Synthesis, Characterization, and High-Pressure Studies of a 3D Berkelium(III) Carboxylate Framework Material

Journal:	*ChemComm*
Manuscript ID	CC-COM-12-2021-006958.R1
Article Type:	Communication

COMMUNICATION

Synthesis, Characterization, and High-Pressure Studies of a 3D Berkelium(III) Carboxylate Framework Material

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Joseph M. Sperling,[a] Nicholas Beck,[a] Benjamin Scheibe,[a] Zhuanling Bai,[a] Jacob Brannon,[a] Daniela Gomez-Martinez,[a] Dennis Grödler,[b] Jason A. Johnson,[c] Xinsong Lin,[a] Brian M. Rotermund,[a] and Thomas E. Albrecht-Schönzart[a,*]

A berkelium(III) mellitate, $Bk_2[C_6(CO_2)_6](H_2O)_8\cdot 2H_2O$, was synthesized and rapidly crystallized by reacting mellitic acid, $C_6(CO_2H)_6$, and $BkBr_3\cdot nH_2O$ in an aqueous medium. Single crystal X-ray diffraction shows that the compound crystallizes as a three-dimensional framework isostructural with Pu(III), Am(III), and Cm(III) mellitates. UV-vis-NIR spectroscopic studies as a function of pressure were performed using a diamond anvil cell and show that the 5*f* → 5*f* transitions of Bk^{3+} display enhanced hypsochromic shifting when compared to other An(III) mellitates.

All elements beyond lead ($Z = 82$) are unstable and undergo radioactive decay. In some cases, the activity can be essentially dismissed because the half-lives are long enough that nuclear instability is not an impediment to experimental studies. Examples of this include ^{209}Bi ($t_{½} = 1.9 \pm 0.2 \times 10^{19}$ years)[1] and ^{238}U ($t_{½} = 4.5 \times 10^9$ years). Understanding electronic and nuclear structure beyond uranium is important for both practical and fundamental reasons such as recycling used nuclear fuel[2, 3] in the former case and gaining insight into relativistic effects on electronic structure in the latter.[4, 5]

Relativistic effects scale nonlinearly with nuclear charge and the optimal place to search for manifestations of these effects is where Z is also large as possible. The final two elements that can be prepared (by neutron irradiation of curium) at synthetically meaningful (milligram) levels are berkelium and californium. Beyond this, yields drop off precipitously for einsteinium ($Z = 99$, ~1 μg) and fermium ($Z = 100$, ~1 pg).[6] No known isotope of Fm undergoes β decay, and thus fusion methods are required for forging elements beyond $Z = 100$.

Thus, for macroscopic experimental studies, the final two elements that can be probed are berkelium and californium. Even though Cf lies beyond Bk, far less is known about its chemistry because the only available isotope, ^{249}Bk, suffers from the so-called odd-odd rule where both the proton number and atomic mass are odd giving rise to a lower stability and a half-life of only 330 days.[7] By comparison, ^{249}Cf has a half-life of 351 years and already poses significant synthetic hurdles. A calculation shows that a crystal the size of a grain of sand (75 μm cube) of *o*-BkF_3[8] (YF_3 structure type) needed for structural analysis would undergo over 10^8 decays/sec leading to rapid degradation, and thus early attempts to refine single crystal

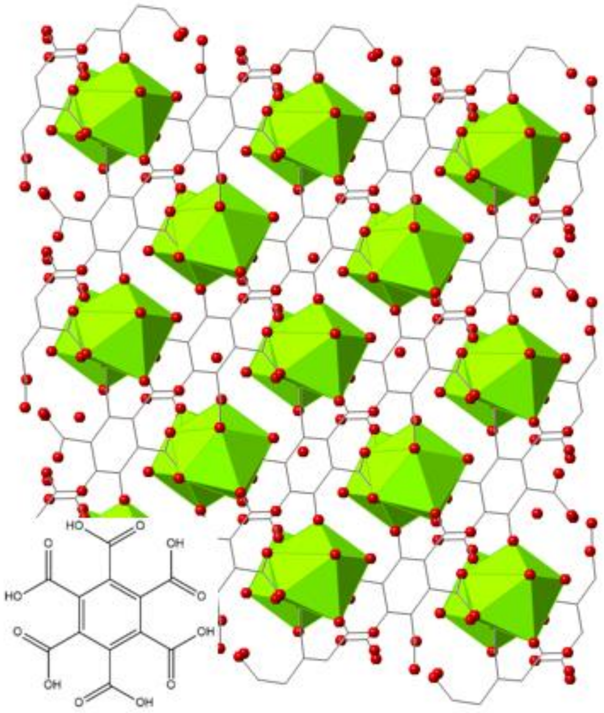

Fig. 1 The extended structure of **Bk1** viewed along the *b*-axis. (Bk, yellow-green; C, black; O, red) Hydrogen atoms omitted for clarity. A ChemDraw of mellitic acid (bottom left).

