

COMMUNICATION

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

DOI: 10.1039/x0xx00000x

Exploring Crown-Ether Functionalization on the Stabilization of Hexavalent Neptunium.

Mikaela M. Pynch, James M. Williams, and Tori Z. Forbes*

Crown-ether molecules are used in radiochemical separations due to their high selectivity for a range of metal cations. Previous investigations regarding the interactions of 18-crown-6 (18C6) with ^{237}Np suggested the formation of a Np(V) inclusion complex, but also reported rapid reduction of Np(VI) to Np(V) in the presence of the ether molecule. Herein, we investigate the impact of crown ether functionalization by exploring the Np(V) and Np(VI) dicyclohexano-18-crown-6 (DCH-18C6) systems. Two $[\text{X}(\text{DCH-18C6})_2[\text{Np(VI)O}_2\text{Cl}_4]]$ compounds (X = K (1) and Na (2)) were crystallized and characterized by [single crystal X-ray diffraction and Raman spectroscopy](#). Additional studies of Np(VI), Np(V), and Np(V)/Np(VI) in solution indicated redox stability in the presence of functionalized crowns and preferential crystallization of Np(VI) DCH-18C6 solids. These results indicate that functionalization of the crown can lead to higher resistance to radiolysis and increased stability of the Np(VI) oxidation state in solution.

Macrocyclic ether molecules are of interest for radiochemical separations due to their ability to selectively chelate a multitude of metal cations.¹ Initially, crown ether molecules were explored for the liquid-liquid extraction of fission products and were found to be quite effective in the separation process. Crown ether molecules have been utilized in several radiochemical separation schemes, including CSEX-SREX, SRTALK, and ALSEP.¹ Studies done by Matel and Bilbao² and Vibhute *et al.*³ reported distribution coefficients of > 1000 for ^{90}Sr and ^{137}Cs within dibenzo- and dicyclohexano-functionalized crown ethers. These functionalized crown ether molecules, particularly dicyclohexano-18-crown-6 (DCH-18C6), also exhibit high selectivity toward [tetravalent U, Np, and Pu](#) cations, with distribution coefficients of up to 64.^{4,5}

Further use of crown ether molecules to encapsulate and extract actinides in the pentavalent and hexavalent oxidation states is enticing due to the unique coordination geometries

associated with these elements in aqueous conditions.^{6,7} Actinides in these higher oxidation state will form the nearly linear dioxo actinyl cation ($\text{AnO}_2^{7/2+}$) that can be further coordinated about the equatorial plane by four, five, or six equatorial ligands. The actinide cation is a hard Lewis acid and prefers coordination with O donor groups; thus, macrocyclic ethers seemed like ideal candidates to encapsulate the actinyl cation around the equatorial plane. Again, DCH-18C6 was found to have a higher affinity for the U(VI)O_2^{2+} cation, but the distribution coefficients were lower (<5.6) compared to the tetravalent state.⁸ Rogers and coworkers⁹⁻¹¹ determined that in aqueous conditions U(VI)O_2^{2+} tends to form an outer sphere complex with crown ether molecules, but subtle differences were observed for Np(V). Clark *et al.*¹² demonstrated that Np(V) strongly favours encapsulation by the unfunctionalized 18C6 molecule to form a stable inclusion complex. Shamov *et al.* then utilized DFT calculations to demonstrate that the smaller solvation energy of the Np(V)O_2^{2+} supports the formation of the inner sphere complex, in contrast to the behaviour in the U(VI)O_2^{2+} and Np(VI)O_2^{2+} systems.¹³

Clark *et al.*¹² also noted in this initial work that it was difficult to stabilize Np(VI) stock solutions in the presence of the 18C6 molecule due to rapid reduction to Np(V) and subsequent formation of the $[\text{NpO}_2(18\text{C6})]^+$ inclusion complex. This reduction would occur even in the presence of strong oxidizers, such as ozone. We noted a similar occurrence in a related study involving the interaction of Np(VI) with the 18C6 molecule.¹⁴ In all cases, we observed rapid reduction of the Np(VI) stock resulting in Np(V) or a mixed Np(V)/Np(VI) solution. Solid products formed from an initial Np(VI) stock solution typically included the $[\text{NpO}_2(18\text{C6})]^+$ inclusion complex, although biphasic systems could be produced [with isolation of only that included the Np\(V\) compound and](#) minor amounts of the Np(VI) products.

