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Cesium Fluorides

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Molecular CsF_5 and CsF_2^+**

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Abstract: *D_{5h} star-like CsF_5, formally isoelectronic with known XeF_5^- ion, is computed to be a local minimum on the potential energy surface of CsF_5, surrounded by reasonably large activation energies for its exothermic decomposition to $CsF+2F_2$, or to CsF_3 (three isomeric forms) $+F_2$, or for rearrangement to a significantly more stable isomer, a classical Cs^+ complex of F_5^-. Similarly the CsF_2^+ ion is computed to be metastable in two isomeric forms. In the more symmetrical structures of these molecules there is definite involvement in bonding of the formally core 5p levels of Cs.*

Near the bottom (or should it be the top?) of the periodic table, for high atomic numbers, the distinction between valence and core orbitals becomes less well defined. For good reasons, as the energetic separation of all potentially occupiable levels becomes small. For instance, it has been suspected that some sub-valence levels of uranium are involved in uranium–ligand bonding.[1] And a compound of mercury in oxidation state IV, HgF_4, involving the d block in bonding, was predicted and observed.[2,3] This is at $p=1$ atm; at higher pressures, calculated compositions of matter stepping well outside of normal valence regularities abound.[4]

We report herein, at least in theory, another clear $p=1$ atm instance of the involvement of orbitals thought to be core orbitals in bonding. Our investigation derives from the theoretical finding of CsF_5 and CsF_2^+ molecular units in a study of cesium fluorides under elevated pressure.[5] Given that the molecules are isoelectronic with known species XeF_5^-[6] and XeF_2, respectively, we decided to examine their potential (even if fleeting) existence as discrete molecules at ambient or low pressure.[7] We predict the thermodynamic metastability and likely kinetic persistence of molecular CsF_5 and CsF_2^+. In certain isomers of these compounds, Cs is in formal oxidation state V and III, respectively, and forms polar Cs–F bonds.[8] We note some excellent recent experimental and theoretical work on CsF_3 and CsF_5 ion pairs by Vent-Schmidt et al.[9]

To obtain reliable results, a reasonably high level of theory has to be used and relativistic effects need to be taken into account (details in the Methods Section at the end of the paper, and in the Supporting Information). Computational pathologies pose obstacles, as we will describe.

The D_{5h} CsF_5 structure is a local minimum (Hessian matrix eigenvalues all positive) in our calculations (PBE0/TZVP/ZORA level; the same geometry is obtained with other methods; please see the Methods Section and the Supporting Information), and is shown in Figure 1. The star-like planar geometry mirrors its isoelectronic anionic XeF_5^-. The calculated Cs–F distance is 2.05 Å.[10] Essentially the same results were obtained by the CCSD(T) method (Cs–F distance is 2.08 Å, see the Supporting Information for details), thus providing important support for the reliability of PBE0 geometry calculations.

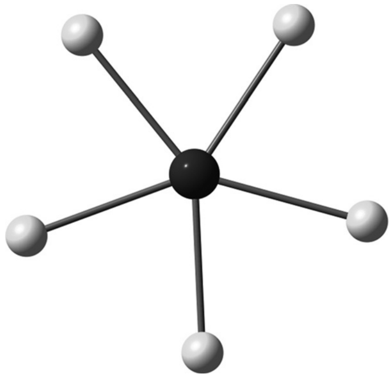

Figure 1. Calculated equilibrium geometry of CsF_5.

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How stable (or unstable) is D_{5h} CsF$_5$ with respect to its expected decomposition products CsF + 2 F$_2$? That turned out to be a difficult question to answer—there was a huge discrepancy of more than 60 kcal mol^{-1} in the ΔE between CCSD(T)/TZVP (or CCSD(T)/QZVPP or MP2/TZVP, all with ZORA corrections) calculations on one hand, and PBE0 calculations with the same basis sets on the other. The PBE0/TZVP/ZORA level (the results are also supported by other methods[11]) gives −45 kcal mol^{-1} as the energy for decomposition. The products have computed distances of 2.375 Å for CsF (experimental: 2.345 Å[12]) and 1.383 Å for F$_2$ (experimental: 1.412[13]). To get more reliable estimations, we then turned to multireference (MR) perturbation theory in the XMCQDPT2 variant (these results will be used throughout the subsequent discussion; please see the Methods Section and the Supporting Information for details). This method gives $\Delta E = -44$ kcal mol^{-1}, which agrees well with the DFT value. Subsequent analysis of the wavefunction revealed that the leading closed-shell singlet configuration contributes 83 % (see the Supporting Information for details). Importantly, the weight of any other electronic configuration that contributes to the final wavefunction was found to be no more than 2 %. We conclude that the ground state of D_{5h} CsF$_5$ can be approximately described by single-reference methods.

