CHARACTERIZATION OF BERKELIUM(III) DIPOCILINATE AND BORATE COMPOUNDS IN SOLUTION AND THE SOLID STATE

Mark A. Silver,* Samantha K. Cary,* Jason A. Johnson, Ryan E. Baumbach, Alexandra A. Arico, Morgan Luckey, Matthew Urban, Jamie C. Wang, Matthew J. Polinski, Alexander Chemey, Guokui Liu, Kuan-Wen Chen, Shelley M. Van Cleve, Matthew L. Marsh, Teresa M. Eaton, Lambertus J. van de Burgt, Ashley L. Gray, David E. Hobart, Kenneth Hanson, Laurent Maron, Frédéric Gendron, Jochen Autschbach, Manfred Speldrich, Paul Kögerler, Ping Yang, Jenifer Braley,* Jason A. Johnson, Ryan E. Baumbach, Ashley L. Gray, David E. Hobart, Kenneth Hanson, Laurent Maron, Frédéric Gendron, Jochen Autschbach, Manfred Speldrich, Paul Kögerler, Ping Yang, Jenifer Braley,* Thomas E. Albrecht-Schmitt†

INTRODUCTION: Developing the chemistry of late actinides is hindered by the lack of availability of isotopes, the need for specialized research facilities, and the nuclear instability of the elements. Berkelium represents one of the last elements that can be prepared on a milligram scale in nuclear reactors. However, its only available isotope, $^{249}$Bk, has a half-life of only 320 days, which has greatly curtailed the expansion of its chemistry and fundamental exploration of how large relativistic and spin-orbit coupling effects alter its electronic structure. Furthermore, data gathered from Bk(III) in aqueous media suggest that its coordination may be different from that of earlier actinides. However, a single-crystal structure of a berkelium compound has remained elusive, leaving answered whether these structural changes occur in the solid state.

RATIONALE: This work focuses on characterizing two distinct berkelium compounds on the milligram scale. In particular, the goal was to obtain crystals of these compounds that could be used in structure determinations and physical property measurements. Two compounds were selected: a coordination complex of dipicolinate and a borate. Dipicolinate complexation occurs with most other lanthanides and actinides in the $+3$ oxidation state, facilitating comparisons across the series to discern periodic trends. In the borate family, the structural frameworks are hypersensitive to the nature of the bonding at the metal center and are rearranged accordingly. Modeling the experimental data using a variety of computational techniques allows us to deconvolute the role of covalent bonding and spin-orbit coupling in determining the electronic properties of berkelium.

RESULTS: Experiments with milligram quantities of $^{249}$Bk were choreographed for 6 months before the arrival of the isotope because the total quantity used in the studies was 13 mg, which corresponds to a specific activity of 21 Ci. Although this isotope is a low-energy $\beta$ emitter, it decays to $^{249}$Cf at a rate of about 1.2% per week, and the latter produces hard $\gamma$ radiation that represents a serious external hazard. In addition, the samples described in this work undergo about $10^{12}$ decays per second. This rapid decomposition necessitated the development of techniques for swiftly preparing and encapsulating samples and for collecting all structural and spectroscopic data within 24 hours of crystal formation. After this preparation, the single-crystal structures of Bk(III)tris(dipicolinate) and Bk(III) borate were determined. The latter compound has the same topology as that of californium(III) (Cf) and contains an eight-coordinate BkO$_8$ unit. This reduction in coordination number is consistent with previous solution-phase X-ray absorption measurements and indicates that a drop in coordination number in the actinide series from nine to eight begins at berkelium. The magnetic and optical properties of these samples were also measured. The red luminescence from Bk(III) was similar in nature to that of curium(III) and is primarily based on an $f/f$ transition. The ingrowth of the broad green luminescence from Cf(III), which is caused by a ligand-to-metal charge transfer, was shown to be distinct in nature from that originating from Bk(III). Ligand-field, density functional theory, and wave-function calculations were used to understand the spectroscopic features and revealed that the single largest contributor to the unexpected electronic properties of Bk(III) is spin-orbit coupling. This effect mixes the first excited state with the ground state and causes a large deviation from a pure Russell-Saunders state. The reduction in the measured magnetic moment for these samples that calculated for an $f^0$ electron configuration is primarily attributable to this multiconfigurational ground state.

CONCLUSION: The crystallographic data indicate that Bk(III) shares more structural similarities with Cf(III) than with Cm(III). However, ligand-field effects are more similar between Bk(III) and Cm(III). Terbium (Tb), in the lanthanide series, represents the closest analog of Bk because the trivalent cations possess $4f^0$ and $5f^0$ configurations, respectively. Spin-orbit coupling in Bk(III) creates mixing of the first excited state ($^7G_6$) with the ground state. In contrast, the ground state of the Tb(III)tris(dipicolinate) contains negligible contributions of this type. An overall conclusion from this study is that spin-orbit coupling plays a large role in determining the ground state of late actinide compounds. *These authors contributed equally to this work. †Corresponding author. Email: jbraley@mines.edu (J.B.); albrecht-schmitt@chem.fsu.edu (T.E.A.-S.)

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*These authors contributed equally to this work.

†Corresponding author. Email: jbraley@mines.edu (J.B.); albrecht-schmitt@chem.fsu.edu (T.E.A.-S.)