Controlling the redox of ^{237}Np in the presence of organic ligands, such as crown ethers, is important for effective separations processes. The redox behaviour is crucial for controlling neptunium removal because Np(VI) is considered an

* Department of Chemistry, University of Iowa, Iowa City, IA 52242 *tori-forbes@uiowa.edu

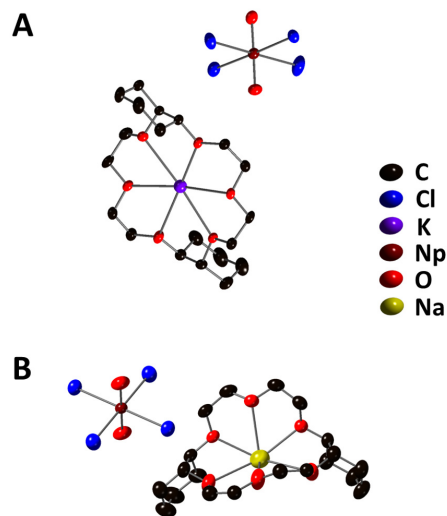
Electronic Supplementary Information (ESI) available: Synthetic details, Single-crystal X-ray diffraction data, Raman spectroscopy. See DOI: 10.1039/x0xx00000x

extractable species whereas Np(V) is inextractable in processes such as PUREX and TALSPEAK.^{15,16} In the current study, we set out to evaluate the behaviour of the neptunyl cation in the presence of functionalized crown ether molecules (DCH-18C6). This molecule was chosen because has been previously investigated for use in radiochemical extractions, exhibits higher solubility than other functionalized crown ether molecules, and is commercially available. During this process, we noted significant differences in the redox behaviour of the system and the resulting material when compared to the simple 18C6 system. Herein, we describe the crystallization of Np(VI) tetrachloro species in the presence of dicyclohexano-18-crown-6 ($[\text{X}(\text{DCH-18C6})]_2[\text{NpO}_2\text{Cl}_4]$ (X = K (1), Na (2)) and structural features determined via single crystal X-ray diffraction. We also provide characterization using Raman spectroscopy and discuss the behaviour of Np(V) and Np(V)/Np(VI) DCH-18C6 solutions.

Crystallization of **1** and **2** occurred through a room-temperature evaporation process. Compound **1** precipitated from a Np(VI) stock in the presence of the DCH-18C6 ligand. The K⁺ cation was not added as a separate synthetic ingredient in this case, but was present in the stock solution as a by-product of the Np reprocessing procedure. Crystallization of compound **2** occurred by adding a Np(VI) stock solution in 1 M HCl to a Na⁺-DCH-18C6 complex dissolved in methanol. The crystallization process was explored under various molar ratios of metal to ligand (Np:crown ratios of 1:2, 1:4). The material was highly reproducible under all of these conditions. Liquid scintillation counting indicated that the overall yield of solid-state products was approximately 90% based upon Np.

