



**Soft-donor dipicolinamide derivatives for selective actinide(III) / lanthanide(III) separation: The role of S- vs. O-donor sites**

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-09-2018-007683.R3
Article Type:	Communication

SCHOLARONE™  
Manuscripts

## Soft-donor dipicolinamide derivatives for selective actinide(III) / lanthanide(III) separation: The role of S- vs. O-donor sites†

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

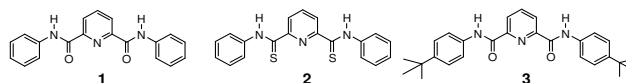
Ingrid Lehman-Andino<sup>a</sup>, Jing Su<sup>b</sup>, Konstantinos E. Papanthanasou<sup>a</sup>, Teresa M. Eaton<sup>c,§</sup>, Jiwen Jian<sup>c</sup>, David Dan<sup>d</sup>, Thomas E. Albrecht-Schmitt<sup>d</sup>, Christopher J. Dares<sup>a</sup>, Enrique R. Batista<sup>b,\*</sup>, Ping Yang<sup>b,\*</sup>, John K. Gibson<sup>c,\*</sup>, and Konstantinos Kavallieratos<sup>a,\*</sup>

**Selectivity for An(III) vs. Ln(III) binding and extraction using dipicolinamide analogs containing the C=O vs. C=S groups was investigated in solution, gas-phase, and by DFT calculations. The results show higher selectivity for complex formation and extraction for Am(III) vs. Eu(III) for the softer dithioamide vs. the diamide ligand, while in CH<sub>3</sub>CN the diamide binds more strongly than the thioamide to several Ln(III), forming 1:1 complexes.**

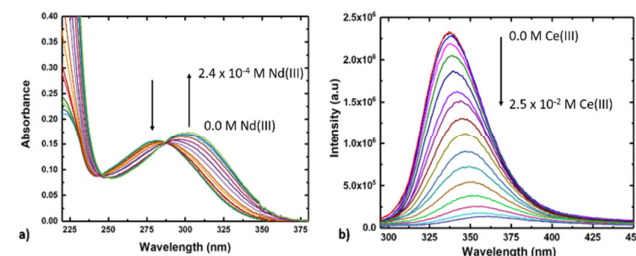
Long-lived minor actinides (An) such as <sup>241</sup>Am, <sup>245</sup>Cm, and <sup>237</sup>Np are present together with fission products in used nuclear fuel (UNF) and are responsible for much of the radiotoxicity and heat generation that limit the capacity of geological repositories.<sup>1–7</sup> Thus, removing minor An from UNF can reduce storage time from thousands of years to a few hundred years.<sup>1,8</sup> Furthermore, large neutron cross-sections of lanthanide (Ln) fission products interfere with transmutation and compromise long-term geological disposal.<sup>9</sup> Selective An(III)/Ln(III) separation based on complexation and extraction must overcome difficulties due to similar properties of these elements in their dominant +III oxidation state.<sup>10,11</sup> The An(III) 5*f* valence orbitals allow for a stronger covalent component in metal-ligand interactions with soft donor ligands, as compared to Ln(III) 4*f* orbitals.<sup>12–19</sup>

Since the 1980s a variety of soft- N- and O-donor ligands have been introduced for selective An(III) vs. Ln(III) complexation and extraction, some with excellent separation properties.<sup>2,9,20–25</sup> S-donors, such as the P=S ligand Cyanex 301,<sup>10,12</sup> have been studied less, with concerns including stability under the highly acidic and oxidizing conditions of UNF, as well as adherence to the CHON principle for safe

disposal.<sup>26</sup> Thioamide derivatives of dipicolinic acid have been known to complex softer transition metals, but their An(III) vs. Ln(III) coordination chemistry remains unknown, even though they are more stable than other thio-ligands<sup>27</sup> with the N=C=S group<sup>28–29</sup> offering higher basicity, polarizability, and covalent character than the analogous N-C=O.<sup>30</sup>



**Figure 1.** *N,N'*-bis(phenyl)pyridine-2,6-dicarboxamide (**1**), *N,N'*-bis(phenyl)pyridine-2,6-bis(carbothioamide) (**2**) and *N,N'*-bis(4-*tert*-butyl)phenyl)pyridine-2,6-dicarboxamide (**3**).



