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The $[\text{U}_2\text{F}_{12}]^{2-}$ anion of $\text{Sr}[\text{U}_2\text{F}_{12}]$.**

Benjamin Scheibe, Clemens Pietzonka, Otto Mustonen, Maarit Karppinen, Antti J. Karttunen, Mihail Atanasov, Frank Neese, Matthias Conrad and Florian Kraus*

Dedicated to Professor Wolfgang Schnick on the occasion of his 60th birthday

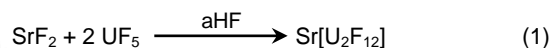
Abstract: The D_{2h} -symmetric dinuclear complex anion $[\text{U}_2\text{F}_{12}]^{2-}$ of pastel green $\text{Sr}[\text{U}_2\text{F}_{12}]$ shows a hitherto unknown structural feature: The coordination polyhedra around the U atoms are edge-linked monocapped trigonal prisms, the U^{V} atoms are therefore seven-coordinated. This leads to a U–U distance of 3.8913(6) Å. A weak $\text{U}^{\text{V}}\text{–U}^{\text{V}}$ interaction is observed for the dinuclear $[\text{U}_2\text{F}_{12}]^{2-}$ complex and described by the antiferromagnetic exchange J_{exp} of circa -29.9 cm^{-1} . The crystalline compound can be easily prepared from SrF_2 and $\beta\text{-UF}_5$ in anhydrous hydrogen fluoride (aHF) at room temperature. It was studied by means of single crystal X-ray diffraction, IR, Raman and UV/VIS spectroscopy, magnetic measurements, and by molecular as well as by solid state quantum chemical calculations.

Compounds containing a central atom with coordination number seven may exhibit in principle three different idealized geometric ligand arrangements.^[1–3] These are the monocapped octahedron (C_{3v} , 1/3/3 arrangement), the monocapped trigonal prism (C_{2v} , 1/4/2 arrangement) and the pentagonal bipyramid (D_{5h} , 1/5/1 arrangement). Binary main group species seem to prefer the 1/5/1 arrangement, which was reported for $[\text{XeF}_7]^+$, IF_7 , $[\text{TeF}_7]^-$ and $[\text{SbF}_7]^{2-}$, but also some transition metal compounds show this motif, like ReF_7 , $[\text{Re}(\text{CN})_7]^{3-}$ and $[\text{U}(\text{N}_3)_7]^{3-}$.^[4–9] The 1/4/2 arrangement is observed for the anions $[\text{NbF}_7]^{2-}$, $[\text{TaF}_7]^{2-}$, $[\text{Nb}(\text{N}_3)_7]^{2-}$ and $[\text{Ta}(\text{N}_3)_7]^{2-}$, but also by $[\text{XeF}_7]^-$ in $[\text{Xe}_2\text{F}_{13}]^-$.^[10–12] The 1/3/3 arrangement is featured in the complex anions containing homoleptic ligands $[\text{MoF}_7]^-$, $[\text{WF}_7]^-$, $[\text{Mo}(\text{CH}_3)_7]^-$ and $[\text{U}(\text{N}_3)_7]^{3-}$.^[9,13,14]

To the best of our knowledge, there are so far only two reported cases with condensed homoleptic complex anions exhibiting a coordination number of seven for their central atoms. One being the $[\text{Zr}_2\text{F}_{12}]^{4-}$ anion (C_i symmetry) in $[\text{Co}(\text{en})_3]_2[\text{Zr}_2\text{F}_{12}][\text{SiF}_6]\cdot 4\text{H}_2\text{O}$, which can be described as a distorted edge-linked pentagonal

bipyramid.^[15] The other case can be described as an association of two $[\text{IF}_6]^-$ anions in $[\text{N}(\text{Me})_4][\text{IF}_6]$, forming a $[\text{I}_2\text{F}_{12}]^{2-}$ anion, which consists of edge-sharing monocapped trigonal prisms (C_i symmetry). However, the I–(μ -F) distances are very different due to the sterically active lonepairs of the I atoms.^[16] An example for a compound with a condensed heteroleptic complex anion and coordination number seven for the central atoms is $\text{K}[\text{HF}_2]\cdot 2\text{IF}_5$, where an infinite chain structure is observed in which HF_2^- ions are bridged by IF_5 molecules.^[17]

