Supporting Information

# Synthesis and characterization of homo- and heteronuclear molecular $Al^{3+}$ and $Th^{4+}$ species chelated by the ethylenediaminetetraacetate (edta) ligand.

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Crystals for all four compounds were isolated from the mother liquor, coated in Infinium oil to prevent dehydration, and mounted on a Nonius Kappa CCD single crystal X-ray diffractometer equipped with MoKα radiation (λ=0.7107 Å) and a Cryostream low temperature cryostat. Diffraction experiments were performed at 210 K using the Nonius Collect software and unit cell parameters, data integration, and Lorentzian and polarization corrections were completed using the APEX II suite of software. Semi-empirical absorption corrections were applied using the Scale program within the APEX II software. Atomic scattering factors for each atom were taken from the International Table of X-ray Crystallography. Thorium and Al atoms were determined in each crystal, where present, by direct methods solutions and O, C, and N atoms were identified in the difference Fourier maps calculated following refinement of partial-structure models. Structures were then refined on the basis of $F^2$ for all unique data using the Bruker SHELXTL version 5.01 software. Hydrogen atoms associated with the edta molecules were constrained to either O or C atoms using a riding model with the HFIX command. Also, in compounds **Th1** and **Al2**, H atoms were also determined for $H_2O$ and OH groups and constrained using the DFIX command. For compounds **Th4Al10** and **Th2Al6**, H atoms associated with structural OH and $H_2O$ and interstitial $H_2O$ molecules were not determined due

to the lack of consistent Q peaks within the difference Fourier map, as is common for large aqueous clusters.

Crystallographic information files were checked using the online checkCIF program hosted by the IUCr and alerts of concern are as follows. For compound **Al2**, a B-level alert was issued due to a low Data to Parameter ratio caused by crystallization of the material in a non-centrosymmetric space group. For structures **Th2Al6** and **Th4Al10**, B-level alerts were issued for interstitial O water molecules with missing H atoms, and predictable C-level alerts for disorder about the cleating EDTA molecules complexed to Th atoms of the heterometallic clusters.

Table S1. Selected bond distances for **Th1**

| | |
|---|---|
| Th(1)-O(2) | 2.402(2) |
| Th(1)-O(5) | 2.413 (2) |
| Th(1)-O(3) | 2.440 (2) |
| Th(1)-O(7) | 2.458(2) |
| Th(1)-O(1) | 2.490 (2) |
| Th(1)-O(4) | 2.524 (2) |
| Th(1)-O(8) | 2.545 (2) |
| Th(1)-O(6) | 2.570 (2) |
| Th(1)-N(2) | 2.790(2) |
| Th(1)-N(1) | 2.819(2) |

Table S2. Selected bond distances for **Al2**

| | |
|---|---|
| Al(1)-O(1) | 1.841(2) |
| Al(1)-O(3) | 1.851 (2) |
| Al(1)-O(1)[a] | 1.855(2) |
| Al(1)-O(5) | 1.883 (2) |
| Al(1)-O(4) | 1.884(2) |
| Al(1)-N(1) | 2.110(2) |
| Al(1)-Al(1)[a] | 2.855(1) |

[a] -x+2,y,-z+2

Table S3. Selected bond distances for **Th4Al10**

| | | | |
|---|---|---|---|
| Th(1)-O(6) | 2.373(4) | Al(2)-O(12) | 1.837(5) |
| Th(1)-O(9) | 2.389(4) | Al(2)-O(5) | 1.872(5) |
| Th(1)-O(22) | 2.424(5) | Al(2)-O(7) | 1.879(5) |
| Th(1)-O(10) | 2.434(5) | Al(2)-O(2) | 1.882(5) |
| Th(1)-O(25) | 2.469(6) | Al(2)-O(3) | 1.943(5) |
| Th(1)-O(26) | 2.469(5) | Al(2)-O(4) | 1.957(5) |
| Th(1)-O(8) | 2.522(5) | | |
| Th(1)-O(16) | 2.736(4) | Al(3)-O(9) | 1.831(5) |
| Th(1)-N(4) | 2.843(6) | Al(3)-O(1) | 1.857(5) |
| Th(1)-N(3) | 2.869(6) | Al(3)-O(3) | 1.882(5) |
| | | Al(3)-O(16) | 1.902(5) |

