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**Two poly-oxo cluster complexes of tetravalent neptunium (Np(IV)),  $\text{Np}_{38}\text{O}_{56}\text{Cl}_{18}(\text{bz})_{24}(\text{THF})_8 \cdot n\text{THF}$  and  $\text{Np}_{38}\text{O}_{56}\text{Cl}_{42}(\text{ipa})_{20} \cdot \text{mipa}$  (bz = benzoate, THF = tetrahydrofuran, and ipa = isopropanol), were obtained via solvothermal synthesis and structurally characterised by single-crystal X-ray diffraction. The  $\{\text{Np}_{38}\}$  clusters are comparable to the analogous  $\{\text{U}_{38}\}$  and  $\{\text{Pu}_{38}\}$  motifs, filling the gap in this largest poly-oxo cluster series of tetravalent actinides.**

Owing to its diversity as well as its technological importance in the nuclear industry, the polymer and cluster chemistry of actinides (An) has been flourishing since the last decade.<sup>1–5</sup> In particular, the poly-oxo/hydroxo polymer and cluster complexes of tetravalent actinides (An(IV)) have received considerable attention,<sup>6–20</sup> as the formation of these complexes stems primarily from their hydrolysis<sup>21–24</sup> and, hence, it would have significant implications for the natural and engineered aqueous systems associated with the nuclear industry.<sup>25</sup> The largest poly-oxo An(IV) cluster reported thus far is the  $\{\text{An}_{38}\}$  complex, consisting of 38 An(IV) centres bridged by 56 oxygens. This type of cluster complex has been synthesised and characterised for U(IV)<sup>9,26</sup> and Pu(IV),<sup>13,15</sup> and this cluster motif could be stable in solution in a colloidal form.<sup>13,15,27</sup> In the periodic table, neptunium ( $_{93}\text{Np}$ ) is present between  $_{92}\text{U}$  and  $_{94}\text{Pu}$ . Despite its importance in nuclear fuel reprocessing and radioactive waste management,<sup>25</sup> the research on Np always lags behind those on U and Pu,<sup>28</sup> which is also the case for the chemistry of poly-oxo/hydroxo polymers and clusters. In order to fill the gap between the  $\{\text{U}_{38}\}$  and  $\{\text{Pu}_{38}\}$  clusters and to complete a series of these largest poly-oxo An(IV)

cluster complexes, we report herein the synthesis and characterisation of the first  $\{\text{Np}_{38}\}$  cluster complexes, which are also the largest single molecules of Np reported thus far.

The first  $\{\text{Np}_{38}\}$  complex,  $\text{Np}_{38}\text{O}_{56}\text{Cl}_{18}(\text{bz})_{24}(\text{THF})_8 \cdot n\text{THF}$ † (1, bz = benzoate, THF = tetrahydrofuran), was obtained via solvothermal synthesis with  $\text{NpCl}_4$ , benzoic acid, THF and deionised water (Sections 1 and 2 in the ESI†), which is a slight modification of the synthesis of the  $\{\text{U}_{38}\}$  complex.<sup>9</sup> After 1 day of heating at 400 K, purple/brown crystals with an octahedral shape were deposited (Fig. 1, left). Single-crystal X-ray diffraction (SC-XRD) measurements on the obtained crystals reveal the discrete  $\{\text{Np}_{38}\}$  motif shown in Fig. 2a. The second  $\{\text{Np}_{38}\}$  complex,  $\text{Np}_{38}\text{O}_{56}\text{Cl}_{42}(\text{ipa})_{20} \cdot \text{mipa}$ † (2, ipa = isopropanol), was synthesised solvothermally from a mixture of  $\text{NpCl}_4$  and benzoic acid in isopropanol (Sections 1–3 in the ESI†). Heating the sample mixture at 370 K for 3 days resulted in the formation of purple/brown crystals with an octahedral shape (Fig. 1, right). The complex structure determined by SC-XRD shows another  $\{\text{Np}_{38}\}$  motif, as illustrated in Fig. 2b.