**Figure 2.** a) UV-Visible titration in CH<sub>3</sub>CN of **1** ( $1.3 \times 10^{-5}$  M) with Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O ( $1.0 \times 10^{-3}$  M). b) Fluorescence titration in CH<sub>3</sub>CN of **1** ( $1.2 \times 10^{-4}$  M) with Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O ( $1.1 \times 10^{-2}$  M).  $\lambda_{\text{exc.}} = 282$  nm.

Herein we present a selective dithioamide ligand for An(III) vs. Ln(III) separation from highly acidic aqueous media via solvent extraction (**2** in Fig. 1), a detailed Ln(III) binding study of the diamide **1**, and a direct comparison of C=O vs. C=S analogs and their complexation properties. Experiments and theory indicate 1:1 stoichiometry in solution in the presence of coordinating NO<sub>3</sub><sup>-</sup>, while the X-ray structure of the *t*-Bu analog **3** with Nd(III) in the presence of I<sup>-</sup> reveals a 1:3 metal:ligand stoichiometry. Collision Induced Dissociation Electrospray Ionization Mass Spectrometry (CID-ESI-MS) and DFT theoretical calculations corroborate the extraction and solution complexation studies. This N-C=S vs. N-C=O comparison points to potential future applicability of

<sup>a</sup> Department of Chemistry and Biochemistry and Biomolecular Sciences Institute, Florida International University. kavallie@fiu.edu

<sup>b</sup> Theoretical Division, Los Alamos National Laboratory. pyang@lanl.gov, erb@lanl.gov

<sup>c</sup> Chemical Sciences Division, Lawrence Berkeley National Laboratory. jkgibson@lbl.gov

<sup>d</sup> Department of Chemistry and Biochemistry, Florida State University.

†Electronic Supplementary Information (ESI) available: CCDC 1854275. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

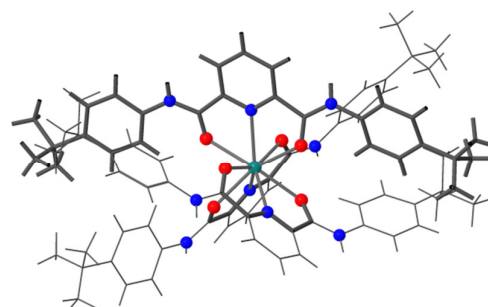
<sup>§</sup> Current Address: Embry-Riddle Aeronautical University, Prescott, AZ

optimized thioamide analogs for selective minor actinide separations.

Initial Ln(III) binding experiments were carried out by NMR, UV-Vis and fluorescence titrations. The diamide **1** shows maximum absorption at  $\lambda_{\text{max}} = 282$  nm and fluorescence emission at  $\lambda_{\text{em}} = 338$  nm, (Fig. 2), while the dithioamide **2** shows an absorption maximum at  $\lambda_{\text{max}} = 311$  nm and no significant fluorescence emission. Upon addition of several Ln(III) salts in CH<sub>3</sub>CN (under constant concentration of **1**), a new lower energy band was observed, with clear isosbestic points. Figure 2a shows the UV-Vis titration with Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, with similar results obtained for La(III), Eu(III), and Lu(III) (ESI). Fluorescence titrations with the same Ln(III) salts showed fluorescence quenching at 338 nm with a slight red shift (Figure 2b). Titration of dithioamide **2** with the same Ln(III) salts showed no significant changes upon Ln(III) addition (ESI). <sup>1</sup>H-NMR titrations with La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in acetone-d<sub>6</sub> showed chemical shift changes for diamide **1** but no observable changes for dithioamide **2** under the same conditions (ESI). UV-Vis continuous variation method (Job plot) experiments (plots of Abs x [1]/([Ln(III)]+[1]) vs. mol. fraction) showed maxima at 0.5, consistent with 1:1 binding stoichiometry (ESI). Fluorescence titration curves were also found consistent with a 1:1 Ln(III):1 binding stoichiometry. The di(*t*-Bu)diamide analog **3** showed similar spectroscopic changes with **1** upon Ln(III) addition (ESI).