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Crystal structure of a berkelium coordination compound. The central Bk(III) ion is coordinated by three monoprotonated dipicolinate ligands in tridentate O,N,O fashion. Bk, yellow; C, gray; N, blue; O, red; H, white.
Characterization of berkelium(III) dipicolinate and borate compounds in solution and the solid state

Mark A. Silver,1,1 Samantha K. Cary,1,1 Jason A. Johnson,2 Ryan E. Baumbach,3 Alexandra A. Arico,4 Morgan Luckey,4 Matthew Urban,4 Jamie C. Wang,1 Matthew J. Polinski,5 Alexander Chemey,1 Guokui Liu,6 Kuan-Wen Chen,3 Shelley M. Van Cleve,7 Matthew L. Marsh,1 Teresa M. Eaton,1 Lambertus J. van de Burgt,1 Ashley L. Gray,2 David E. Hobart,1 Kenneth Hanson,1 Laurent Maron,8 Frédéric Gendron,9 Jochen Autschbach,9 Manfred Speldrich,10 Paul Kögerler,10 Ping Yang,11 Jenifer Braley,4,12 Laurent Maron,8 Frédéric Gendron,9 Jochen Autschbach,9 Manfred Speldrich,10 Paul Kögerler,10 Ping Yang,11 Jenifer Braley,4,12 Thomas E. Albrecht-Schmitt1

Berkelium is positioned at a crucial location in the actinide series between the inherently stable lawrencium \((Z = 103)\) lies in a \(p\) orbital rather than \(d\) as would have been predicted by extrapolating from earlier elements (1). Beyond the actinide series, the situation is no less complex with superheavy elements like seaborgium \((Z = 106)\) exhibiting chemical behavior similar to the triad above (i.e., Cr, Mo, and W) (2), whereas reactivity of rutherfordium \((Z = 104)\) and dubnium \((Z = 105)\) can deviate significantly from expectations (3, 4).

Although the exotic electronic structure of superheavy elements is now accepted, the validity of simple chemical principles to predict electron configuration, and thus chemical behavior, is questionable throughout the entire actinide series. Plutonium demonstrates these qualities best, and after seven decades of interrogation, only now do we understand that its electronic structure must be framed within the context of electronic states that are fluctuating on a sub-picosecond time scale (5). Similarly, at californium \((Z = 98)\) a metastable electronic state is observed near ambient conditions that also manifests in the spectroscopic features of complex molecules containing Cr(III) ions (6–10).

However, as is often true with heavy elements, our ability to probe chemical and physical properties is hampered by nuclear instability. This creates gaps that impede the feedback between experiment and theory. One such gap occurs just before californium at the element berkelium. Berkelium has no long-lived isotopes that can be isolated. The only accessible isotope is \(^{249}\text{Bk}\), with a half-life of only 320 days. Compounds that contain isotopes with half-lives of less than hundreds of thousands of years undergo rapid degradation because of the high energetics and ionization nature of nuclear decay processes that can be up to a million times larger than the strength of any chemical bond.

Although measurements and crystal-field modeling of the optical spectra of aqueous solutions of \(\text{Bk(III)}\), as well as solid-state samples doped with low levels of \(\text{Bk(III)}\) and \(\text{Bk(IV)}\), have been reported (11–13), single-crystal x-ray analysis of a berkelium compound proved elusive (14–16). Spectroelectrochemical measurements of berkelium’s speciation in aqueous media have been accomplished using x-ray absorption spectroscopy and provided evidence that a break in the trend of complexation with actinides might begin at berkelium (17). This latter study points to the need for obtaining high-resolution structural data for berkelium compounds to investigate whether a transition also occurs in the solid state (18–20). Furthermore, the optical measurements obtained from hydrated \(\text{Bk(III)}\), \(\text{LnCl}_{3}\text{Bk}\) (where \(\text{Ln}\) is generic for lanthanide), and \(\text{CeF}_{3}\text{Bk}\) do not reveal the full range of the effects of ligation on the electronic properties of \(\text{Bk(III)}\) because water and chloride coordination induce relatively small electronic perturbations (11–13, 20).

Data fitting using early crystal-field models, based on electrostatic interactions between point...
charges, did not account for the possible involvement of the frontier orbitals in bonding (21).

For meaningful comparisons to be made between the chemistry of berkelium and other actinides, two divergent systems were selected for investigation. The first of these is an archetypal coordination complex that forms via the chelation of An3+ cations by 2,6-pyridinedicarboxylate [dipicolinate (DPA)] yielding An(HDPA)3·nH2O in the solid state (An is Pu, Am, Cm, Bk, or Cf) or [An(DPA)3]n−, [An(DPA)3]2−, and [An(DPA)3]3+ in solution (6, 19, 22–24). These complexes have a predictable coordination environment (a feature often absent in the f-block), and serve as a benchmark for examining trends in bond distances, spectroscopy, and thermodynamics. The second system is one that has proven to be exquisitely sensitive to the nature of the actinide ions employed in the reaction. In this case, we have shown that polyborates form unique structural topologies with each of the different actinide ions from Pu(III) to Cf(III) (7–9, 25).

