Main Group Metal–Actinide Magnetic Coupling and Structural Response Upon U⁴⁺ Inclusion Into Bi, Tl/Bi, or Pb/Bi Cages

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S *Supporting Information*

ABSTRACT: The encapsulation of actinide ions in intermetalloid clusters has long been proposed but was never realized synthetically. We report the isolation and experimental, as well as quantum chemical, characterization of the uranium-centered clusters $[U@Bi_{12}]^{3-}$, $[U@Tl_2Bi_{11}]^{3-}$, $[U@Pb_7Bi_7]^{3-}$, and $[U@Pb_4Bi_9]^{3-}$, upon reaction of $(EE'Bi_2)^{2-}$ (E = Ga, Tl, E' = Bi; E = E' = Pb) and $[U(C_5Me_4H)_3]$ or $[U(C_5Me_4H)_3Cl]$ in 1,2-diaminoethane. For $[U@Bi_{12}]^{3-}$, magnetic susceptibility measurements rationalize an unprecedented antiferromagnetic coupling between a magnetic U^{4+} site and a unique radical Bi_{12}^{7-} shell.

Ligand-free metal clusters, often described as superatomic systems,[1] show intriguing size-dependent electronic properties, which define their optoelectronic behavior, reactivity, and magnetism.[2] Moreover, multimetallic clusters can be viewed as nanosized alloys or as doped (semi)metal particles, making them attractive to experimentalists as well as theorists in this field.[3] They are regarded as promising catalysts and as precursors to novel intermetallic phases with new structural patterns. Here, intermetalloid clusters $[M@E_n]$ that are obtained by encapsulation of transition and lanthanide metal atoms (M) in main group element clusters (E_n) turned out to be ideal candidates for such systems. They have been intensely studied over the past two decades by a variety of synthetic approaches[4] and by spectroscopy[5] and quantum chemistry.[6]

In contrast, stable actinide-centered main group metal clusters have been predicted theoretically but heretofore not confirmed experimentally.[7] The realization of such clusters would be of great interest in regard to their structural, bonding, and magnetic properties, and would further complement the dynamic research taking place in the field of actinide chemistry.[8] Binary main group metal shells display remarkable flexibility of composition, nuclearity, and charge and thus represent ideal systems for trapping metal atoms with flexible oxidation states.

Herein we report the successful transfer of a synthetic approach, formerly applied to the syntheses of ternary lanthanide-centered main group metal clusters,[9] to their first actinide-centered analogs $[K(crypt-222)]_3[U@Bi_{12}]$·tol·1.5en (**1**), $[K(crypt-222)]_2[K(crypt-222)(en)][U@Tl_2Bi_{11}]$·tol (**2**), and $[K(crypt-222)]_3[U@Pb_7Bi_7]_{0.66}[U@Pb_4Bi_9]_{0.34}$·2tol (**3**). Compounds **1**–**3** exhibit unique structural and electronic peculiarities not observed in the Ln congeners. They were first synthesized by reactions of $[K(crypt-222)]_2(EE'Bi_2)$·en (E = Ga, Tl, E' = Bi; E = E' = Pb)[10] with $[U(C_5Me_4H)_3]$[11] (denoted as $[UCp^{\#}_3]$ in the following) in 1,2-diaminoethane (en) and were characterized by means of X-ray diffraction, electrospray ionization (ESI) mass spectrometry, micro X-ray fluorescence spectroscopy (μ-XFS), quantum chemistry, and magnetic measurements.

Compound **1** was obtained as black crystalline prisms in ~13% yield upon using $(GaBi_3)^{2-}$ as the binary precursor. In the anion in compound **1** (Figure 1), a U atom is surrounded by an unprecedented polybismuthide architecture (U–Bi_B 3.119(3)–3.167(3) Å; U–Bi_A 3.463(3)–3.545(3) Å). The doughnut-like Bi_{12} shell may be described as an assembly of three Bi_4 butterfly-like moieties (Bi_A–Bi_B 3.051(4)–3.109(4) Å), which are linked by three shorter Bi_A–Bi_A contacts along
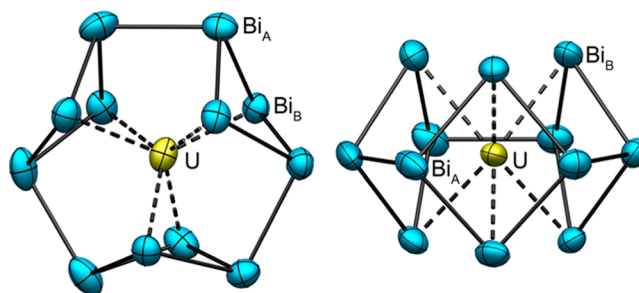

