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Mixed-valent neptunium oligomer complexes based on cation-cation interactions†‡

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Mixed-valent tri- and tetranuclear complexes of neptunium, $[\{\text{Np}^{\text{IV}}\text{Cl}_4\}\{\text{Np}^{\text{V}}\text{O}_2\text{Cl}(\text{THF})_3\}_2]\cdot\text{THF}$ and $[\{\text{Np}^{\text{IV}}\text{Cl}_3\}\{\text{Np}^{\text{V}}\text{O}_2(\mu_2\text{-Cl})(\text{THF})_2\}_3\{\mu_3\text{-Cl}\}]$ (THF = tetrahydrofuran), were synthesised and characterised. Both the complexes are formed *via* the cation-cation interactions between the Np(IV) centre and the axial oxygens of the neptunyl(V) unit (i.e. transdioxo NpO_2^+ cation), demonstrating the potential of cation-cation interactions for further exploring the oligomer/cluster chemistry of actinides.

The oligomer and cluster complexes of actinides (An) have attracted considerable attention over the last few decades, not only from the fundamental chemical interest in a series of these heavy metal elements appearing at the bottom of the periodic table, but also for their technological applications and implications for the nuclear waste treatment and management.^{1–4} Although a considerable number of An oligomer and cluster complexes have been reported to date, the majority of these oligomer/cluster complexes are oxo/hydroxo-bridged^{2,3} and/or supported by chelating ligands, such as carboxylates⁵ or phosphonates.⁶ The former oxo/hydroxo-bridged oligomer/cluster complexes are formed via hydrolysis and subsequent condensation reactions, whilst the latter ligand-supported oligomers/clusters utilise the chelating function of the ligand to bridge the metal centres. In addition to these two strategies to materialise An oligomer/cluster complexes, there is another way to encourage the link between the metal centres for potentially producing oligomer/cluster complexes, that is, cation-cation interactions (CCIs).^{7,8} The CCIs in An complexes are observed as the interaction between the axial oxygen of the actinyl unit (transdioxo AnO_2^{n+} cation, where $n = 1$ or 2) and another

adjacent cationic centre. Such CCIs were reported not only for homo-valent actinyl compounds (U(V),⁹ -(VI),¹⁰ Np(V),^{11,12} -(VI)¹³ and Pu(V)¹⁴), but also for mixed-valent An compounds including small oligomer complexes (U¹⁵ and Np^{16,17}). All these facts indicate the potential of CCIs for triggering the formation of new types of An oligomer/cluster complexes. This motivates us to perform the current study to explore the oligomer/cluster chemistry of Np, the chemical enquiries into which always lags behind those on the adjacent An of U and Pu,¹⁸ based on CCIs.

Our synthetic attempt commenced with the dissolution of a starting Np(IV) tetrachloride compound into tetrahydrofuran (THF). It has been reported that the dissolution of pure Np(IV) tetrachloride compounds (e.g. $\text{NpCl}_4(\text{DME})_2$, DME = 1,2-dimethoxyethane) in THF results in the exchange of solvent molecules to yield $\text{Np}^{\text{IV}}\text{Cl}_4(\text{THF})_3$.¹⁹ The preparation of our starting Np(IV) tetrachloride compound is based on the simultaneous reduction and chlorination of Np(VI) nitrate in hexachloropropene.²⁰ With this synthetic route, it is difficult to achieve the complete reduction to Np(IV) and the final product contains a small amount of Np(V) (neptunyl(V) chlorides) as impurity. The amount of Np(V) impurity in the final product depends on the synthetic conditions (reaction time, temperature, etc.) and, therefore, varies from one batch to another. When the Np(IV) source with a lower content of Np(V) impurity was dissolved in THF, the trinuclear Np(IV/V) complex, $[\{\text{Np}^{\text{IV}}\text{Cl}_4\}\{\text{Np}^{\text{V}}\text{O}_2\text{Cl}(\text{THF})_3\}_2]\cdot\text{THF}$ (**1**) was obtained (Section 1–2 in the ESI). The compound **1**, the first mixed-valent An(IV/V) trinuclear complex to the best of our knowledge, was crystallised in the monoclinic space group $P2_1/c$ and deposited as pale green plate crystals (Fig. S1 in the ESI). The molecular structure of **1** consists of one Np(IV) centre linked with two neptunyl(V) cations via CCIs, and the two neptunyl(V) units are bridged by two μ_2 -chlorides (Fig. 1). The trinuclear arrangement of **1** is comparable with the reported Np(V/VI) trinuclear complex, $[\{\text{Np}^{\text{VI}}\text{O}_2\text{Cl}_2\}\{\text{Np}^{\text{V}}\text{O}_2\text{Cl}(\text{THF})_3\}_2]\cdot\text{THF}$,¹⁶ although the different valence states of the Np centres result in the distinct structural difference between these mixed-valent trinuclear complexes. The Np1 atom in **1** (Fig. 1) is tetravalent and, hence, its CCIs with the adjacent