While the basic structural features for **1** and **2** are similar, there are observable differences in the configuration of the DCH-18C6 molecule (Fig. 1). Compound **1** crystallizes in the monoclinic $P2_1/c$ space group with the asymmetric unit consisting of two unique $[\text{NpO}_2\text{Cl}_4]^{2-}$ complexes, and three $[\text{K}(\text{DCH-18C6})]^+$ molecules. Structure **2** formed in the same space group and the asymmetric unit contains one unique $[\text{NpO}_2\text{Cl}_4]^{2-}$ moiety and one $[\text{Na}(\text{DCH-18C6})]^+$ complex. The neptunyl (Np=O) and Np-Cl bonds for the $[\text{NpO}_2\text{Cl}_4]^{2-}$ complexes range from 1.734(6) to 1.744(4) Å and 2.645(2) to 2.665(2) Å, respectively. Bond distances observed for **1** and **2** are similar to previously reported $[\text{NpO}_2\text{Cl}_4]^{2-}$ species, confirming the hexavalent oxidation state of the Np cation.^{17,18} The major difference between the two compounds is the configuration of the DCH-18C6 molecule, which is observed in *cis-anti-cis* and *cis-syn-cis* configurations for **1** and **2**, respectively. There is additional buckling of the DCH-18C6 with the encapsulation of the Na⁺ cation, which may be caused by a mismatch between the diameter of alkali cation and crown ether molecule.

Raman spectroscopy on the solid-state material was performed to further confirm the oxidation state of the neptunyl cation in these coordination compounds (Fig. S5 and S6). The spectral window of interest for the neptunyl symmetric stretch (ν_1) is located between 700 to 950 cm^{-1} . In the case of both **1** and **2**, the spectra are quite complex with 10 vibrational bands noted in this region. The most intense spectral features in **1** and **2** are located at 793 and 930 cm^{-1} , respectively, and these bands were assigned to DCH-18C6 modes based upon



previous work by Takeuchi *et al.*¹⁹ Most of the features in this

Figure 1. $[\text{Na}(\text{DCH-18C6})]^+$ and $[\text{NpO}_2\text{Cl}_4]^{2-}$ complexes observed in compounds (a) **1** and (b) **2**. The Np, Cl, O, C, K, and Na atoms are represented by maroon, blue, red, black, purple, and yellow ellipsoids, respectively. The H atoms have omitted from the image for clarity.

region can also be assigned to the crown ether, with variations in the position and intensity of the bands corresponding to the different conformations of the DCH-18C6 molecule. A single spectral feature could not be assigned to the crown ether; thus, we concluded that it was associated with the $[\text{NpO}_2\text{Cl}_4]^{2-}$ complex. The Raman active Np(VI)O₂ symmetric stretch is located at 805 and 802 cm^{-1} for **1** and **2**, respectively. These values are similar to previously reported solid-state compounds containing the $[\text{Np(VI)O}_2\text{Cl}_4]^{2-}$ complex.^{18,20} The Np(V)O₂⁺ symmetric stretching bands are typically observed at 780 cm^{-1} or lower, confirming that the presence of hexavalent Np complexes in compounds **1** and **2**.²¹

To further evaluate the effect of the DCH-18C6 molecule on the oxidation state of Np, we performed additional syntheses with pure Np(V) and mixed Np(V)/Np(VI) stock solutions. The mixed oxidation state stock was confirmed via Raman spectroscopy (SI Fig.3). We were unable to crystallize a Np(V) DCH-18C6 solid, which was surprising given the ease of forming the $[\text{NpO}_2(\text{18C6})]^+$ inclusion complex with a variety of different counterions. Instead, evaporation of the solution resulted in clear salt crystals surrounded by an amorphous solid. In the mixed Np(V)/Np(VI) solution, the DCH-18C6 molecule selectively crystallized **1**, leaving the emerald green Np(V) behind in solution (Fig. S4). Due to the small volume of the remaining solution, we were unable to collect spectroscopic data to confirm oxidation state. However, the colour is indicative of a concentrated Np(V) solution.