| | | | |
|---|---|---|---|
| Th(2)-O(24) | 2.384(5) | Al(3)-O(4) | 1.952(5) |
| Th(2)-O(19) | 2.391(4) | Al(3)-O(13) | 1.983(5) |
| Th(2)-O(15) | 2.402(5) | | |
| Th(2)-O(27) | 2.416(4) | Al(4)-O(15) | 1.828(5) |
| Th(2)-O(28) | 2.441(5) | Al(4)-O(5) | 1.835(5) |
| Th(2)-O(21) | 2.480(5) | Al(4)-O(17)[a] | 1.854(5) |
| Th(2)-O(23) | 2.553(5) | Al(4)-O(14) | 1.887(5) |
| Th(2)-N(2) | 2.801(6) | Al(4)-O(4) | 1.959(5) |
| Th(2)-O(14) | 2.806(4) | Al(4)-O(13) | 2.022(5) |
| Th(2)-N(1) | 2.869(6) | | |
| | | Al(5)-O(17) | 1.863(5) |
| Al(1)-O(19) | 1.848(5) | Al(5)-O(2)[a] | 1.870(5) |
| Al(1)-O(6) | 1.850(4) | Al(5)-O(7) | 1.875(5) |
| Al(1)-O(14) | 1.908(5) | Al(5)-O(1) | 1.878(5) |
| Al(1)-O(18) | 1.921(5) | Al(5)-O(20) | 1.963(5) |
| Al(1)-O(16) | 1.930(5) | Al(5)-O(11) | 2.001(5) |
| Al(1)-O(13) | 1.962(5) | | |

[a] -x+1,-y+1,-z+1

Table S4. Selected bond distances for **Th2Al6**

| | | | |
|---|---|---|---|
| Th(1)-O(3) | 2.374(4) | Al(2)-O(3) | 1.828(4) |
| Th(1)-O(6) | 2.374(4) | Al(2)-O(4) | 1.857(4) |
| Th(1)-O(12) | 2.426(5) | Al(2)-O(14) | 1.896(5) |
| Th(1)-O(10) | 2.447(4) | Al(2)-O(2) | 1.905(5) |
| Th(1)-O(16) | 2.454(5) | Al(2)-O(11)[a] | 1.954(5) |
| Th(1)-O(9) | 2.460(5) | Al(2)-O(1) | 1.961(5) |
| Th(1)-O(15) | 2.579(5) | | |
| Th(1)-O(1) | 2.680(4) | Al(3)-O(5)[a] | 1.843(5) |
| Th(1)-N(2) | 2.822(6) | Al(3)-O(2) | 1.861(5) |
| Th(1)-N(1) | 2.857(6) | Al(3)-O(7) | 1.918(5) |
| | | Al(3)-O(19) | 1.928(5) |
| Al(1)-O(6) | 1.837(5) | Al(3)-O(18) | 1.934(5) |
| Al(1)-O(5) | 1.853(5) | Al(3)-O(8) | 1.945(5) |
| Al(1)-O(4)[a] | 1.855(5) | | |
| Al(1)-O(1) | 1.920(5) | | |
| Al(1)-O(11) | 1.959(4) | | |
| Al(1)-O(11)[a] | 1.973(5) | | |