Herein we describe the synthesis and properties of the salt $\text{Sr}[\text{U}_2\text{F}_{12}]$, strontium di- μ -fluorido-decafluorodiduranate(V). The bulk phase of the compound appears pastel green, for a photograph see Figure S1, while single crystals are yellowish. It can be synthesized from the reaction of SrF_2 and $\beta\text{-UF}_5$ in anhydrous hydrogen fluoride (aHF) at room temperature, see Equation 1 and the SI for details. During the course of the synthesis the HF solution turns bluish, which is characteristic for the solvated $[\text{UF}_6]^-$ ion.^[18] The title compound was always obtained together with a small percentage (1–3 %) of crystalline, paramagnetic $\text{Sr}[\text{UF}_5(\text{FHF})_2]$ as an impurity. This compound will be reported elsewhere.



However, unlike other hexafluoroduranates(V), such as $\text{NO}[\text{UF}_6]$ or KUF_6 , which contain isolated $[\text{UF}_6]^-$ ions or more complex anionic structure motifs, the title compound $\text{Sr}[\text{U}_2\text{F}_{12}]$ contains the highly symmetric di- μ -fluorido-decafluorodiduranate(V) anion, $[\text{U}_2\text{F}_{12}]^{2-}$ (Figure 1), in its solid state structure as evidenced by single crystal X-ray diffraction.^[19–21] The compound crystallizes in the tetragonal space group type $I4/mcm$ with $a = 9.2149(13)$, $c = 11.361(2)$ Å, $V = 964.7(3)$ Å³, and $Z = 4$ at $T = 100$ K. Further crystallographic details are available from Table S1.

The anion can be formally described as a dimer of $[\text{UF}_6]^-$ ions. The coordination sphere around each U atom is then best described as a monocapped trigonal prism with C_{2v} symmetry for these formal “ UF_7 ” subunits. Linkage via the edge (see Figure 1,

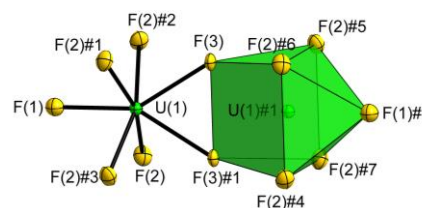


Figure 1. A section of the crystal structure of $\text{Sr}[\text{U}_2\text{F}_{12}]$ showing the $[\text{U}_2\text{F}_{12}]^{2-}$ anion. The green coordination polyhedron highlights the first coordination sphere of a uranium atom. Displacement ellipsoids are shown at 70% probability level at 100 K. Selected atomic distances in [Å] and angles in [°]: U(1)–F(1) 2.079(10), U(1)–F(2) 2.081(4), U(1)–F(3) 2.281(4), U(1)–U(1)#1 3.8913(10), F(1)–U(1)–F(2) 81.23(12), F(1)–U(1)–F(3) 148.54(17), F(2)–U(1)–F(2)#1 162.5(2), F(3)–U(1)–F(3)#1 62.9(3), U(1)–F(3)–U(1)#1 117.1(3). See the SI and CSD-433765 for crystallographic details.

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the F(3) atoms) leads to the $[\text{U}_2\text{F}_{12}]^{2-}$ anion with ideal D_{2h} symmetry. Their arrangement in the crystal structure is shown in Figure S2.