Attempts to crystallize the Ln(III) complexes with **1-3** in the presence of Ln(III)-nitrate salts were unsuccessful. However, when the more weakly-coordinating I<sup>-</sup> salt was used, instead of NO<sub>3</sub><sup>-</sup>, crystals of the complex of diamide **3** with several Ln(III) were obtained. The structure of [Nd(**3**)<sub>3</sub>]<sub>3</sub>·3CH<sub>3</sub>CN (Fig. 3) consists of Nd<sup>3+</sup>, an Am<sup>3+</sup> structural surrogate,<sup>31-32</sup> complexed by three tridentate ligands creating a distorted, 9-coordinate environment. The I<sup>-</sup> anions are in the outer sphere, with the closest contacts between the three I<sup>-</sup> anions and the arene rings at 3.67(6), 3.52(6), and 3.53(6) Å.<sup>33-35</sup> The average Nd–N and Nd–O bond distances are 2.593(3) and 2.469(3) Å respectively. The structure is instructive of how distortions due to bulky donors allow for high M:L coordination ratios. The ligand ability to extract Am(III) vs. Eu(III) under acidic conditions was investigated by solvent extraction experiments

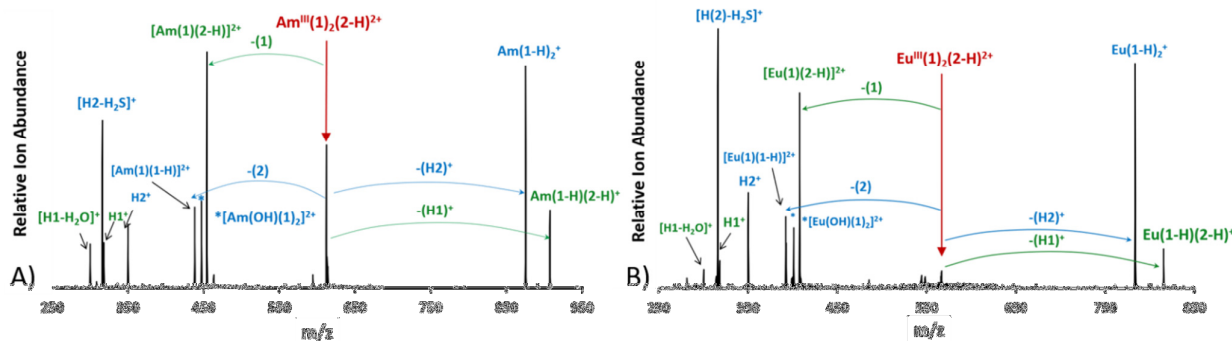
with <sup>243</sup>Am and <sup>154</sup>Eu in CH<sub>2</sub>Cl<sub>2</sub>/HNO<sub>3</sub> (6.5 M). Both **1** and **2** exhibit stronger extraction for Am(III) vs. Eu(III) into dichloromethane solutions saturated with ligand. Specifically, a Am/Eu separation factor (SF) of 5 (±2) was determined for C=O ligand **1**, while a SF of 17 (±3) was measured for C=S ligand **2** (ESI), with the thioamide ligand **2** also showing substantially higher solubility, and thus stronger extraction. Slightly weaker extraction is observed from 1.0 M HNO<sub>3</sub> (ESI). Our SF<sub>Am/Eu</sub> of 17 while lower than the system reported by Geist,<sup>1</sup> it is slightly higher than most reported systems for extraction from highly acidic media (Table S1, ESI)



**Figure 3.** Structure of [Nd(**3**)<sub>3</sub>]<sub>3</sub>·3CH<sub>3</sub>CN. *N,N'*-bis(4-*tert*-butyl)phenylpyridine-2,6-dicarboxamide complex with Nd<sup>3+</sup>, showing a three-face centered trigonal prism (D<sub>3h</sub>) coordination sphere (CN 9) surrounding the metal center.