---

[a] Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way, RM. 118 DLC, Tallahassee, Florida 32306, USA
[b] Department of Chemistry, Institute for Inorganic Chemistry, University of Cologne, Greinstr. 4-6, 50939 Cologne, Germany
[c] Environmental Health and Safety, Florida State University, Tallahassee, Florida 32310, USA
*Email: talbrechtschoenzart@gmail.com

† Electronic Supplementary Information (ESI) available: Experimental details, photographs, extra crystallographic information, and supplementary electronic absorption spectra for berkelium mellitate. CCDC 2125963. For ESI and CIF files see DOI: 10.1039/x0xx00000x

data on berkelium compounds failed.[9] Modern instrumentation, such as diffractometers with area detectors and bright X-ray sources have allowed for detailed structural characterization to finally be performed. Although, to date, only six single crystal structures (with accompanying spectroscopic data and theory) of berkelium compounds have been published.[10-13] Herein we expand our understanding of this enigmatic element a bit further by preparing and characterizing a berkelium coordination polymer and subjecting it to high pressures.

Mellitic acid (benzene hexacarboxylic acid, $C_6(CO_2H)_6$) is formed in the dissolution of actinide carbides, a nuclear fuel form of interest, in nitric acid (>4M) making it a molecule of interest to study across the actinide series.[14, 15] The formation of trivalent *f*-element mellitate crystals can also occur in short time frames suitable for high activity actinide isotopes.[16] Recently, our group has studied a series of trivalent actinide mellitates for plutonium,[17] americium,[18] curium,[19] and californium.[20]

The Bk(III) mellitate, $Bk_2[C_6(CO_2)_6](H_2O)_8{\cdot}2H_2O$ (**Bk1**), was obtained by layering a green aqueous solution of $BkBr_3{\cdot}nH_2O$ (3.5 mg, 14 μmol $^{249}Bk^{3+}$ content) and mellitic acid with ethanol. Yellowish-green crystals of **Bk1** grew in three hours from this solution (further details are given in the ESI). All isolated crystals exhibited a uniform habit (Fig. S4-7, ESI) and were found by single crystal X-ray diffraction to be isostructural with $An_2[C_6(CO_2)_6](H_2O)_8{\cdot}2H_2O$ (An = β-Pu, Am, and Cm).[17-19] **Bk1** crystallizes in the monoclinic space group $P2_1/n$ (#14) with a three-dimensional framework as shown in Fig. 1. The berkelium metal centre resides on a general position and has a total coordination number of nine with two bidentate carboxylate groups (O1–O4), one monodentate carboxylate group (O1B), and four coordinating water molecules (O1W–O4W), Fig. 2, Tables S2-3. This connectivity results in the Niggli-type formula $^{3}_{\infty}\{[\mathrm{Bk(OH_2)_4}(\kappa^1\text{-}mel)_{1/6}(\kappa^2\text{-}mel)_{2/6}]{\cdot}\mathrm{H_2O}\}$. The Bk^{3+} molecular geometry most closely resembles muffin-type (1 + 5 + 3) geometry.[21]

