Giant Hollow Heterometallic Polyoxoniobates with Sodalite-Type Lanthanide–Tungsten–Oxide Cages: Discrete Nanoclusters and Extended Frameworks

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Abstract: The first series of niobium–tungsten–lanthanide (Nb-W-Ln) heterometallic polyoxometalates \([\text{Ln}_n\text{W}_{12}\text{O}_{36-(Ln-n)}(\text{H}_2\text{O})_{24}]\) (Ln = Y, La, Sm, Eu, Yb) have been obtained, which are comprised of giant cluster-in-cluster-like \((f[\text{Ln}_n\text{W}_{12}\text{O}_{36-(Ln-n)}] \text{in-[Nb}_{32}\text{O}_{96})\) structures built from 12 hexaniobate \([\text{Nb}_{32}\text{O}_{96}]\) clusters gathered together by a rare 24-nuclearity sodalite-type heterometal–oxide cage \([\text{Ln}_n\text{W}_{12}\text{O}_{36}(\text{H}_2\text{O})_{24}]\). The Nb-W-Ln clusters present the largest multi-metal polyoxoniobates and a series of rare high-nuclearity 4d-5d-4f multicomponent clusters. Furthermore, the giant Nb-W-Ln clusters may be isolated as discrete inorganic alkali salts and can be used as building blocks to form high-dimensional inorganic–organic hybrid frameworks.

Polyoxometalates (POMs) of V, Mo, and W have been developed over the past two decades, in pursuit of unique structural characteristics (for example, high negative charge, oxygen-rich surface, and rich redox properties) and wide potential applications\,[1,2] Moreover, new discoveries are becoming more and more frequent and abundant. In contrast, the development of polyoxoniobate (PONb) chemistry is still at a nascent stage because of some major limiting factors, including the lack of soluble niobate oxoanion precursors, low activity and the narrow working pH region of niobate species\,[3] For a long time, PONb chemistry was dominated by the isopolyoxoniobates \([\text{Nb}_{32}\text{O}_{96}]\) and \([\text{ Nb}_{32}\text{O}_{96}]\). Some new isopolyoxoniobates were obtained in recent years, including \([\text{ Nb}_{32}\text{O}_{96}]\)[4a] \([\text{H}_9\text{Nb}_{24}\text{O}_{72}]\)[4b] \([\text{H}_9\text{Nb}_{27}\text{O}_{76}]\) \([\text{H}_{10}\text{Nb}_{31}\text{O}_{93}-(\text{CO}_3)}\)[4c] and the largest, \([\text{Nb}_{32}\text{O}_{96}]\).[4d] Therefore, the exploration of elusive PONb chemistry is of great interest.

The introduction of metals (for example, transition metals and lanthanides) into POMs is an effective strategy for construction of POMs with diverse chemical compositions, structures, and functionalities. For instance, this strategy has achieved great success in creating transition-metal-substituted polyoxotungstates.[5] Especially, this strategy can allow access to a greater level of self-assembly to form surprising high-nuclearity heterometallic POMs\,[6–8] such as the recently reported examples \([\text{H}_2\text{Zr}_2\text{Ag}_2\text{Cl}(\text{TeW}_{31}\text{O}_{90})_2]^{2+}\)[5b] \([\text{Zr}_2\text{O}_2\text{Ag}(\text{OH})_4(\text{H}_2\text{O})_4(\text{W}_{29}\text{O}_{87})\text{GeW}_{5}\text{O}_{31}\text{GeW}_{3}\text{O}_{11}\)]\.[5c]