Figure 1. Top (left) and side (right) views of the molecular structure of one of the two individual anions, $[U@Bi_{12}]^{3-}$, in **1** (thermal ellipsoids at 50% probability). Structural details are given in Table S2.

the molecular "equator" (3.018(4)–3.046(4) Å). The structure is related to that of known lanthanide-centered 14-atom cages (Figure S13). However, the $[U@Bi_{12}]^{3-}$ anion lacks two atoms at the molecular "poles" that would otherwise complete a spherical cluster shell like that of $[Ln@Sn_7Bi_7]^{4-}$ or the oblate cluster $[Pd_3@Sn_8Bi_6]^{4-}$.[9b,12] The relatively large number of 69 valence electrons in **1** precludes the adoption of any known 12-atom topology, like an icosahedron, a recently reported D_{2d} symmetric structure, or a hexagonal prism.[6b,13]

Despite reacting a binary anion, $(GaBi_3)^{2-}$, we did not obtain a ternary cluster anion. However, it is known that $(GaBi_3)^{2-}$ is sensitive to disproportionation into elemental Ga^0 and polybismuthides, cf. the formation of Bi_{11}^{3-} and Bi_4^{2-} from $(GaBi_3)^{2-}$ in pyridine.[14] The structure of the anion in **1** suggests that $(GaBi_3)^{2-}$ again undergoes disproportionation and concomitant formation of Ga^0 beside Bi_4^{2-}, the latter of which successively replace precursor ligands. As illustrated in Scheme 1, organic 6π Hückel aromatic systems are thus replaced with inorganic ones.

Scheme 1. Calculated Minimum Structures Showing Folding and Coupling of Bi_4^{2-} Rings (turquoise) As They Replace $Cp^\#$ Ligands Around the U Ion during Formation of $[U@Bi_{12}]^{3-}$
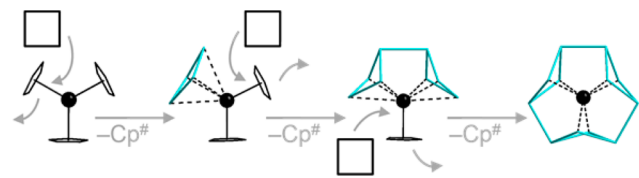
Quantum chemical calculations reproduce the folding and thus dearomatization of the Bi_4^{2-} rings upon substitution of the second and third ligand and subsequent Bi–Bi bond formation. The third exchange step produces the unique $[U@(Bi_4)_3]^{3-} = [U@Bi_{12}]^{3-}$ anion in **1**. We consider the shown pathway to be chemically more plausible than trapping of a U ion by an anionic Bi_{12} shell preformed without a (templating) metal atom.

One might assume that the cluster anion in **1** consists of a U^{3+} ion that is surrounded by a diamagnetic Bi_{12}^{6-} shell. However, magnetic measurements of **1** (*vide infra*) indicate the presence of U^{4+}. The anion in **1** should thus be formally described as $[U^{4+}@Bi_{12}^{7-}]^{3-}$, with a radical Bi_{12}^{7-} shell. An odd electron number is a very uncommon feature of main group polyanions and has so far only been observed for the polygermanide shell of the intermetalloid cluster anion $[Ru@Ge_{12}]^{3-}$.[13a] To confirm the findings, we produced compound **1** directly from a U^{4+} precursor, $[UCp^\#_3Cl]$,[11a] thus corroborating the preference for this oxidation state in the present system.

DFT calculations[15] helped to rationalize the experimental findings of an oxidation state higher than U^{3+} and shorter Bi–Bi distances between the Bi_4 rings than within them. The most favorable orbital occupation (in D_{3h} symmetry) is a doublet state (with slight spin contamination, $\langle S^2 \rangle = 0.79$) at level ECP78,[15c,h] TZVP,[15f,h] B3LYP,[15b,d] COSMO.[15e] Bi–Bi distances are 3.090 Å within the Bi_4 rings and 2.971 Å between them, reproducing the experimental trend. Notably, this is reverse of calculations of a bare Bi_{12}^{6-} unit with respective values of 3.043 and 3.138 Å. This indicates that the f electrons are involved in the bonding (otherwise a quartet state would be expected), leading to strengthening of the Bi_A–Bi_A bonds. For

