

## SmF<sub>6</sub><sup>4-</sup> CONFORMATION CAUSED BY 5d–2p ORBITAL INTERACTIONS

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**Abstract**—Despite having almost equivalent sizes, Sm<sup>2+</sup> and Sr<sup>2+</sup> prefer opposite conformations if coordinated by six F<sup>-</sup> ligands. Using qualitative molecular orbital calculations, we find that the disparity originates from different amounts of metal *d* level bonding participation which is greater for Sm<sup>2+</sup> than for Sr<sup>2+</sup>. The influences of ligand repulsion, the participation of the 4*f* orbitals of Sm<sup>2+</sup>, and relativistic effects are insignificant. We emphasize the crucial importance of covalency in an essentially ionic system.

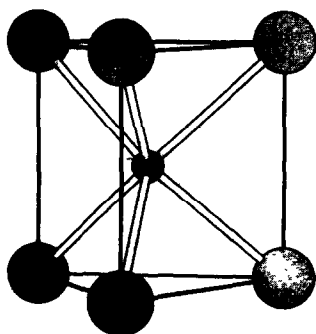
**Keywords:** Molecular orbital calculation, conformational difference, ionicity vs covalency, *d* level participation.

Most structural discussions within crystal chemistry are still based on three classic bonding paradigms. Interpretations are given in terms of packing considerations via ionic radii [1], bond length–bond strength recipes [2], as well as calculations of purely electrostatic interactions between fictively charged particles [3]. Despite the large number of persuasive references, in particular those dealing with highly ionic materials, the complete renunciation of wave mechanics will, at some point, lead to problems in understanding. Here is one example.

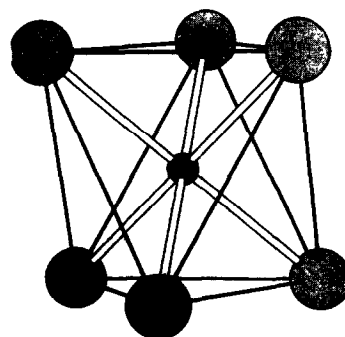
The crystal structure of the recently discovered phase LiSmAlF<sub>6</sub> [4] contains the SmF<sub>6</sub><sup>4-</sup> complex anion, geometrically related to an ideal *D*<sub>3h</sub> trigonal prism [5] (see Sketch 1). This was unexpected since the well-known crystal structure of LiSrAlF<sub>6</sub> [6] shows the presence of a corresponding SrF<sub>6</sub><sup>4-</sup> unit with perfect *D*<sub>3d</sub> symmetry [7] (see Sketch 2). Why the great difference in geometry? It cannot be explained by size effects [8] because the difference in metal–F bond lengths is only 1.5%, corresponding to the tiny 4 pm

difference in cation radii [1]. Remarkably, Madelung energy calculations predict the LiSrAlF<sub>6</sub> structure type to be *more* stable than the LiSmAlF<sub>6</sub> structure type by approximately 25 kJ mol<sup>-1</sup> [9], i.e. all divalent cations with sizes close or equal to Sm<sup>2+</sup> or Sr<sup>2+</sup> should, if coordinated by six F<sup>-</sup> ligands, crystallize in *D*<sub>3d</sub> (2) instead of *D*<sub>3h</sub> (1) point symmetry, in clear conflict with observation. *With only classical arguments at hand, SmF<sub>6</sub><sup>4-</sup> should have no right to adapt its actual structure.*

However, the key to the above puzzle is easy. A simple LCAO molecular orbital method (extended Hückel theory) based on sophisticated atomic data [10] reproduces the correct geometries. To achieve the most reliable relative energies and to address the high degree of ionicity, MO calculations including charge iteration for on-site Hamiltonian matrix elements [11, 12] were performed for the complex anions, stepwise twisting them from *D*<sub>3h</sub> to *D*<sub>3d</sub> geometry. As a result (see Fig. 1), covalent bonding contributions would favor *both* SmF<sub>6</sub><sup>4-</sup> by 32.3 kJ mol<sup>-1</sup> and SrF<sub>6</sub><sup>4-</sup>