[a] -x,-y+1,-z+1

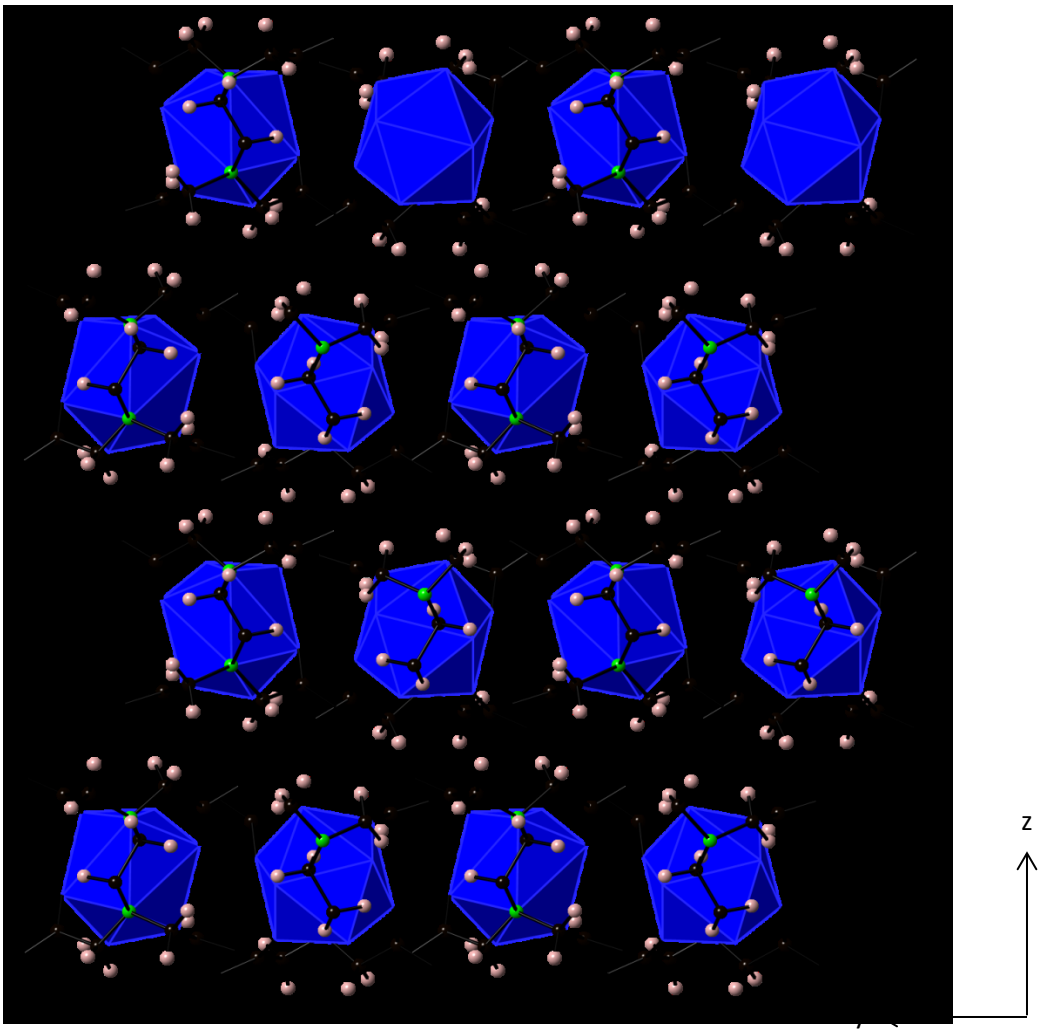


Figure S1. Extended structure for **Th1** is given as a polyhedral representation. The $Th^{4+}$ coordination is shown as a dark blue polyhedra and the C, N, and H of the EDTA ligand are black, green, and light pink spheres, respectively. The O atoms associated with the EDTA and ligated water are not shown for clarity.