Since the first heteropolyoxoniobate \([\text{SiNb}_{12}\text{O}_{40}]\)\[5b–5d\] was reported by Nyman et al. in 2002,\[5b\] intensive efforts have been invested into development of novel heterometallic PONbs by the introduction of metals. Nevertheless, the integration of metals into PONbs remains largely undeveloped to date because the working pH region (ca. 10.5–12.5) of PONbs is incompatible with the solubility of most metal cations (acidic nature). Among known heterometallic PONbs (except for some new types of structures)\,[10,11] the major structure types are derived from isopolyoxoniobates \([\text{Nb}_{32}\text{O}_{96}]\), \([\text{Nb}_{32}\text{O}_{96}]\), or heteropolyoxoniobates \([\text{XNb}_{32}\text{O}_{96}] (X = \text{Si}, \text{Ge}, \text{P}, \text{V})\) by the attachment of a few addendum metals or by the substitution of one or several Nb metals with addendum metals\,[12–15] Especially, compared with giant high-nuclearity heterometallic POMs of Mo and W, the majority of known heterometallic PONbs are low-nuclearity (<20) structures. Based on the current research status of PONbs and their promising applications in fields such as nuclear-waste treatment, virology, and photochemistry,\[5c\] the synthesis of whole new types of heterometallic PONbs (especially with giant high-nuclearity structures) is challenging and scientifically interesting.

Herein, we report a series of unprecedented giant high-nuclearity heterometallic PONbs \([\text{Ln}_n\text{W}_{12}\text{O}_{36}(\text{H}_2\text{O})_{24}]\) \((\text{Ln}=\text{Y, La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb})\) which possess the following remarkable features: 1) \([\text{Ln}_n\text{W}_{12}\text{Nb}_{72}]\) is the first series of Nb-W-Ln heterometallic POMs, and of rare 4d-5d-4f composite clusters; 2) \([\text{Ln}_n\text{W}_{12}\text{Nb}_{72}]\) PONbs are by far the largest multi-metal PONbs reported thus far; 3) the incorporated 12\(W^{6+}\) and 12\(Ln^{3+}\) ions in \([\text{Ln}_n\text{W}_{12}\text{Nb}_{72}]\) form novel nanoscale 24-nuclearity hollow sodalite-type heterometal–oxide cages \([\text{Ln}_n\text{W}_{12}\text{O}_{36}(\text{H}_2\text{O})_{24}]\); 4) \([\text{Ln}_n\text{W}_{12}\text{Nb}_{72}]\) acts as a giant building block for three-dimension inorganic–organic hybrid framework \([\text{Na}_8\text{K}_2\text{Cu}(\text{en})_3]_[\text{Ln}_n\text{W}_{12}\text{O}_{36}(\text{H}_2\text{O})_{24}]\text{HNb}_{32}\text{O}_{96}\text{OH}^-\text{OH}_2^+]\text{solv} \ ([\text{1Ln}]n-\text{ethylene diamine, solv = solvents} )\) that can be isolated as discrete inorganic sodium–potassium salts, as shown by isolation of a Y-based PONb \([\text{Na}_8\text{K}_2\text{Y}_{12}\text{W}_{12}\text{O}_{36}(\text{H}_2\text{O})_{24}]\text{HNb}_{32}\text{O}_{96}\text{OH}^-\text{OH}_2^+]\text{solv} \ (29\text{H}_2\text{O})\). The overall structures of \([\text{1Ln}]n\) can be viewed as a multi-layered self-assembly.

Solid \([\text{1Eu}]n\) was first obtained and employed for single-crystal X-ray diffraction analyses. The results show that \([\text{1Eu}]n\) is a really interesting composite material based on various kinds of metals. Specifically, \([\text{1Eu}]n\) exhibits an anionic 3D inorganic–organic hybrid framework built by 4d-5d-4f heterometallic clusters \([\text{Eu}_{2}\text{W}_{13}\text{Nb}_{72}]\) bridged together by 3d Cu-complexes \([\text{Cu}(\text{en})]^+\), which is charge-balanced by s-block metals Na+. 

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and K⁺. The giant Eu₃W₁₂Nb₇₂ consists of 12Eu³⁺, 12W⁶⁺, and 72Nb⁵⁺ (12 [Nb₆O₁₉]) metal ions, forming the first Nb-W-Ln heterometallic PONb with an intriguing cluster-in-cluster-like ([Eu₁₂W₁₂]-in-[Nb₇₂]) structure.