To the best of our knowledge, such a coordination polyhedron has not been observed for complex anions containing homoleptic ligands, previously. Furthermore, the anion is the first example of a dinuclear fluoridouranate(V) complex. There are three crystallographically different kinds of fluoride ligands, of which F(1) and F(2) are terminal ligands with almost equal U–F distances of 2.079(10) and 2.081(4) Å, respectively. Such distances are in good agreement with the literature.^[19,22] In comparison, the μ -bridging fluoride ligand F(3) shows an increased distance to the U atoms with 2.281(4) Å, which is expected due to its higher coordination number. With 3.8913(10) Å, the U–U distance within the dinuclear complex is small for a U^{V} fluoride compound. In comparison, α - UF_5 shows a U–U interchain distance of circa 4.5 Å and β - UF_5 shows U–U distances of 4.5 and 4.6 Å.^[23,24]

If the centers of gravity of the $[\text{U}_2\text{F}_{12}]^{2-}$ anions are thought of as an atom (B), then, together with the Sr atoms (A), a simple AB structure type results, where each of the A and B atoms shows a distorted cubic coordination sphere. Therefore, $\text{Sr}[\text{U}_2\text{F}_{12}]$ can be derived from the simple CsCl structure type. The crystallographic relation is shown in Scheme S1. The surrounding of the Sr atoms by F atoms is square-antiprismatic and is shown in Figure S3.

Quantum chemical calculations using a well-established protocol within the ab-initio ligand field theory implemented in the program ORCA were carried out to elucidate the antibonding effect of the F^- ligands on the 5f orbitals of the uranium atoms, which also leads to the ligand field splitting and gives rise to the f–f absorption spectra.^[25–27] From a chemical perspective this can be done by using the angular overlap model (AOM), which defines the antibonding effects on f-orbitals for well aligned orbitals of the U and F atoms with overlap of σ - and π -symmetry (see SI for details).^[28,29] These effects are quantified by the AOM parameters e_σ and e_π , which depend on the nature of the ligand and the metal–ligand bond length. The trend of the U–F distances correlates with

the computed AOM parameters for the three inequivalent fluoride donors, which classify the relative σ - and π -donor strength – the F(1) atom being the strongest, the F(2) atom weaker and the μ -F(3) atom the weakest σ - and π -donor towards the uranium atom, see Figure 2. Population analyses, carried out for the bulk phase of $\text{Sr}[\text{U}_2\text{F}_{12}]$ using quantum chemical solid state calculations within the CRYSTAL 14 program package on the PBE0-TZVP level of theory (see the SI),^[44,45] also suggest such a trend with the μ -F(3) atoms being the most ionic ones.

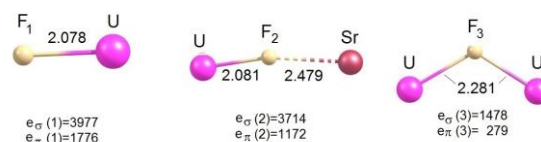


Figure 2. σ - and π -donor character of the three types of fluoride ligands as given by the AOM parameters e_σ and e_π (in cm^{-1}) and their correlation with the number and strength of their interactions with their nearest neighbors in the crystal structure of $\text{Sr}[\text{U}_2\text{F}_{12}]$.

The vibrational spectra of the compound show three different regions: At approximately 610 cm^{-1} the symmetric U–F stretching modes, at circa 450 cm^{-1} the asymmetric U–F stretching modes and at circa 270 cm^{-1} the F–U–F deformation modes are observed. Using quantum chemical solid state calculations within the CRYSTAL14 program package, the experimentally obtained Raman and IR spectra of $\text{Sr}[\text{U}_2\text{F}_{12}]$ were nicely reproduced and allowed the assignment of the observed bands (the spectra and irreducible representations are given in the SI). Overall, the observed bands are in good agreement with other hexafluoridouranate(V) salts.^[19,20]

Additionally, we were interested in the absorption spectrum of the highly symmetric $[\text{U}_2\text{F}_{12}]^{2-}$ anion, in which the uranium(V) atoms have the electron configuration $[\text{Rn}]5f^1$, where on-site f–f electron interaction is absent and thus only a few absorptions can be observed.^[21,30] We recorded the solid state absorption spectrum and performed Complete Active Space Self-Consistent Field