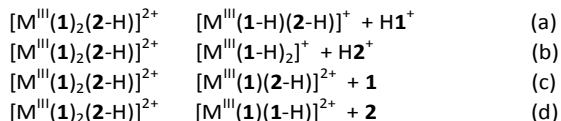
Although solvent effects, including entropy, may be important in actual separations, fragmentation of bare gas-phase coordination complexes can offer fundamental insights into metal-ligand binding in the absence of such effects. The CID-ESI-MS of mixed ligand complexes with Am(III) and Eu(III) show i) a higher relative stability of the Am(III) vs Eu(III) complex, and ii) based on the four different decomposition pathways for ligand loss: A higher tendency of Eu(III) for **2** vs **1** ligand loss, as determined by the relative intensity ratios.

The gas-phase complexes [M(1)<sub>2</sub>(2-H)]<sup>2+</sup>/[M(1)(2)(1-H)]<sup>2+</sup> (these two isomers are denoted hereafter as [M(1)<sub>2</sub>(2-H)]<sup>2+</sup>, where M = Am or Eu, were produced by ESI and subjected to CID in a quadrupole ion trap. The L-H notation (for L = **1** or **2**) indicates H<sup>+</sup> loss. The tricationic gas-phase complexes [M(1)<sub>2</sub>(2)]<sup>3+</sup>, which might be more directly comparable to



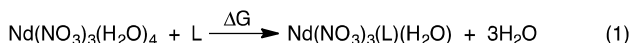
**Figure 4.** CID results for mixed-ligand complexes with **1** and **2** of (a) Am(III), and (b) Eu(III), at nominal CID energies of 0.6 V and 0.5 V, for (a) and (b), respectively.

solution species, were not produced in appreciable yields by ESI. CID of mixed-ligand complexes such as  $[M(\mathbf{1})_2(\mathbf{2-H})]^{2+}$  can illuminate relative binding strengths of the two ligands **1** and **2**. The dominant CID fragmentation pathways apparent in Figure 4 for  $[M(\mathbf{1})_2(\mathbf{2-H})]^{2+}$  are given by reactions **a-d**. Reactions **b** and **c** were dominant over **a** and **d** for both  $M = \text{Am}$  and  $M = \text{Eu}$ .



The results in Figure 4 show that the Eu(III) complex fragments more easily, as revealed by near complete depletion of the parent peak in Fig. 4b at a lower CID energy, nominally 0.5 V, than Am(III), nominally 0.6 V (Fig. 4a), where substantial unfragmented Am(III) parent complex remains. This more facile fragmentation of the Eu(III) complex is in accord with the greater affinity of both **1** and **2** for Am(III) versus Eu(III) in solution. Another apparent difference is that the contribution of reaction **a** relative to reaction **b** is greater for Am(III) versus Eu(III). Even though the change from an O- to an S- ligand affects not only the relative covalency of M-L bonding, these gas-phase results suggest that the direct bonding interactions between ligands and metal center are the dominant factor determining metal-ligand affinities, and the solvation and/or entropy may be secondary effects. Notably, this is precisely the effect observed in solution, where the Am/Eu SF is higher for **2** vs. **1**. The key gas-phase fragmentation results, and the remarkable parallels with the observed solution affinities, suggest that the SFs are, at least partly, governed by intrinsic differences in binding of Am(III) and Eu(III) to **1** and **2**.

