\{\text{Np}_{38}\} \text{ clusters: the missing link in the largest poly-oxo cluster series of tetravalent actinides}^\dagger

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Two poly-oxo cluster complexes of tetravalent neptunium (Np(IV)), \text{Np}_{38}\text{O}_{56}\text{Cl}_{42}(\text{bz})_{24}(\text{THF})_{8}\text{THF} and \text{Np}_{38}\text{O}_{56}\text{Cl}_{42}(\text{ipa})_{20}\text{mipa} (\text{bz} = \text{benzoate}, \text{THF} = \text{tetrahydrofuran}, \text{and ipa} = \text{isopropanol}), were obtained \textit{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.\textsuperscript{1–5} In particular, the poly-oxo-hydroxo polymer and cluster complexes of tetravalent actinides (An(IV)) have received considerable attention,\textsuperscript{6–20} as the formation of these complexes stems primarily from their hydrolysis\textsuperscript{21–24} and, hence, it would have significant implications for the natural and engineered aqueous systems associated with the nuclear industry.\textsuperscript{25} The largest poly-oxo An(IV) cluster reported thus far is the \{\text{An}_{38}\} motif shown in Fig. 2a. The second \{\text{Np}_{38}\} complex, \text{Np}_{38}\text{O}_{56}\text{Cl}_{42}(\text{ipa})_{20}\text{mipa} (\text{ipa} = \text{isopropanol}), was synthesised \textit{via} solvothermal synthesis with \text{NpCl}_{4}, benzoic acid, \text{THF} and deionised water (Sections 1 and 2 in the ESI\textsuperscript{†}). Heating the sample mixture at 370 K for 3 days resulted in the formation of 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}_{18}\text{O}_{35}\text{Cl}_{25}(\text{ipa})_{20}\text{mipa} (\text{ipa} = \text{isopropanol}), was synthesised \textit{via} solvothermal synthesis with \text{NpCl}_{4} and benzoic acid in isopropanol (Sections 1–3 in the ESI\textsuperscript{†}). 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 \textit{I}4/\textit{m} (Table S1 in the ESI\textsuperscript{†}), which is the same as that observed for the analogous \{\text{U}_{38}\} clusters \text{U}_{18}\text{O}_{35}\text{Cl}_{18}(\text{bz})_{24}(\text{THF})_{8}\text{THF} and \text{U}_{18}\text{O}_{35}\text{Cl}_{18}(\text{ipa})_{20}\text{ipa}.\textsuperscript{26} Both the \{\text{Np}_{38}\} clusters are composed of a \{\text{Np}_{18}\} core (light green polyhedra in Fig. 2) surrounded by six tetranuclear \{\text{Np}_{4}\} subunits (blue and dark brown crystals with an octahedral shape (Fig. 1, right)).
brown polyheda 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. 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_{18}\} 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_{18}\} clusters; \(\mu_{4}\)-O with Np–O distances of 2.294(9)–2.408(9) and 2.284(4)–2.424(4) Å for 1 and 2, respectively, and \(\mu_{2}\)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 bulk NpO_2. The eight corners of the cubic \{Np_{14}\} core are all occupied by the oxygen atoms of THF- or isopropanol molecules (Fig. 3a) is composed of three distinct Np centres (Np4, Np5 and Np6), all of which form an eightfold coordination geometry with a dodecahedron around the Np7 atom (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 benzoato groups are involved in the formation of the \{Np_{18}\} 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⁻ ions and the O oxo 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 oxo groups shared with the \{Np_{14}\} core and four Cl⁻ 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}\}m subunits decorate the exterior of the cubic \{Np_{14}\} core to form an \{Np_{18}\} cluster.

The chemical formulae of \([\text{Np}_{38}\text{O}_{56}\text{Cl}_{18}(\text{bz})_{24}(\text{THF})_{8}]\) (1) and \([\text{Np}_{38}\text{O}_{56}\text{Cl}_{18}(\text{ipa})_{20}]\) (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. \(\text{Np}^{4+}\)). No cationic species are identified in the crystal packing of 1 and 2 either, indicating that the \{Np_{18}\} cluster units should be neutral. This discrepancy can be, however, explained by the partial replacement of chloride anions (Cl⁻) with neutral water molecules (H₂O) in the \{Np_{4}\} subunits and/or the replacement of the \(\mu_{4}\)-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. $\text{U}_{38}$, $\text{Pu}_{38}$) in this study, and $\text{Pu}_{38}$ clusters were successful 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 oxolation/oxolation tendency,$^{11}$ An$^{(iv)}$ can form a variety of oligomer species$^{3}$ including soluble $\mu_2$-hydroxo-bridged dinuclear species, which could further evolve into hexanuclear species via hydrolysis.$^{6,10,11,14}$ A similar evolution of such oligomer species was also observed for Ce$^{(iv)}$, a chemical analogue of An$^{(iv)}$. The union of $\text{di-}$ and hexanuclear species could also lead to the formation of $\text{An}_{12}$ complexes. However, to the best of our knowledge, no $\text{An}_{12}$ 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 $\text{An}_{14}$ complexes have been characterised for Th$^{(iv)}$, 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 (i.e. $\text{An}^{(vi)}$) 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 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 (i.e. $\text{An}^{(vi)}$) can form poly-oxo clusters larger than 100-mer based on the cage structure which is not directly comparable with open clusters, 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 oxolation/oxylation (i.e. hydrolysis) behaviour amongst these lighter An$^{(iv)}$ species. A comparison of the series of $\text{An}_{38}$ clusters with the large poly-oxo clusters of other metals (e.g. Ti$^{(iv)}$ or Bi$^{(iv)}$) 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.$^{5,6}$ 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 the collected SC-XRD data show disorder, statistically populating at two close sites with equivalent occupancy. This disorder is, however, not illustrated in Fig. 2a and 3a for clarity.