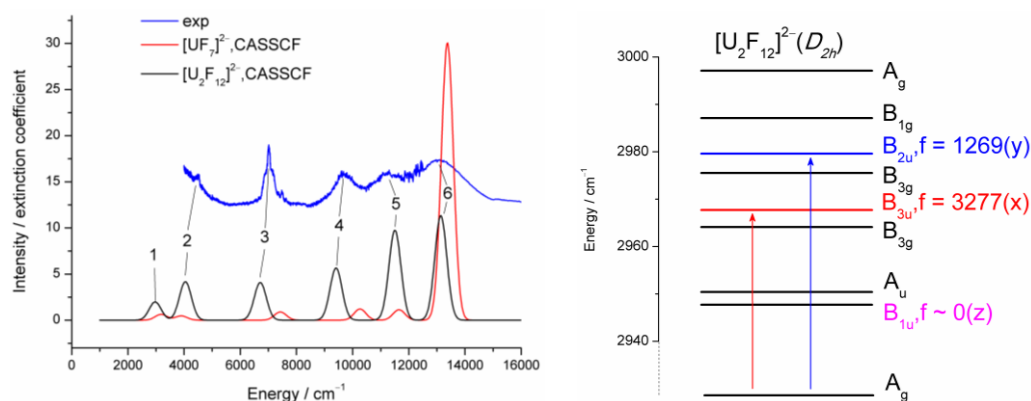


Figure 3. Left: Experimental (blue) and simulated (CASSCF, Gaussians with half width at half maximum of 500 cm^{-1} , black lines) absorption spectra due to f–f transitions of $[\text{U}_2\text{F}_{12}]^{2-}$ and their comparison with the computed spectrum of the formal $[\text{UF}_7]^{2-}$ subunit with the same geometry and charge as the dimer (red lines). Based on CASSCF calculations (see SI for further details) assignment of the six parity allowed transitions 1, 2, 3, 4, 5 and 6 are assigned as $A_g \rightarrow B_{2u}$, B_{3u} ; $A_g \rightarrow B_{1u}$, B_{2u} , B_{3u} ; $A_g \rightarrow B_{1u}$, B_{2u} , B_{3u} ; $A_g \rightarrow B_{1u}$, B_{2u} , B_{3u} and $A_g \rightarrow B_{1u}$, B_{2u} , B_{3u} , respectively. Symmetry notations refer to spin-orbit wavefunctions classified according to the irreducible representations of the D_{2h} point group. Right: Eight possible f–f transitions of $[\text{U}_2\text{F}_{12}]^{2-}$ arising from the coupling of the lowest two I_3 electronic states within each $[\text{UF}_7]^{2-}$ subunit with respective irreducible representations from CASSCF calculations and additionally the oscillator strengths f are shown.

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(CASSCF) calculations for the $[\text{U}_2\text{F}_{12}]^{2-}$ anion and a hypothetical $[\text{UF}_7]^{2-}$ subunit, see Figure 3. The calculations for the $[\text{U}_2\text{F}_{12}]^{2-}$ anion were carried out for D_{2h} symmetry and are in excellent agreement with the recorded spectrum regarding relative intensities and computed energies. Upon comparison of the two calculated anions, the f-f transitions for the hypothetical $[\text{UF}_7]^{2-}$ anion change strongly both in energy and intensity when going to the dinuclear $[\text{U}_2\text{F}_{12}]^{2-}$ anion, showing the effect of f¹-f¹ pair interactions on the f-f transitions. Thus, from the eight possible f-f excitations stemming from the lowest $\Gamma_5 \rightarrow \Gamma_5$ excitation within each $[\text{UF}_7]^{2-}$ subunit only two, $A_g \rightarrow B_{3u}$ and $A_g \rightarrow B_{2u}$, are computed to appear with an appreciable intensity (Figure 3, right). For the $[\text{U}_2\text{F}_{12}]^{2-}$ anion we calculated eight possible f-f transitions, of which six could be observed in the spectrum. Comparing the spectrum with the spectra of $\text{Cs}[\text{UF}_6]$, $\text{NO}[\text{UF}_6]$ or RbUF_6 , the distinctive ligand field effects of the surroundings of the U^{V} atoms become visible.^[19,31,32] This is characteristic for the actinides, where ligand field splitting and spin-orbit coupling can be in the same order of magnitude.^[21]

