

Syntheses and crystal structures of thorium(IV) and uranium(IV) tripodal metalloligands



Yingjie Zhang^{a,*}, Mohan Bhadbhade^b, Linggen Kong^a, Inna Karatchevtseva^a, Rongkun Zheng^c

^a Nuclear Fuel Cycle Research Theme, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

^b Mark Wainwright Analytical Centre, University of New South Wales, Kensington, NSW 2052, Australia

^c School of Physics and the Australian Institute for Nanoscale Science and Technology, University of Sydney, NSW 2006, Australia

ARTICLE INFO

Article history:

Received 27 April 2017

Accepted 15 September 2017

Available online 23 September 2017

Keywords:

Thorium

Uranium

Schiff base

Tripodal

Metalloligand

ABSTRACT

Two tetravalent actinide tripodal metalloligands, [Th(H₃L)(NO₃)(MeO)]·2NO₃ (**1**) and [U(H₃L)Cl(MeO)]₂[(UO₂)Cl₄]_{0.5}·3 Cl·2CH₃OH·2H₂O (**2**) (H₃L = tris{[2-((imidazole)methylidene) amino]ethyl}amine; CH₃O = methoxide), were synthesized and structurally characterized. Both **1** and **2** contain the expected tripodal shape with the heptadentate Schiff base wrapping around Th(IV) or U(IV) ion. Further coordination of nitrate/chlorine and methoxide makes a ten-fold and a nine-fold coordination environments for Th(IV) ion (**1**) and U(IV) ion (**2**), respectively. Metalloligand **2** is a mixed valent uranium complex due to partial oxidation of U(IV) to U(VI). These tripodal metalloligands will have the potential to link secondary metal ions via deprotonated imidazole nitrogen donors to form either discrete heterometallic cages or supramolecular assemblies containing tetravalent actinide ions.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

As potential building units, the metalloligands with appended electron donors fixed in a rigid structure capable of coordinating to secondary metal ions have attracted recent attention [1–7]. Due to their unique abilities for the construction of various metallo-supramolecular entities such as heterometallic coordination cages, considerable effort has been devoted to the synthesis of various metalloligands and their further use in producing supramolecular architectures, especially for heterometallic systems [8–14].

The tripodal metalloligands constructed from Schiff base condensation of tris(2-aminoethyl)amine (tren) with additional functional groups have been demonstrated to form complexes with a wide range of metal ions, e.g. d-transition metal ions [9–14]. In particular, tripodal metal complexes incorporating uncoordinated secondary donor sites consisting of pyridine [8,14–16] and imidazole [8,11] nitrogens are of interest as the uncoordinated nitrogen donor sites at the terminus of each arm are available for further coordination to secondary metal ions after deprotonation. As an example, condensation of 2-pyridinecarboxaldehyde with tren in a 3:1 molar ratio yields the tris-imine derivative, tris-2-(2-pyridylimine ethyl)amine (H₃L), whose ability for coordinating metal ions has been well documented [8,11]. The recent successes

of using Fe(III) [11] and Dy(III) [8] tripodal metalloligands with H₃L in preparing heterometallic coordination cages via coordination of secondary Cu(II) ions highlight the potential applications for these metalloligands.

Despite the recent advances on the tripodal metalloligands of H₃L, the central metal ions are still dominated by d-transition metal ions with only a few examples involving lanthanide ions [8,17]. Hardly has any tetravalent metal ion or any actinide ion been attempted in this particular tripodal ligand system, which has been the prime motivation for undertaking the current work. Herein we report the synthesis of two new tripodal metalloligands of H₃L with either Th(IV) or U(IV) ion. Each metalloligand was formed by Schiff base condensation of 4-imidazole carboxaldehyde with tren in the presence of Th(IV) nitrate/U(IV) chloride in a 3:1:1 molar ratio (Scheme 1). Their crystal structures have been confirmed by X-ray diffraction studies.

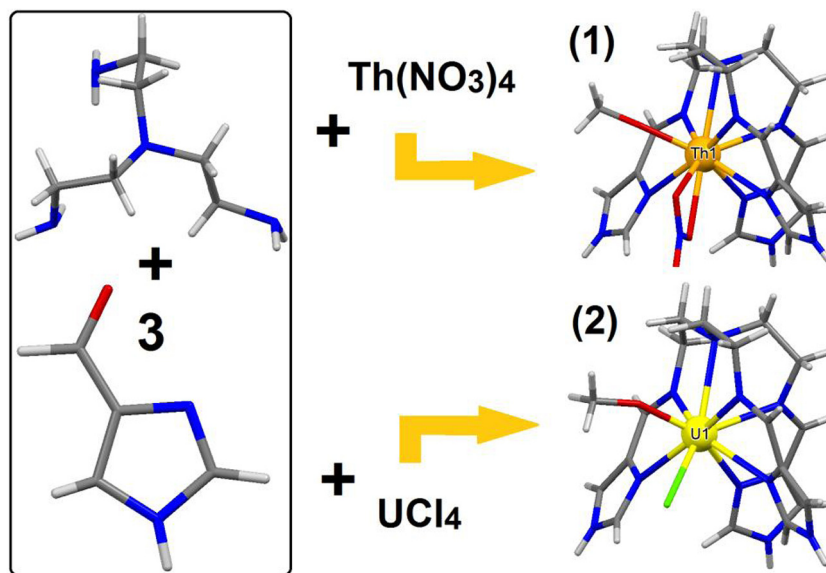
2. Results and discussion

2.1. Synthesis and characterizations

Tripodal metalloligands **1** and **2** were prepared via the coordination of H₃L to Th(IV) nitrate (**1**) or U(IV) chloride (**2**) in MeOH solutions. Backscattered SEM micrographs of **1** and **2** (Fig. S1) show large blocks of crystals for **1** and needle crystals for **2**. EDS analysis results were consistent with the expected elemental compositions

* Corresponding author.