Sketch 1



Sketch 2

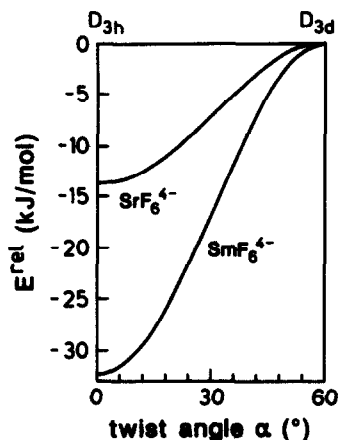


Fig. 1. Relative total energies of  $\text{SmF}_6^{4-}$  and  $\text{SrF}_6^{4-}$  while moving between  $D_{3h}$  (left) and  $D_{3d}$  (right) symmetry.

by  $13.7 \text{ kJ mol}^{-1}$  to adopt  $D_{3h}$  symmetry. To our surprise, this finding even stands for *quantitative* agreement with experiment, despite the crude approximations employed. Thus, taking the electrostatic MAPLE considerations into account,  $D_{3h}$  is allowed for  $\text{SmF}_6^{4-}$  since covalency is obviously overcompensating the Madelung energy difference by  $7 \text{ kJ mol}^{-1}$  [13], in contrast to  $\text{SrF}_6^{4-}$  whose  $D_{3h}$  stabilization by covalent contributions is too small by  $11 \text{ kJ mol}^{-1}$ .

It is clear that, in principle, the external Madelung field, taken into account by us only as an *additional* contribution to the total energy, may also slightly shift the orbital energies localized on metal (Sm, Sr) and nonmetal (F) atoms, thus changing the difference in covalent energies. In other words, covalency and electrostatics cannot be strictly separated from each other. But the detailed comparison between the electrostatic potentials at the Sm and Sr atoms in both phases shows them to be different by only 5.2%, whereas the difference for F atoms is practically nonexistent (0.2%). This is the consequence of the identical ionic host environment for both complex anions. Because of this, any additional shift in covalent energies arising from the non-zero Madelung field will have the same effect for both  $\text{SmF}_6^{4-}$  and  $\text{SrF}_6^{4-}$ , giving rise to a new relative zero point in energy without changing the qualitative result presented above.

The trend for the relative energies in Fig. 1 is paralleled by the trend in the absolute hardnesses [14] of  $\text{SmF}_6^{4-}$  and  $\text{SrF}_6^{4-}$ , serving as resistance indicators of the species against electronic perturbations. In  $D_{3h}$  these numbers were found to be 4.17 and 6.46 eV, respectively, higher by 90 and 20 meV than those in  $D_{3d}$  geometry. In other words, covalent bonding increases the hardnesses and strengthens the

electronic resistances of the complex anions more in  $D_{3h}$  than in  $D_{3d}$ . Interestingly, the change in atomic contributions to the absolute hardnesses, the so-called gross atomic reactivity increments [15], is one order of magnitude larger for  $\text{Sm}^{2+}$  and  $\text{Sr}^{2+}$  than for  $\text{F}^-$  while going from  $D_{3d}$  to  $D_{3h}$  symmetry. In Pearson's acid-base language, it is essentially the metals becoming *harder* in  $D_{3h}$  in order to match the very hard fluorine ligands.

Examining the reason for the covalent preference of  $D_{3h}$  symmetry, it is reasonable to focus first on the influences of the coordinating  $\text{F}^-$ . We note that the stepwise Walsh calculations were performed by twisting one of the  $\text{F}_3$  triangles around the  $C_3$  axis, safely keeping all metal-F bond distances constant and treating the  $\text{F}_3$  triangles as rigid groups. In the solid, such a twisting *only* affects the first coordination sphere of Sm and Sr since it is equivalent to a twisting of two neighboring  $\text{LiAlF}_6$  slabs. Within the complex anions themselves, covalent ligand repulsion is *not* very important, in good agreement with a guess based on tabulated Van der Waals radii [16]. F-F distances exceed twice the latter by more than 40 pm, and, consequently, there are vanishingly small F-F overlap populations between triangles, practically unaffected by a specific geometry.

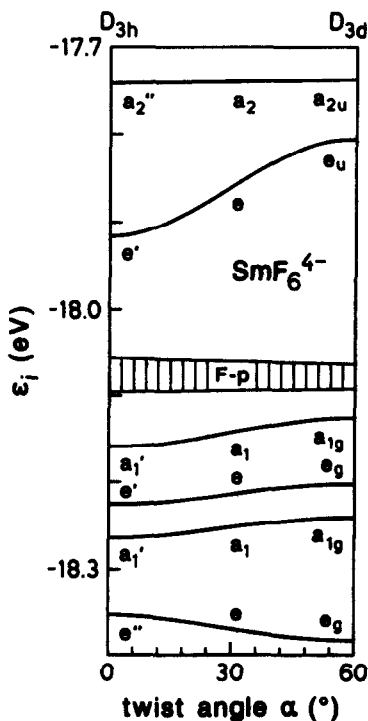


Fig. 2. Walsh diagram of  $\text{SmF}_6^{4-}$ . The top molecular orbital  $a_2$  is the HOMO. The labelling between  $D_{3h}$  (left) and  $D_{3d}$  (right) symmetry corresponds to point group symmetry  $D_3$  which is retained during the geometrical twist.