elucidation, we considered the frontier orbitals of the bare Bi_{12}^{6-} unit and inspected the changes upon inserting a U atom (Figure 2). The LUMO of Bi_{12}^{6-} (a_2'') is a combination of p_z
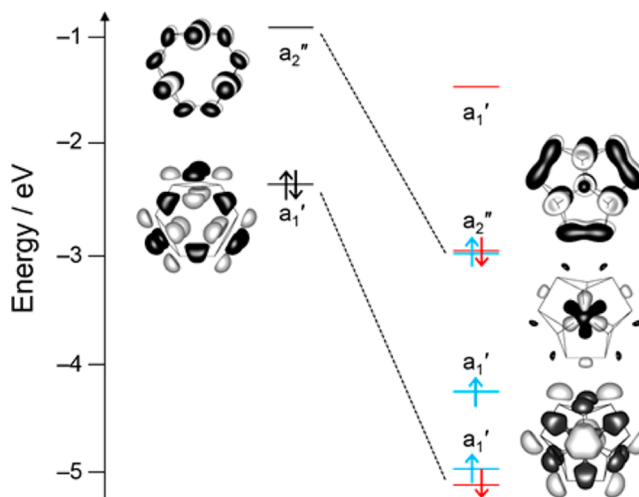

Figure 2. Frontier orbitals of Bi_{12}^{6-} and $[U@Bi_{12}]^{3-}$. Contours are drawn at ±0.025 au. The (singly occupied) open shell orbitals of $[U@Bi_{12}]^{3-}$ are indicated by blue (α) or red (β) color.

orbitals, being antibonding within the Bi_4 rings, but bonding between them. Insertion of a U atom stabilizes this MO by admixture of the f_{z^3} orbital (also a_2'') and its occupation. This results in elongation of bonds within the Bi_4 rings and shortening between them. The unpaired (f) electron occupies an a_1' orbital; a second a_1' orbital is a bonding combination of the HOMO of the Bi_{12}^{6-} unit and the d_{z^2} of U, again being antibonding within the Bi_4 rings and bonding between them. Further f (as well as d and s) contributions occur in the other MOs, leading to a (Mulliken)[16] population of 1.80 electrons and (weak) antiferromagnetic coupling. This is reflected by a surplus of 1.36 α electrons at U and 0.05 β electrons for each of the six Bi atoms closest to U, in line with the magnetic measurements that indicate antiferromagnetic coupling (*vide infra*) and the slight deviation of $\langle S^2 \rangle$ from the ideal value of 0.75.

The crucial role of the f electrons becomes even more evident when they are included in the effective core potential, MWB-ECP-81.[15g] This restricts the bonding activity of the U atom to its s and d electrons and its maximum oxidation state to +3. Calculated distances within the Bi_4 rings are then shorter (3.027 Å), while between them they are longer (3.200 Å). Hence, the use of f electrons, formally producing U^{4+}, must be considered for the computed structural trend to agree with the experimental observation.

A similar anion was reported very recently for Ln^{3+}/Sb clusters.[17] However, as f electrons are not involved in the bonding of Ln^{3+} ions, no folding of the main group metal four-membered rings is observed, and the bond lengths within/between the main group metal four-membered rings comply with the trend that was calculated for $[U@Bi_{12}]^{3-}$ when forcing it into a U^{3+} situation. This supports once more the involvement of f electrons in the bonding of **1** and rationalizes its electronic and magnetic peculiarities.

To explore whether the result obtained with $(GaBi_3)^{2-}$ was due to the group 13/15 elemental combination in general or due to the inhomogeneous Ga/Bi combination in particular, we

further tested the pseudo-homoatomic anion $(TlBi_3)^{2-}$. This afforded **2** in a 65% yield. The cluster anion in **2**, $[U@Tl_2Bi_{11}]^{3-}$, adopts a 13-atom cage structure with a 2:11 ratio of the group 13:15 elements, as confirmed by μ-XFS analysis (see Table S6). The composition is in agreement with quantum chemical studies applying DFT methods[15] along with first-order perturbation theory that also allows for the assignment of atomic positions of atoms of similar nuclear charge.[18] Although the overall topology and formation mechanism of the 13-atom cage is known,[13c] the anion in **2** exhibits some structural peculiarities (Figure 3). A notable folding of the basal face is
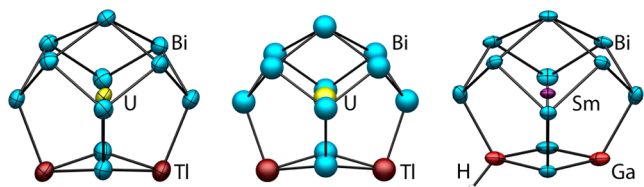

Figure 3. Experimentally determined structures (thermal ellipsoids at 50% probability) of $[U@Tl_2Bi_{11}]^{3-}$ (left, for structural parameters see Table S3) and $[Sm@Ga_2HBi_{11}]^{3-}$ (right)[9d] and the optimized structure of $[U@Tl_2Bi_{11}]^{3-}$, as obtained from DFT calculations (center).

observed, in agreement with DFT calculations for $[U@Tl_2Bi_{11}]^{3-}$. This is probably due to the relatively large (anionic) Tl atoms that do not allow for a planar four-membered Tl_2Bi_2 ring.