To understand the complexation thermodynamics of the ligands **1** and **2** with Nd(III), and the UV-Vis absorption spectral changes in the titrations, DFT calculations were performed on the reactant  $\text{Nd}(\text{NO}_3)_3(\text{H}_2\text{O})_4$ , obtained by removing two  $\text{H}_2\text{O}$  molecules in the 2<sup>nd</sup> coordination sphere in the X-ray structure of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,<sup>36</sup> to form a model 1:1 Nd(III):L product,  $\text{Nd}(\text{NO}_3)_3(\text{L})(\text{H}_2\text{O})$  ( $L = \mathbf{1}$  or  $\mathbf{2}$ ). Even though we can't claim that these 1:1 M-L species are exclusively formed under extraction conditions and higher complexation is also possible, these products are likely formed in the extraction experiment as shown in prior work with analogous tridentate ligands.<sup>23,37</sup> The optimized structures are shown in Figure S14 (ESI) and show tridentate coordination. The calculated Gibbs free energies ( $\Delta G$ ) of the complexation reaction 1 are  $-15.49$  and  $-3.77$  kcal/mol for ligands **1** and **2**, respectively (ESI): Ligand complexation with Nd(III) is thermodynamically favorable, with **1** the stronger complexant.



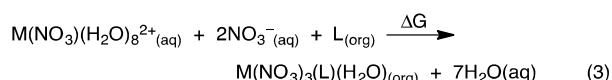
The calculated UV-Vis spectra (ESI) show a red shift of the lowest energy absorption from 267 nm for unbound **1** to 288 nm for  $\text{Nd}(\text{NO}_3)_3(\mathbf{1})(\text{H}_2\text{O})$ , which is consistent with the UV-Vis titration results. The DFT-derived UV-Vis for **2** and  $\text{Nd}(\text{NO}_3)_3(\mathbf{2})(\text{H}_2\text{O})$  show a slight blue shift of maximum absorption from 304 nm in **2** to 294 nm in the complex, also in accord with the minimal changes in UV-Vis titrations.

The binding affinity of **1** versus **2** towards M(III) ( $M = \text{Nd}, \text{Eu}, \text{Am}$ ) was evaluated from ligand exchange reaction 2:

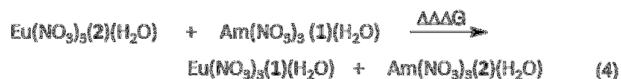


The calculated  $\Delta G$  values in Table S4 are negative with the values slightly different depending on solvents; the  $\Delta G$  for solvent  $\text{CH}_2\text{Cl}_2$  are  $-11.93$ ,  $-15.10$  and  $-14.53$  kcal/mol for  $M = \text{Nd}, \text{Eu}$  and  $\text{Am}$ , respectively, which suggests stronger binding of **1** vs. **2** towards both Ln(III) and An(III).

The extraction selectivity of **1** vs. **2** for Eu(III) and Am(III) in  $\text{CH}_2\text{Cl}_2/\text{HNO}_3$  was also assessed in a two-phase extraction system by the reaction 3 where  $\text{M}(\text{NO}_3)_3(\text{H}_2\text{O})_8^{2+}$  (optimized structure in ESI) and  $\text{M}(\text{NO}_3)_3(\text{L})(\text{H}_2\text{O})$  are taken as the dominant species of both Am(III) and Eu(III) in aqueous and organic phases, respectively ( $M = \text{Am}/\text{Eu}$  and  $L = \mathbf{1}$  or  $\mathbf{2}$ ):<sup>9</sup>



From the  $\Delta G(\text{Eu})$ ,  $\Delta G(\text{Am})$  and  $\Delta\Delta G(\text{Am-Eu})$  values (Table S5, ESI), it is shown that  $\Delta G(\text{Am})$  is more negative than  $\Delta G(\text{Eu})$ , resulting in  $\Delta\Delta G(\text{Am-Eu})$  of  $-1.03$  and  $-1.60$  kcal/mol, for **1** and **2**, respectively. These values are in excellent agreement with the corresponding experimental results of  $-0.93$  and  $-1.68$  kcal/mol, which follow from SFs 5 for **1** and 17 for **2**, according to the formula  $\Delta\Delta G = -RT \ln SF_{\text{Am/Eu}}$  ( $T = 298$  K). The calculated  $\Delta\Delta G(\text{Am-Eu}) = -1.03$  kcal/mol for **1** is also very close to the previously computed value of  $-0.76$  kcal/mol for Et-Tol-PyDA,<sup>9</sup> which is an analog of **1**. The Am(III)/Eu(III) extraction selectivity into  $\text{CH}_2\text{Cl}_2$  was evaluated according to reaction 4:



The  $\Delta\Delta\Delta G$  is calculated to be  $-0.57$  kcal/mol, which is consistent with experimental value of  $-0.77$  kcal/mol for Am(III) vs. Eu(III) extraction (ESI-Figure S7). The reason for higher selectivity of **2** towards Am(III) is that replacement of thioamide **2** with oxoamide **1** stabilizes Eu(III) vs. Am(III) ( $-15.10$  versus  $-14.53$  kcal/mol - Eq. 2). This thermodynamic preference is possibly due to increased covalency in Am-S vs. Eu-S bonding, as discussed elsewhere.<sup>38-42</sup> Although replacing  $\text{M}(\text{NO}_3)_3(\text{H}_2\text{O})_8^{2+}$  with  $\text{M}(\text{H}_2\text{O})_9^{3+}$  in Eq. 3 significantly changes  $\Delta G$ , it has an insignificant overall influence on  $\Delta\Delta G(\text{Am-Eu})$  (ESI) or  $\Delta\Delta\Delta G$  (Eq. 4).  $\Delta\Delta\Delta G$  values have been valuable for evaluating relative separation selectivities.<sup>43</sup>

In conclusion, our investigation of binding and An(III) vs. Ln(III) extraction selectivity of C=O vs. C=S dipicolinamide analogs demonstrates the potential of simple dithiopicolinamides as selective extractants for minor actinides under highly acidic conditions consistent with UNF reprocessing. DFT results reveal a stronger affinity of diamide **1** vs. dithioamide **2** for both Ln(III) and An(III), while also demonstrating that **2** has a higher Am(III)/Eu(III) separation selectivity. Titrations with  $\text{NO}_3^-$  salts show strong Ln(III) binding by the diamide ligand with 1:1 metal-to-ligand stoichiometry, while X-ray crystallography indicates a 1:3 stoichiometry when  $\Gamma^-$  is used. Such solvent and

counteranion-dependent coordination effects<sup>44-46</sup> can affect speciation under UNF extraction conditions.

This research was supported by the Center for Actinide Science and Technology (CAST), an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (Award DE-SC0016568). ILA was supported by a U.S. Nuclear Regulatory Commission fellowship (NRC-HQ-84-14-G-0040/NRC-HQ-84-15-G-0038). JS, a Glenn T. Seaborg postdoctoral fellow, acknowledges use of DOE-EMSL facility. We are grateful to Dr. Travis S. Grimes (Idaho National Lab) for solvent extraction experimental help and advice.