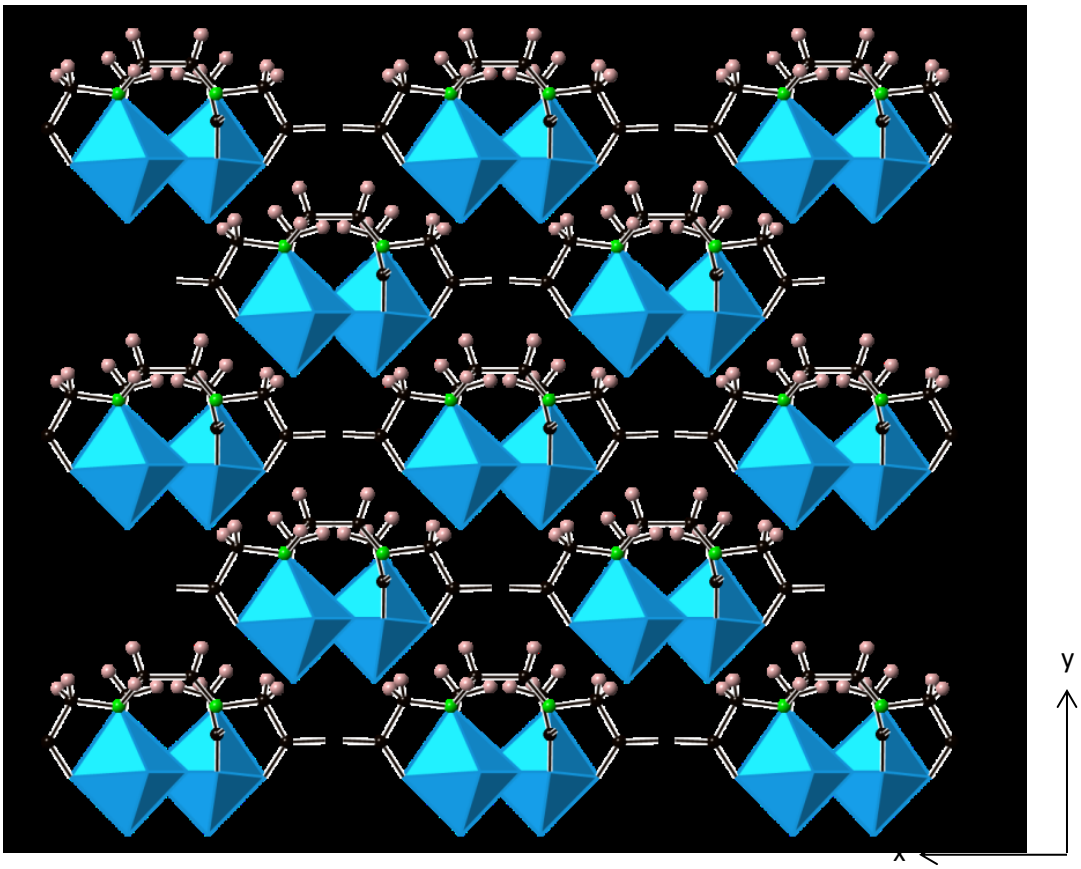


Figure S2. The crystalline packing of the dimeric species within the **Al2** compound is provided as a polyhedral representation. The $Al^{3+}$ is displayed as light blue polyhedra and the EDTA is pictured as a ball and stick model.