Experiments with milligram quantities of 249Bk were choreographed for 6 months before the arrival of the isotope because the total quantity used in the studies was 13 mg, which corresponds to a staggering activity of 21 Ci. Although this isotope is a low-energy β emitter, it decays to 249Cf at a rate of ~1.2% per week, and the latter produces hard γ radiation that represents a serious external hazard. In addition, the samples described in this work undergo ~109 decays per second. This rapid decomposition necessitated the development of techniques for swiftly preparing and encapsulating samples and collecting all structural and spectroscopic data within 24 hours of crystal formation. Crystals of these compounds underwent Coulombic explosions within 4 days, although they did not exhibit the color changes that often occur with high specific activity α emitters (6). With the exception of the magnetic susceptibility measurements, all of the data described below were acquired from isolated single crystals.

**Synthesis**

250BkCl3·nH2O, freshly prepared at the High Flux Isotope Reactor at Oak Ridge National Laboratory, was treated with a five-fold excess of dipicolinic acid in a 1:1 water:ethanol mixture. The initial solution was lime green and emitted faint green light as the result of electronic excitation from the high specific activity of 249Bk (i.e., self-luminescence). The addition of DPA resulted in an immediate color change and precipitation of a golden-yellow crystalline product. Mild heating of the reaction mixture led to ripening of the microcrystals and formation of golden crystals of Bk(HDPA)3·nH2O with an approximate hexagonal prismatic shape (see fig. SI). Much like the reaction with Cf(III) (6), the precipitation of Bk(HDPA)3·nH2O was nearly quantitative, and little Bk(III) remained in solution at the end of the reaction. This sharply contrasts with curium(III), where a substantial portion of the 248Cm remained in solution in the form of [Cm(HDPA)2(H2DPA)(H2O)2]Cl+ (20).

**Crystallography**

Single-crystal x-ray diffraction studies revealed that Bk(HDPA)3·nH2O is isomorphous with the other members of the trivalent lanthanide and actinide series (table S1) (6). In short, the Bk(III) ions are complexed by three tridentate, mono-protonated dipicolinate ligands, constituting a nine-coordinate, tricapped, trigonal prismatic coordination environment with approximate D3 symmetry. The nitrogen atoms from the pyridine rings are located in the capping positions, and the oxygen atoms from the carboxylate anions fill the six prismatic sites. Tris-chelate complexes, where the metal center is octahedral or nine-coordinate, are chiral. The two enantiomers are designated Δ and Λ, and unless stereoselective processes are involved, a racemate mixture of both enantiomers should be present in every system. Bk(HDPA)3·nH2O crystallizes in a centrosymmetric space group, indicating that a racemic mixture is present. In addition, a hydrogen-bonding network is present between the cocrystallized water molecules and the berkelium complexes. These interactions cause minor distortions of the local coordination around the Bk(III) centers. Each enantiomer is present in the structure in two distinct positions (see Δ and Λ in Table 1), one more distorted than the other because of these intermolecular interactions. A view of the Δ and Λ enantiomers is shown in Fig. 1A. Table 2 highlights bond distance changes in the tris(dipicolinate) series spanning Am(III) through Cf(III).

The preparation of Bk(III) borate followed the same procedure used for preparing all other An(III) borates (An is Pu, Am, Cm, or Cf) (9, 25–27) and yielded golden tablets of Bk2O3(OH)3 (see fig. S2). The synthesis and crystal growth of Bk2O3(OH)3 required 10 days during which time nearly 2% of the 249Bk converted to 249Cf. We initially posited that this compound would remain stable under

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**Table 1.** Selected bond lengths (Å) for An(HDPA)3 (An is Am, Cm, Bk, or Cf) complexes.

<table>
<thead>
<tr>
<th>An</th>
<th>Am Δ</th>
<th>Cm Δ</th>
<th>Bk Δ</th>
<th>Cf Δ</th>
<th>Am Δ′</th>
<th>Cm Δ′</th>
<th>Bk Δ′</th>
<th>Cf Δ′</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>2.472(3)</td>
<td>2.462(3)</td>
<td>2.457(3)</td>
<td>2.455(4)</td>
<td>2.507(3)</td>
<td>2.496(3)</td>
<td>2.483(3)</td>
<td>2.476(4)</td>
</tr>
<tr>
<td>O12</td>
<td>2.491(3)</td>
<td>2.483(3)</td>
<td>2.475(4)</td>
<td>2.473(4)</td>
<td>2.441(3)</td>
<td>2.433(3)</td>
<td>2.421(3)</td>
<td>2.413(4)</td>
</tr>
<tr>
<td>O15</td>
<td>2.430(3)</td>
<td>2.417(3)</td>
<td>2.410(3)</td>
<td>2.387(4)</td>
<td>2.405(3)</td>
<td>2.389(3)</td>
<td>2.372(3)</td>
<td>2.363(3)</td>
</tr>
<tr>
<td>O16</td>
<td>2.468(3)</td>
<td>2.459(3)</td>
<td>2.440(3)</td>
<td>2.422(3)</td>
<td>2.512(3)</td>
<td>2.498(3)</td>
<td>2.482(3)</td>
<td>2.476(3)</td>
</tr>
<tr>
<td>O17</td>
<td>2.516(3)</td>
<td>2.508(3)</td>
<td>2.500(3)</td>
<td>2.494(3)</td>
<td>2.494(3)</td>
<td>2.480(3)</td>
<td>2.464(3)</td>
<td>2.441(3)</td>
</tr>
<tr>
<td>O18</td>
<td>2.499(3)</td>
<td>2.481(3)</td>
<td>2.433(3)</td>
<td>2.411(4)</td>
<td>2.457(3)</td>
<td>2.448(3)</td>
<td>2.437(3)</td>
<td>2.417(3)</td>
</tr>
<tr>
<td>N1</td>
<td>2.550(4)</td>
<td>2.533(4)</td>
<td>2.512(4)</td>
<td>2.512(4)</td>
<td>2.553(4)</td>
<td>2.520(4)</td>
<td>2.533(4)</td>
<td>2.518(4)</td>
</tr>
<tr>
<td>N3</td>
<td>2.551(4)</td>
<td>2.536(4)</td>
<td>2.518(4)</td>
<td>2.508(4)</td>
<td>2.531(4)</td>
<td>2.535(4)</td>
<td>2.503(4)</td>
<td>2.506(4)</td>
</tr>
<tr>
<td>N5</td>
<td>2.591(3)</td>
<td>2.581(4)</td>
<td>2.558(4)</td>
<td>2.545(4)</td>
<td>2.573(4)</td>
<td>2.569(4)</td>
<td>2.542(4)</td>
<td>2.526(4)</td>
</tr>
</tbody>
</table>