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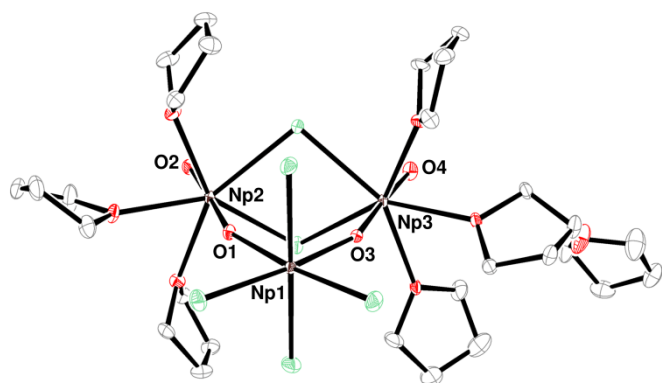


Fig. 1 ORTEP representation of the molecular structure of **1**, $[\{\text{Np}^{\text{IV}}\text{Cl}_4\}\{\text{Np}^{\text{V}}\text{O}_2\text{Cl}(\text{THF})_3\}_2]\cdot\text{THF}$. Thermal ellipsoids are drawn at 50% probability level and hydrogen atoms are omitted for clarity. Colour code: carbon (C, grey), chlorine (Cl, light green), oxygen (O, red) and neptunium (Np, dark brown).

neptunyl(V) units are expected to be stronger than those between the neptunyl(VI) (as a divalent NpO_2^{2+}) and the adjacent neptunyl(V) units in the reported Np(V/VI) complex. (Fig. S2 in the ESI). As a result, the Np1 atom in **1** attracts the adjacent neptunyl(V) oxygens (O1 and O3) much more strongly with the Np1–O1 and Np1–O3 distances of 2.25 and 2.27 Å, respectively. These Np–O distances in the Np(IV/V) complex **1** are significantly shorter than those in the Np(V/VI) complex (2.30 and 2.32 Å) (Table S1 in the ESI). The stronger CClIs in **1** also shrinks its trinuclear arrangement slightly as compared with that in the Np(V/VI) complex, which is indicated by the shorter Np–Np distances in **1** than those in the Np(V/VI) complex (Table S1 in the ESI).

When the Np(IV) source with a higher content of Np(V) impurity was dissolved in THF, the tetranuclear Np(IV/V) complex, $[\{\text{Np}^{\text{IV}}\text{Cl}_3\}\{\text{Np}^{\text{V}}\text{O}_2(\mu_2\text{-Cl})(\text{THF})_2\}_3\{\mu_3\text{-Cl}\}]$ (**2**) was obtained (Section 1-3 in the ESI). The compound **2** was crystallised in the monoclinic space group $C2/c$ and deposited as pale blue/purple plate crystals (Fig. S1 in the ESI). The molecular structure of **2** consists of one Np(IV) centre linked with three neptunyl(V) cations via CClIs, and the three neptunyl(V) units are linked by three μ_2 - and one μ_3 -chlorides (Fig. 2). In the compound **2**, one Np(IV) and three Np(V) atoms are arranged at the vertices of a pseudo-tetrahedron. Such a (pseudo-)tetrahedral arrangement has been reported for single-valent tetranuclear complexes of Th(IV)^{21, 22} and U(IV),^{23, 24} as well as for a mixed-valent U(III/IV) complex.²⁴ Some transition metals, such as Ti/Ir,²⁵ Mo and W,²⁶ and Ru,²⁷ can also form such (pseudo-)tetrahedral tetranuclear complexes. However, to the best of our knowledge, a tetrahedral arrangement has never been reported for the polynuclear complexes based on CClIs. The compound **2** is therefore the first mixed-valent tetranuclear actinide complex with a pseudo-tetrahedral arrangement via CClIs. The reported mixed-valent Np(IV/V) tetranuclear complex¹⁷ forms a planar triangle with three Np(V) apices and one Np(IV) at the centre of the triangle (Fig. S3 in the ESI). Hence, the tetranuclear arrangement of **2** differs significantly from that of the reported one, but is rather comparable with the compound **1** possessing one Np(IV) apex. The average distance between the Np(IV) centre (Np1) and the adjacent neptunyl(V)