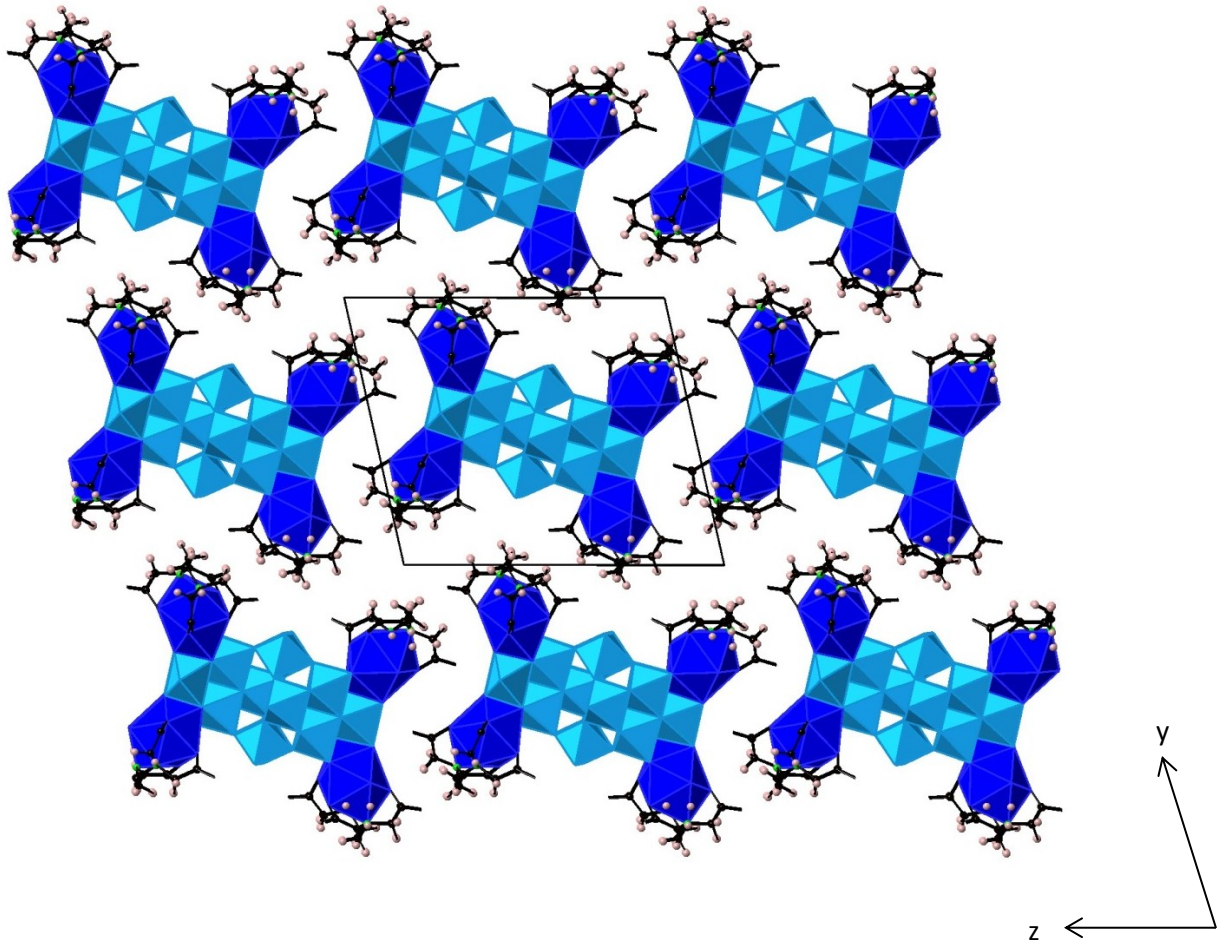


Figure S3. Extended structure for **Th4Al10** is shown as a polyhedral representation. The light blue octahedra are the $Al^{3+}$ coordination shell and the dark blue dodecahedron is the $Th^{4+}$ cation. Solvent molecules were removed from the figure for clarity.