**Table 2.** Comparison of bond lengths (Å) between the Δ and Δ′ molecules of An(HDPA)3 (An is Am, Cm, Bk, or Cf) complexes.

<table>
<thead>
<tr>
<th>An</th>
<th>Am Δ</th>
<th>Cm Δ</th>
<th>Bk Δ</th>
<th>Cf Δ</th>
<th>Am Δ′</th>
<th>Cm Δ′</th>
<th>Bk Δ′</th>
<th>Cf Δ′</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longest An-N</td>
<td>2.515(4)</td>
<td>2.509(4)</td>
<td>2.457(3)</td>
<td>2.494(4)</td>
<td>2.519(4)</td>
<td>2.501(4)</td>
<td>2.483(3)</td>
<td>2.477(4)</td>
</tr>
<tr>
<td>Shortest An-N</td>
<td>2.431(4)</td>
<td>2.416(4)</td>
<td>2.410(3)</td>
<td>2.386(4)</td>
<td>2.401(4)</td>
<td>2.388(4)</td>
<td>2.372(3)</td>
<td>2.363(4)</td>
</tr>
<tr>
<td>Average An-N</td>
<td>2.482(4)</td>
<td>2.468(4)</td>
<td>2.449(3)</td>
<td>2.436(4)</td>
<td>2.468(4)</td>
<td>2.457(4)</td>
<td>2.442(3)</td>
<td>2.431(4)</td>
</tr>
<tr>
<td>Longest An-O</td>
<td>2.589(4)</td>
<td>2.582(4)</td>
<td>2.558(4)</td>
<td>2.545(4)</td>
<td>2.573(4)</td>
<td>2.566(4)</td>
<td>2.542(4)</td>
<td>2.526(4)</td>
</tr>
<tr>
<td>Shortest An-O</td>
<td>2.555(4)</td>
<td>2.532(4)</td>
<td>2.512(4)</td>
<td>2.508(4)</td>
<td>2.532(4)</td>
<td>2.519(4)</td>
<td>2.503(4)</td>
<td>2.506(4)</td>
</tr>
<tr>
<td>Average An-O</td>
<td>2.564(4)</td>
<td>2.550(4)</td>
<td>2.529(4)</td>
<td>2.522(4)</td>
<td>2.554(4)</td>
<td>2.540(4)</td>
<td>2.526(4)</td>
<td>2.517(4)</td>
</tr>
</tbody>
</table>
steady β emission, but the buildup of positive charge in the crystals led to violent fracture within 4 days of isolation. Bk[B₂O₆(OH)₃] has the same formula but is not isomorphous with Cf [B₂O₆(OH)₃] (table S1), but distinct from all other actinide borates previously synthesized. The Bk(III) ions are present as eight-coordinate, distorted square antiprisms (Fig. 1B), in contrast to the nine- and ten-coordinate motifs in the Pu(III), Am(III), and Cm(III) borates (9, 25–27).

**Thermodynamics of complexation**

The thermodynamics of Bk(III) complexation with dipicolinic acid are presented in Table 3, with the association constants presented in table S2. The Bk(III) β₁₀¹[BP(DPA)⁺], β₁₀²[BP(DPA)₂⁺], and β₁₀³[BP(DPA)³⁺] constants at 25°C and 1 M ionic strength are larger than values reported for Sm(III), Eu(III), or Gd(III). These lanthanides have ionnic radii comparable to those proposed for Bk(III) (28). The enthalpic binding contribution for the berkelium 1:3 DPA complex is more exothermic than observed with any of the lanthanide dipicolinic acid complexes (29). The 1:1 and 1:2 complexes are comparable or slightly more exothermic than other lanthanide DPA complexes.