The Raman spectra of the initial Np(VI) and Np(V) DCH-18C6 solutions used in the crystallization process show subtle shifts in the crown ether bands and the appearance of the ν_1 symmetric stretch of the neptunyl cation (Figure 2). Spectral features at 788 and 809 cm^{-1} remain in similar positions for the free crown ether molecule, as well as in the presence of Np(V)O_2^+ and Np(VI)O_2^{2+} cations. Notable differences in the spectra of the free DCH-18C6 molecule compared to the Np(VI) DCH-18C6 solution occurs in the window between 820–870 cm^{-1} . Most markedly is the increased intensity of the band at 838 cm^{-1} and the appearance of a broad feature with peak centroid at 854 cm^{-1} . We assigned the feature at 838 cm^{-1} to the DCH-18C6 molecule, which is supported by Takeuchi *et al.*¹⁹ who noted an increase in the intensity and a narrowing of this peak in the presence of alkali cations. The broader feature at 854 cm^{-1} is assigned to the symmetric stretch of the Np(VI)O_2 moiety due to similarities in peak position and the FWHM (24 cm^{-1}) for the Np stock solution. Spectral features observed in the Np(V) DCH-18C6 solution between 820–870 cm^{-1} are red shifted compared to the free ligand and may indicate additional complexation or encapsulation of the neptunyl cation. An additional band centred at 767 cm^{-1} appears in the spectrum that is associated with the ν_1 Np(V)O_2^+ symmetric stretch. Both solutions were monitored over time and there is no evidence of significant changes in the Np oxidation state. This is also supported by the fractional crystallization of the Np(V)/Np(VI) system that was described *vide supra*.

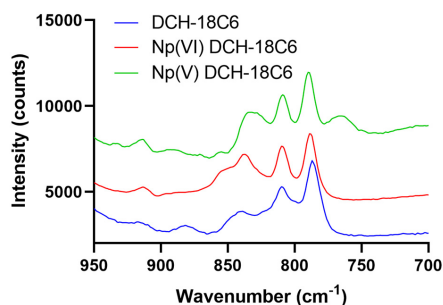


Figure 2. Solution-phase Raman spectroscopy of the pure DCH-18C6 ligand (blue), Np(VI) stock with the DCH-18C6 ligand (red), and Np(V) stock with the DCH-18C6 ligand (green).

To compare the impact of the crown functionalization on the Np redox stability, we monitored the same Np(VI) stock solution for 72 hours in the presence of 18C6 or DCH-18C6 using Raman spectroscopy for 72 hours. In the case of the Np(VI) DCH-18C6 solution, the spectral features remained the same throughout the experiment. A subtle shoulder does appear in the spectra centred at 786 cm^{-1} and that can be contributed to the presence of both DCH-18C6 isomers in solution.¹⁹ Differences are observed with the Np(VI) 18C6 solutions, namely the ingrowth of a band at 767 cm^{-1} . As noted earlier,

this band is assigned to the Np(V)O_2^+ symmetric stretch (ν_1) in solution and indicates reduction of the Np(VI) stock. The intense spectral feature at 861 cm^{-1} is associated with the ν_{43} of 18C6 ligand obscures ν_1 band of the Np(VI)O_2^{2+} that should be present at $\sim 855 \text{ cm}^{-1}$. This makes it difficult to assess the amount of reduction that has occurred within this experiment. However, using data from a previous Np(V) 18C6 titration experiment¹⁴ allowed us to evaluate the relationship between the intensity ratio of the two bands and the mole ratio of the two components in solution (see supporting information for additional details). From the linear regression ($R^2 = 0.988$), we can approximate the Np(VI) reduction in this system. The

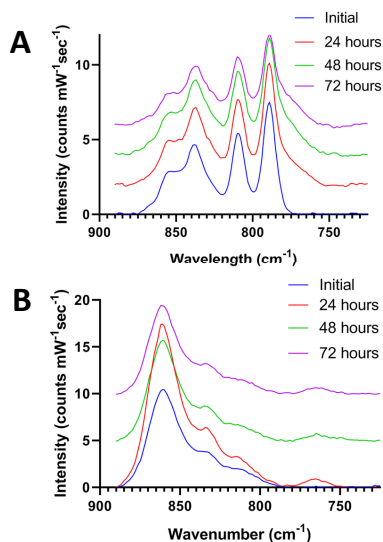


Figure 3. Solution-phase Raman spectroscopy of the initial (A) Np(VI) DCH-18C6 and (B) Np(VI)-18C6 solution and after 24, 48, and 72 hours.

original mole Np(VI): mole 18C6 ratio was 0.325 and the resulting mole Np(V):mole 18C6 ratio was calculated as 0.29 after 24 hours. This translates to 88% of the original Np(VI) reduced over the course of 24 hours and 96% reduction after three days.