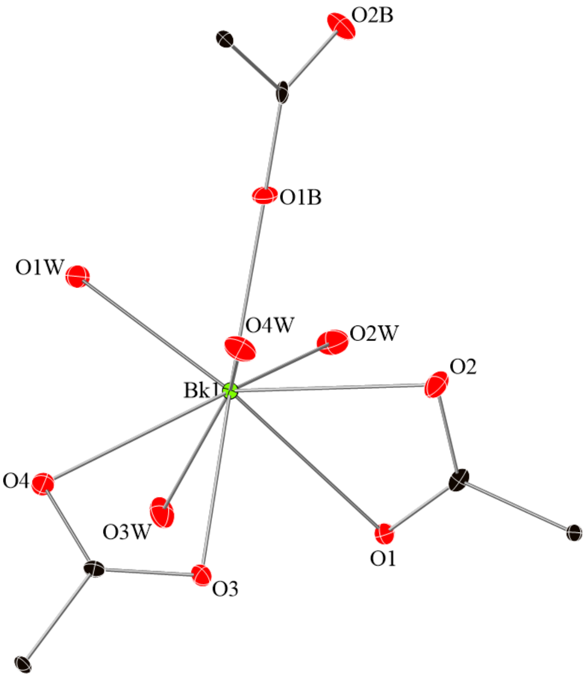

Fig. 2 Bk coordination environment in **Bk1** drawn with displacement ellipsoids at the 50% probability level at 100 K. (Bk, yellow-green; C, black; O, red) Hydrogen atoms omitted for clarity.

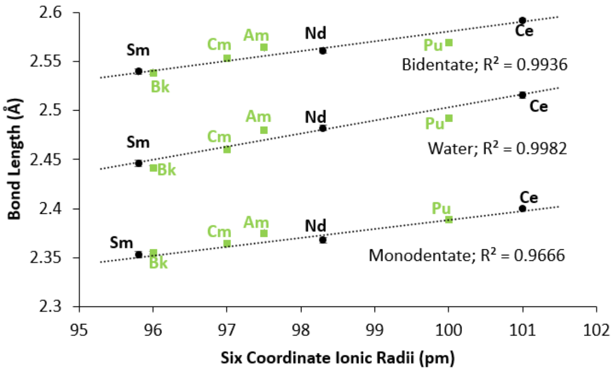

Fig. 3 Average bond lengths (in Å) of isostructural *f*–element mellitates with trend lines drawn for the lanthanide series. (lanthanides, black circles; actinides, green squares)

Owing to the scarcity of berkelium structural data, accurate comparisons between **Bk1** and other berkelium compounds cannot be made except for the monodentate carboxylate groups present in $Bk(Hdpa)_3{\cdot}nH_2O$ (H_2dpa = 2,6-pyridinedicarboxylic acid) that has a Bk–O range of 2.372(3) – 2.498(3) Å.[10] This bond length range does not overlap with the monodentate carboxylic acid bond length found in **Bk1** of 2.3552(16) Å. The bond length found in **Bk1** is likely much shorter because the $Hdpa^{1-}$ ligand acts as a tridentate ligand forming a tris chelate versus a dense extended framework formed with mellitate. This short Bk–O bond length also falls out of the bond length range of $Bk(DOPO^q)_3$ ($DOPO^{q-}$ = 2,4,6,8-tetra-*tert*-butyl-1-oxo-1*H*-phenoxazin-9-olate)[12] and $Bk[B_6O_8(OH)_5]$.[10] However, the broad Bk–O bond length range in $Bk(IO_3)_3$ (2.327(6) – 2.870(6) Å)[11] does overlap with all of the bond lengths found in **Bk1**.

Bond length analysis shows that the average lengths steadily decrease as the actinide series (Fig. 3, Table S3). This correlates with the decrease in the ionic radii caused by the actinide contraction.[22] Since the nine-coordinate radius of curium is yet to be determined, the bond lengths are plotted against the six-coordinate ionic radii. The actinide bond lengths do not substantially deviate from the lanthanide trendline showing that the bond lengths are what would be expected based on their radii. This trend is also observed in $An^{III}(IO_3)$ (An = Am, Bk, Cf),[11] $[An^{III}(H_2O)_9](CF_3SO_3)_3$ (M = U – Cf, excl. Bk),[23] $An^{III}{}_2(HPO_3)_3(H_2O)$ (An = Pu, Am),[24] and $An^{III}{}_2(C_4O_4)_3(H_2O)_4$ (An = Am, Cf).[25] The opposite effect is found in softer donor systems such as $An^{III}(dtc)_3(phen)$ (dtc^- = diethyldithiocarbamate; phen = 1,10-phenanthroline, An = Am, Cm, Cf),[26] $[K(crypt)][Pu^{III}(COT)_2]$ (crypt = 2.2.2-cryptand, COT^{2-} = cyclooctatetrenide),[27] and $An^{IV}L_2$ (H_2L = N,N′-bis[(4,4′-diethylamine)salicylidene]-1,2-phenylenediamine, An = Th, U, Np, Pu)[28, 29] where the actinide bond lengths fall significantly below the lanthanide-ligand bond trendline meaning the actinide bond lengths are shorter than expected based on their ionic radii.