Both compounds 1 and 2 crystallise in the tetragonal space group  $I4/m$  (Table S1 in the ESI†), which is the same as that observed for the analogous  $\{\text{U}_{38}\}$  clusters  $\text{U}_{38}\text{O}_{56}\text{Cl}_{18}(\text{bz})_{24}(\text{THF})_8 \cdot 8\text{THF}$ <sup>9</sup> and  $\text{U}_{38}\text{O}_{56}\text{Cl}_{42}(\text{H}_2\text{O})_2(\text{ipa})_{20} \cdot \text{xipa}$ .<sup>26</sup> Both the  $\{\text{Np}_{38}\}$  clusters are composed of a  $\{\text{Np}_{14}\}$  core (light green polyhedra in Fig. 2) surrounded by six tetranuclear  $\{\text{Np}_4\}$  subunits (blue and dark

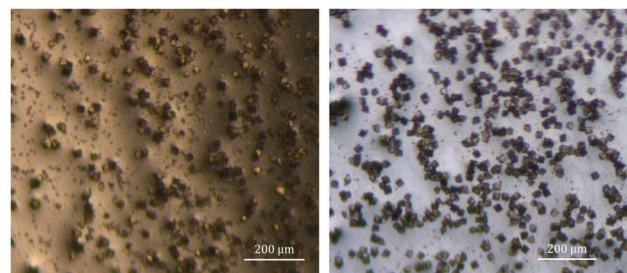


Fig. 1 Optical micrographs of single crystals of the  $\{\text{Np}_{38}\}$  compounds synthesised from THF (1, left) and isopropanol (2, right).

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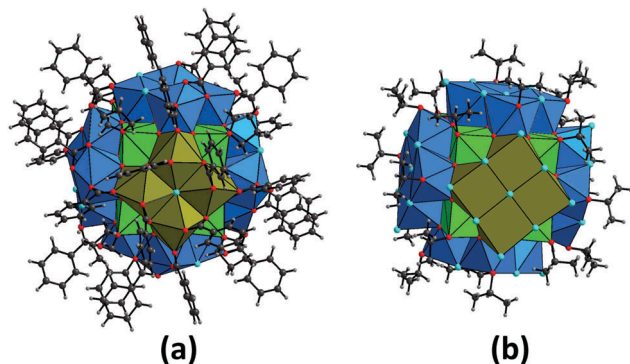


Fig. 2 Molecular structures of the two  $\{Np_{38}\}$  clusters  $Np_{38}O_{56}Cl_{18}(bz)_{24}(THF)_8$  (**1**, a) and  $Np_{38}O_{56}Cl_{42}(ipa)_{20}$  (**2**, b).§ The coordination geometry around neptunium atoms (as  $Np^{4+}$ ) is illustrated with coloured polyhedra, whilst carbon (black), chlorine (light blue), hydrogen (grey) and oxygen (red) atoms are shown as balls. The cubic  $\{Np_{14}\}$  cores are depicted with light green, whilst the exterior  $\{Np_4\}^{tetra}$  and  $\{Np_4\}^m$  subunits adhering to the  $\{Np_{14}\}$  core are illustrated with blue and dark brown, respectively.

brown polyhedra in Fig. 2). In the  $\{Np_{14}\}$  core, three crystallographically distinct Np atoms (Np1, Np2 and Np3) are packed in a dense manner, forming a primitive unit of the fluorite structure (Fig. S1 in the ESI†) which is the basis of bulk  $NpO_2$ .<sup>29,30</sup> The eight corners of the cubic  $\{Np_{14}\}$  core are all occupied by the oxygen atoms of THF- or isopropanol molecules for **1** and **2**, respectively (Fig. S1 in the ESI†). Each face of the cubic  $\{Np_{14}\}$  core is further decorated with the  $\{Np_4\}$  subunits, where there is a significant difference between **1** and **2**. In both the  $\{Np_{38}\}$  compounds, two types of  $\{Np_4\}$  subunits appear. The first type (referred to as “ $\{Np_4\}^{tetra}$ ” hereafter) appears four times by symmetry operation with respect to the tetragonal axis, whilst the second type (referred to as “ $\{Np_4\}^m$ ” hereafter) appears twice around the  $\{Np_{14}\}$  core as a result of the perpendicular mirror plane operation. The coordination polyhedra of the Np atoms in the inner  $\{Np_{14}\}$  core are cubic, whilst those in the exterior  $\{Np_4\}$  subunits are square antiprismatic polyhedra (Fig. 3). This results in two different types of oxo-bridging groups in the  $\{Np_{38}\}$  clusters;  $\mu_4$ -O with Np–O distances of 2.294(9)–2.408(9) and 2.28(4)–2.42(4) Å for **1** and **2**, respectively, and  $\mu_3$ -O with Np–O distances of 2.203(9)–2.335(10) and 2.15(4)–2.305(3) Å for **1** and **2**, respectively. These Np–O distances are comparable to those in the fluorite-based  $NpO_2$  structure (2.353–2.354 Å),<sup>29,30</sup> suggesting that the Np–O framework in the  $\{Np_{38}\}$  clusters could also be comparable to that in the bulk  $NpO_2$ .