As shown in Figure 1a, 12Eu³⁺ and 12W⁶⁺ ions are alternately linked by 36 μ₂-O bridges to form a centrosymmetric hollow 24-nucelarity heterometal-oxide cluster [Eu₁₂W₁₂O₃₆]³⁻ (Supporting Information, Figure S1), forming a closed cage. The free diameter of the largest sphere that can fit into the cage is approximately 0.7 nm (after consideration of the van der Waals radii of Eu and W). In the cage, some disordered water molecules are found to serve as the pore-filling species (Supporting Information, Figure S1). With the W⁶⁺ ions, each Eu³⁺ ion is simplified as a triangle, and three vertex oxygen atoms from three adjacent [Nb₆O₁₉]⁸⁻ anions can be viewed as an icosahedron with [Nb₆O₁₉]⁸⁻ anions held together by one Eu³⁺ ion of the [Eu₁₂W₁₂O₃₆]³⁻ cage further coordinates with three vertex oxygen atoms from three adjacent [Nb₆O₁₉]⁸⁻ anions, forming an eight-coordinate bicapped trigonal prism configuration (Eu-H₂O bonds: 2.586(8)–2.628(8) Å; Supporting Information, Table S1). With the W⁶⁺ and Eu³⁺ ion linkers, the 12 polyoxoanions [Nb₆O₁₉]⁸⁻ are gathered together by the nanosized [Eu₁₂W₁₂O₃₆]³⁻ cage to generate the largest multimetal PONbs Eu₁₂W₁₂Nb₇₂ thus far, with the dimensions 2.5 x 2.5 x 2.5 nm (Figure 1c); the Nb, W, and Eu contents were further confirmed by energy dispersive X-ray spectroscopy (EDS) element analyses (Supporting Information, Figure S3). With the W⁶⁺ and Eu³⁺ ion linkers, the 12 polyoxoanions [Nb₆O₁₉]⁸⁻ are gathered together by the nanosized [Eu₁₂W₁₂O₃₆]³⁻ cage to generate the largest multimetal PONbs Eu₁₂W₁₂Nb₇₂ thus far, with the dimensions 2.5 x 2.5 x 2.5 nm (Figure 1c); the Nb, W, and Eu contents were further confirmed by energy dispersive X-ray spectroscopy (EDS) element analyses (Supporting Information, Table S1). Interestingly, if every three adjacent [Nb₆O₁₉]⁸⁻ polyoxoanions held together by one Eu³⁺ ion is simplified as a triangle, the geometric arrangement of the 12 [Nb₆O₁₉]⁸⁻ polyoxoanions can be viewed as an icosahedron with [Nb₆O₁₉]⁸⁻ as vertices. Thus, the complicated giant Eu₃W₁₂Nb₇₂ can be regarded as a sodalite cage in an icosahedron cage, that is a ([Eu₁₂W₁₂O₃₆(H₂O)₁₂]³⁻-in-[(Nb₆O₁₉)₁₂]) configuration.

Except for the 4f Eu³⁺, 4d Nb⁵⁺, and 5d W⁶⁺ metal ions, the 3d Cu²⁺ metal ions are also integrated into the structure of 1Eu to act as linkers. As shown in Figure 2, each Eu₁₂W₇₂Nb₂₂ is linked to eight adjacent units by eight Cu-complex cations [Cu(en)₂]²⁺ to give a three-dimensional eight-connected uninodal network with bctu-type topology, in which each six-coordinate Cu²⁺ ion is defined by four N atoms from two chelating en ligands (Cu–N bonds: 2.006(14)–2.029(14) Å) and two terminal oxo atoms from two polyoxoanions [Nb₆O₁₉]⁸⁻ (Cu–O bonds: 2.449(1)–2.756(2) Å). On the basis of valence sum (Σ) calculations,[16] in 1Eu the oxidation states of all Nb, W, Eu, and Cu atoms is +5 (Σₑ = 4.89–5.08), +6 (Σₑ = 5.80–5.96), +3 (Σₑ = 2.97–3.21), and +2 (Σₑ = 1.60), respectively.
Notably, the overall structure of \( \text{Eu} \) can be regarded as an intriguing multi-layered self-assembly. The innermost species are some neutral water molecules, which are enclosed into a cationic cage \([\text{Eu}_{12}\text{W}_{12}\text{O}_{36}]^{24+}\). Twelve anionic \([\text{Nb}_{6}\text{O}_{19}]^{8-}/\text{C}_{0}\) centered around the cationic cage give a larger anionic \(\text{Eu}_{12}\text{W}_{12}\text{Nb}_{72}\) cluster. Finally, the anionic \(\text{Eu}_{12}\text{W}_{12}\text{Nb}_{72}\) cluster is further surrounded by eight \(\text{Cu}^{2+}\) cations (Supporting Information, Figure S4).