### Conflicts of Interest

There are no conflicts to declare

### Notes and references

- A. Geist, C. Hill, G. Modolo, M. R. S. J. Foreman, M. Weigl, K. Gompper and M. J. Hudson, *Solvent Extr. Ion Exch.*, 2006, **24**, 463–483.
- P. J. Panak and A. Geist, *Chem. Rev.*, 2013, **113**, 1199–1236.
- M. J. Hudson, L. M. Harwood, D. M. Laventine and F. W. Lewis, *Inorg. Chem.*, 2013, **52**, 3414–3428.
- S. Demir, N. K. Brune, J. F. Van Humbeck, J. A. Mason, T. V. Plakhova, S. Wang, G. Tian, S. G. Minasian, T. Tyliczszak, T. Yaita, T. Kobayashi, S. N. Kalmykov, H. Shiwaku, D. K. Shuh and J. R. Long, *ACS Cent. Sci.*, 2016, **2**, 253–265.
- E. Macerata, E. Mossini, S. Scaravaggi, M. Mariani, A. Mele, W. Panzeri, N. Boubals, L. Berthon, M.-C. Charbonnel, F. Sansone, A. Arduini and A. Casnati, *J. Am. Chem. Soc.*, 2016, **138**, 7232–5.
- A. Geist, U. Müllich, D. Magnusson, P. Kaden, G. Modolo, A. Wilden and T. Zevaco, *Solvent Extr. Ion Exch.*, 2012, **30**, 433–444.
- P. R. Zalupski, K. L. Nash and L. R. Martin, *J. Solut. Chem.*, 2010, **39**, 1213–1229.
- J. Magill, V. Berthou, D. Haas, J. Galy, R. Schenkel and G. Heusener, *Nuclear Energy*, 2003, **42**, 263–277.
- Q.-Y. Wu, Y.-T. Song, L. Ji, C.-Z. Wang, Z.-F. Chai and W.-Q. Shi, *Phys. Chem. Chem. Phys.*, 2017, **19**, 26969–26979.
- G. Modolo and R. Odoj, *J. Alloys Compd.*, 1998, **271–3**, 248–251.
- A. Bhattacharyya, Mohapatra P. K. and V. K. Manchanda, *Solvent Extr. Ion Exch.*, 2006, **24**, 1–17.
- K. L. Nash, *Solvent Extr. Ion Exch.*, 2015, **33**, 1–55.
- Y. A. Ustynyuk, I. P. Gloriov, S. N. Kalmykov, A. A. Mitrofanov, V. A. Babain, M. Y. Alyapyshev and N. A. Ustynyuk, *Solvent Extr. Ion Exch.*, 2014, **32**, 508–528.
- C. Marie, M. Miguiditchian, D. Guillaumont, A. Tosseng, C. Berthon, P. Guilbaud, M. Duvail, J. Bisson, D. Guillauneux, M. Pipelier and D. Dubreuil, *Inorg. Chem.*, 2011, **50**, 6557–6566.
- B. J. Mincher, L. R. Martin and N. C. Schmitt, *Solvent Extr. Ion Exch.*, 2012, **30**, 445–456.
- J. C. Braley, T. S. Grimes and K. L. Nash, *Ind. Eng. Chem. Res.*, 2012, **51**, 629–638.
- J. N. Cross, J. Su, E. R. Batista, S. K. Cary, W. J. Evans, S. A. Kozimor, V. Mocko, B. L. Scott, B. W. Stein, C. J. Windorff and P. Yang, *J. Am. Chem. Soc.*, 2017, **139**, 8667–8677.
- M. P. Kelley, J. Su, M. Urban, M. Luckey, E. R. Batista, P. Yang and J. C. Shafer, *J. Am. Chem. Soc.*, 2017, **139**, 9901–9908.
- M. P. Kelley, G. J.-P. Deblonde, J. Su, C. H. Booth, R. J. Abergel, E. R. Batista and P. Yang, *Inorg. Chem.*, 2018, **57**, 5352–5363.
- D. M. Whittaker, T. L. Griffiths, M. Helliwell, A. N. Swinburne, L. S. Natrajan, F. W. Lewis, L. M. Harwood, S. A. Parry and C. A. Sharrad, *Inorg. Chem.*, 2013, **52**, 3429–3444.
- J. Wang, D. Su, D. Wang, S. Ding, C. Huang, H. Huang, X. Hu, Z. Wang and S. Li, *Inorg. Chem.*, 2015, **54**, 10648–10655.