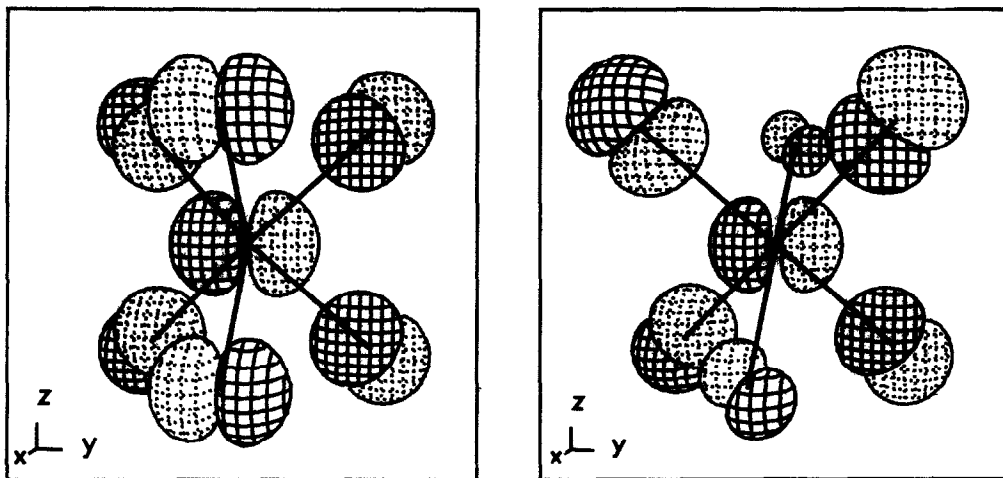


Fig. 3. Molecular orbitals  $e'$  ( $D_{3h}$ , left) and  $e_u$  ( $D_{3d}$ , right) of  $\text{SmF}_6^{4-}$ . The surface value of the wave function is 0.02. For clarity, atomic orbital contributions have been contracted by a factor of 1.5.

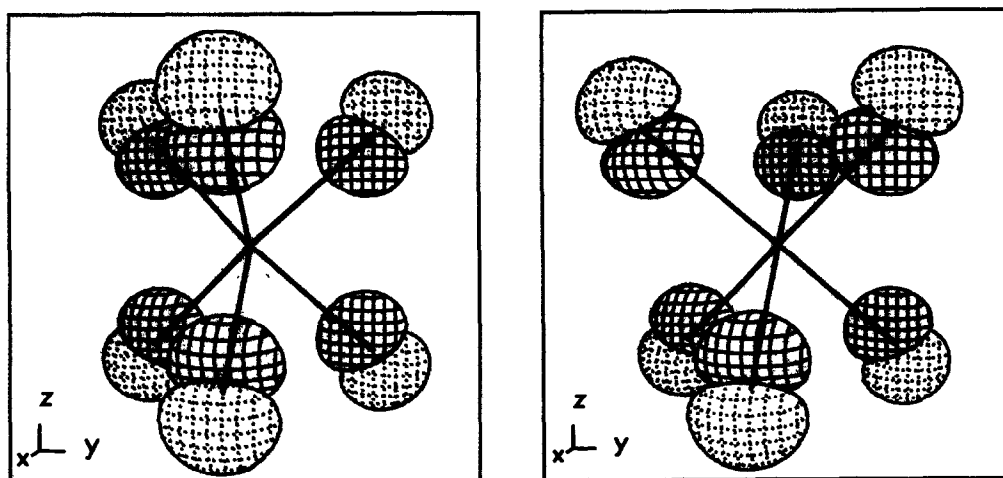


Fig. 4. As in Fig. 3, but showing molecular orbitals  $a_1'$  ( $D_{3h}$ , left) and  $a_{1g}$  ( $D_{3d}$ , right).