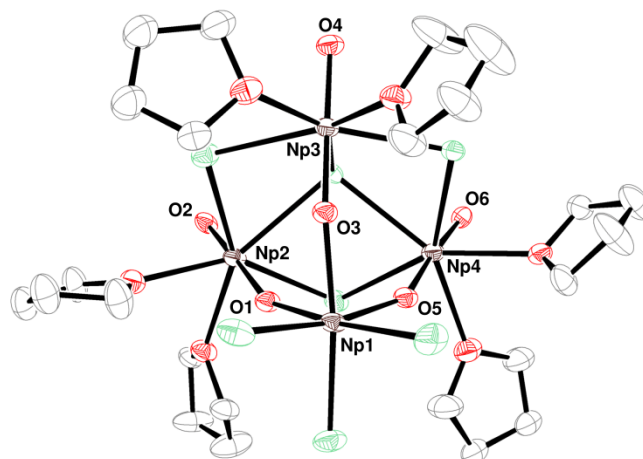


Fig. 2 ORTEP representation of the molecular structure of **2**, $[\{\text{Np}^{\text{IV}}\text{Cl}_3\}\{\text{Np}^{\text{V}}\text{O}_2(\mu_2\text{-Cl})(\text{THF})_2\}_3\{\mu_3\text{-Cl}\}]$. Thermal ellipsoids are drawn at 50% probability level and hydrogen atoms are omitted for clarity. Colour code: carbon (C, grey), chlorine (Cl, light green), oxygen (O, red) and neptunium (Np, dark brown).

oxygen atoms (O1, O3 and O5) in **2** (2.23 Å) are the shortest amongst the three mixed-valent Np(IV/V) complexes characterised thus far (average distances; 2.26 and 2.29 Å for **1** and the planar complex¹⁷, respectively) (Tables S1 and S2 in the ESI). This suggests the strongest CClIs in **2** amongst the mixed-valent polynuclear Np complexes reported thus far.

In order to estimate the valence state of Np atoms in the compounds **1** and **2**, the bond valence model²⁸ was applied. Shown in Tables 1 and 2 are lists of the bond valence sum (BVS) values (V), one measure of the apparent atomic valence state, calculated for the Np atoms in **1** and **2** with different parameters reported for $\text{Np}^{\text{V}}\text{-O}$ and $\text{Np}^{\text{V}}\text{-Cl}$ bonds. The V values for the “ γ ” Np atoms in **1** and **2** (Np2 and Np3 for **1**, and Np2, Np3 and Np4 for **2**) are consistent with a localised valence of +5 for the pentavalent state (Np(V)). The Np1 atoms in both **1** and **2** shows, however, the V values that are significantly higher than a localised valence of +4, possibly indicating a delocalisation of the charge within the clusters.^{29, 30} The deviation of the V values from the localised valence of +4 is more significant in **2** than **1**, potentially suggesting the more prominent charge delocalisation in **2** than **1**.

Table 1 Bond valence sum (BVS) values (V) of Np atoms in the trinuclear Np(IV/V) complex **1**. Details of the calculations are described in Section 3-3 in the ESI. Parameters for $\text{Np}^{\text{V}}\text{-O}$ and $\text{Np}^{\text{V}}\text{-Cl}$ bonds were taken from the references listed in the table, whilst the other parameters were taken from the reference.³¹

| Np(IV) | Np(V) | | | Reference |
|--------|-------|------|---------|-----------|
| | Np2 | Np3 | Average | |
| 4.14 | 5.00 | 4.93 | 4.97 | 12 |
| | 4.93 | 4.87 | 4.90 | 32 |
| | 4.95 | 4.88 | 4.92 | 33 |