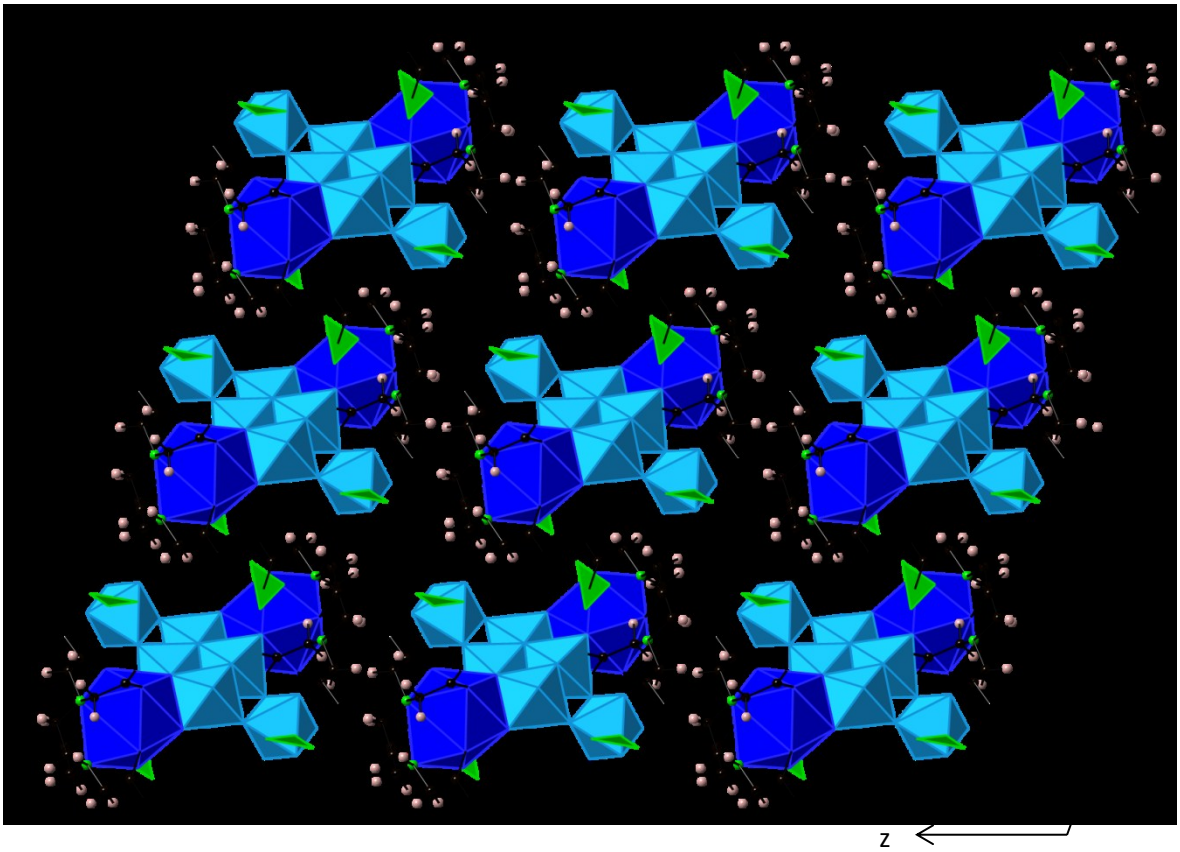


Figure S4. **Th2Al6** packs into a triclinic crystalline lattice and that bond through hydrogen bonding interactions with the interstitial water molecules (not shown for clarity) and the nitrate anions (green triangles). The $Al^{3+}$ and $Th^{4+}$ are represented by the light and dark blue polyhedra, respectively.