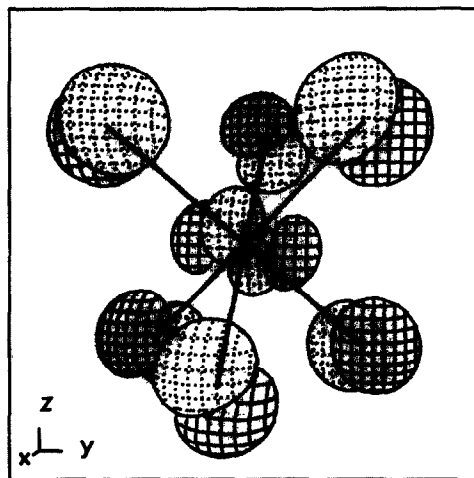
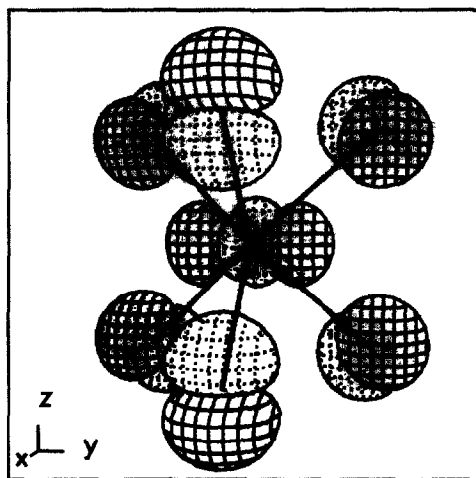


Fig. 5. As in Fig. 3, but showing molecular orbitals  $e'$  ( $D_{3h}$ , left) and  $e_g$  ( $D_{3d}$ , right).

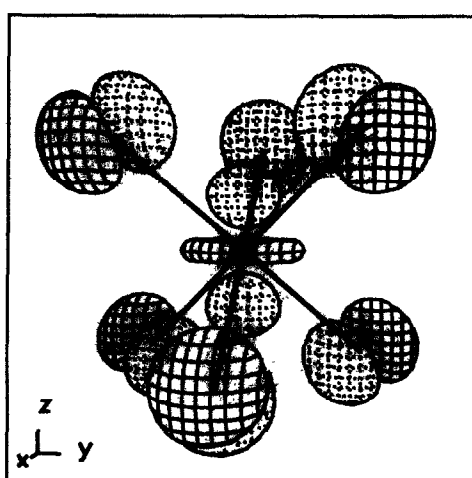
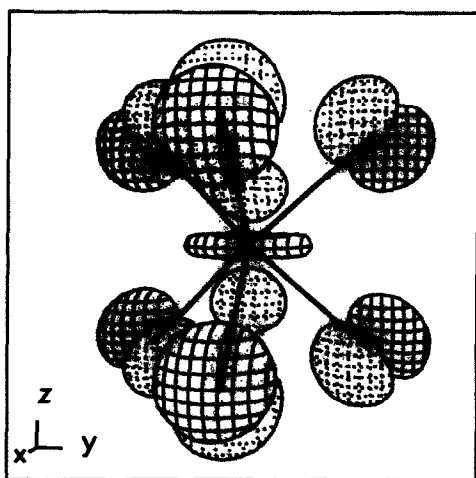


Fig. 6. As in Fig. 3, but showing molecular orbitals  $a_1'$  ( $D_{3h}$ , left) and  $a_{1g}$  ( $D_{3d}$ , right).

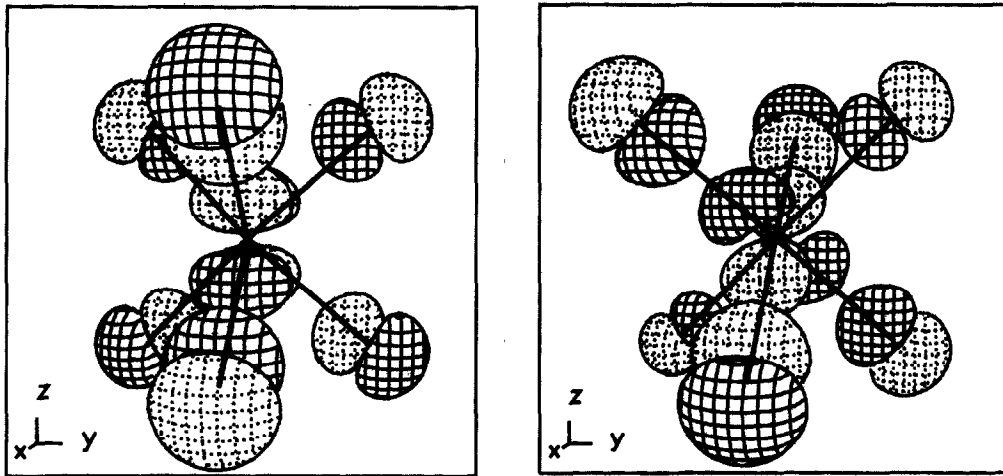


Fig. 7. As in Fig. 3, but showing molecular orbitals  $e''$  ( $D_{3h}$ , left) and  $e_g$  ( $D_{3d}$ , right).