The decomposition of CsF$_5$ to CsF + 2 F$_2$ is allowed (no level crossings) along a least-motion reaction coordinate. The transition state (TS) we found for this process is shown in Figure 2; the same results were obtained with (C_{2v}) and without (C_1) symmetry restrictions applied. An activation energy of + 39 kcal mol^{-1} was computed for the process at the XMCQDPT2 level. In contrast to the ground state of the star-like isomer, the C_{2v} TS wavefunction is substantially multireference; it corresponds to an open-shell singlet configuration, with two leading configurations of equal weight (44 %). Still another highly exothermic channel is to F$_2$ and CsF$_3$ (the Cs$^+$ complex of the trifluoride ion,[8] more on this species soon[14]). This channel could be viewed as an asymmetric fragmentation, with a computed ΔE of −9 kcal mol^{-1} and E_a of + 73 kcal mol^{-1}. The TS was found to be open-shell singlet in nature, 70 % coming from two leading configurations.

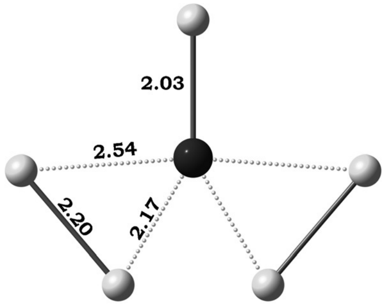

Figure 2. Transition-state geometry for decomposition of CsF$_5$ to CsF and two molecules of F$_2$. Selected geometrical parameters are shown.

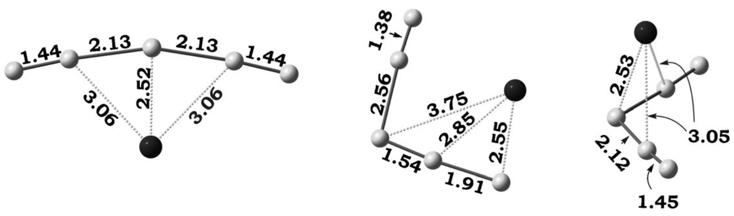

Figure 3. Three calculated less-symmetrical low-energy structures for CsF$_5$.

Symmetry is not a good guide to stability; in addition to the beautiful star-shaped structure for CsF$_5$ (and weakly bound complexes of CsF and two F$_2$ molecules described in the Supporting Information), we have also discovered some less-symmetrical and quite stable CsF$_5$ structures. Three local minima are shown in Figure 3; they may be viewed as Cs$^+$ complexes of F$_5^-$[9,15] or F$_3^-$[15c,16] and F$_2$, stabilized much as Ault and Andrews originally reasoned for CsF$_3$.[8] The structures are 42 to 49 kcal mol^{-1} more stable than the D_{5h} star.[17] All these isomers of CsF$_5$ can be approximately described by a closed-shell singlet electronic configuration with a weight of the leading term of more than 86 %. The barriers between the three Cs$^+$ + F$_5^-$ structures were found to be small (no more than 3 kcal mol^{-1}, see the Supporting Information); it appears this is a single easily deformed family of structures. In terms of geometrical distortions, we think these structures are far away from the star, and a distortion to them will encounter substantial barriers. The various CsF$_5$ isomers have quite distinct vibrations (see the Supporting Information, which also has a calibration on F$_2$ and F$_3^-$), so they should be distinguishable.