Solid-state absorption spectra of **Bk1** were measured at ambient conditions (Fig. 4). The transition energies and relative intensities of the Laporte forbidden 5*f* → 5*f* transitions correlate well with the

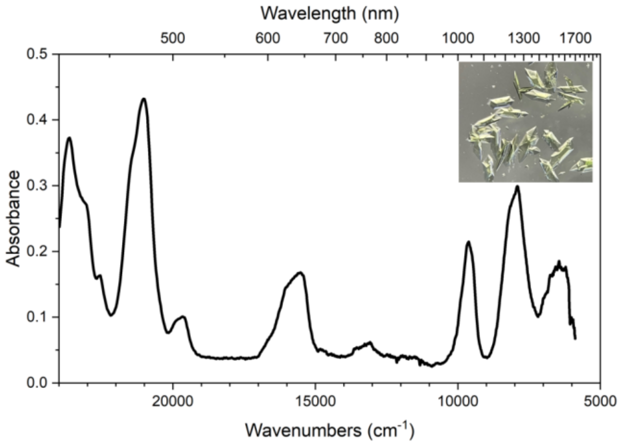

Fig. 4 Solid-state absorption spectrum of **Bk1** under ambient pressure and temperature with a photograph of a crop of the crystals.

solution spectrum of Bk^{3+} in $HClO_4/DClO_4$.[30] The most intense feature are the Groups E transitions ($^7F_6 \rightarrow {}^7F_2$, $^5H_{5,7}$, ^5L)[31,‡] where the maximum is located at 20,965 cm^{-1} (476 nm). This is also observed in several other solid-state spectra namely that of *h*- and *o*–$BkCl_3$.[32] However, this transition is obscured in $Bk(Hdpa)_3{\cdot}nH_2O$[10] and $Bk(IO_3)_3$.[11] There is a large gap between the transitions centred at 15,400 cm^{-1} (650 nm; Group C, $^7F_6 \rightarrow {}^7F_{6'}$, $^5D_4$, $^7F_4$, $^3H_6$) and 9,500 cm^{-1} (1,050 nm; Group B, $^7F_6 \rightarrow {}^7F_{0,1}$). This is with the exception of two small features between 11,000 and 13,900 cm^{-1} (720 and 900 nm). These are the Group C (11,000 cm^{-1}, 900 nm; $^6H_{15/2} \rightarrow {}^2H_{11/2}$) and Group D (13,900 cm^{-1}, 720 nm; $^6H_{15/2} \rightarrow {}^6H_{9/2}$, $^6F_{7/2}$) transitions for Cf^{3+}.[31, 33] This impurity is due to the high specific activity of ^{249}Bk that results in the ingrowth of ^{249}Cf at almost 1.5% per week. Since this experiment was completed 34 days after the initial Bk/Cf separation at ORNL that leads to the Cf content being roughly 6.8%. Since the Group D transitions for Cf^{3+} have amongst the highest molar absorptivity (~6.4 $M^{-1}cm^{-1}$) in 1 M $DClO_4$[34] and are close to the molar absorptivity of the Group E transitions of Bk^{3+} (~7 $M^{-1}cm^{-1}$),[35, 36] this observation makes sense. The other more intense Cf^{3+} transitions overlap with the intense transitions of Bk^{3+} which is why only the Group D and E transitions of Cf^{3+} are observed. Similar spectra with both Bk^{3+} and Cf^{3+} features are found in the literature such as *h*,*o*–$BkCl_3$[32] and $BkBr_3$[37] where the decay of $BkBr_3$ with the $PuBr_3$ structure type lead to the previously uncharacterized isostructural $CfBr_3$. Spectra taken at −180 °C show the same features with some line groups being slightly more resolved, namely in the Group E transitions (Fig. S9, ESI).