More quantitatively, a numerical energy partitioning shows that covalent F–F interactions between triangles *alone* would favor  $D_{3d}$  with respect to  $D_{3h}$  geometry by only about 1 kJ mol<sup>-1</sup> (SmF<sub>6</sub><sup>4-</sup>) and 4 kJ mol<sup>-1</sup> (SrF<sub>6</sub><sup>4-</sup>).

Moreover, the effect found does *not*, as one might anticipate, originate from the inclusion of 4*f* orbitals on Sm; downfolding them led to no appreciable change in relative energies. Consequently, 4*f* orbitals were omitted in the sequel, making the MO scheme more transparent. Also, corresponding calculations for SmF<sub>6</sub><sup>4-</sup> and SrF<sub>6</sub><sup>4-</sup> based on relativistic atomic data [17, 18] did not show any significant differences.

We can *understand* why these anions adopt their respective conformations by looking at a Walsh diagram of the HOMO region of SmF<sub>6</sub><sup>4-</sup> (see Fig. 2), giving a deeper insight within the one-electron approximation. Contour plots of the corresponding wave functions [19] are depicted in Figs 3–7. The HOMO of  $a_2$  symmetry in  $D_3$  has only a tiny amount of Sm  $p_z$  character and is practically unaffected by the geometrical twist. The doubly degenerate  $e$  wave function around -17.85 eV has some Sm contribution, composed of 56%  $d_{x^2-y^2,xy}$  character and 44%  $p_{x,y}$  character in  $D_{3h}$ . But, while moving to  $D_{3d}$  symmetry, all  $d$  character is lost, raising its energy (see Fig. 3). Below  $e$ , there is a region of nine molecular orbitals which are almost completely centered on the F ligands. Note that their dispersion stays practically constant over the whole geometrical range, a clear sign for small ligand–ligand interaction. One of the two exceptions is found in the ligand combination  $a_1$  around -18.15 eV, composed of  $p$  hybrids forming weakly *bonding* interactions in  $D_{3h}$  which are reduced in  $D_{3d}$  (see Fig. 4).

There is considerable  $d$  character in the molecular orbital  $e$  below -18.1 eV. Specifically, we find the Sm contribution to consist of 98%  $d_{x^2-y^2,xy}$  character in  $e'$ , having some overlap with F  $p$  hybrids. The bonding interaction is weakened in  $e_g$  although 20%  $d_{xz,yz}$  character is mixed in to address the changing geometry of the upper F<sub>3</sub> triangle, depicted in Fig. 5. The  $a'_1$  wave function around -18.25 eV is the second example of weak ligand–ligand interaction. There is a little Sm  $d_{z^2}$  mixing in, but the small dispersion, favoring  $D_{3h}$  geometry, is due to the better ligand  $p$  hybrid overlap (see Fig. 6). Finally, we have a molecular orbital  $e$  below -18.35 eV, the only one favoring  $D_{3d}$  to  $D_{3h}$  symmetry. Having a look at Fig. 7, the Sm contribution in  $e''$  appears to consist of almost only a  $d_{xz}$  orbital, whereas there is roughly 23%  $d_{x^2-y^2}$  character in the  $e_g$  wave function. So there is an interesting build-up of four  $\sigma$  orbital lobe interactions in  $D_{3d}$  which is stronger than the two  $\sigma$

interactions and the two approximate  $\pi$ -like interactions in  $D_{3h}$ .