We note that an extended CsF$_5$ phase containing Cs$^+$ and F$_5^-$ ions, in a relative geometry resembling the right-hand structure in Figure 3, has been calculated to be stable at $p =$ 1 atm by Zhu, Oganov, and Zeng.[18]

Like the XeF$_5^-$ ion, CsF$_5$ has a well-defined high-lying molecular orbital (MO) that is mainly 5p$_z$ on Cs (the two MOs are illustrated in the Supporting Information). For CsF$_5$, this MO lies 0.69 eV lower than the HOMO of the molecule. We have recently predicted relatively high stability for organometallic Lewis acid adducts of XeF$_5^-$.[19] And we find that a hypothetical transition-metal complex [W(CO)$_5$CsF$_5$], W–Cs bonded, corresponds to a local minimum. Weakly bound as it is, by 6 kcal mol^{-1} (at the PBE0 level, see the SI), this adduct represents a rare case of activated reactivity of near-core (in this case 5p$_z$) orbitals.

We turn next to the CsF$_2^+$ ion which is isoelectronic with XeF$_2$. Interestingly, two local minima emerge on its potential surface as shown in Figure 4. The bent isomer is unstable by

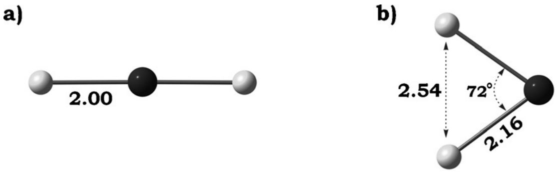

Figure 4. Equilibrium geometry configurations for a) linear and b) bent isomers of CsF$_2^+$.

about 25 kcal mol^{-1} relative to the linear one, as calculated at the XMCQDPT2 level. For both isomers, the ground state is a singlet. However, for the linear form, the contribution from the leading (closed-shell) configuration is 86 %, while another 13 % come from a second component. At the same time, for the bent analogue, the two leading configurations have weights of 57 % and 41 % and correspond to closed-shell and open-shell singlets, respectively. Both systems thus appear as significantly multireference in nature.

The reaction $CsF_2^+ \rightarrow Cs^+ + F_2$ is calculated to be exothermic with $\Delta E = -61$ kcal mol^{-1} (again in excellent agreement with the DFT value of -59 kcal mol^{-1}). Calculations of the reaction pathway led to a two-step mechanism (Figure 5) with one intermediate, the abovementioned bent isomer of the CsF_2^+ ion. Despite the large exothermicity, this reaction encounters a high reaction barrier ($E_a(1) = +29$ kcal mol^{-1}, the first barrier of the reaction considered). The asymmetrical C_s transition states are drawn out in the Supporting Information. As we have seen already in the case of CsF_5 systems, both transition states, TS1 and TS2, are highly multireference (see the Supporting Information).

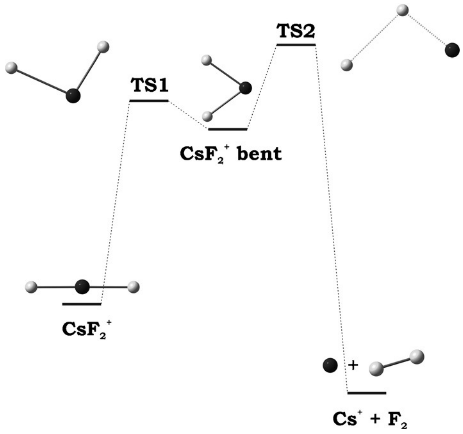

Figure 5. Schematic energy profile for the reaction $CsF_2^+ \rightarrow Cs^+ + F_2$.

We mentioned above an asymmetric CsF_3 species, a complex of Cs^+ with F_3^-. Actually, we located at least three local minima for this stoichiometry. The low-symmetry structure of the most stable isomer is close to the geometry of the right-hand structure in Figure 3, with F_2 removed (see the Supporting Information). A second structure derives from a D_{3h} star-shaped molecule. Such a species would share the electronic characteristics of the isoelectronic (and known[20,21]) XeF_3^- ion in being a classic Jahn–Teller system. Two electrons would occupy an e' orbital, with deformations to T and Y shapes expected.[20] The T shape for both XeF_3^- and CsF_3 is not a local minimum, while the Y shape is.[20–23] The energy of this minimum is about 32 kcal mol^{-1} (26 kcal mol^{-1} by DFT) above the asymmetric structure mentioned above. Finally, there is a pyramidal C_{3v} isomer, 46 kcal mol^{-1} (38 kcal mol^{-1} at the PBE0 level) higher in energy. The T and Y shaped isomers are closed-shell singlets, with 83 % and 90 % contribution, respectively, from the leading configuration. In contrast, the pyramidal CsF_3 has an open-shell singlet as the ground state.