Reduction of $^{237}\text{Np(VI)}$ to Np(V) has been previously noted in aqueous conditions and the redox behaviour can be impacted by radiolysis and the presence of organic molecules.^{7, 22} Under acidic conditions, Np(VI) will reduce to Np(V) as a consequence of its own self radiolysis. The rate constant for this reaction was determined to be $3.1 \times 10^{-9} \text{ s}^{-1}$ in 0.044–0.3 M Np(VI) solutions and the radiochemical yield was calculated at 0.66 $\mu\text{mol/J}$.²³ Radiolysis in solution can also be enhanced by the presence of the ^{233}Pa ($t_{1/2} = 27$ days) daughter product, which decays through β^- to form $^{233}\text{Uranium}$.⁷ Release of ionizing radiation from ^{237}Np and its daughters can form free radicals (produced from the radiolysis of water) in solution and results in the slow

Formatted: Superscript

reduction of Np(VI) to Np(V) in aqueous conditions. Organic molecules can also form radicals under ionizing radiation and influence the Np(V)/Np(VI) redox couple by partaking in fast electron transfer reactions, either as oxidizing or reducing agents.

Our results suggest that the resistance of the DCH-18C6 molecule to radiolysis leads to stability of the Np(VI) oxidation state and ultimately the formation of the $[\text{Na}(\text{DCH-18C6})_2[\text{NpO}_2\text{Cl}_4]]$ compound. Crown ether molecules are chemically robust, but can be impacted by radicals that form in solution. Radiolysis effects on crown-ether molecules have been previously explored by several groups, and functionalization impacts the formation rate of radicals in the system. Zatonksy and Povolotskaya²⁴ measured the radiation resistance of 18C6 compared to the dicyclohexano and dibenzo derivatives to gamma radiation and monitored the production of H₂ gas to determine radical formation and molecular degradation rates. The 18C6 molecule produced twice as much H₂ gas under these conditions as the dicyclohexano functionalized molecule, suggesting higher susceptibility to ionizing radiation. Further studies by Abashkin *et al.*²⁵ found that no radiolysis products were observed for DCH-18C6 molecule at absorbed radiation doses of less than 500 kGy. This is in contrast to 18C6 where radiation effects and degradation of the molecule are noted at levels of 0.45 kGy.

In conclusion, we have successfully synthesized and characterized two related DCH-18C6 neptunyl tetrachloro complexes. The stability of the Np(VI)DCH-18C6 solution and [production of a single oxidation state as a monophasic isolation of the Np\(VI\) solid in high yields](#) is unusual, given the redox activity that has been previously associated with the neptunyl 18C6 system. We have observed that compounds **1** and **2** are highly reproducible under a range of conditions [with high yields](#), and that the reduction of Np(VI) upon addition of the functionalized crown-ether molecule does not occur. This redox behaviour diverges from previously observed work by Clark *et al.*¹² and highlights the importance of the functionalized crown ether molecule in stabilizing the hexavalent oxidation state. We have also demonstrated that Np(VI) can be stabilized in the presence of DCH-18C6, but reduces to Np(V) in the presence of 18C6. This may be associated with differences in radiolysis caused by ²³⁷Np and related daughter products. These results also provide additional knowledge on the behaviour of neptunium in the presence of functionalized crown ether molecules, which may have implications in future separations processes.

Conflicts of interest

The Authors declare no conflict of interest.

Acknowledgements

We would like to acknowledge the Department of Energy Basic Energy Sciences Early Career Award (DE-SC0013980) for supporting this work.