*Powder XRD.*

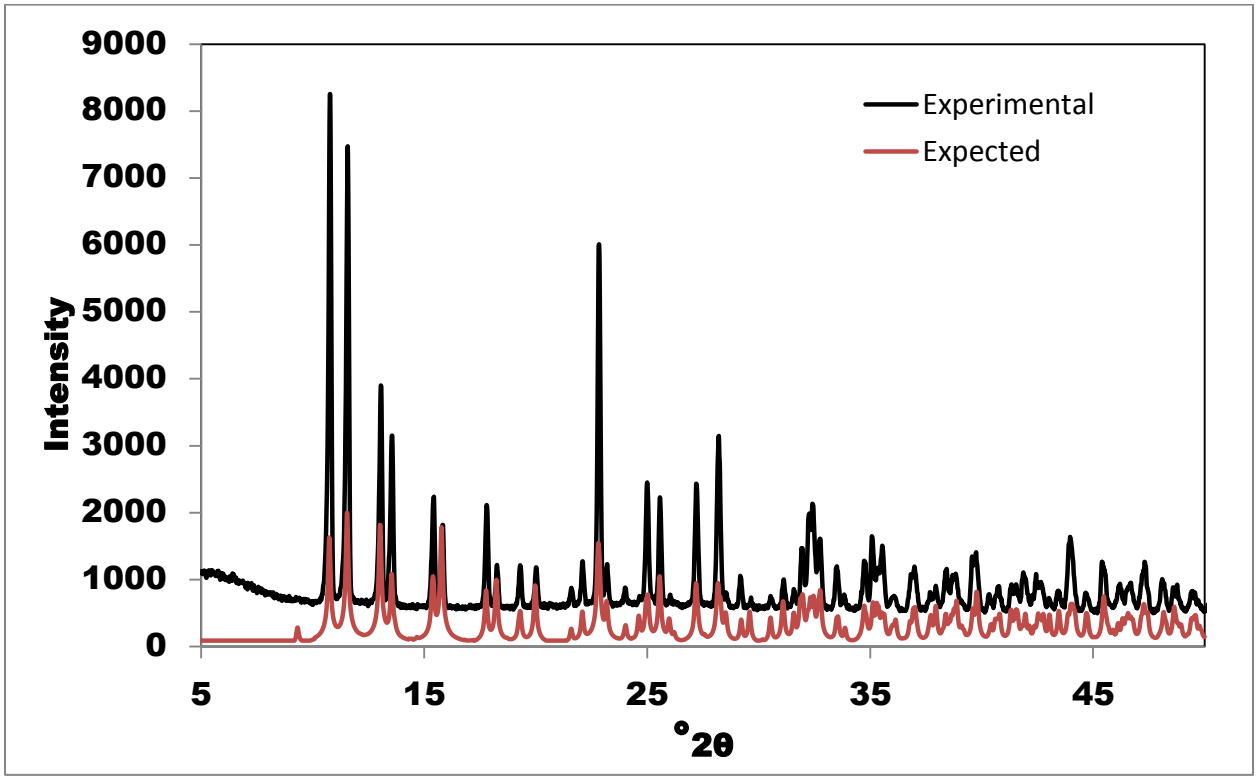


Figure S5. Experimental (black) and predicted (red) powder X-ray diffraction pattern for **Th1**.