What about the bonding in these cesium fluorides? The question refers to the structures that are not ion pairs of Cs^+ with F_3^- or F_5^-. Oxidation states are a convenient fiction, so one must not conclude from them that one breaks into the hypothetical "core" 5s and 5p orbitals of Cs. But a population analysis in fact indicates that 5p orbitals are involved in the bonding: the total population of 5p orbitals in CsF_5 ($q(Cs) = +2.40$) and CsF_2^+ ($q(Cs) = +1.79$) is 4.41 e and 5.12 e, respectively. In the case of CsF_5, Cs $5p_x$ and $5p_y$ orbitals both are occupied by about 1.20 e (notably below 2.00 e, owing to the participation of $5p_x$ and $5p_y$ in hypervalent bonding), whereas the population of $5p_z$ (which does not take part in bonding) is exactly 2.00 e. A similar situation occurs for the CsF_2^+ ion, in which only the $5p_x$ orbital on Cs has a low occupancy of 1.25 e through its participation in 4e–3c bonding, whereas two other orbitals, $5p_y$ and $5p_z$, are close to doubly occupied (1.88 e and 2.00 e, respectively). In contrast, the same analysis performed for CsF ($q(Cs) = +0.93$) revealed that none of the 5p orbitals of the cesium center (5p total population is essentially 6.00 e) is involved in interaction with fluorine atoms.

We look forward to the detection of these intriguing higher fluorides of cesium.

Methods

DFT geometry explorations were performed with the help of the PBE0 correlation–exchange functional (within the RIJCOSX approximation). Full-electron relativistically recontracted basis sets of triple-Z quality (TZVP) were used for all atoms. Scalar relativistic effects were incorporated by applying the zero-order regular approximation (ZORA); the influence of spin–orbit coupling (SO) was evaluated through the ZORA approximation at the PBE0/TZ2P level with help of the ADF program.[24] The methods used were thus PBE0/QZVPP/ZORA; PBE0/TZVP/DKH2; MP2/TZVP/ZORA. The SO contribution was found to be about 1.33 kcal mol^{-1} and, thus, considered as negligible.[25]

Test calculations were also carried out for PBE0/TZVP-optimized geometries at the following levels of theory: MP2/TZVP and its orbital-optimized spin-scaled version OO-SCS-MP2/TZVP, CCSD(T)/TZVP and CCSD(T)/QZVPP (all with help of the RIJCOSX approximation). These calculations were performed by using the ORCA program suite (version 2.9.1).[26] The natural bond orbitals (NBOs, GENNBO (version 5.0) program) of the optimized geometries were then examined to gain some insight into the electronic structures. The nature of all stationary points on the potential energy surfaces (PES) was determined by calculation of the full Hessian matrix and the harmonic vibrational frequencies. All structures reported were found to be true minima on corresponding PES (no imaginary frequencies), whereas all TSs were found to possess only one imaginary frequency, corresponding to the transition between reactants and the products intended. The nature of all TSs was probed through the IRC technique connecting the target products and reactants. IRC calculations were carried out with help of the Firefly program (version 8.0) at the PBE0/def2-TZVP level of theory.

All MR calculations were performed for PBE0-optimized geometries. The active space includes the full valence space for fluorine atoms (7 electrons distributed over 1 orbital of s-type and 3 orbitals of p-type; altogether 7 electrons and 4 orbitals per F atom). For the cesium atom, 1 electron in the 6s orbital, 8 electrons in the 5s and 5p orbitals were included in the active space. This approach produced

(44 e, 22 orb), (30 e, 16 orb), and (22 e,12 orb) active spaces for CsF_5, CsF_3, and CsF_2^+, respectively. Converged CASSCF wavefunctions were then used as reference wavefunctions for subsequent calculations by the XMCQDPT2 method.[27] The conventional intruder-state avoidance technique (ISA) was used with a shift of 0.02 au in these calculations. All MR calculations were performed with help of the Firefly program suite (version 8.1.0). To avoid the problem of self-consistency of MR perturbation theory calculations, all products of the reaction(s) were considered in the calculation with the same active space as for the original molecule, but separated by about 20 Å. Albeit deficient in the absence of evaluation of ZPE and entropy contributions (which can notably change the final numbers), the method provides a unique opportunity to precisely analyze different contributions to the total wavefunction, especially in the case when the system cannot be described by a single determinant. This is precisely the case for any transition state considered herein, as well as a significant number of ground-state molecules.