Notes and references

- S. V. Nesterov, *Russian-Russ. Chemical-Chem. Reviews*, 2000, **69**, 769-782.
- L. Matel and T. Bilbao, *Journal of Radioanalytical Radioanalyt. and Nucl. Chem. Letters*, 1989, **137**, 183-190.
- R. G. Vibhute and S. M. Khopkar, *Journal of Radioanalyt. and Nucl. Chem. Letters*, 1991, **152**, 487-496.
- J. P. Shukla, R. K. Singh and A. Kumar, *Radiochim. Acta*, 1991, **54**, 73-77.
- A. G. Godbole, N. V. Thakur, R. Swarup and S. K. Patil, *Journal of Radioanalytical and Nuclear Chemistry Letters*, 1987, **108**, 89-98.
- P. C. Burns, *The Canadian Mineralogist*, 2005, **43**, 1839-1894.
- L. R. Morss, N. Edelstein, J. Fuger and J. J. Katz, eds., *The Chemistry of the Actinide and Transactinide Elements*, Springer-Verlag Publishing, Berlin, Germany, 2011.
- V. Guyon, J. Foss, A. Guy, T. Moutarde, R. Chomel, M. Draye and M. Lemaire, *Separation Science and Technology*, 1995, **30**, 1961-1980.
- R. D. Rogers, A. H. Bond and W. G. Hipple, *Journal of Crystallographic and Spectroscopic Spectrosc. Research Res.*, 1990, **20**, 611-616.
- R. D. Rogers, A. H. Bond, W. G. Hipple, A. N. Rollins and R. F. Henry, *Inorganic Chemistry*, 1991, **30**, 2671-2679.
- R. D. Rogers, A. H. Bond and W. G. Hipple, *Journal of Crystallographic and Spectroscopic Spectrosc. Research Res.*, 1992, **22**, 365-369.
- D. L. Clark, D. W. Keogh, P. D. Palmer, B. L. Scott and C. D. Tait, *Angew. Chem. Int. Ed.*, 1998, **37**, 164-166.
- G. A. Shamov, G. Schreckenbach, R. L. Martin and P. J. Hay, *Inorganic-Inorg. Chemistry*, 2008, **47**, 1465-1475.
- M. Basile, E. Cole and T. Z. Forbes, *Inorganic-Inorg. Chemistry Chem.*, 2018, **57**, 6016-6028.
- H. Zhang, Z. Y. Liu, X. M. Zhou and L. Li, *Journal of Radioanalytical and Nuclear Nucl. Chemistry Chem.*, 2017, **312**, 173-180.
- B. J. Mincher, *Journal of Radioanalytical Radioanalyt. and Nuclear Nucl. Chemistry Chem.*, 2018, **316**, 799-804.
- S. M. Cornet, M. P. Redmond, D. Collision, C. A. Sharrad, M. Helliwell and J. Warren, *C. R. Chim.*, 2010, **13**, 832-838.
- D. D. Schnaars and R. E. Wilson, *Inorg. Chem.*, 2018, **57**, 3008-3016.
- H. Takeuchi, T. Arai and I. Harada, *Journal of Molecular Molec. Structure Struct.*, 1990, **223**, 355-364.
- J. L. Bjorklund, M. M. Pyrch, M. C. Basile, S. E. Mason and T. Z. Forbes, *Dalton Trans.*, 2019, [Advance Article](#), **48**, 8861-8871.
- B. Guillaume, G. M. Begun and R. L. Hahn, *Inorganic-Inorg. Chemistry Chem.*, 1981, **21**, 1159-1166.
- B. J. Mincher, M. Precek and A. Paulenova, *J. Radioanal. Nucl. Chem.*, 2016, **308**, 1005-1009.
- A. K. Pikaev, V. P. Shilov and A. V. Gogolev, *Russian-Russ. Chemical-Chem. Reviews*, 1997, **66**, 763-788.
- S. V. Zatonksy and O. S. Povolotskaya, *Journal of Radioanalytical Radioanalyt. and Nuclear Nucl. Chemistry Chem. Letters*, 1987, **117**, 361-367.