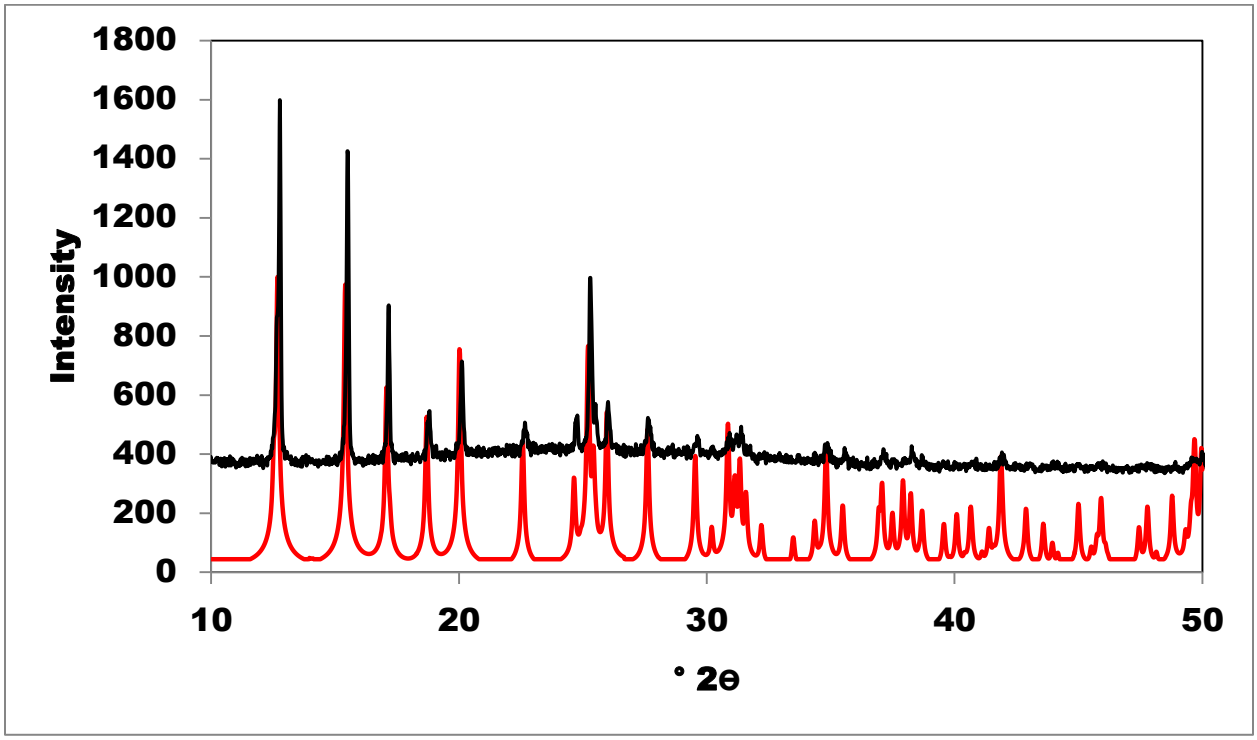

Figure S6. Experimental (black) and predicted (red) powder X-ray diffraction pattern for **Al2**.

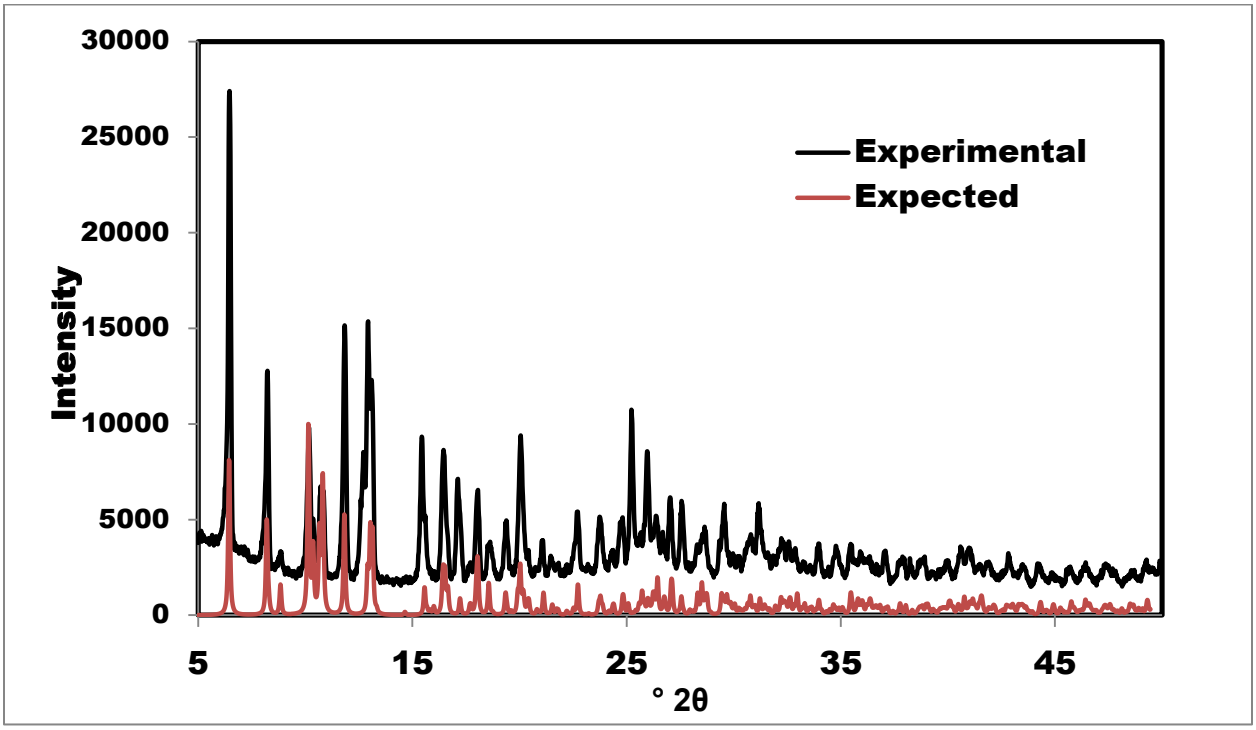


Figure S7. Experimental (black) and predicted (red) powder X-ray diffraction pattern for **Th2Al6**.