- Kolarik, Z.; Müllich, U.; Gassner, F., *Solvent Extr. Ion Exch.*, 1999, **17**, 1155–1170.
- M. Y. Alyapyshev, V. A. Babain, L. I. Tkachenko, A. Paulenova, A. A. Popova and N. E. Borisova, *Solvent Extr. Ion Exch.*, 2014, **32**, 138–152.
- C.-L. Xiao, C.-Z. Wang, L.-Y. Yuan, B. Li, H. He, S. Wang, Y.-L. Zhao, Z.-F. Chai and W.-Q. Shi, *Inorg. Chem.*, 2014, **53**, 1712–1720.
- J. Bisson, J. Dehaut, M.-C. Charbonnel, D. Guillauneux, M. Miguiditchian, C. Marie, N. Boubals, G. Dutech, M. Pipelier, V. Blot and D. Dubreuil, *Chem. Weinh. Bergstr. Ger.*, 2014, **20**, 7819–7829.
- A. Geist, M. Weigl, U. Müllich and K. Gompper, *Nuclear Fuel Cycle And Fuel Materials*, 2001, **32**, 641–647.
- Y. Komiyama, J. Kuwabara and T. Kanbara, *Organometallics*, 2014, **33**, 885–891.
- T. S. Jagodziński, *Chem. Rev.*, 2003, **103**, 197–228.
- Q.-Q. Wang, R. Ara Begum, V. W. Day and K. Bowman-James, *Inorg. Chem.*, 2012, **51**, 760–762.
- F. Berny and G. Wipff, *J. Chem. Soc. Perkin Trans. 2*, 2001, 73–82.
- J. N. Cross, E. M. Villa, S. Wang, J. Diwu, M. J. Polinski, and T. E. Albrecht-Schmitt, *Inorg. Chem.*, 2012, **51**, 8419–8424.
- D. Lundberg, *J. Radioanal. Nucl. Chem.* 2018, **2**, 849–854.
- M. Albrecht, C. Wessel, M. de Groot, K. Rissanen and A. Lüchow, *J. Am. Chem. Soc.*, 2008, **130**, 4600–4601.
- G. Garau, A. Frontera, D. Quiñonero, P. Ballester, A. Costa and P. M. Deyà, *J. Phys. Chem. A*, 2004, **108**, 9423–9427.
- B. P. Hay and R. Custelcean, *Cryst. Growth Des.*, 2009, **9**, 2539–2545.
- M. Quarton and D. Svoronos, *J. Solid State Chem.*, 1982, 325–7.
- M. G. B. Drew, P. B. Iveson, M. J. Hudson, J. O. Liljenzin, L. Spjuth, P.-Y. Cordier, Å. Enarsson, C. Hill and C. Madic, *J. Chem. Soc. Dalton Trans.*, 2000, 821–830.
- K. I. M. Ingram, M. J. Tassell, A. J. Gaunt and N. Kaltsoyannis, *Inorg. Chem.*, 2008, **47**, 7824–7833.
- L. P. Spencer, P. Yang, B. L. Scott, E. R. Batista and J. M. Boncella, *Inorg. Chem.*, 2009, **48**, 2693–2700.
- J. N. Cross, J. A. Macor, J. A. Bertke, M. G. Ferrier, G. S. Girolami, S. A. Kozimor, J. R. Maassen, B. L. Scott, D. K. Shuh, B. W. Stein and S. C. E. Stieber, *Angew. Chem. Int. Ed.*, 2016, **55**, 12755–12759.
- 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. V. Alstine, F. D. White and P. Yang, *Dalton Trans.*, 2018, **47**, 14452–14461.
- M. Kaneko and M. Watanabe, *J. Radioanal. Nucl. Chem.*, 2018, **316**, 1129–1137.
- J. M. Keith and E. R. Batista, *Inorg. Chem.*, 2012, **51**, 13–15.
- B. Qiao, A. Sengupta, Y. Liu, K. P. McDonald, M. Pink, J.R. Anderson, K. Raghavachari, and A. H. Flood, *J. Am. Chem. Soc.* 2015, **137**, 9746–9757.
- J. M. Mahoney, A. M. Beatty, and B. D. Smith, *J. Am. Chem. Soc.*, 2001, **123**, 5847–5848.
- T. M. Jonah, L. Mathivathanan, A. N. Morozov, A. M. Mebel, R. G. Raptis, and K. Kavallieratos, *New J. Chem.*, 2017, **41**, 14835–14838.