Polyhedron 42 (2012) 271-275

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Copper and uranyl extraction from aqueous solutions using bis-dithiophosphinate ligands have been characterized

Michael A. DeVore II, Anne E.V. Gorden*

179 Chemistry, Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, USA

ARTICLE INFO

Article history: Received 5 April 2012 Accepted 22 May 2012 Available online 30 May 2012

Keywords: Uranyl Copper Bis-dithiophosphinite Extraction

1. Introduction

The availability of adequate energy at a reasonable price is considered a requirement of modern society [1]. Experts predict that the maximum allowable oil production using current methods will occur in the next 5-25 years, and consequently the need to have alternative energy sources to eventually replace oil is growing [1]. Currently 13–14% of the world's electricity is produced using nuclear sources, and nuclear power is the dominant source of electrical power for most of Europe [2]. The applications of nuclear energy for the production of electricity for general civilian use, military applications, as well as in satellite and space exploration applications are plagued with waste management risks that must be addressed [3]. During the past 60 years, more than 1800 metric tonnes of Plutonium, and substantial quantities of the "minor" actinides, such as Neptunium, Americium, and Curium, have been generated in nuclear reactors [4]. There are two basic strategies concerning the disposition of these heavy elements: (1) to "burn" or transmute the actinides using nuclear reactors or accelerators [5]; (2) to "sequester" the actinides in chemically durable, radiation-resistant materials that are suitable for geologic disposal [6]. While reprocessing is not currently performed in the United States due to proliferation concerns subsequent to the Cold War, other nations using nuclear power technology reprocess their spent fuel to recycle the remaining fissile fractions [1,7]. Such a process can provide up to 96% more energy than the once-through cycle using the same initial amount of enriched uranium fuel [1].

ABSTRACT

Dithiophosphinate ligands with groups linked together by a bridging spacer to take advantage of a chelate effect for improved selectivity have been characterized. Extractions with each ligand were performed with the ligands dissolved in methylene chloride and the metal salts dissolved in aqueous phase at pH 4. H₂L1 was found to have good differentiation between $UO_2^{2^+}$ and Gd^{3^+} , but only resulted in 50% extraction. H₂L2 had lower selectivity; however, copper extractions approached 95% after 24 h.

© 2012 Elsevier Ltd. All rights reserved.

Currently, the most widely used effective process for the extraction and separation of plutonium and uranium from the lanthanides is the Plutonium Uranium Recovery by Extraction (PUREX) process [8–10]. This process uses the extractant tributyl phosphate (TBP) (Fig. 1) in a hydrocarbon solvent such as kerosene or dodecane [6,11]. While this process is well described, it still leaves room for improvement, and a resurgence of interest in the coordination chemistry of the actinides has been inspired by a need to address these environmental concerns, to develop new separations and remediation technologies, and to continue to develop our fundamental understanding of the chemical behavior of the actinides [12–17].

Organophosphorous extractants have played a major role in actinide extraction [18]. These extractants are generally stable, inexpensive, and commercially available, and have been widely studied in the past few decades, in particular with respect to cobalt–nickel separation from weakly acidic sulfate media [19]. The earliest work was performed by Ritcey et al., as well as Flett and co-workers in which they used an alkylphosphoric acid, di-(2-ethylhexyl)-phosphoric acid (D2EHPA) (Fig. 1) [19]. Subsequently, the development of the phosphonic and phosphinic acid extractants 2ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) and bis-(2,4,4,-trimethylpentyl)-phosphinic acid (Cyanex 272) have led to further improved separation factors in the order: phosphoric ric < phosphonic < phosphinic acid [19–21].

In recent years, Cyanex 301 and Cyanex 302 (Fig. 1), have received considerable attention both for their ability to extract soft transition metals [22], and for their ability to differentiate between the chemically similar trivalent lanthanides and actinides [23,24]; however, Cyanex 301 can only differentiate between the trivalent





^{*} Corresponding author. Tel.: +1 334 844 4043.

E-mail address: gordeae@auburn.edu (A.E.V. Gorden).

^{0277-5387/\$ -} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.05.026



Fig. 1. Current and previously used extractants.

lanthanides and trivalent actinides in solutions of a pH lower than 3 [25]. Several methods of separations of spent nuclear fuel (SNF) have focused on extraction agents containing a single dithiophosphinic acid group like Cyanex 301. Here, we report the preparation and simple extractions with a class of compounds – the bisdithiophosphinites [26,27]. The purpose of this design was to incorporate two dithiophosphinic acid groups connected by a linker to take advantage of a potential chelate effect to increase selectivity for actinides.