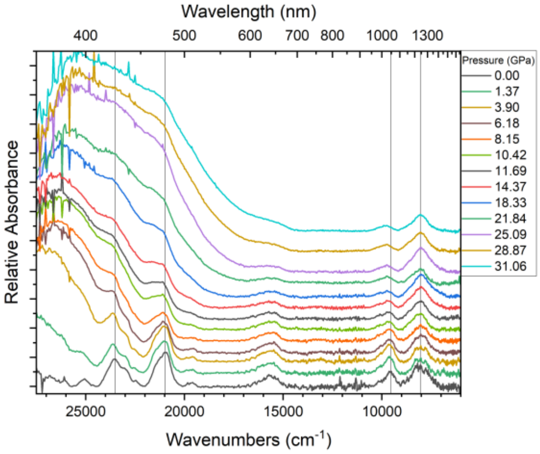

Fig. 5 Solid-state absorption spectra of **Bk1** measured at different pressures, with lines centred at several transitions at ambient pressure for guidance.

Crystals of **Bk1** were placed into a diamond anvil cell (DAC) to investigate how the 5*f* → 5*f* transitions are affected under pressure (Fig. 5). Compared to the americium,[18] curium,[19] and californium[20] mellitate, it appears that the average shift of a transition is hypsochromic (blue shifting) as opposed to bathochromic (red shifting) (Fig. S11, ESI). One clear example of a blue shifting peak are from the Group B ($^7F_6 \rightarrow {}^7F_{0,1}$) transitions centred at 9,630 cm^{-1} which shift 7.6 ± 0.7 cm^{-1}/GPa (Figs. S11, S13). Several other Bk^{3+} transitions feature blue shifting, a trend not observed in any of the other *f*-element mellitates. Another anomaly found in **Bk1** is that there is an intense transition appearing as pressure is applied in the high-energy region of the spectra that grows to lower energies as more pressure is applied causing a colour change from pale yellowish green to a deep red-orange (Fig. S15, ESI). The feature extends into lower energy at 3.90 GPa in **Bk1** than at over 10 GPa in the americium mellitate.[18] The intense feature is also reversible and therefore is not a result of degradation of the compound since the spectra of before and after the application of pressure are nearly identical (Fig. S14, ESI). Since this feature does not appear in any other actinide or lanthanide mellitates under pressure, it attributed to a metal-to-ligand charge transfer (MLCT) caused by the lower reduction potential compared to the other *f* -element mellitates studied so far ($Bk^{4+/3+}$, +1.3 V, 1 M $HClO_4$, vs. S.C.E).[38] This spectroscopic trend has also been found in *f*-element hexahalido complexes where MLCT peaks are found in lower energies if the reduction potential is smaller.[39]

In summary, $Bk_2[C_6(CO_2)_6](H_2O)_8{\cdot}2H_2O$ has been prepared from the reaction of $BkBr_3{\cdot}nH_2O$ with mellitic acid. This mellitate was found to be isostructural with previously reported plutonium (β-phase), americium, and curium analogues. Absorption spectra were measured for **Bk1** adding further details for the 5*f* → 5*f* transitions of Bk^{3+} in the solid-state. Unlike other reported actinide mellitates (Am, Cm, and Cf) where the typical 5*f* → 5*f* transitions experience bathochromic shifts, several Bk^{3+} transitions experience substantial hypsochromic shifts under pressure. This is likely due to the greater destabilization of some excited states with respect to the clear destabilization of the ground state evidenced by the ingrowth of an MLCT band not found in other actinide mellitates.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Heavy Elements Chemistry Program under Award Number DE-FG02-13ER16414. The crystallography work using a Rigaku Synergy-S single-crystal X-ray diffractometer was acquired through the NSF MRI program award number CHE-1828362. We are also grateful for the supplying of the isotopes by the U.S. Department of Energy Isotope Program, managed by the Office of Science for Nuclear Physics and the Radiochemical Engineering Development Centre (REDC) at Oak Ridge National Laboratory (ORNL) for purifying and processing the ^{249}Bk.