The correlation between coordination exothermicity and degree of bonding covalency is a subject of current debate. Comparisons of the interactions of aromatic nitrogen donors with Nd(III) and Am(III), using 2-amino-4,6-di-(pyridin-2-yl)-1,3,5-triazine (ADPTZ) have been assessed (28–31). The ADPTZ studies show the formation of the Am(III)-ADPTZ complex to be 9 kJ·mol⁻¹ more exothermic than the Nd(III)-ADPTZ complex. When the thermodynamics of the 1:3 berkelium and samarium DPA complexes are considered, a ΔH of 9 kJ·mol⁻¹ for the 1:3 metal: dipicolinic acid complex of 9 kJ·mol⁻¹ is observed.

**Experimental electronic structure analysis**

The absence of the greenish self-luminescence of Bk(III) upon complexation by DPA is an indication of increased ion-ligand interactions that alter Bk(III) electronic structure and transition dynamics. Absorption, excitation, and photoluminescence spectra are shown in Fig. 2 and in figs. S3 and S4. The low-lying energy levels (<20,000 cm⁻¹ or 2.5 eV) of the 5f electronic states do not differ grossly from the corresponding states in the aquo complex (11), indicating relatively small changes in ligand-field splitting. Similar to the 5f photoluminescence in Cm(HDPA)₃ (6, 20), the narrowband near 14,700 cm⁻¹ (680 nm) most likely arises from an intra-5f transition. As shown in Fig. 2C, the 5000 cm⁻¹ energy gap between the emitting state and the next 5f state is critical for the red luminescence to be competitive with nonradiative phonon relaxation, whereas the smaller gap of ~35,000 cm⁻¹ above the emitting state effectively eliminates green luminescence from the excited state near 20,000 cm⁻¹ (11, 12).

However, starting from 21,000 cm⁻¹ in the blue and ultraviolet (UV) region, a broad band lacking 5f characteristics appears in the absorption and excitation spectra. The 6d levels of Bk(III) are much lower in energy than those of Am(III) or Cf(III) with the same ligands (8, 11, 12, 32), and we attribute this transition in the Bk(III) spectra to 5f⁸ to 5f⁶⁶d transitions. The narrow and intense peak at 21,350 cm⁻¹ in the excitation spectrum has an energy and bandwidth consistent with the scheme of the 5f⁵ states but an intensity on the same scale as the parity allowed 5f⁶d transitions. These observations are consistent with crystal-field induced coupling of the 5f and 6d orbitals, which is expected in a molecule with D₃h symmetry (11, 12).

For overlapping 5f⁵ and 5f⁶d states enhances this orbital hybridization. The low-lying 6d states and the enhanced 5f⁷d hybridization contribute to Bk(III)-ligand bonding and coordination and therefore, put Bk(III) in a unique position in the heavy actinide group. These studies also provide a direct comparison between Bk(III) photoluminescence and the in-growth of Cf(III)-based luminescence. The latter is ligand-to-metal charge transfer-based and is therefore an allowed transition. In contrast, although the 5f⁶d mixing does provide some relaxation of the selection rules and hence greater intensity than a pure intra-f transition, the intensity from the Cf(III) is larger than that of the Bk(III) despite a sample composition of ~97%²⁴⁹Bk and only ~3%²⁴⁹Cf.

**Magnetic properties**

To further elucidate the ligand-field effects on Bk(III), as well as enhance our understanding of electronic structure, magnetic susceptibility data were measured in the 4 to 300 K temperature

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**Table 3. Thermodynamic parameters for Bk(III)-dipicolinic acid complexation at 1.0 M ionic strength and various temperatures (in molality).**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Log β₁₀¹</th>
<th>Log β₁₀²</th>
<th>Log β₁₀³</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>9.30(9)</td>
<td>17.65(4)</td>
<td>23.90(2)</td>
</tr>
<tr>
<td>15</td>
<td>9.15(3)</td>
<td>17.50(2)</td>
<td>23.45(7)</td>
</tr>
<tr>
<td>25</td>
<td>9.07(7)</td>
<td>17.23(2)</td>
<td>23.14(1)</td>
</tr>
<tr>
<td>45</td>
<td>8.8(1)</td>
<td>16.85(6)</td>
<td>22.43(4)</td>
</tr>
</tbody>
</table>