2. Experimental

2.1. General procedure

Lawesson's reagent, uranyl nitrate, cuprous chloride, gadolinium chloride, 1,3-propanediol, and 1,5-pentanediol, were purchased from Acros and used without any purification. The pH was recorded on a Fischer Scientific AR15 pH meter. UV–Vis data was collected on a Cary 50 UV–Vis spectrophotometer with a xenon lamp in the range of 200–1200 nm. The ¹H, ¹³C, and ³¹P NMR was recorded on a Bruker AV 250 spectrophotometer with d₄-MEOD, d₁-CDCl₃, or d₆-DMSO as the solvent using tetramethylsilane as the reference. 100 ppm standards were purchased and diluted to ~2 ppm and used for calibration of the ICP-OES.

2.2. Synthesis of ligands

Ligands were prepared according to literature procedures [26,27]. To a solution of diol (10 mmol) in toluene (30 mL), 4.0 g (10 mmol) of Lawesson's Reagent (1) was added. The mixture was stirred at 70 °C until all the solids had dissolved and left overnight. The solvent was removed on a roto-vap until the remaining volume was ~10 mL. Hexane (30 mL) was added to precipitate the product as a green oil (Scheme 1).

2.3. Extraction and hydrolysis studies

Two-phase extraction studies in methylene chloride/water (DCM/ H_2O) were performed to determine the extraction capability for the removal of Cu²⁺ ions from aqueous solution. The ligand

 H_2L1 and H_2L2 , quantitatively soluble in DCM, were used for extraction studies. Fresh solutions of $CuCl_2 \cdot 2H_2O$, $UO_2(NO_3)_2$ $6H_2O$, or $GdCl_3$ were prepared in DI water, and the pH was adjusted with HNO_3 and KOH (±0.05). Simple extractions were tested at pH 4 with a ratio of 1:1 metal to ligand for compounds H_2L1 and H_2L2 . The phases were agitated by stirring for time periods indicated, allowed 24 h to equilibrate, and the organic layer drawn off into a separate vial.

3. Results and discussion

The ligands H₂L1 and H₂L2 each possess 4 potential donor atoms to complex with metal atoms and take advantage of the chelate effect to enhance extractions. While there are few metal complexes with similar ligands, it has been shown through mass spectrometry that these complexes can be monomer or dimers, and mononuclear or dinuclear [27]. Ligands without the carbon chain bridge can form many crystallographic species. Verani et al. reported crystal structures with Pt²⁺, Pd²⁺, and Ni²⁺ that have a 1-2 metal to ligand structure [28,29], while Karakus et al. have described a 2-4 metal to ligand crystal structure with cadmium in which two ligands have both donors coordinating to cadmium metal, and the other two ligands have their donors split between the two metal centers [30]. While crystals suitable for X-ray diffraction were not able to be grown, based on above papers and what was observed for extraction we would expect coordination as shown in Fig. 2.

3.1. Hydrolysis and extraction studies

Stock solutions of H_2L1 and H_2L2 were prepared by dissolving the respective compound in methylene chloride (100 mL each). An equivalent amount of an aqueous solution at pH 1–14 (±0.05) (adjusted with HNO₃ and KOH) was added to separate vials containing H_2L1 or H_2L2 in organic solvent and shaken for 60 s. The solution was left undisturbed overnight, and the organic layer isolated for hydrolysis studies employing UV–Vis. The extent of hydrolysis was interpreted relative to the spectra of the ligand at neutral pH.



Scheme 1. Synthesis of ligands.



Fig. 2. Proposed coordination of uranyl and ligand.

The two-phase hydrolysis study of H_2L1 indicates that the ligand hydrolyzes in extreme pH conditions (pH 1, 2 and 12–14) while H_2L2 also hydrolyzes in at these pH conditions (pH 1, 2 and 11–14). The hydrolysis profile of compounds H_2L1 and H_2L2 are shown in Fig. 3.

The two-phase extraction studies described here are at pH 4.0 only since H₂L1 and H₂L2 hydrolyze in the acidic region. H₂L1 and H₂L2 were dissolved in methylene chloride (10 μ M) while the metal salts were dissolved in the aqueous phase (10 μ M). The two phases were agitated by stirring on a magnetic stir plate for the indicated time. At higher concentrations- above 10 μ M, a third layer can clearly be seen, and hence, using UV–Vis spectroscopy to track the uranyl peak was undesirable.

The H₂L1 ligand was found to extract about 48% of the copper ion after 8 h and 57% after 12 h (Fig. 4); however, after 24 h, the concentration of the metal ion increased in the aqueous phase to about 50% of the original solution, again indicative of a possible third laver formation. The third laver formation was observed at higher concentrations of the metal and ligand when initial studies were to employ the use of UV-Vis spectroscopy. Since the layers would often be cloudy because of this third layer, it was impossible to use that technique. The extraction of uranyl ion was modest at about 41% after 8 and 12 h, but as in the case with the copper ion after 24 h, there is an increase in the uranyl ion concentration after 24 h. With the four sulfur donors being "softer" donors, better able to overlap and bond with the 5*f* orbital of the uranyl, it was expected that the extraction of gadolinium would not be very good and for H₂L1 it was not with only 17% being the highest extraction after 8 h. With the smaller binding pocket associated with H₂L1, the gadolinium metal ion would be small enough to fit but the bond distances from the donors could be far enough away as to not form stable complexes. The concentration in the aqueous phase does increases as it does with the other metal ions.

