Assembly of a family of mixed metal \{\text{Mo:V}\} polyoxometalates templated by TeO₃²⁻: \{\text{Mo}_{12}V_{12}\text{Te}_3\}, \{\text{Mo}_{12}V_{12}\text{Te}_2\} and \{\text{Mo}_{17}V_8\text{Te}\}†

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The influence of the pyramidal heteroanion, TeO₃²⁻, in the self-assembly of mixed metal (Mo/V) systems, is demonstrated by the isolation of three novel mixed-metal, mixed-valence architectures, \{\text{Mo}_{12}V_{12}\text{Te}_3\} (1), \{\text{Mo}_{12}V_{12}\text{Te}_2\} (2) and \{\text{Mo}_{17}V_8\text{Te}\} (3) with the tellurium centres exhibiting the novel \(\mu_2\)–TeO₄ and \(\mu_5\)–TeO₃ coordination modes while compounds 1 and 2 were discovered utilizing ESI mass spectrometry.

Polyoxometalate chemistry has undergone an exponential growth over the last few decades due to the vast range of properties and applications that this diverse family of inorganic materials presents. In this respect, there are numerous reported examples in the recent literature, where the architecture of new heteropolyoxometalates (HPOMs) is mainly templated by tetrahedral heteroanions, such as phosphates and sulfates. However, HPOMs templated by non-conventional (pyramidal or octahedral) heteroanions are relatively rare. Moreover, it has been demonstrated that the incorporation of pyramidal heteroanions with a non-bonding, but stereochemically active lone pair of electrons, influences the assembly process and consequently the observable structural features leading finally to unique archetypes with extraordinary properties. In an effort to investigate the implication of the heteroanions mentioned above, we recently reported the characterization of two novel sulfito-based polyoxometalates with unprecedented mixed-metal/valence archetypes, \[\text{Mo}_2\text{V}_6\text{O}_{24}(\mu_3\text{-SO}_3)^{11-} (\text{M}_18\text{S})\] and \[\text{Mo}_2\text{V}_6(\mu_5\text{-SO}_3)(\text{Mo}_6\text{V}_6\text{O}_{20})^{9-} (\text{M}_2\text{S}),\] and we showed the use of reactive POM-based species as secondary building units towards the design of higher complexity architectures.

Herein, in order to investigate the effect of the geometry and the size of the incorporated heteroanions on the self-assembly process and the final structural motif, we report the synthesis, solid state and solution characterization of three novel tellurite-based mixed-metal and mixed-valence polyoxometalates, namely: \((\text{NH}_4)\text{_K}[\text{Mo}^{\text{VI}}\text{V}^{\text{V}}\text{V}^{\text{IV}}\text{V}^{\text{IV}}\text{O}_{60}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)]_2\cdot 2\text{H}_2\text{O}\) 1, \(\text{K}_4[\text{Mo}^{\text{VI}}\text{V}^{\text{V}}\text{V}^{\text{IV}}\text{V}^{\text{IV}}\text{V}^{\text{IV}}\text{O}_{60}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)]_2\cdot 2\text{H}_2\text{O}\) 2, which is isostructural with a tellurium centre gating the square shaped window on the cap of 1; and \(\text{K}_4[\text{Mo}^{\text{VI}}\text{V}^{\text{V}}\text{V}^{\text{IV}}\text{V}^{\text{IV}}\text{O}_{52}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)(\text{Mo}^{\text{VI}}\text{V}^{\text{IV}}\text{O}_{22})]_1\text{H}_2\text{O}\) 3. To the best of our knowledge 1, 2 and 3 are the largest tellurite-based mixed-metal polyoxometalate clusters reported to date, and it is the first time that the tellurite anion exhibits the \(\mu_5\)- and the rare \(\mu_9\)-coordination modes respectively. All three compounds were characterized in the solid state by X-ray structural analysis while compounds 1 and 2 were also characterized in solution by electrospray mass spectrometry studies. The sequential addition of \((\text{NH}_4)_2\text{V}^{\text{V}}\text{O}_3\), \(\text{K}_2\text{Te}^{\text{IV}}\text{O}_3\) and \(\text{NH}_4\text{NH}_2\text{HCl}\) in an aqeous solution of \((\text{NH}_4)_2\text{Mo}^{\text{VI}}\text{O}_{24}\), followed by the adjustment of the pH by conc. HCl, resulted in the formation of dark green crystals of 1; when \(\text{KV}^{\text{V}}\text{O}_3\) and \(\text{K}_2\text{MoO}_4\) were used instead of the ammonium salts, crystals of 2 were formed in similar yield. Even though sulphur and tellurium, belong to the same group of the periodic table and present similar behaviour under the same experimental conditions, the much larger size of the tellurium influenced the self-assembly process and the architecture of the final product (Fig. 1).