In compound **1**, the  $\{Np_4\}^{tetra}$  subunit (blue polyhedra in Fig. 2a and 3a) is composed of three distinct Np centres (Np4, Np5 and Np6). The four Np atoms are linked *via* either  $\mu_2/\mu_4$ -Cl atoms or bidentately coordinating the carboxylate groups of bz, forming a ninefold coordination geometry with distorted trideca- and undecahedra around Np4 and Np5, respectively, and an eightfold geometry with a distorted nonahedron around Np6 (Fig. 3a). Each  $\{Np_4\}^{tetra}$  subunit adheres to one side of the cubic  $\{Np_{14}\}$  core *via* twelve O atoms facing the core, covering the four sides of the  $\{Np_{14}\}$  cube. On the other hand, the  $\{Np_4\}^m$  subunit (dark brown polyhedra in Fig. 2a and 3b) is composed of a single type of a distinct Np centre (Np7). The four Np atoms in the

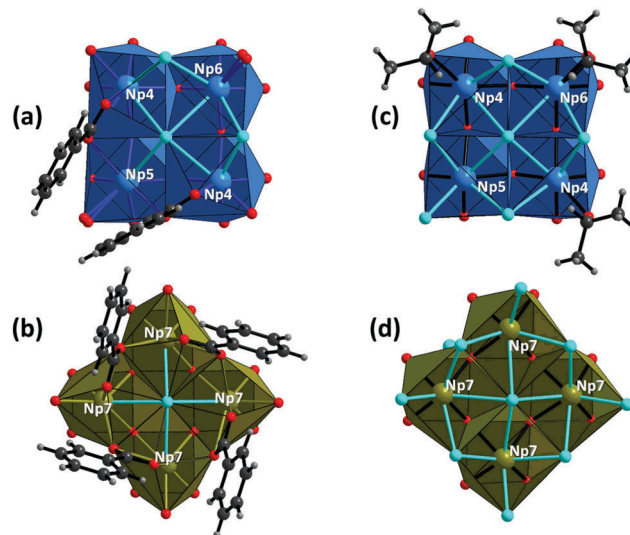


Fig. 3 Top-side views of the  $\{Np_4\}$  subunits in **1** and **2**; the  $\{Np_4\}^{tetra}$  and  $\{Np_4\}^m$  subunits in **1** (a and b, respectively) and those in **2** (c and d, respectively).§ All these subunits contain unique  $\mu_4$ -bridging Cl atoms. The coordination geometry around neptunium atoms (as  $Np^{4+}$ ) is illustrated with blue and dark brown polyhedra ( $\{Np_4\}^{tetra}$  and  $\{Np_4\}^m$ , respectively), whilst carbon (black), chlorine (light blue), hydrogen (grey) and oxygen (red) atoms are shown as balls.

$\{Np_4\}^m$  subunit are linked *via* one  $\mu_4$ -Cl atom and four carboxylate groups of bz, forming a ninefold coordination geometry with a dodecahedron around the Np7 atoms (Fig. 3b). This  $\{Np_4\}^m$  subunit covered the rest of the two sides of the  $\{Np_{14}\}$  cube, and is further connected with the  $\{Np_4\}^{tetra}$  subunit by the bidentate carboxylate groups of bz to overlay the  $\{Np_{14}\}$  core (Fig. 2a).

Despite the presence of benzoic acid in the initial sample solution, no benzoate groups are involved in the formation of the  $\{Np_{38}\}$  cluster in **2**, which is in contrast to **1**. The exterior  $\{Np_4\}$  subunits in **2** are composed of the O atoms of isopropanol molecules, Cl<sup>−</sup> ions and the O<sub>oxo</sub> groups shared with the  $\{Np_{14}\}$  core. The  $\{Np_4\}^{tetra}$  subunit in **2** is composed of three distinct Np centres (Np4, Np5 and Np6), all of which form an eightfold square antiprismatic geometry (Fig. 3c). In the  $\{Np_4\}^m$  subunit of **2**, there is only a single distinct Np centre (Np7) which is surrounded by four O<sub>oxo</sub> groups shared with the  $\{Np_{14}\}$  core and four Cl<sup>−</sup> ions, eventually forming an eightfold square antiprismatic geometry as well (Fig. 3d). In a similar manner to the arrangement in **1**, the six  $\{Np_4\}$  subunits decorate the exterior of the cubic  $\{Np_{14}\}$  core to form an  $\{Np_{38}\}$  cluster.