Table 2 Bond valence sum (BVS) values (V) of Np atoms in the tetranuclear Np(IV/V) complex **2**. Details of the calculations are described in Section 3-3 in the ESI. Parameters for $\text{Np}^{\text{V}}\text{-O}$ and $\text{Np}^{\text{V}}\text{-Cl}$

bonds were taken from the references listed in the table, whilst the other parameters were taken from the reference.³¹

| Np(IV) | Np(V) | | | | Reference |
|--------|-------|------|------|------|-----------|
| | Np1 | Np2 | Np3 | Np4 | |
| 4.30 | 5.14 | 5.06 | 5.12 | 5.11 | 12 |
| | 5.00 | 4.94 | 4.99 | 4.98 | 32 |
| | 5.03 | 4.97 | 5.02 | 5.01 | 33 |

Tetrachloride An(IV) species are stable in THF.^{19,34} The THF employed in this study was a pure anhydrous solvent (Sections 3-4 and 3-5 in the ESI) and, therefore, there was no oxygen source in the synthetic route to form trans-dioxo neptunyl(V) units from Np(IV). These facts confirm that the neptunyl(V) components in **1** and **2** originate not in the possible oxidation of Np(IV) to neptunyl(V) during the synthetic process, but in the original Np sources employed for the syntheses. As discussed above, the synthesis using the original source with a lower Np(V) content resulted in the formation of a smaller oligomer of the trinuclear complex **1**, whilst the synthesis with a higher Np(V) content yielded a larger oligomer of the tetranuclear complex **2**. Hence, the nuclearity of the resultant complex is governed by the ratio of Np(IV)/Np(V) in the starting material (Section 3-6 in the ESI). The mixed-valent polynuclear An complexes reported thus far were obtained by spontaneous oxidation/reduction of the original An source containing a single oxidation state¹⁵⁻¹⁷ and, therefore, the formation and nuclearity of the resultant mixed-valent polynuclear complexes are rather contingent and uncontrollable. However, this study indicates the potential for controlling the formation and nuclearity of the mixed-valent An oligomer complex based on CCIs by adjusting the original source. For instance, the precise adjustment of the Np(IV)/Np(V) ratio by mixing pure Np(IV) and -(V) sources potentially results in the formation of other smaller or larger oligomeric complexes. Given the fact that the polynuclear actinyl-containing complexes based on CCIs have recently been spotlighted as peculiar functional materials, such as single-molecule magnets^{35,36} or single-chain magnets,³⁷ the findings of this study could have significant implications not only for further exploring the fundamental oligomer/cluster chemistry of An, but also for expanding their applications for material science.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ **Caution!** Neptunium (²³⁷Np) is a radioactive nuclide (α emitter) and, therefore, precautions with suitable equipment and facility for radiation protection are required for handling this radionuclide. All the experiments using ²³⁷Np were carried out in a controlled laboratory at the Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Germany.

§ Crystal data for **1**: C₂₈H₅₆Cl₆Np₃O₁₁, *Mr* = 1492.42, Monoclinic P2₁/c, *a* = 15.3447(17), *b* = 24.156(3), *c* = 11.5292(8) Å, β = 90.060(3)°, *V* = 4273.5(7) Å³, *Z* = 4, ρ_{calcd} = 2.320 g cm⁻³, Mo-K α radiation, λ = 0.71073 Å, μ = 7.664 mm⁻¹, *T* = 100.(2) K. 65035 collected reflections, 10184 unique reflections (*R*_{int} = 0.0334), *R*1 = 0.0207, *wR*2 = 0.0382, GOF on *F*² = 1.072. Largest difference peak and hole were observed at 1.294 and -1.101 eÅ⁻³, respectively. CCDC No. 1884777.

§§ Crystal data for **2**: C₂₄H₄₈Cl₇Np₄O₁₂, *Mr* = 1724.77, Monoclinic C2/c, *a* = 15.009(4), *b* = 14.159(3), *c* = 40.069(9) Å, β = 91.406(2)°, *V* = 8513.(3) Å³, *Z* = 8, ρ_{calcd} = 2.692 g cm⁻³, Mo-K α radiation, λ = 0.71073 Å, μ = 10.173 mm⁻¹, *T* = 100.(2) K. 31324 collected reflections, 6089 unique reflections (*R*_{int} = 0.0596), *R*1 = 0.1402, *wR*2 = 0.3249, GOF on *F*² = 1.358. Largest difference peak and hole were observed at 6.554 and -5.350 eÅ⁻³, respectively. CCDC No. 1884778. The crystallographic data for **2** have a lower quality than those for **1** due to a high mosaicity of the crystal, etc. The treatment and interpretation of the collected/analysed data for **2** are detailed in Section 2-1 of the ESI.

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