There are scarce reports on the magnetic properties of homoleptic uranium(V) fluoro complexes.^[19,33–36] However, several heteroleptic dinuclear uranium(V) complexes have been magnetically characterized and most of them show antiferromagnetic coupling with susceptibility maxima in the range of 5 to 70 K.^[37–42] To the best of our knowledge, no magnetic data for a homoleptic dinuclear uranium(V) complex, such as in $\text{Sr}[\text{U}_2\text{F}_{12}]$, have been reported as yet. We carried out DC magnetic measurements on $\text{Sr}[\text{U}_2\text{F}_{12}]$ and also computed data for the $[\text{U}_2\text{F}_{12}]^{2-}$ anion with the CASSCF and N-Electron Valence Perturbation Theory to second order (NEVPT2) methods, see Figure 4 (left) for χ versus T data (additional details are given in the SI, for field dependent magnetic data see Figure S4). The paramagnetic $\text{Sr}[\text{UF}_5(\text{FHF})_2]$ impurity leads to an increase of the molar susceptibility at temperatures below 5 K. The compound $\text{Sr}[\text{U}_2\text{F}_{12}]$ shows molecular antiferromagnetic behavior, with a maximum of the molar susceptibility at approximately $T_{\text{max}} = 26$ K. This temperature should not be regarded as a Néel temperature, as the $[\text{U}_2\text{F}_{12}]^{2-}$ anions are separated by the Sr cations which results in a very large inter-dimer separation with next-nearest $\text{U}\cdots\text{U}$ distances of 4.9672(7) Å. This large separation and the very

ionic nature of the $\text{Sr}\cdots\text{F}$ bond causes only very weak inter-dimer interactions.

The magnetic data were fitted with a modified Heisenberg-Dirac-van-Vleck model, in which the paramagnetic impurity was considered (see Figure S7 and the SI for further details). The exchange coupling parameter J_{exp} , which indicates the strength of the antiferromagnetic coupling of the U(V) atoms, is determined as -29.86 cm⁻¹, whereas the CASSCF calculations lead to -10.74 cm⁻¹ and the NEVPT2 calculations to -38.22 cm⁻¹.

Furthermore, temperature independent paramagnetism (van Vleck paramagnetism) is observed for $\text{Sr}[\text{U}_2\text{F}_{12}]$, and this behavior is also predicted by our calculations. Field-dependent measurements at 15 K yield a molar susceptibility of $3.8300(5) \cdot 10^{-3}$ cm³·mol⁻¹ for $\text{Sr}[\text{U}_2\text{F}_{12}]$. In the temperature region between 50 and 300 K, the data was fitted with a modified Curie-Weiss law (Figure S5) resulting in an effective magnetic moment of $1.02(1)$ μ_{B} per uranium atom and a Weiss constant of $-32(2)$ K, which also demonstrates the antiferromagnetic interaction of the U(V) atoms. In Figure 4 (right) the temperature dependence of the effective magnetic moment per $\text{Sr}[\text{U}_2\text{F}_{12}]$ formula unit is shown. A strong influence of the temperature below 50 K can be observed, while a linear course of the data above 100 K is found. The effective magnetic moment approaches a non-zero value at very low temperatures, which is common for uranium(III) and (V) compounds.^[33]

In general, the magnetic exchange J depends on the overlap of the magnetic orbitals on the U^{V} centers which is controlled by the U–L–U angle (α) and the nature of the bridging ligand L . For angles close to 90° this overlap is weak resulting in a ferromagnetic exchange. For the complex reported here a significant deviation of the U–F–U bridging angle from 90° with $\alpha = 117.1(3)^\circ$ is observed. This results in a significant overlap and leads to antiferromagnetic exchange as Figure 5 shows for the lowest pair of singly occupied molecular orbitals – the lowest MO, being an almost non-bonding orbital, and the antibonding one which is 2304 cm⁻¹ higher in energy. Equation 2 shows the approximation of J by the antiferromagnetic contribution J_{af} only. As an approximation, the ferromagnetic contribution to J was neglected as the deviation of α from 90° is very large.^[43]