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

‡ The reference here is found specifically in the 103 page ESI which breaks down the Russel-Saunders terms of electronic transitions from the trivalent actinides U^{3+} to No^{3+} (Fm^{3+} - No^{3+} calc. only)

1 P. De Marcillac, N. Coron, G. Dambier, J. Leblanc and J.-P. Moalic, Nature, 2003, 422, 876-878.
2 J. Bruno and R. C. Ewing, Elements, 2006, 2, 343-349.
3 T. Taiwo, T. Kim, J. Stillman, R. Hill, M. Salvatores and P. Finck, Nucl. Technol., 2006, 155, 34-54.
4 P. Pyykko and J. P. Desclaux, Acc. Chem. Res., 1979, 12, 276-281.
5 M. Seth, M. Dolg, P. Fulde and P. Schwerdtfeger, J. Am. Chem. Soc., 1995, 117, 6597-6598.
6 J. Roberto, C. W. Alexander, R. A. Boll, J. Burns, J. Ezold, L. Felker, S. L. Hogle and K. Rykaczewski, Nucl. Phys. A, 2015, 944, 99-116.
7 V. Polyukhov, G. Timofeev and B. Levakov, Radiokhimiya, 1981, 23, 884-888.
8 J. Peterson and B. Cunningham, J. Inorg. Nucl. Chem., 1968, 30, 1775-1784.
9 P. G. Laubereau and J. H. Burns, Inorg. Chem., 1970, 9, 1091-1095.
10 M. A. Silver, S. K. Cary, J. A. Johnson, R. E. Baumbach, A. A. Arico, M. Luckey, M. Urban, J. C. Wang, M. J. Polinski, A. Chemey, G. Liu, K.-W. Chen, S. M. Van Cleve, M. L. Marsh, T. M. Eaton, L. J. van de Burgt, A. L. Gray, D. E. Hobart, K. Hanson, L. Maron, F. Gendron, J. Autschbach, M. Speldrich, P. Kögerler, P. Yang, J. Braley and T. E. Albrecht-Schmitt, Science, 2016, 353.
11 M. A. Silver, S. K. Cary, A. J. Garza, R. E. Baumbach, A. A. Arico, G. A. Galmin, K.-W. Chen, J. A. Johnson, J. C. Wang, R. J. Clark, A. Chemey, T. M. Eaton, M. L. Marsh, K. Seidler, S. S. Galley, L. van de Burgt, A. L. Gray, D. E. Hobart, K. Hanson, S. M. Van Cleve, F. Gendron, J. Autschbach, G. E. Scuseria, L. Maron, M. Speldrich, P. Kögerler, C. Celis-Barros, D. Páez-Hernández, R. Arratia-Pérez, M. Ruf and T. E. Albrecht-Schmitt, J. Am. Chem. Soc., 2017, 139, 13361-13375.
12 S. S. Galley, S. A. Pattenaude, C. A. Gaggioli, Y. Qiao, J. M. Sperling, M. Zeller, S. Pakhira, J. L. Mendoza-Cortes, E. J. Schelter and T. E. Albrecht-Schmitt, J. Am. Chem. Soc., 2019, 141, 2356-2366.
13 A. N. Gaiser, C. Celis-Barros, F. D. White, M. J. Beltran-Leiva, J. M. Sperling, S. R. Salpage, T. N. Poe, D. Martinez Gomez, T. Jian, N. J. Wolford, N. J. Jones, A. J. Ritz, R. A. Lazenby, J. K. Gibson, R. E. Baumbach, D. Páez-Hernández, M. L. Neidig and T. E. Albrecht-Schönzart, Nat. Commun., 2021, 12, 7230-7238.
14 P. L. Pauson, J. McLean and W. J. Clelland, Nature, 1963, 197, 1200.
15 L. M. Ferris and M. J. Bradley, J. Am. Chem. Soc., 1965, 87, 1710-1714.
16 L. L. da Luz, R. Milani, J. F. Felix, I. R. B. Ribeiro, M. Talhavini, B. A. D. Neto, J. Chojnacki, M. O. Rodrigues and S. A. Júnior, ACS Appl. Mater. Interfaces, 2015, 7, 27115-27123.
17 J. M. Sperling, A. N. Gaiser, C. J. Windorff, B. E. Klamm, M. A. Whitefoot, A. T. Chemey, B. N. Long, J. G. Campbell and T. E. Albrecht-Schmitt, Inorg. Chem., 2020, 59, 3085-3090.
18 J. M. Sperling, E. Warzecha, B. E. Klamm, A. N. Gaiser, C. J. Windorff, M. A. Whitefoot and T. E. Albrecht-Schönzart, Inorg. Chem., 2021, 60, 476-483.