ΔH (kJ mol⁻¹) = −19(1)  
ΔS (J mol⁻¹ K⁻¹) = −64(3)
range for Bk(HDPA)$_3$·nH$_2$O and 7 to 300 K range for Bk[B$_2$O$_6$(OH)$_3$] under an applied field of 1 kOe (Fig. 3). The experimental $\mu_{\text{eff}}$ values of 9.24 $\mu_B$ (Bk[B$_2$O$_6$(OH)$_3$]) and 9.27 $\mu_B$ (Bk(HDPA)$_3$·nH$_2$O) at 300 K are close to the simulated value of 9.32 $\mu_B$ derived from spectroscopic data by Carnall (12). The susceptibility data were fitted to a full-model Hamiltonian (33), where the relevant spin-orbit coupling parameter ($\zeta = 3210$ cm$^{-1}$) and Slater-Condon parameters ($F^2 = 57,697$ cm$^{-1}$, $F^4 = 45,969$ cm$^{-1}$, and $F^6 = 32,876$ cm$^{-1}$) were chosen on the basis of the optical spectra of BkCl$_3$ (11, 12) and used as constants. To restrict the number of independent ligand-field parameters, a least-squares fit of the magnetic data for Bk(HDPA)$_3$·nH$_2$O requires assumption of an idealized $C_{3v}$ symmetry for the BkN$_3$O$_6$ coordination sphere. Initial sets of most ligand-field ($B^d_{1g}$) (Wybourne notation) parameters were again adopted from spectroscopically determined energy levels for BkCl$_3$; the Bk$^{3+}$ site symmetry reduction from $D_{3h}$ (BkCl$_3$) to $C_{3v}$ mandates two additional ligand-field parameters ($B^d_{2g}$ and $B^d_{3g}$). The signs of the $B^d_{kg}$ values were assigned from point-charge electrostatic model calculations for a regular tricapped trigonal prism and fixed throughout the fitting procedure. This approach resulted in a near-perfect fit (quality of fit, SQ = 0.5%), yielding a ligand field characterized by $B^d_{2g} = 59$ cm$^{-1}$, $B^d_{3g} = -870$ cm$^{-1}$, $B^d_{4g} = 150$ cm$^{-1}$, $B^d_{5g} = -2310$ cm$^{-1}$, $B^d_{6g} = -420$ cm$^{-1}$, and $B^d_{7g} = 800$ cm$^{-1}$. The composition of the ground term [5$F$ (70%); 2$G$ (23%)] is in good agreement with CASSCF-SO results (vide infra). The total splitting of the $J = 6$ ground state into $m_J$ substates amounts to 147.9 cm$^{-1}$, with a small energy gap of 4.9 cm$^{-1}$ between the ground state and the first excited state. The observed temperature dependence of $\mu_{\text{eff}}(-T^{3/2})$ below 15 K arises from the composition of the ground state (mixture of 50% $m_J = 0$ and 50% $m_J = 6$ states), not from exchange interactions.

For Bk[B$_2$O$_6$(OH)$_3$], bridging borate anions provide exchange pathways between neighboring Bk$^{3+}$ centers; therefore, 5f-5f coupling interactions were assumed to be significant and were accounted for in a molecular-field approach. Approximating the distorted square-antiprismatic geometry of the BkO$_6$ environments as $C_{3v}$ symmetric, an analogous least-squares fit (SQ = 0.7%) then yielded $B^d_{2g} = 140$ cm$^{-1}$, $B^d_{3g} = -910$ cm$^{-1}$, $B^d_{4g} = -550$ cm$^{-1}$, $B^d_{5g} = 460$ cm$^{-1}$, $B^d_{6g} = -860$ cm$^{-1}$, and the molecular-field parameter $\lambda_{\text{eff}} = -9400$ mol m$^{-3}$ (corresponding to a Weiss temperature of ~1.3 K). In comparison to Bk(HDPA)$_3$·nH$_2$O, the composition of the ground term [5$F$ (73%); 2$G$ (24%)] is nearly identical; however, the ground state multiplet here is exclusively composed of the $m_J = 6$ states. The total splitting of the $7F_6$ Russell-Saunders ground state amounts to 173 cm$^{-1}$, with a very low separation (0.4 cm$^{-1}$) between ground and first excited state (Fig. 3).
orbitals involved in the bonding. Among others, the two highest bonding orbitals are depicted in Fig. 4. In particular, the 5f2 orbital is delocalized with a 2p orbital from a carboxylic acid oxygen atom. These orbitals involve hybrid 7s/6d/5f orbitals on berkelium and are consistent with the energetic availability of the 6d orbitals. Therefore, to probe the contribution of the 6d orbitals to bonding, an f Core competition, as applied to lanthanides, was carried out. In this calculation, the 5f orbital is kept frozen in the core of the relativistic effective core potential (RECP) so that the 5f orbital cannot participate in bonding. In the latter calculation, the bonding situation is very similar to that described in Fig. 4 (see fig. S5), indicating that the 6d orbitals are crucial to describing the bonding in Bk(HDPA)3, as is often true in actinide compounds.

The electronic structure and magnetic properties of Bk(HDPA)3 were also probed using relativistic all-electron multireference wave-function theory, including spin-orbit (SO) coupling (see the supplementary materials). The lowest-energy level of the free Bk3+ ion is 7Fg with L = 3, S = 3, and J = L + S = 6. An idealized D3 symmetric ligand environment would split the 13-fold degeneracy (2J + 1) into four non-Kramers doublets (E) and five singlets (A). The SO interaction mixes ion levels with the same J = 6. The calculated electronic states deriving from the 7Fg level are characterized in Table 4 for the 100 K Δ′ structure. The ground state corresponds to a non-Kramers doublet that is slightly split due to the distorted D3 geometry in the crystal. An admixture (~1%) of states from the excited 5Gg level of the ion contributes to each entry in Table 4 (table S6 and fig. S7). The fact that these states derive mainly from the 7FG0 and 7G10 levels indicates that for the 5f shell the ligand-field interactions are secondary to the SO coupling, in line with the 5f-in-core DFT results. The split Δ′ ground-state doublet can be described by a pseudo-spin 1/2 Hamiltonian with a large electronic g factor along the magnetic axis (g = 15.65). As shown in Fig. 5, the calculated orbital (L) and spin (S) angular momentum are parallel, as expected, leading to a ground state with a large magnetic anisotropy. The calculated magnetic susceptibility χ(T) is in reasonable agreement with the experimental data (Fig. 5, inset). Due to the relatively small energetic spread of the states derived from the 7Fg level (417 cm⁻¹) from the ligand field, χ reflects contributions from several electronic states even at relatively low T. See figs. S8 and S9 for comparative results of a structure.