It is interesting to point out the chemical and structural information common to all three compounds: (a) the existence of the oxidized form of V in the presence of a reducing agent, even though the V⁴⁺ is reduced rapidly to V⁴⁺ by the hydrazine (in the present case there are 4 V⁴⁺ for compounds 1 and 2, and 2 for compound 3); (b) the plethora of geometries adopted by the metal centres in the same structure, as shown by structural analysis (dioxo-/oxo-Mo⁶⁺ and octahedrally/ tetrahedrally coordinated V⁴⁺/⁵⁺ centres); and (c) the second reported

![Fig. 1 Polyhedral representation of the three tellurite-based clusters.](image-url)

Colour code: Mo: blue polyhedra; V: grey polyhedra; Te: yellow spheres.
example of $\mu_2$-Te$^{IV}$O$_3$ coordination mode in the literature and the new $\mu_3$-Te$^{IV}$O$_4$ coordination mode in 1 (Fig. 2).

It is worth noting that the heteroanion size has a profound effect on the self-assembly of the metal oxide units in solution: the bigger the heteroanion becomes, the more spatial restrictions are introduced and this leads to new architectures with higher nuclearity as in the case of compounds 1 and 2.

Crystallographic studies revealed that 1a and 2a can be formulated as [Mo$^{VI}$(V$^4$)$_3$(V$^4$)$_6$(V$^2$)$_3$] and [Mo$^{VI}$(V$^4$)$_6$(V$^4$)$_3$(V$^2$)$_3$]_{10} respectively where the molybdovanadate-tellurite anions 1a and 2a adopt a “capsule” like structure which consists of two hemispheres. The upper hemisphere, which is structurally related to the lacunary Keggin structure [X$_{12}$O$_{40}$]$^{10-}$, incorporates five V (3 $^4$V and 2 $^2$V) and four Mo$^{VI}$ centres crystallographically disordered over the nine positions. Its cavity is occupied by one $\mu_2$-Te$^{IV}$O$_4$ anion with the lone pair of electrons pointing downwards. In the case of 1a a tellurium ion gates one of the square shaped windows of the $\{M_{24}Te_3\}$ building block, $\{MoVI_{8}V^{IV}_{5}V^{IV}_{2}Te^{IV}O_{8}\}$, see Fig. 3. In the case of 2a there is a triad of edge-shared MoO$_6$ octahedra capping the $\{Mo^{VI}_{8}V^{IV}_{3}V^{IV}_{2}Te^{IV}O_{8}\}$ unit, connected further to the “crown”-shaped, $\{Mo^{VI}_{6}V^{IV}_{2}\}$, formation while in the case of 1a and 2a the common building unit is capped by a $\{Mo^{VI}_{8}V^{IV}_{3}V^{IV}_{2}O_{3}\}$ and $\{Mo^{IV}_{4}V^{IV}_{2}V^{IV}_{2}Te^{IV}O_{3}\}$ respectively. In a similar fashion to the $\{M_9S\}$ cluster in compounds 1a and 2a, the “crown” formation and the upper part of the capsule is crystallographically well resolved. The “crown”-shaped, $\{Mo^{VI}_{6}V^{IV}_{2}\}$ fragment is attached to the three Mo$^{VII}$ centres located at the top of the ‘egg-shaped’ structure through six oxo-bridges. The metal sites in the lower hemisphere are crystallographically disordered over nine positions and the Mo, VO$_4$ and Te atoms can be assigned the oxidation states of VI, V and IV respectively (shown by BVS). Also, the V atoms in the VO$_4$ are coordinated by three $\mu_3$-O$^{2-}$ moieties, with V–O bonds spanning 1.730(6)–1.767(10) Å, and one terminal oxo group with V–O distances of the order of 1.628(11)–1.647(14) Å. The Mo atoms in the MoO$_6$, belonging to the upper hemisphere are coordinated by two terminal oxo groups in cis-positions, with Mo=O distances of 1.702(10)–1.731(12) Å, one $\mu_2$-O$^{2-}$, with Mo–O bond lengths between 1.882(10)–1.905(14) Å, and three $\mu_3$-O$^{2-}$ bridges, with Mo–O bond lengths of 1.988(10)–2.280(10) Å.†

During the course of this study, ESI-MS+ has proved to be a valuable tool in our effort to discover the $\{M_{24}Te_3\}$ 1a and $\{M_{24}Te_2\}$ 2a clusters in solution. This was performed either directly in aqueous media or by precipitating solid from the various reaction mixtures via ion exchange with tetrabutyl ammonium (TBA) followed by using mass spectrometry in CH$_3$CN. In this study, the TBA salt of the $\{M_{24}Te_3\}$ cluster 1a, dissolved in CH$_3$CN confirmed that the tellurite inorganic cage retains its integrity in solution (Fig. S1, ESI†), and peaks were seen that were assigned to the $\{M_{11}Te_2\}$ species organized in two groups of envelopes (Fig. 4).