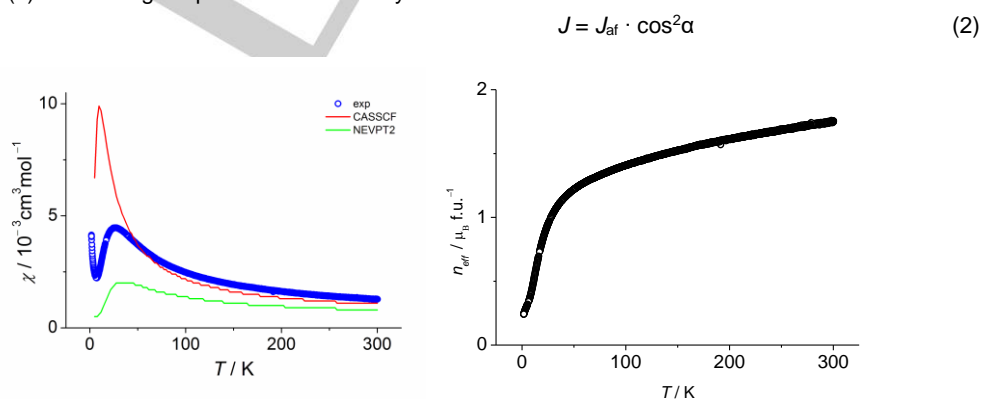


Figure 4. Left: χ vs. T data of $\text{Sr}[\text{U}_2\text{F}_{12}]$ at 1 T (blue) and computed data (red: CASSCF; green: NEVPT2) for $[\text{U}_2\text{F}_{12}]^{2-}$. The figure also shows the presence of the paramagnetic impurity of $\text{Sr}[\text{UF}_5(\text{FHF})_2]$, see the ascent below 5 K and the Figures S6 and S8. Right: Temperature dependence of the effective magnetic moment per $\text{Sr}[\text{U}_2\text{F}_{12}]$ formula unit.

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Values of experimentally obtained J_{exp} and calculated $|J_{\text{af}}|$ for other dinuclear U^V complexes with the same bridging topology but with μ -oxido and μ -imido ligands have been compared in Table 1. In order to eliminate the differences of J_{exp} due to the different bridging angles of these complexes, J_{af} has been calculated from the reported J values by normalization with $\cos^2\alpha$. This allows us to compare the $|J_{\text{af}}|$ values and formulate the following sequence of ligands with regards to their super exchange abilities: $O^{2-} > NR_2^- > F^-$. This observed trend is likely due to the higher ionicity of the U–F bond in comparison to a U–N or a U–O bond.

Table 1. Comparison of dinuclear U^V complexes and their calculated (mean) negative J_{af} values given as the modulus of J_{af} . L stands for the μ -bridging atoms F, NR_2^- , and O. The ligand Z is a polypyrrrolic macrocycle.^[40]

U^V complexes	$d(U_1-L) / \text{\AA}$	$d(U_2-L) / \text{\AA}$	$\alpha / ^\circ$	$T_{\text{max}} / \text{K}$	$J_{\text{exp}} / \text{cm}^{-1}$	$ J_{\text{af}} / \text{cm}^{-1}$
$\{[U(\mu-F)F_3]_2\}^{2-}$	2.281(4)	2.281(4)	117.1(3)	26	-29.9	144
$\{[U(\mu-NtBu)_2(l)(tBu_2bpy)]_2\}^{[39]}$	2.067(5) 2.380(5)	2.387(5) 2.078(5)	106.7(2) 106.5(2)	13	-14.4	176
$\{[Me_3SiOUO)_2(Z)]^{[40]}$	2.099(4) 2.098(4)	2.085(4) 2.094(4)	106.3(2) 106.6(2)	17	-33.0	412
$\{[(^{n\text{P}},\text{Me}^e\text{ArO})_3\text{tacn}]U_2(\mu-O)_2\}^{[42]}$	2.206(2)	2.066(2)	109.18(7)	70	-77.8	721