The chemical formulae of  $[Np_{38}O_{56}Cl_{18}(bz)_{24}(THF)_8]$  (**1**) and  $[Np_{38}O_{56}Cl_{42}(ipa)_{20}]$  (**2**) derived from SC-XRD both exhibit an excess negative charge of  $-2$ , assuming that the Np atoms in the clusters are all tetravalent (*i.e.*  $Np^{4+}$ ). No cationic species are identified in the crystal packing of **1** and **2** either, indicating that the  $\{Np_{38}\}$  cluster units should be neutral. This discrepancy can be, however, explained by the partial replacement of chloride anions (Cl<sup>−</sup>) with neutral water molecules (H<sub>2</sub>O) in the  $\{Np_4\}$  subunits and/or the replacement of the  $\mu_3$ -oxo groups with the hydroxo ones in the inner  $\{Np_{14}\}$  core. Further detailed discussions are provided in the ESI† (Section 3).



Albeit a series of  $\{\text{An}_{38}\}$  clusters (*i.e.*  $\{\text{U}_{38}\}$ ,<sup>9,26</sup>  $\{\text{Np}_{38}\}$  in this study, and  $\{\text{Pu}_{38}\}$ <sup>13,15</sup>) were successfully characterised, their formation mechanism has been unrevealed even to date. All the  $\{\text{An}_{38}\}$  clusters characterised thus far are composed of an inner  $\{\text{An}_{14}\}$  core decorated with six exterior  $\{\text{An}_4\}$  subunits. Given this construction manner, it is reasonable to infer that the formation of the primary  $\{\text{An}_{14}\}$  core is followed by the attachment of the  $\{\text{An}_4\}$  subunits to the surface of the cubic  $\{\text{An}_{14}\}$  core. Owing to their strong ololation/oxolation tendency,<sup>31</sup> An(IV) can form a variety of oligomer species<sup>2</sup> including soluble  $\mu_2$ -hydroxo-bridged dinuclear species,<sup>7,17,32</sup> which could further evolve into hexanuclear species *via* hydrolysis.<sup>6,10,11,14</sup> A similar evolution of such oligomer species was also observed for Ce(IV),<sup>33,34</sup> a chemical analogue of An(IV). The union of di- and hexanuclear species could also lead to the formation of  $\{\text{An}_{12}\}$  complexes.<sup>8</sup> However, to the best of our knowledge, no  $\{\text{An}_{14}\}$  complexes have been characterised for An(IV) thus far, indicating that the  $\{\text{An}_{14}\}$  motif is probably not stable at least as a discrete species. In contrast, several discrete  $\{\text{An}_4\}$  complexes have been characterised for Th(IV)<sup>35</sup> and U(IV),<sup>36–43</sup> seven of which exhibit a planar tetranuclear arrangement that is structurally comparable with the  $\{\text{An}_4\}$  subunits in the  $\{\text{An}_{38}\}$  clusters (Section 4 in the ESI†). A striking difference between the  $\{\text{An}_4\}$  subunits and the discrete tetranuclear An(IV) complexes is, however, the presence/absence of  $\mu_4$ -bridging groups. As illustrated in Fig. 3, there are unique  $\mu_4$ -bridging Cl atoms situated at the centre of the  $\{\text{Np}_4\}$  subunits, which are observed for the whole series of  $\{\text{An}_{38}\}$  clusters. On the other hand, none of the discrete tetranuclear An(IV) complexes contains  $\mu_4$ -bridging groups (Table S2 and Fig. S2 in the ESI†), except one Th(IV) complex<sup>35</sup> containing a  $\mu_4$ -bridging oxo group to form a unique non-planar boat conformation arrangement (Fig. S3 in the ESI†). Instead, these discrete tetranuclear complexes are composed of  $\mu_2$ - and  $\mu_3$ -bridging groups (Table S2 and Fig. S3 in the ESI†), suggesting that the planar  $\{\text{An}_4\}$  motif with a  $\mu_4$ -bridging group may also not be stable as a discrete species. Given all these facts, the formation process of the  $\{\text{An}_{38}\}$  clusters could be surmised as follows:

(1) the primitive but transient  $\{\text{An}_{14}\}$  core is formed *via* the ololation/oxolation of precursor species (*e.g.* dinuclear and/or hexanuclear species),

(2) owing to an extremely large negative charge of the primitive  $\{\text{An}_{14}\}$  core ( $-72$  based on the formula  $\text{An}_{14}\text{O}_{64}$  (Fig. S1 in the ESI†)), cationic species in the system (*i.e.*  $\text{An}^{4+}$ ) are further attracted to the surface of the  $\{\text{An}_{14}\}$  core immediately after the formation of the primitive core, forming dense  $\{\text{An}_4\}$  subunits containing  $\mu_4$ -bridging groups on the surface, and

(3) the attachment of six  $\{\text{An}_4\}$  subunits on each face of the cubic  $\{\text{An}_{14}\}$  core neutralises the negative charge of the  $\{\text{An}_{14}\}$  core, eventually stabilising the whole unit as  $\{\text{An}_{38}\}$ .