Keywords: breaking into cores · cesium · fluorides · polyfluoride anions · quantum chemistry

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Angew. Chem. **2015**, *127*, 8393–8396

[1] a) P. F. Walch, D. E. Ellis, *J. Chem. Phys.* **1976**, *65*, 2387–2392; b) V. A. Gubanov, A. Rosén, D. E. Ellis, *J. Inorg. Nucl. Chem.* **1979**, *41*, 975–986; c) K. Tatsumi, R. Hoffmann, *Inorg. Chem.* **1980**, *19*, 2656; d) P. Belanzoni, E. J. Baerends, E. Van Lenthe, *Mol. Phys.* **2005**, *103*, 775–787; e) "Theoretical Studies of the Electronic Structure of Compounds of the Actinide Elements": N. Kaltsoyannis, P. J. Hay, J. Li, J.-P. Bladeau, B. E. Bursten in *The Chemistry of the Actinide and Transactinide Elements, Vol. 3* (Eds.: L. Morss, N. M. Edelstein, J. Fuger), Springer, Berlin, 1893–2011, **2006**; f) R. G. Denning, *J. Phys. Chem. A* **2007**, *111*, 4125; g) P. Pyykkö, *Chem. Rev.* **2012**, *112*, 371–384; h) M. D. Neidig, D. L. Clark, R. L. Martin, *Coord. Chem. Rev.* **2013**, *257*, 394.

[2] a) S. Riedel, M. Straka, M. Kaupp, *Chem. Eur. J.* **2005**, *11*, 2743, and references therein; b) X. Wang, L. Andrews, S. Riedel, M. Kaupp, *Angew. Chem. Int. Ed.* **2007**, *46*, 8371; *Angew. Chem.* **2007**, *119*, 8523.

[3] In recent work, one of us found that pressure can stabilize high oxidation states of Hg in an extended material: J. Botana, X. Wang, D. Yang, H. Lin, Y. Ma, M. Miao, unpublished results.

[4] W. Grochala, R. Hoffmann, J. Feng, N. W. Ashcroft, *Angew. Chem. Int. Ed.* **2007**, *46*, 3620; *Angew. Chem.* **2007**, *119*, 3694.

[5] M. Miao, *Nat. Chem.* **2013**, *5*, 846–852.

[6] K. O. Christe, *J. Am. Chem. Soc.* **1991**, *113*, 3351.

[7] The possible existence of cesium fluorides has been probed experimentally: a) H. Bode, *Naturwissenschaften* **1950**, *37*, 477; b) K. Moock, K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1676; *Angew. Chem.* **1989**, *101*, 1713; c) L. B. Asprey, J. L. Margrave, M. E. Silverthorne, *J. Am. Chem. Soc.* **1961**, *83*, 2955; d) C. Jehoulet, A. J. Bard, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 836–838; *Angew. Chem.* **1991**, *103*, 882–884; the experimental verdict so far appears to be "not proven".

[8] CsF_3 is known from matrix isolation studies. This fascinating molecule is a Cs^+ complex of the trifluoride ion: B. S. Ault, L. Andrews, *J. Am. Chem. Soc.* **1976**, *98*, 1591.

[9] T. Vent-Schmidt, F. Brosi, J. Metzger, T. Schlöder, X. Wang, L. Andrews, C. Müller, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2015**, *54*, 8279–8283; *Angew. Chem.* **2015**, *127*, 8397–8401.

[10] CsF is a common ionic solid with a distance in the solid of 3.01 Å: W. Pies, A. Weiss, *a1, I.1.1 Simple fluorides and their solid solutions*. SpringerMaterials—The Landolt-Börnstein Database (Eds.: K.-H. Hellwege, A. M. Hellwege), (http://www.springermaterials.com). DOI: 10.1007/10201462_2.