Terbium represents the closest analog of berkelium because the trivalent cations possess 4f⁶ and 5f⁶ configurations, respectively. However, the distinct electronic properties of these elements is attributable to several factors. First, the 5f2 orbital of Bk(III) overlaps with the 2p orbital on the oxygen atoms in the dipicolinate ligands. This covalency is absent with the 4f orbitals of Tb(III). These ligand-field effects, however, are secondary to spin-orbit coupling in Bk(III) that creates mixing of the first excited state 7G5 with the ground state. In contrast, the ground state of Tb(HDPA)3 contains negligible contributions of this type. Furthermore, although spin-orbit coupling also dominates the electronic structure of Cr(III), the magnitude of ligand-field splitting can be an order of magnitude larger in Cr(III) than in Bk(III). Ligand-field effects on berkelium are much more similar to that of curium. Hence, although the structural chemistry of berkelium is akin to that of californium, its electronic structure is more similar to that of earlier actinides.

Materials and methods

Syntheses

Caution! 249Bk (I/2 = 320 d; specific activity = 1.6 - 10³ Ci/g) β-decays to 249Cf (I/2 = 351 y; activity = 4.1 Ci/g), which represents a serious external hazard because of its γ-emission (0.388 MeV). There is also a small α-decay branch for 249Bk that yields 249Am. While this does not contribute in a meaningful way to hazards, 249Am β-decays to 249Cm. Reports attributing luminescence near 600 nm to a second 249Bk emission feature in the red are in error. This peak is from 246Cm (38). All studies with transuranium elements were conducted in a laboratory dedicated to these studies. This laboratory is equipped with HEPA filtered hoods and negative pressure glove boxes that are ported directly into the hoods. A series of counters continually monitor radiation levels in the laboratory. The laboratory is licensed by the State of Florida (an NRC-compliant state).

All experiments were carried out with approved safety operating procedures. All free-flowing solids were worked with in glove boxes, and products were only examined when coated with either water or Krytox oil. Thick lead sheets, respirators, and long lead vests were used as much as possible to shield researchers from radiation.

2,6-Pyridinedicarboxylic acid (99%, Sigma-Aldrich), ethanol (100%, Koptec), hydrobromic acid (ACS reagent 48%, Sigma-Aldrich), and berkelium (249Bk) obtained from ORNL in the form of BkCl₃ were used without further purification. PTFE-lined Parr 4749 autoclaves with a 10 mL internal volume, and Millipore water were used in all of the following reactions. All solvents that were used in a glove box were sparged with argon.

Bk(HDPA)₃-nH₂O

Bk (4.33 mg, 0.0173 mmol) in the form of BkCl₃ was combined with an excess of DPA (17.2 mg, 0.1029 mmol) in 200 μL of a 1:1 mixture of ethanol and water. The reaction mixture was heated in a PTFE-lined Parr 4749 autoclave with a 10 mL internal volume for 4 hours at 150°C, and then slowly cooled to 40°C over a 22-hour period. The reaction was performed inside a negative-pressure glovebox that was surrounded by thick lead sheets. The reaction yielded gold-yellow crystals that had both hexagonal prismatic and columnar habits (see fig. S1).

Bk[B₂O₆(OH)₃]₂

Bk (4.33 mg, 0.0173 mmol) in the form of BkCl₃ was dissolved in deionized water (30 mL) and transferred to a PTFE-lined Parr 4749 autoclave with a 10 mL internal volume. Boric acid (69.6 mg, 1.125 mmol) was added to the autoclave, and the reaction mixture was heated to 240°C for seven days. The reaction was cooled slowly over the course of three days. The product was washed with deionized water to dissolve the excess flux and yield small, yellow-orange crystals with a tablet habit (see fig. S2).

Crystallographic studies

Single crystals of Bk₃(HDPA)₉·3H₂O and Bk[B₂O₆(OH)₃] were glued to Mitegen mounts with epoxy and optically aligned on a Bruker D8 Quest x-ray diffractometer using a digital camera. Initial
control the temperature from room temperature down to 80 K.

**Magnetic susceptibility measurements and magnetochemical modeling**

Magnetism measurements were performed on polycrystalline samples using a Quantum Design VSM Magnetic Properties Measurement System under an applied field of 10 kOe for 4 K < 300 K, and for 0 < H < 70 kOe at T = 4 K and 50 K. The samples were sealed inside two different, custom-built Teflon capsules. The outermost capsule was also taped closed using Kapton. In order to extract the intrinsic magnetic behavior of the Bk-containing sample, we subtracted measurements of an empty capsule from those of the filled capsule. All magnetic parameters are given in SI units.