The distribution ratio (defined as $D = \frac{[M]org}{[M]aq}$, Table 1) of copper with H₂L1 was found to be ~1 while it is much less for the other metal ions. The separation factor of uranyl over gadolinium is 3–5, which while low, indicates a preference of uranyl of gadolinium and use in the separation of trivalent actinides from trivalent lanthanides is perhaps possible with additional suitable modifications to the ligand.

 H_2L2 with the five carbon chain has a bigger binding pocket for which a metal ion or metal ions to bind and be extracted into the organic phase (Fig. 5). After 8 h, 80% of the copper in the aqueous phase had been extracted with 95% after 24 h. This was interesting, so a shorter time scale was used to see how quickly the copper could be extracted (Fig. 6). After only 5 min of stirring, 87% of the copper ions had been extracted out of the aqueous phase. The per-



Fig. 3. Absorption spectra showing hydrolysis of H₂L1 and H₂L2 between pH 1–14. The bands indicated by \times correspond to spectra at neutral pH. The bottom graph is a close up expansion of the previous graph from 290 to 380 nm.



Fig. 4. Percent extraction of various metals by H₂L1 at 8, 12, and 24 h (Cu²⁺ = •; Gd³⁺ = - -; UO₂²⁺ = -).

Table 1

Distribution of metal ions after extraction by H₂L1 at 8, 12, and 24 h.

Metal	8 h	12 h	24 h
Copper	0.91	1.28	0.98
Gadolinium	0.21	0.13	0.18
Uranyl	0.72	0.70	0.47



Fig. 5. Percent extraction of various metals by H_2L1 at 8, 12, and 24 h (Cu^{2+} = $\bullet;$ Gd^{3+} = - -; UO_2^{-2+} = -).

cent extracted from the aqueous layer is consistent until about 8 h in when it drops to 80%, before more is extracted at 12 and 24 h. While the bigger pocket does help the uranyl extractions, it also allows for better extraction of gadolinium as the percent extracted increases from ~20% with H₂L1 to ~50% with H₂L2. H₂L2 also had issues of a third layer formation at higher concentrations, although not as severe as H₂L1, still significant enough to not be



Fig. 6. % Copper extraction at shorter time lengths.

Table 2	
Distribution of metal ions after extraction of H_2L2 at 8, 12, and 24 h.	

Metal	8 h	12 h	24 h
Copper	4.17	11.69	20.68
Gadolinium	0.85	1.30	0.76
Uranyl	1.00	0.81	0.95

able to employ the use of UV–Vis spectroscopy to track extraction of uranyl ion.

Distribution (Table 2) of the copper ion increases after 8 h to a max of 20 after 24 h while gadolinium peaks at 12 h and falls at 24 h. Uranyl does the opposite where the distribution decreases between 8 and 12 h but then increases at 24 h.

The separation factor values of H_2L2 of copper over uranyl increases, as there is an increase in time. While the goal would be to have a higher separation factor of uranyl over copper, this is still in interesting result and confirmation of the problem of uranyl and copper binding in the same coordination pocket of a ligand [31].

4. Conclusions

Extractions were performed on three metals (Cu^{2+} , Gd^{3+} , and UO_2^{2+}) using two bisdithiophophinate ligands H_2L1 and H_2L2 . Unlike the Cyanex 301 ligand, H_2L1 and H_2L2 hydrolyze under very acidic conditions so all extractions were performed at pH 4. While H_2L1 had about 50% extraction for copper and 40% for uranyl, it was not very good at extraction of gadolinium expected, according to the Pearson theory of Hard and Soft Acids and Bases [32]. The H_2L2 with the bigger binding pocket was a much better ligand for the extraction of all three metals, especially copper where there was nearly 100% extraction. Until modifications can be made such that the ligands are more soluble in more suitable solvents like kerosene, extractions could prove to be difficult with the formation of third layer systems or metallopolymer byproducts.

Acknowledgements

The research was sponsored in part by the Fuel Cycle Research and Development Program, Office of Nuclear Energy, US Department of Energy and in part by Auburn University. The authors would like to thank Dr. Paul Cobine for use of the ICP-OES.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.05.026.