The total charge of the cluster is 3−. However, unlike the situation in the Sm^{3+} clusters in $[K(crypt-222)]_3[Sm@Ga_2HBi_{11}]_{0.9}[Sm@Ga_3H_3Bi_{10}]_{0.1}\cdot en\cdot tol$,[9d] there is no indication for a protonation of the (Lewis-basic) "Tl^{2-}" atoms in the high-resolution mass spectrum (see Figure S18). This, along with the magnetic measurements (*vide infra*), confirms the formal 4+ oxidation state of the U atom. Again, a formation from $[UCp^\#_3Cl]$ is successful, in accordance with the given oxidation state.

As another validation of the observed inclusion of U^{4+}, we reacted $[UCp^\#_3]$ with the $(Pb_2Bi_2)^{2-}$ anion,[19] from which well-studied Ln^{3+} compounds have been previously derived.[9e] Compound **3** crystallizes from this reaction in ~28% yield. It is isomorphic with the known Nd^{3+} compound, $[K(crypt-222)]_3[Nd@Pb_6Bi_8]_{0.545}[Nd@Pb_3Bi_{10}]_{0.455}\cdot 2tol$.[9e] Again, magnetic measurements (*vide infra*) are in agreement with a 4+ oxidation state for the U atom, which agrees with the observation that compound **3** can also be directly obtained from $[UCp^\#_3Cl]$. Because the clusters in **3** have overall 3− charges, their formulations differ from those in the Nd^{3+} congener: $[U^{4+}@(Pb_7Bi_7)^{7-}]^{3-}$ and $[U^{4+}@(Pb_4Bi_9)^{7-}]^{3-}$ in agreement with all further analytic data.

As shown in Figure 4, the χT product is about 0.66 cm^3 K/mol for **1** and 1.0 cm^3 K/mol for **2** and **3** at 270 K. The high temperature value for **2** and **3** most likely indicates the presence of a U^{4+} center here, although these data alone cannot exclude 3+ and 5+ oxidation states.[8b] In the case of **1**, the lower χT product at 270 K supports a strong antiferromagnetic coupling between the $S = 1/2$ radical Bi_{12}^{7-} shell and the U^{4+} magnetic center. The almost identical temperature dependence of the magnetic susceptibility, and particularly the low 1.8-K χT values for **2** and **3** (0.09 and 0.11 cm^3 K/mol, respectively), leave no doubt of the 4+ oxidation state of the U site,[8b] in agreement with the above-mentioned compositions and total charges of
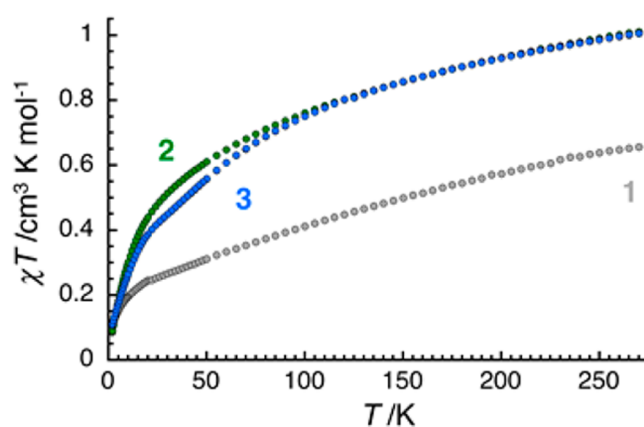

Figure 4. Temperature dependence of χT (magnetic susceptibility $\chi = M/H$ per mole of cluster at 0.1 and 1 T below and above 100 K, respectively) for **1**−**3**.

the anions in **2** and **3**. For **1**, the strong antiferromagnetic coupling between the radical Bi_{12}^{7-} shell and the U^{4+} centers induces a thermal decrease of the χT product that is superposed to the intrinsic magnetic properties of the actinide ion seen in **2** and **3**. The low 1.8 K χT value (0.10 cm^3 K/mol) suggests that the resulting magnetic entity has a singlet or weakly paramagnetic ground state.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04363.

Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Details on syntheses, single-crystal XRD, EDX, μ-XFS, ESI-MS, magnetic measurements, DFT studies (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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