The structure of \( \text{Eu} \) is quite flexible in chemical compositions, and a series of isomorphic compounds (\(\text{Ln} \)) with other Ln ions, such as lighter \(\text{Y}^{3+}\), light \(\text{La}^{3+}\), heavy \(\text{Sm}^{3+}\), and heavier \(\text{Yb}^{3+}\), have also been obtained (Supporting Information, Figures S5–9, Table S2). Additionally, the giant \(\text{Ln}_{12}\text{W}_{12}\text{Nb}_{72}\) can also be isolated as discrete PONbs, as shown in a Y-based PONb (2), composed of a discrete \([\text{Y}_{12}\text{W}_{12}\text{O}_{39-}(\text{H}_{2}\text{O}_{2})_{12}\text{H}_{1}\text{Nb}_{6}\text{O}_{19}]^{24+}\) polyoxoanion charge-balanced by alkali metal ions Na\(^{+}\) and K\(^{+}\) (Supporting Information, Figure S10). Single crystal X-ray diffraction reveals that the discrete \([\text{Y}_{12}\text{W}_{12}\text{O}_{39-}(\text{H}_{2}\text{O}_{2})_{12}\text{H}_{1}\text{Nb}_{6}\text{O}_{19}]^{24+}\) polyanion in 2 is isostuctural with \(\text{Ln}_{12}\text{W}_{12}\text{Nb}_{72}\) in \(\text{Ln} \).

Notably, Su and Wang et al. reported a 96-Nb-containing PONb \(\text{K}_{12}[\text{Nb}_{6}\text{O}_{27}\text{H}_{13}]_{107}\text{H}_{2}\text{O}\) in 2012,\(^{[46]}\) which is constructed from three isopolyoxoniobate clusters \([\text{H}_{1}\text{Nb}_{6}\text{O}_{19}]^{3-}\) linked together by eight alkali metal ions (K\(^{+}\)). Generally, alkali metal ions are regarded as extra-cluster charge-balancing cations in POM chemistry. Without regard to the linkage of alkali metals, the \(\text{Ln}_{12}\text{W}_{12}\text{Nb}_{72}\) series is the largest among heterometallic PONbs reported thus far, and contains the largest number of Nb centers in a discrete POM. Additionally, almost all known Nb-W-based POMs allow adaptation of niobate chemistry to tungstate chemistry, forming tungsten-rich structures. The \(\text{Ln}_{12}\text{W}_{12}\text{Nb}_{72}\) series is a rare example in which tungstate chemistry has been adapted to niobate chemistry.