Based on this hypothetical formation process, it is obvious that the faces of the primitive  $\{\text{An}_{14}\}$  core provide a sort of “substrate” for the formation of unique planar  $\mu_4$ -bridged  $\{\text{An}_4\}$  subunits. In other words, such a planar  $\mu_4$ -bridged  $\{\text{An}_4\}$  motif could be formed and stabilised only when an appropriate substrate exists in the system.

As previously mentioned, the inner  $\{\text{An}_{14}\}$  core in the  $\{\text{An}_{38}\}$  cluster is a primitive unit of the fluorite-based  $\text{AnO}_2$  structure.

The  $\{\text{An}_4\}$  subunits in the cluster also show a closer structural conformity to the bulk  $\text{AnO}_2$  structure as compared with the discrete tetranuclear An(IV) complexes (Fig. S4 in Section 4, ESI†). All these facts indicate that the poly-oxo  $\{\text{An}_{38}\}$  clusters can be the origin of the formation of  $\text{AnO}_2$  in solution. As a matter of fact, the  $\{\text{An}_{38}\}$  clusters can easily evolve into bulk  $\text{AnO}_2$  by moderate hydrolysis.<sup>9,26</sup> Given the electroneutrality of the  $\{\text{An}_{38}\}$  clusters, the  $\{\text{An}_{38}\}$  motif will no longer attract additional metal cations (*i.e.*  $\text{An}^{4+}$ ) to form larger clusters. Hence, the  $\{\text{An}_{38}\}$  unit is probably the largest poly-oxo An(IV) cluster stabilised in solution, which is also the limiting point that defines the border between discrete poly-oxo oligomer/cluster complexes and insoluble bulk  $\text{AnO}_2$ , including colloidal species or aggregates.

In summary, this study succeeded in synthesising and structurally characterising the two poly-oxo Np(IV) cluster complexes **1** and **2** which are composed of 38 Np atoms. The characterised  $\{\text{Np}_{38}\}$  clusters are the largest discrete Np complexes reported thus far, filling the gap between the already reported  $\{\text{U}_{38}\}$  and  $\{\text{Pu}_{38}\}$  clusters to complete a series of  $\{\text{An}_{38}\}$  cluster complexes. Although hexavalent An cations (as actinyl(VI) cations:  $\text{AnO}_2^{2+}$ ) can form poly-oxo clusters larger than 100-mer based on the cage structure which is not directly comparable with open clusters,<sup>3</sup> the  $\{\text{An}_{38}\}$  motif is probably the largest open cluster unit for the poly-oxo An(IV) complexes that can be stabilised as a discrete species in solution. A series of poly-oxo  $\{\text{An}_{38}\}$  clusters (An = U, Np and Pu) exhibits a significant structural similarity, suggesting a similar ololation/oxolation (*i.e.* hydrolysis) behaviour amongst these lighter An(IV) series. A comparison of the series of  $\{\text{An}_{38}\}$  clusters with the large poly-oxo clusters of other metals (*e.g.*  $\text{Ti}^{4+}$  or  $\text{Bi}^{4+}$ ) will further highlight the peculiarity or generality of the chemistry of An(IV) on the periodic table, particularly in terms of hydrolysis and coordination chemistry.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

‡ The Fourier maps of electronic density residues on the collected SC-XRD data show diffused peaks in the void between the  $\{\text{Np}_{38}\}$  units. These peaks probably correspond to neutral solvent molecules (*i.e.* THF in **1** and isopropanol in **2**) intercalated in the crystal structures, as observed in the analogous  $\{\text{U}_{38}\}$  compounds.<sup>9,26</sup> However, owing to the limited quality of the collected SC-XRD data, it is difficult to determine the positions of these intercalated solvent molecules. For this reason, the number of solvent molecules is not specified in the chemical formulae of **1** and **2**.

§ The carbon atoms of some benzoate (bz) molecules in **1** show disorder, statistically populating at two close sites with equivalent occupancy. This disorder is, however, not illustrated in Fig. 2a and 3a for clarity.

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