19 J. M. Sperling, E. J. Warzecha, C. Celis-Barros, D.-C. Sergentu, X. Wang, B. E. Klamm, C. J. Windorff, A. N. Gaiser, F. D. White, D. A. Beery, A. T. Chemey, M. A. Whitefoot, B. N. Long, K. Hanson, P. Kögerler, M. Speldrich, E. Zurek, J. Autschbach and T. E. Albrecht-Schönzart, Nature, 2020, 583, 396-399.
20 J. M. Sperling, E. Warzecha, C. J. Windorff, B. E. Klamm, A. N. Gaiser, M. A. Whitefoot, F. D. White, T. N. Poe and T. E. Albrecht-Schönzart, Inorg. Chem., 2020, 59, 10794-10801.
21 A. Ruiz-Martínez, D. Casanova and S. Alvarez, Chem. Eur. J., 2008, 14, 1291-1303.
22 R. D. Shannon, Acta Crystallogr., Sect. A: Found. Crystallogr., 1976, 32, 751-767.
23 C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis, O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R. G. Haire, J. Rabizant, F. Bruchertseifer and T. Fanghänel, Angew. Chem. Int. Ed., 2010, 49, 6343-6347.
24 J. N. Cross, E. M. Villa, S. Wang, J. Diwu, M. J. Polinski and T. E. Albrecht-Schmitt, Inorg. Chem., 2012, 51, 8419-8424.
25 N. Brenner, J. M. Sperling, T. N. Poe, C. Celis-Barros, K. Brittain, E. M. Villa, T. E. Albrecht-Schmitt and M. J. Polinski, Inorg. Chem., 2020, 59, 9384-9395.
26 S. K. Cary, J. Su, S. S. Galley, T. E. Albrecht-Schmitt, E. R. Batista, M. G. Ferrier, S. A. Kozimor, V. Mocko, B. L. Scott, C. E. Van Alstine, F. D. White and P. Yang, Dalton Trans., 2018, 47, 14452-14461.
27 C. J. Windorff, J. M. Sperling, T. E. Albrecht-Schönzart, Z. Bai, W. J. Evans, A. N. Gaiser, A. J. Gaunt, C. A. Goodwin, D. E. Hobart, Z. K. Huffman, D. N. Huh, B. E. Klamm, T. N. Poe and E. Warzecha, Inorg. Chem., 2020, 59, 13301-13314.
28 B. E. Klamm, C. J. Windorff, M. L. Marsh, D. S. Meeker and T. E. Albrecht-Schmitt, Chem. Commun., 2018, 54, 8634-8636.
29 B. E. Klamm, C. J. Windorff, C. Celis-Barros, M. J. Beltran-Leiva, J. M. Sperling and T. E. Albrecht-Schönzart, Inorg. Chem., 2020, 59, 18035-18047.
30 W. T. Carnall, J. Beitz and H. Crosswhite, J. Chem. Phys., 1984, 80, 2301-2308.
31 W. T. Carnall, J. Chem. Phys., 1992, 96, 8713-8726.
32 J. Peterson, J. Young, D. Ensor and R. Haire, Inorg. Chem., 1986, 25, 3779-3782.
33 W. T. Carnall, S. Fried and F. Wagner Jr, J. Chem. Phys., 1973, 58, 1938-1949.
34 J. Conway, S. Fried, R. Latimer, R. McLaughlin, R. Gutmacher, W. Carnall and P. Fields, The Solution Absorption Spectrum of Cf3+, Report UCRL-16971, Ernest O. Lawrence Radiation Laboratory, 1966.
35 R. Gutmacher, E. Hulet, R. Lougheed, J. Conway, W. Carnall, D. Cohen, T. Keenan and R. Baybarz, J. Inorg. Nucl. Chem., 1967, 29, 2341-2345.
36 W. Carnall and S. Fried, Spectroscopic Properties of Bk3+ and Cf3+, Argonne National Lab., Ill.(USA), Argonne National Lab, 1975.
37 J. Young, R. Haire, J. Peterson, D. Ensor and R. Fellows, Inorg. Chem., 1980, 19, 2209-2212.
38 J. R. Stokely, R. D. Baybarz and J. R. Peterson, J. Inorg. Nucl. Chem., 1972, 34, 392-393.
39 L. Nugent, R. Baybarz, J. Burnett and J. Ryan, J. Inorg. Nucl. Chem., 1971, 33, 2503-2530.