25. V. M. Abashkin, D. W. Wester, J. A. Campbell and K. E. Grant, *Radiat. Phys. Chem.*, 1996, **48**, 463-472.
1. S. V. Nesterov, *Russian Chemical Reviews*, 2000, **69**, 769-782.
 2. L. Matel and T. Bilbao, *Journal of Radioanalytical and Nuclear Chemistry Letters*, 1989, **137**, 183-190.
 3. R. G. Vibhute and S. M. Khopkar, *Journal of Radioanalytical and Nuclear Chemistry Articles*, 1991, **152**, 487-496.
 4. J. P. Shukla, R. K. Singh and A. Kumar, *Radiochimica Acta*, 1991, **54**, 73-77.
 5. P. C. Burns, *The Canadian Mineralogist*, 2005, **43**, 1829-1894.
 6. L. R. Morss, N. Edelstein, J. Fuger and J. J. Katz, eds., *The Chemistry of the Actinide and Transactinide Elements*, Springer-Verlag Publishing, Berlin, Germany, 2011.
 7. V. Guyon, J. Foes, A. Guy, T. Moutarde, R. Chemel, M. Draye and M. Lemaire, *Sep. Sci. Techn.*, 1995, **30**, 1961-1980.
 8. R. D. Rogers, A. H. Bond and W. G. Hipple, *Journal of Crystallographic and Spectroscopic Research*, 1990, **20**, 611-616.
 9. R. D. Rogers, A. H. Bond, W. G. Hipple, A. N. Rollins and R. F. Henry, *Inorganic Chemistry*, 1991, **30**, 2671-2679.
 10. R. D. Rogers, A. H. Bond and W. G. Hipple, *Journal of Crystallographic and Spectroscopic Research*, 1992, **22**, 265-269.
 11. D. L. Clark, D. W. Keogh, P. D. Palmer, B. L. Scott and C. D. Tait, *Angew. Chem. Int. Ed.*, 1998, **37**, 164-166.
 12. G. A. Shamov, G. Schreckenbach, R. L. Martin and P. J. Hay, *Inorganic Chemistry*, 2008, **47**, 1465-1475.
 13. M. Basile, E. Cole and T. Z. Forbes, *Inorganic Chemistry*, 2018, **57**, 6016-6028.
 14. H. Zhang, Z. Y. Liu, X. M. Zhou and L. Li, *Journal of Radioanalytical and Nuclear Chemistry*, 2017, **312**, 173-180.
 15. B. J. Mincher, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, **316**, 799-804.
 16. S. M. Cornet, M. P. Redmond, D. Collison, C. A. Sharrad, M. Helliwell and J. Warren, *C. R. Chim.*, 2010, **13**, 832-838.
 17. D. D. Schnaars and R. E. Wilson, *Inorg. Chem.*, 2018, **57**, 2008-2016.
 18. H. Takeuchi, T. Arai and I. Harada, *Journal of Molecular Structure*, 1990, **223**, 355-364.
 19. J. L. Bjorklund, M. M. Pynch, M. C. Basile, S. E. Mason and T. Z. Forbes, *Dalton Trans.*, 2019, **Advance Article**.
 20. B. Guillaume, G. M. Begun and R. L. Hahn, *Inorganic Chemistry*, 1981, **21**, 1159-1166.
 21. B. J. Mincher, M. Precek and A. Paulenova, *J. Radioanal. Nucl. Chem.*, 2016, **308**, 1005-1009.
 22. A. K. Pikaev, V. P. Shilov and A. V. Gogolev, *Russian Chemical Reviews*, 1997, **66**, 763-788.