Solid \(\text{Sm} \) is taken as a representative example for the investigation of solid-state photoluminescent properties. The phase purity of as-synthesized \(\text{Sm} \) was confirmed by PXRD (Supporting Information, Figure S6). The temperature-dependent photoluminescent properties of the powder sample \(\text{Sm} \) are displayed in Figure 3. Under 336 nm UV light excitation at 300 K, \(\text{Sm} \) exhibits a broad emission band in the range of 350–450 nm, which is attributed to O\(^{-}\)-Nb charge transfer.\(^{[15c,d]}\) When sample \(\text{Sm} \) is cooled, its luminescence intensity gradually increases with decreasing temperature from 300 to 80 K. A series of emission peaks at 371, 383, and 411 nm become more and more clear with increased luminescence intensity, which is attributed to the existence of different NbO\(_6\) octahedral environments. Interestingly, the luminescence intensity of the series of emissions at 371, 383, and 411 nm increases linearly with decreasing temperature in the range of 80–300 K (Figure 3b), which can be fitted as a function of \(I = aT + b\) with very good correlation.
coefficients $R^2=0.993$, 0.995, and 0.996 for the respective emissions intensities (luminescence intensity (I), temperature (T)). Furthermore, the luminescence of 1Sm has good reversibility without an obvious loss of emission intensity for at least three cycles (Supporting Information, Figure S11), suggesting that compound 1Sm is a potential sensor as a luminescent thermometer in a broad temperature range of 80–300 K.

In summary, we have successfully integrated mixed metals W and Ln into PONb chemistry to prepare a series of the largest multi-metal composite PONbs \{Ln\textsubscript{12}W\textsubscript{12}O\textsubscript{36}\}, reported to date, which are also the first family of Nb-W-Ln heterometallic POMs. The giant PONbs {Ln\textsubscript{12}W\textsubscript{12}O\textsubscript{36}·(H\textsubscript{2}O)\textsubscript{24}} reveal the potential of introducing mixed metals into PONb chemistry to prepare a series of the largest multi-metal composite PONbs {Ln\textsubscript{12}W\textsubscript{12}O\textsubscript{36}·(H\textsubscript{2}O)\textsubscript{24}·(Nb\textsubscript{6}O\textsubscript{19})\textsubscript{12}} present intriguing high-nuclearity and dimensional hybrid framework materials. Among these new materials, 1Sm exhibited a very good linear relationship $I = 0.993$, $I = 0.995$, and $I = 0.996$ for the respective temperature coefficients $R^2=0.993$, 0.995, and 0.996 for the respective emissions intensities (luminescence intensity (I), temperature (T)). Furthermore, the luminescence of 1Sm has good reversibility without an obvious loss of emission intensity for at least three cycles (Supporting Information, Figure S11), suggesting that compound 1Sm is a potential sensor as a luminescent thermometer in a broad temperature range of 80–300 K. In summary, we have successfully integrated mixed metals W and Ln into PONb chemistry to prepare a series of the largest multi-metal composite PONbs \{Ln\textsubscript{12}W\textsubscript{12}O\textsubscript{36}\}, reported to date, which are also the first family of Nb-W-Ln heterometallic POMs. The giant PONbs {Ln\textsubscript{12}W\textsubscript{12}O\textsubscript{36}·(H\textsubscript{2}O)\textsubscript{24}} reveal the potential of introducing mixed metals into PONb chemistry to prepare a series of the largest multi-metal composite PONbs {Ln\textsubscript{12}W\textsubscript{12}O\textsubscript{36}·(H\textsubscript{2}O)\textsubscript{24}·(Nb\textsubscript{6}O\textsubscript{19})\textsubscript{12}} present intriguing high-nuclearity and dimensional hybrid framework materials. Among these new materials, 1Sm exhibited a very good linear relationship between luminescence intensity and temperature. This work reveals the potential of introducing mixed metals into PONb chemistry for the synthesis of diverse composite PON material, especially for exciting giant PONbs with useful applications. The possibility of integrating s, d, 4d, 5d, and 4f metals into composite structures, as demonstrated by this work, showcases the interesting structural chemistry of different metals and offers promising routes to novel multi-component materials.

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Giant heterometallic polyoxoniobates: A family of polyoxometalate-based frameworks has been made by integrating s, 3d, 4d, 5d, and 4f metals. Multi-component self-assembly offers the first series of niobium–tungsten–lanthanide heterometallic polyoxometalates, which are the largest multi-metal polyoxoniobates and contain rare nanosized hollow sodalite-type tungsten–lanthanide–oxide cages.