[11] For example, PBE0/QZVPP/ZORA gives -34 kcal mol^{-1}, whereas the combination of an MP2 approach with orbital optimization as well as with spin-component-scale techniques (OO-SCS-MP2/TZVP/ZORA) gives -28 kcal mol^{-1}. Details of these calculations are collected in the Supporting Information.

[12] K. P. Huber, G. Herzberg, *Constants of Diatomic Molecules*, **1979**, Van Nostrand Reinhold.

[13] http://webbook.nist.gov/chemistry/.

[14] The previously computed structure of the most stable isomer of CsF_3 (Figure 14 in H. Haller, S. Riedel, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1281) corresponds in our calculations to the transition state between two identical isomers of CsF_3 (side-on isomer, central picture in our Figure S18). Our calculated barrier separating the isomers is low (ca. 1 kcal mol^{-1}).

[15] a) S. Riedel, T. Köchner, X. Wang, L. Andrews, *Inorg. Chem.* **2010**, *49*, 7156; b) for experimental evidence for F_5^- see the discussion in Ref. [14]; c) A. Artau, K. E. Nizzi, B. T. Hill, L. S. Sunderlin, P. G. Wenthold, *J. Am. Chem. Soc.* **2000**, *122*, 10667.

[16] a) A. A. Tuinman, A. A. Gakh, R. J. Hinde, R. N. Compton, *J. Am. Chem. Soc.* **1999**, *121*, 8397–8398.

[17] Since trifluoride F_3^- is known experimentally, we also computed the energetics of fragmentation of D_{5h} CsF_5 to $Cs^+ + F_2 + F_3^-$ ($\Delta E = +61$ kcal mol^{-1} at the PBE0 level).

[18] Q. Zhu, A. R. Oganov, Q. Zeng, *Sci. Rep.* **2015**, *5*, 785.

[19] A. Yu. Rogachev, R. Hoffmann, unpublished results.

[20] I. A. Krouse, C. Hao, C. E. Check, K. C. Lobring, L. S. Sunderlin, P. G. Wenthold, *J. Am. Chem. Soc.* **2007**, *129*, 846–852.

[21] N. Vasdev, M. D. Moran, H. M. Tuononen, R. Chirakal, R. J. Suontamo, A. D. Bain, G. J. Schrobilgeb, *Inorg. Chem.* **2010**, *49*, 8997–9004.

[22] D. J. Grant, T.-H. Wang, D. A. Dixon, *Inorg. Chem.* **2010**, *49*, 261–270.

[23] H. Rzepa, http://www.ch.imperial.ac.uk/rzepa/blog/?p=11681.

[24] a) C. F. Guerra, J. Snijders, G. te Velde, E. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391; b) G. te Velde, F. Bickelhaupt, E. Baerends, C. Guerra, S. Van Gisbergen, J. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

[25] Concerning the SO, it is tempting to note that at the limit of large SO (jj coupling), cesium in the oxidation state V would formally completely empty the semi-core $5p_{3/2}$ subshell, and leave the $5p_{1/2}$ subshell completely filled. A reviewer has suggested the following line of reasoning: Taking the SO from Desclaux's tables (*At. Data Nucl. Data Tables* **1973**, *12*, 312) it is 42.55 kcal mol^{-1}. Multiplying by 4/3, one gets for first-order SO 56.3 kcal mol^{-1}. Actually, in a filled-shell molecule, only second-order SO effects should occur. Guessing an energy denominator of 1 au or 627.5 kcal mol^{-1}, one gets $56.339^2/627.5 = 5.058$ kcal mol^{-1}. This must still be multiplied by the 5p character of these molecular orbitals, and corrections for jj vs. LS coupling. Against this order-of-magnitude estimate, the value of 1.33 kcal mol^{-1} is smallish, but not absurd. For this type of reasoning, see: P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

[26] F. Neese, *ORCA* **2009**, University of Bonn, Bonn, Germany.

[27] A. A. Granovsky, *J. Chem. Phys.* **2011**, *134*, 214113.

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