be viewed as a complex $[FZn]^+(F_2)^-$.[10]

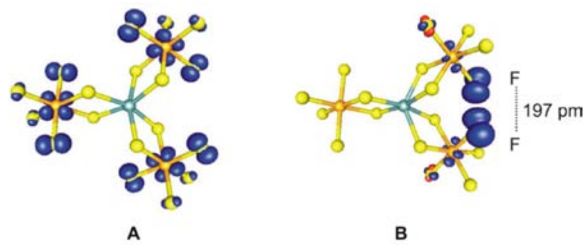

Figure 1. Spin-density distribution of the $Zn(AuF_6)_3$ complex in D_3 (A) and C_2 (B) symmetry at RI-B3LYP/def2-TZVPP level. Isosurface plot ±0.005 au (blue indicates positive spin density, and red indicates negative spin density).

Thus, from a structural point of view, the system is best described as $[(AuF_6)Zn]^+(AuF_5)_2[F_2]^-$. Such a description was ruled out by SJ for reasons that remained unclear to us. In case of such an open-shell system, inspection of the spin-density distribution is particularly informative regarding physical oxidation states. Figure 1 shows spin-density isosurface plots for both minima. In the C_2 structure, the spin density is clearly concentrated on the two above-mentioned fluorine atoms, which approach each other. Indeed, the Mulliken spin densities are +0.477 on each of the two atoms (Table S1 in SI). This is a clear indication of the formation of an $(F_2)^-$ radical anion coordinated as a bridge between two AuF_5 units. In fact, this interaction between two of the AuF_6 ligands is the prime reason for the distortion to C_2 symmetry. Negligible spin density is found on the zinc atom (<0.001 Mulliken spin density), in complete disagreement with the Zn^{III} oxidation-state assignment of SJ. In the second, higher-lying D_3 minimum, the spin density is delocalized over all three AuF_6 moieties, predominantly on the three Au centers and on six terminal fluorine atoms. The spin density on the gold atoms signals their partial oxidation beyond Au^V. However, given the general instability of the complex (see above) and the fact that this is a higher-lying minimum, not too much significance can be attached to this observation. Again, there is no spin density on zinc, and thus characterization of the complex as a Zn^{III} compound can be clearly ruled out. Additional support for this conclusion comes from a comparison of the NPA charges on zinc and gold between $Zn(AuF_6)_3$ and $Zn(AuF_6)_2$: these are identical (cf. Table S1 in SI) within 0.02 for Zn and within 0.04 for Au (for both the C_2 and D_3 structures of the former complex). Closer analysis of d-orbital populations on Zn (Table S1 in SI) indicates furthermore that the metal d-orbitals are not involved in bonding. This also contradicts a Zn^{III} description. In situations as this, formal oxidation states become meaningless and physical oxidation states have to be discussed. In this context, $Zn(AuF_6)_3$ has to be described, beyond any doubt and by all applicable criteria, as a Zn^{II} complex with partial oxidation of the ligand framework. This outcome is reminiscent of our previous results for the above-mentioned complex $[Hg^{II}(cyclam^+)](BF_4)_2$.[8] It is also in line with a very recent matrix-isolation and quantum chemical investigation of mercury oxyfluorides, which showed that the experimentally characterized OHgF molecule is not a Hg^{III} complex.[17] Instead, the spin density localized at the oxygen ligand characterizes that system as a Hg^{II} complex with an oxyl radical ligand.

In conclusion, the recent quantum chemical prediction of a thermochemically stable Zn^{III} complex by SJ cannot be upheld. $Zn(AuF_6)_3$ is neither thermochemically stable nor a Zn^{III} complex. We suggest strongly that extreme care has to be taken in the prediction of novel oxidation states regarding both thermochemical and kinetic stabilities as well as assignments of electronic structure and oxidation state.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details, structures NPA charges, Mulliken spin densities, total energies, and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

sebastian.riedel@psichem.de

Notes

The authors declare no competing financial interest.

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