The higher intensity envelope comprises two overlapping species which can be formulated as \{(C$_{16}$H$_{36}$N)$_2$K$_2$H$_3$[Mo$^{VI}$(V$^4$)$_6$(V$^4$)$_3$(V$^2$)$_3$(V$^2$)$_3$]$_{10}${(H$_2$O)$_{2}\}$ – 4H$_2$O\} at $m/z$ ca. 2227.1 and \{(C$_{16}$H$_{36}$N)$_2$K$_2$H$_3$[Mo$^{VI}$(V$^4$)$_6$(V$^4$)$_3$(V$^2$)$_3$(V$^2$)$_3$]$_{10}${(H$_2$O)$_{3}\}$ – 5H$_2$O\} at $m/z$ ca. 2233.2, respectively. In the case of 2a the studies similarities with compounds 1a and 2a become obvious since the lower part of their structures incorporates the same building block, \{Mo$^{VI}$(V$^4$)$_8$(V$^4$)$_5$(V$^2$)$_2$Te$^{IV}O_{38}\}$, see Fig. 3.

Fig. 2 Wire-stick representation of Te$^{IV}$ coordination modes. $\mu_2$-TeO$_3$ (left) where each oxygen is linked to three metal centres, found in 1a and 2a upper and lower hemisphere and in 3a lower hemisphere $\mu_2$-TeO$_4$ (right) in 1a where every oxygen atom is bridged to two metal centres.
Crystals for data 1: K₄[MoVI₄V⁴IVO₆(TeO₃)₃]·27H₂O: H₄K₂Mo₂O₁₀(Te₂O₃)₂12V₂O₁₆; M₉ = 4033.27, monoclinic, space group C2/m, a = 23.2791(6), b = 13.3972(3), c = 29.3216(8) Å, β = 93.462(2), V = 9127.85(5) Å³, Z = 4, ρc = 3.094 g cm⁻³, δ(Cu-Ka) = 1.5418 Å, T = 150(2)K, 36456 reflections measured, 9042 independent reflections (Rₑ = 0.0746), R(final) = 0.0859, wR₂ = 0.2250, GoF = 1.055.

Crystals for data 2: K₄[MoVI₂V₄V₄IVO₆(TeO₃)₃]·27H₂O: H₄K₂Mo₂O₁₀(Te₂O₃)₂12V₂O₁₆; M₉ = 4251.59, monoclinic, space group C2/m, a = 23.2791(6), b = 13.3972(3), c = 29.3216(8) Å, β = 93.462(2), V = 9127.85(5) Å³, Z = 4, ρc = 3.094 g cm⁻³, δ(Cu-Ka) = 1.5418 Å, T = 150(2)K, 36456 reflections measured, 9042 independent reflections (Rₑ = 0.0746), R(final) = 0.0859, wR₂ = 0.2250, GoF = 1.055.

In conclusion, we have reported the discovery, syntheses and structural investigation of three novel mixed-metal, mixed-valence polyoxomolybdenum/vanadium-tellurite clusters (NH₄)₂[(MoVI₄V⁴IV₄IVO₆(Te₂O₃)₂12V₂O₁₆)²⁻·27H₂O 1, (NH₄)₂[(MoVI₂V₄IV₂V₄IV₄IVO₆(Te₂O₃)₂12V₂O₁₆)²⁻·27H₂O 2 and (NH₄)₂[(MoVI₁V⁵IV₅IV₂IV₂V₄IV₂V₄IV₂V₄IV₄IVO₆(Te₂O₃)₂12V₂O₁₆)²⁻·15H₂O 3 which belong to the “Crown”-Dawson mixed-metal HPOM family templated by heteroanions from group VIa. The above compounds are the largest reported so far for mixed metal POMs which incorporate the pyramidal TeIVO₃ anion. ESI-MS studies proved to be crucial not only for the discovery of the aforementioned compounds, but also to identify unambiguously the additional TeIV atom which is incorporated in 1a. Furthermore, we demonstrated the cooperative effect of the counter-ion along with the size of the hetero-ion which allowed the discovery and isolation of these novel POM-based compounds. We have already further expanded the mixed-metal polyoxometalate family, templated by non-conventional heteroanions, and an extensive heteroanion size/structural correlation study has been performed and will be reported shortly.

Notes and references