The dc-susceptibility data were analyzed with the program framework CONDOR 2.0, employing a complete basis set (full /mf manifolds, i.e., 3,003 functions for Bk\(^{3+}\)) (33). Generally, a full model is required to accurately reproduce all magnetic aspects of 5f compounds, and CONDOR accounts for all relevant single-ion effects, in particular the ligand-field effect (\(H_{\text{lf}}\)), interelectronic repulsion (\(H_{\text{rep}}\)), spin-orbit coupling (\(H_{\text{so}}\)) and the Zeeman effect of an applied field (\(H_{\text{mag}}\)). Whereas for Bk(HDPA)\(_3\)·nH\(_2\)O, the nearest-neighbor Bk-Bk distances exceed 1.1 nm, which rules out significant coupling interactions, for Bk[B\(_6\)O\(_8\)(OH)\(_5\)] the exchange interactions between neighboring Bk\(^{3+}\) centers in the solid state are considered in the molecular field approach

\[
\chi_m^{-1} = \chi_0^{-1} + \sum_{j} B_{\text{mf}} C_{\text{mf}}(i, j) - \lambda_{\text{int}}
\]

where \(\chi_m\) is the single-center susceptibility and \(\lambda_{\text{int}}\) is the molecular field parameter. Positive and negative values of \(\lambda_{\text{int}}\) indicate dominant ferromagnetic and antiferromagnetic interactions, respectively.

As full model magnetic simulations of 5f\(^{8}\) systems had not been performed previously, we benchmarked the spin Hamiltonian implemented in CONDOR against the more comprehensively parameterized model Hamiltonian used by Carnall for the interpretation of optical spectra of TbCl\(_3\) (4f\(^6\)) and BkCl\(_3\) (5f\(^6\)), where the M\(^{3+}\) ions reside in \(D_2h\)-symmetric ligand environments (22).

Here, the ligand-field operator with reference to the threefold rotation axis for the angular part of the wave function reads

\[
B_{\text{mf}} = \sum_{j} B_{\text{mf}} C_{\text{mf}}(i, j) - \lambda_{\text{int}}
\]

**UV–vis-NIR spectroscopy**

Single crystals of each compound were placed on separate quartz slides under Krytox oil. The slide was kept inside a Linkam temperature control stage for an extra layer of containment throughout all the measurements. Using a Crain Technologies 20/20 microspectrophotometer the data were collected from 250 to 1700 nm (fig. S3). The exposure time was auto-optimized by the Crain software. Photoluminescence data were collected using the same microspectrophotometer with excitation wavelengths of 420 nm (fig. S4). The Linkam temperature control stage was used to control the temperature from room temperature down to 80 K.
A constant ($K_{ex}$) was assessed for berkelium at various temperatures. To assess $\beta_{103}$, $\beta_{102}$, and $\beta_{93}$ metal-DPA stability constants, partitioning of berkelium between the HDEHP/o-xylene organic phase and aqueous phase with increasing DPA concentration was measured. The ionization strength of the aqueous phase was maintained at 1.0 M using NaClO$_4$. All phases were pre-equilibrated with an appropriate aqueous or organic phase prior to use in the distribution study at the temperature of a given study. Pre-equilibration contact times were five minutes and contact times for thermodynamic measurements were fifteen minutes. The pH of the aqueous phase was measured after contact by using a series of standardized acid solutions at 1 M NaClO$_4$. Conversions from molality were converted to hydrogen ion concentrations using a harmonic force field. Stationary points have been identified as minima on the potential energy surface.

All complexation thermodynamics were assessed by using competitive solvent extraction investigations with bis-2-ethyl-hexyl-phosphoric acid (HDEHP) dissolved in o-xylene. The extraction constant ($K_{ex}$) was assessed for berkelium at various temperatures. To assess $\beta_{103}$, $\beta_{102}$, and $\beta_{93}$ metal-DPA stability constants, partitioning of berkelium between the HDEHP/o-xylene organic phase and aqueous phase with increasing DPA concentration was measured. The ion strength of the aqueous phase was maintained at 1.0 M using NaClO$_4$. All phases were pre-equilibrated with an appropriate aqueous or organic phase prior to use in the distribution study at the temperature of a given study. Pre-equilibration contact times were five minutes and contact times for thermodynamic measurements were fifteen minutes. The pH of the aqueous phase was measured after contact by using a series of standardized acid solutions at 1 M NaClO$_4$. Conversions from molality were converted to hydrogen ion concentrations using a harmonic force field. Stationary points have been identified as minima on the potential energy surface.

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/353/6302/aaf3762/suppl/DC1
Figs. S1 to S9
Tables S1 to S6
References (50–55)
Characterization of berkelium(III) dipicolinate and borate compounds in solution and the solid state


Editor's Summary

Bonding to berkelium

A geographical theme prevailed in the recent naming of the heaviest chemical elements. The choices brought to mind berkelium (Bk) and californium (Cf), the names chosen for elements 97 and 98 over half a century ago. Silver et al. now revisit the chemistry of Bk, which has proven fiercely challenging to study over the years on account of its vigorous radioactive decay. Synthetic crystallized Bk borate and dipicolinate compounds structurally resembled Cf analogs in the solid state but manifested distinct electronic and magnetic characteristics stemming from spin-orbit coupling effects. Science, this issue p. 888

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