In total, near the frontier levels there are two singly degenerate and two doubly degenerate molecular orbitals favoring  $D_{3h}$  and only one doubly degenerate wave function favoring  $D_{3d}$ . Even including the core-like Sm 5*p* levels (not shown here) which tend to prefer  $D_{3d}$  geometry, results in the above mentioned net preference of 32.3 kJ mol<sup>-1</sup> for  $D_{3h}$ . Of course, the qualitative MO reasoning done so far could equally well be applied for SrF<sub>6</sub><sup>4-</sup>. However, and this is the crucial difference, *the participation of metal-centered d levels is much stronger for Sm than for Sr*. This can be estimated either from the dispersion of metal  $d$  levels in SmF<sub>6</sub><sup>4-</sup> (about 0.6 eV) and SrF<sub>6</sub><sup>4-</sup> (about 0.15 eV) or from the  $d$  occupation of Sm (about 0.55 electrons) and Sr (about 0.31 electrons) within the complex anions [20]. Thus, the higher the degree of  $d$  orbital participation, the stronger the splitting of the one-electron eigenvalues, the greater the favoring of  $D_{3h}$  geometry, in good agreement with related studies [21].

Taking only the spatial extent of the  $d$  wave functions of Sm (considerably contracted) and Sr (more diffuse) into account (see [11] for Slater exponents), one would probably have expected an opposite trend for Sm<sup>2+</sup> and Sr<sup>2+</sup>, arguing with an overlap criterion. However, *here the effect of energy resonance between p orbitals of F and d orbitals on the metal gains the upper hand*; the difference in energy between the metal  $d$  and the F  $p$  orbitals is roughly 8 eV for SmF<sub>6</sub><sup>4-</sup> and more than 12 eV for SrF<sub>6</sub><sup>4-</sup>. Both the stronger contraction and lower energy of Sm  $d$  levels may be interpreted as resulting from the incomplete shielding of the nucleus by “4*f* electrons” [22]. This atomic characteristic may lead to the observed Sm-5*d*-F-2*p* interaction and, if there is practically no ligand–ligand repulsion, to  $D_{3h}$  geometry, despite the fact that there is a smaller electrostatic Madelung energy term [23].

In conclusion, we have shown the strong impact of covalency on chemical bonding within a complex ionic unit. Covalency must be taken into account to achieve understanding of conformations. We hope to stimulate more accurate studies using reliable pseudopotentials and/or density-functional techniques.

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- The one-electron Hamiltonian used is that of charge iterated extended Hückel theory [24]. The starting values for the on-site Hamiltonian matrix elements were approximated by atomic orbital energies from numerical Hartree-Fock and Hartree-Fock-Dirac calculations [25]. The only exception is the Sm 5d level which comes from the calculation of the f to d excited configuration 4f<sup>2</sup>6s<sup>2</sup>5d<sup>1</sup> [26]. Exponents of Slater-type orbitals had been fitted to numerical atomic wavefunctions [25] by Pykkö and Lohr. A complete set of both non-relativistic and relativistic parameters has been compiled by them in [18]. To minimize counterintuitive orbital mixing within the minimal basis set, off-site Hamiltonian matrix elements were computed according to the weighted WH-formula of Ammeter *et al.* [27].
- Charge iterations were performed according to the approximations of Cusachs and Reynolds [28, 29]. The self-consistent energy parameters (eV) were typically achieved within 15 cycles. For SmF<sub>6</sub><sup>2-</sup> in D<sub>3h</sub> (D<sub>3d</sub>) symmetry they are: Sm 6s: -7.257 (-7.338), Sm 5p: -31.341 (-31.422), Sm 5d: -9.961 (-10.042), F 2s: -41.016 (-41.003), F 2p: -18.096 (-18.083). For SrF<sub>6</sub><sup>2-</sup> we arrive at Sr 5s: -7.459 (-7.478), Sr 5p: -5.902 (-5.921), Sr 4d: -5.782 (-5.801), F 2s: -41.023 (-41.020), F 2p: -18.103 (-18.100). The Slater orbital coefficients [18] are: Sm 6s: 1.331, Sm 5p: 3.199, Sm 5d: 2.122, Sr 5s: 1.187, Sr 5p: 1.000, Sr 4d: 1.694; F 2s: 2.497, F 2p: 2.305.
- The gross atomic charges for SmF<sub>6</sub><sup>2-</sup> in D<sub>3h</sub> (D<sub>3d</sub>) symmetry are: Sm: 1.321 (1.361), F: -0.887 (-0.894). For SrF<sub>6</sub><sup>2-</sup> we find: Sr: 1.302 (1.311), F: -0.884 (-0.885). Without charge iteration, the metal atoms are roughly 0.3 higher charged.
- However, the slight twist of SmF<sub>6</sub><sup>2-</sup> away from D<sub>3h</sub> symmetry (see [5]) is not reproduced. This failure may be due to packing effects in the solid or, more likely, to the crude approximations of the present approach.
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