E-mail address: yzx@ansto.gov.au (Y. Zhang).



Scheme 1. Formations of Th(IV) and U(IV) tripodal metallogligands **1** and **2**.

in the tripodal metallogligands: C, N, O and Th in **1**, and C, N, O, Cl and U in **2**. The Raman spectrum of **1** (Fig. 1) revealed typical features expected for the organic ligand H_3L : a strong $\nu_{C=N}$ band at 1642 cm^{-1} ; a strong $\nu_{C=C}$ band at 1627 cm^{-1} ; a weak N–H deformation vibration band at 1562 cm^{-1} ; C–H deformation vibrations within CH_3 – and $-CH_2-$ in the region 1458 – 1293 cm^{-1} ; a very weak ν_{C-C} band at 1221 cm^{-1} and a double ν_{C-N} band at 1170 – 1150 cm^{-1} [18,19]. In addition, a weak ν_{C-O} band located at 1086 cm^{-1} is the characteristic for methoxide whilst a medium ν_{N-O} band at 1036 cm^{-1} is a clear indication for the presence of nitrate anions [19].

2.2. Crystal and molecular structures

The crystal data and structure refinement details for both metallogligands **1** and **2** are summarized in Table 1. Selected bond

Table 1

Crystallographic data and structure refinement details for complexes **1** and **2**.

Complex	1	2
Formula	$C_{19}H_{27}N_{13}O_{10}Th$	$C_{40}H_{62}N_{20}O_6Cl_7U_{2.5}$
Formula weight	829.57	1762.32
Crystal system	orthorhombic	triclinic
Space group	$Pna21$	$P\bar{1}$
a (Å)	18.510(4)	9.3370(19)
b (Å)	15.233(3)	16.369(3)
c (Å)	9.774(2)	21.107(4)
α (°)	90	86.22(3)
β (°)	90	79.21(3)
γ (°)	90	88.39(3)
V (Å ³)	2755.9(10)	3161.7(12)
Z/μ (mm ⁻¹)	4/5.489	2/6.742
Min./Max. θ [°]	1.731/27.874	0.984/33.854
d_{calcd} (g cm ⁻³)	1.999	1.851
GOF	1.048	1.019
Final R_1^a [$I > 2\sigma(I)$]	0.0193	0.0420
Final wR_2^b [$I > 2\sigma(I)$]	0.0481	0.1113

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

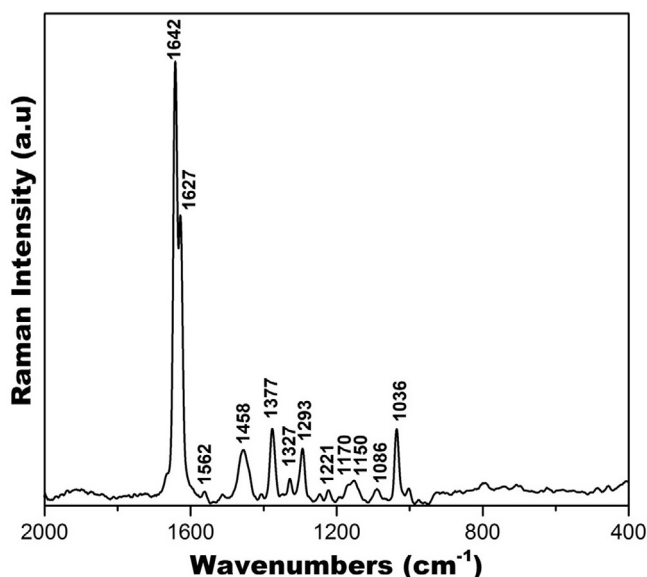


Fig. 1. A Raman spectrum of complex **1** in 2000 – 400 cm^{-1} region.

lengths for the metal coordination polyhedron are listed in Table 2 and calculated potential hydrogen bonds are listed in Table 3. Metallogligand **1** crystallizes in the orthorhombic $Pna21$ space group. The structure of **1** (Fig. 2a) is consistent with the expected tripodal configuration with H_3L wrapping around the Th(IV) ion. The Th(IV) ion is coordinated by the heptadentate ligand with one amine (Th1–N1 = $2.797(4)\text{ Å}$), three imine (Th1–N(2,5,8) = $2.604(4)$ – $2.659(4)\text{ Å}$), three imidazole (Th1–N(3,6,9) = $2.633(4)$ – $2.697(5)\text{ Å}$) N atoms, together with a bidentate coordinated NO_3^- anion (Th1–O(2,3) = $2.624(3)$ – $2.639(3)\text{ Å}$) and a coordinated methoxide (deprotonated methanol with Th1–O1 = $2.144(4)\text{ Å}$) (Fig. 1a) making the Th(IV) ion a ten-fold coordination environment in a distorted bicapped square antiprism polyhedron (Fig. 3a). The coordination of both nitrate and the methoxide caused the metallogligand deviated significantly from the symmetric arrangement of the three arms (Fig. 2b). Hydrogen bonds between lattice nitrate anions (O5, O7, O8 and O10) and imidazole–NH (N4, N7 and N10) groups (Fig. 2c) lead discrete metallogligands into one-dimensional (1D) polymers along the crystallographic c -axis (Fig. 2d, Table 3).

Download English Version:

<https://daneshyari.com/en/article/5153920>

Download Persian Version:

<https://daneshyari.com/article/5153920>

[Daneshyari.com](https://daneshyari.com)