References

- [1] G.R. Choppin, Sep. Sci. Technol. 41 (2006) 1955.
- [2] I.A.E. Agency, Nuclear Technology Review 2011, Vienna, 2011.
- J.L. Sessler, A.E. Vivian, D. Seidel, A.K. Burrell, M. Hoehner, T.D. Mody, A. Gebauer, S.J. Weghorn, V. Lynch, Coord. Chem. Rev. 216 (2001) 411.
 R.C. Ewing, C. R. Geosci. 343 (2011) 219.
- [4] R.C. Ewing, C. R. Geosci. 343 (2011) 219.
 [5] M.B. Schaffer, Energy Policy 39 (2011) 1382.
- [6] I.A.E. Agency, Spent Fuel Reprocessing Options, Vienna, 2008.
- [7] A. Andrews, Nuclear fuel reprocessing options, vielna, 2000.
- Congress (Ed.), Library of Congress, Washington, DC, 2008.
 [8] S. Barboso, A.G. Carrera, S.E. Matthews, F. Arnaud-Neu, V. Bohmer, J.F. Dozol, H. Rouquette, M.J. Schwing-Weill, J. Chem. Soc., Perkin Trans. 2 (1999) 719.
- [9] J.M. Joshi, P.N. Pathak, V.K. Manchanda, Solvent Extr. Ion Exc. 23 (2005) 663.
 [10] I. May, R.J. Taylor, A.L. Wallwork, J.J. Hastings, Y.S. Fedorov, B.Y. Zilberman, E.N.
- Mishin, S.A. Arkhipov, I.V. Blazheva, L.Y. Poverkova, F.R. Livens, J.M. Charnock, Radiochim. Acta 88 (2000) 283.
- [11] G. Choppin, J.-O. Liljenzin, J. Rydberg, The nuclear fuel cycle, in: Radiochemistry and Nuclear Chemistry, Butterworth-Heinemann, Woburn, MA, 2002, pp. 583–641.

- [12] S.-i. Koyama, T. Suzuki, H. Mimura, R. Fujita, K. Kurosawa, K. Okada, M. Ozawa, Prog. Nucl. Energy 53 (2011) 980.
- [13] F.W. Lewis, L.M. Harwood, M.J. Hudson, M.G.B. Drew, J.F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.H. Vu, J.P. Simonin, J. Am. Chem. Soc. 133 (2011) 13093.
- [14] C. Marie, M. Miguirditchian, D. Guillaumont, A. Tosseng, C. Berthon, P. Guilbaud, M. Duvail, J. Bisson, D. Guillaneux, M. Pipelier, D. Dubreuil, Inorg. Chem. 50 (2011) 6557.
- [15] P.V. Achuthan, C. Janardanan, J. Radioanal. Nucl. Chem. 287 (2011) 753.
- [16] J.C. Braley, T.S. Grimes, K.L. Nash, Ind. Eng. Chem. Res. 51 (2012) 627.
- [17] A. Leydier, D. Lecercle, S. Pellet-Rostaing, A. Favre-Reguillon, F. Taran, M. Lemaire, Tetrahedron Lett. 52 (2011) 3973.
- [18] C. Musikas, Inorg. Chim. Acta 140 (1987) 197.
- [19] K.C. Sole, J.B. Hiskey, Hydrometallurgy 30 (1992) 345.
- [20] I. Komasawa, T. Otake, J. Chem. Eng. Jpn. 17 (1984) 417.
- [21] J.S. Preston, Hydrometallurgy 9 (1982) 115.
- [22] K.C. Sole, J.B. Hiskey, Hydrometallurgy 37 (1995) 129.
- [23] C. Hill, C. Madic, P. Baron, M. Ozawa, Y. Tanaka, J. Alloy Compd. 271 (1998) 159.
 [24] A. Bhattacharyya, P.K. Mohapatra, V.K. Manchanda, Sep. Purif. Technol. 50
- (2006) 278. [25] K.E.A. Matloka, C.R. Chimie 10 (2007).
- [26] A.R. Gataulina, D.A. Safin, T.R. Gimadiev, M.V. Pinus, Transition Met. Chem. 33 (2008) 921.
- [27] M. Karakus, H. Yilmaz, E. Bulak, Russ. J. Coord. Chem. 31 (2005) 316.
- [28] M.C. Aragoni, M. Arca, F. Demartin, F.A. Devillanova, C. Graiff, F. Isaia, V. Lippolis, A. Tiripicchio, A. Verani, Eur. J. Inorg. Chem. (2000) 2239.
- [29] M.C. Aragoni, M. Arca, F. Demartin, F.A. Devillanova, C. Graiff, F. Isaia, V. Lippolis, A. Tiripicchio, G. Verani, J. Chem. Soc., Dalton (2001) 2671.
- [30] M. Karakus, H. Yilmaz, Y. Ozcan, S. Ide, Appl. Organomet. Chem. 18 (2004) 141.
- [31] J.L. Sessler, P.J. Melfi, G.D. Pantos, Coord. Chem. Rev. 250 (2006) 816.
- [32] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.