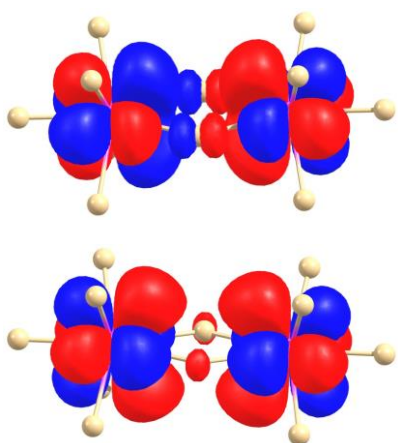


Figure 5. Contour-plot of molecular orbitals for the U–U bonding interaction 2A_g (energy 0 cm^{-1} , bottom) and the U–U antibonding interaction ${}^2B_{1u}$ (energy 2304 cm^{-1}). Contour plots have been constructed using the (hypothetical) one-electron oxidized analogue of $[U_2F_{12}]^{2-}$, i.e. the mixed valence $[U_2F_{12}]$ with the X-ray structure data of the former. The diagram has been constructed using contour isovalues of $0.015 \text{ electron/Bohr}^3$. Color codes: red: positive; blue: negative.

To conclude, we reported on the compound $Sr[U_2F_{12}]$, which contains the highly symmetric and hitherto unknown dinuclear $[U_2F_{12}]^{2-}$ anion. The coordination polyhedra around the U atoms are in the shape of edge-sharing mono-capped trigonal prisms. The different kinds of U–F bonding, with the bridging μ -F atoms being clearly the most ionic ones, could be interpreted within the angular overlap model and with population analyses. The magnetic and spectroscopic properties of $Sr[U_2F_{12}]$ were nicely reproduced and explained utilizing molecular as well as solid state quantum chemical calculations. The $[U_2F_{12}]^{2-}$ anion shows molecular antiferromagnetism caused by the coupling of the $U(V)$ atoms, mediated by the bridging fluorido ligands. Due to the beautiful simplicity of this $[U_2F_{12}]^{2-}$ anion and its D_{2h} symmetry, we

expect it to be the ideal benchmark species for future quantum chemical studies on the U^V – U^V interaction. Investigations of other fluoridouranates(V) with divalent cations, like $Sr[UF_5(FHF)_2]$, are in progress.

Keywords: fluorine • hexafluoridouranate(V) • magnetic properties • quantum chemical calculations • uranium

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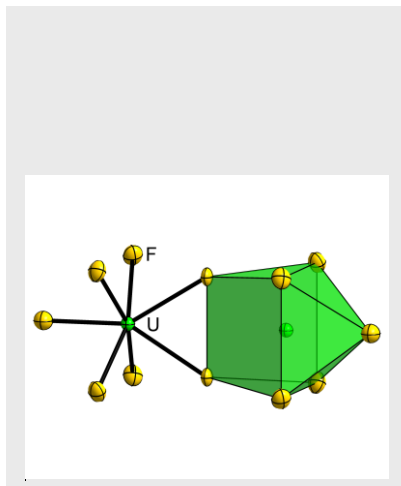
COMMUNICATION

Entry for the Table of Contents

COMMUNICATION

Uranium(V)-Uranium(V) interaction:

The synthesis of $\text{Sr}[\text{U}_2\text{F}_{12}]$ is described. The compound contains the D_{2h} symmetric $[\text{U}_2\text{F}_{12}]^{2-}$ anion, which is the first example of a dinuclear fluoridouranate(V) complex. The spectroscopic and magnetic properties have been studied and could be reproduced by quantum chemical calculations. An antiferromagnetic coupling of the U(V) atoms is observed.



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The $[\text{U}_2\text{F}_{12}]^{2-}$ anion of $\text{Sr}[\text{U}_2\text{F}_{12}]$.