 23. S. V. Zatonksy and O. S. Povolotskaya, *Journal of Radioanalytical and Nuclear Chemistry Letters*, 1987, **117**, 361-367.
 24. V. M. Abashkin, D. W. Wester, J. A. Campbell and K. E. Grant, *Radiat. Phys. Chem.*, 1996, **48**, 463-472.
3. R. G. Vibhute and S. M. Khopkar, *J. Radioanal. Nucl. Chem. Art.*, 1991, **152**, 487-496.
 4. J. P. Shukla, R. K. Singh and A. Kumar, *Radiochim. Acta*, 1991, **54**, 73-77.
 5. P. C. Burns, *Can. Mineral.*, 2005, **43**, 1829-1894.
 6. L. R. Morss, N. Edelstein, J. Fuger and J. J. Katz, eds., *The Chemistry of the Actinide and Transactinide Elements*, Springer Verlag Publishing, Berlin, Germany, 2011.
 7. V. Guyon, J. Foes, A. Guy, T. Moutarde, R. Chemel, M. Draye and M. Lemaire, *Sep. Sci. Techn.*, 1995, **30**, 1961-1980.
 8. R. D. Rogers, A. H. Bond and W. G. Hipple, *J. Cryst. Spectrosc. Res.*, 1990, **20**, 611-616.
 9. R. D. Rogers, A. H. Bond, W. G. Hipple, A. N. Rollins and R. F. Henry, *Inorg. Chem.*, 1991, **30**, 2671-2679.
 10. R. D. Rogers, A. H. Bond and W. G. Hipple, *J. Cryst. Spectrosc. Res.*, 1992, **22**, 265-269.
 11. D. L. Clark, D. W. Keogh, P. D. Palmer, B. L. Scott and C. D. Tait, *Angew. Chem. Int. Ed.*, 1998, **37**, 164-166.
 12. G. A. Shamov, G. Schreckenbach, R. L. Martin and P. J. Hay, *Inorg. Chem.*, 2008, **47**, 1465-1475.
 13. M. Basile, E. Cole and T. Z. Forbes, *Inorg. Chem.*, 2018, **57**, 6016-6028.
 14. H. Zhang, Z. Y. Liu, X. M. Zhou and L. Li, *J. Radioanal. Nucl. Chem.*, 2017, **312**, 173-180.
 15. B. J. Mincher, *J. Radioanal. Nucl. Chem.*, 2018, **316**, 799-804.
 16. S. M. Cornet, M. P. Redmond, D. Collison, C. A. Sharrad, M. Helliwell and J. Warren, *C. R. Chim.*, 2010, **13**, 832-838.
 17. D. D. Schnaars and R. E. Wilson, *Inorg. Chem.*, 2018, **57**, 2008-2016.
 18. H. Takeuchi, T. Arai and I. Harada, *J. Molec. Struct.*, 1990, **223**, 355-364.
 19. J. L. Bjorklund, M. M. Pynch, M. C. Basile, S. E. Mason and T. Z. Forbes, *Dalton Trans.*, 2019, **Advance Article**.
 20. B. Guillaume, G. M. Begun and R. L. Hahn, *Inorg. Chem.*, 1981, **21**, 1159-1166.
 21. B. J. Mincher, M. Precek and A. Paulenova, *J. Radioanal. Nucl. Chem.*, 2016, **308**, 1005-1009.
 22. A. K. Pikaev, V. P. Shilov and A. V. Gogolev, *Russ. Chem. Rev.*, 1997, **66**, 763-788.
 23. S. V. Zatonksy and O. S. Povolotskaya, *J. Radioanal. Nucl. Chem. Lett.*, 1987, **117**, 361-367.
 24. V. M. Abashkin, D. W. Wester, J. A. Campbell and K. E. Grant, *Radiat. Phys. Chem.*, 1996, **48**, 463-472.
1. S. V. Nesterov, *Russ. Chem. Rev.*, 2000, **69**, 769-782.
 2. L. Matel and T. Bilbao, *J. Radioanal. Nucl. Chem. Lett.*, 1989, **137**, 183-190.