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Two Rh^{III}-substituted polyoxoniobates and their base-induced transformation: [H$_2$RhNb$_9$O$_{28}$]$^{6-}$ and [Rh$_2$(OH)$_4$Nb$_{10}$O$_{30}$]$^{8-}$†

Jung-Ho Son*[a] and Willam H. Casey[a,b]

Two new rhodium-substituted polyoxoniobates, [H$_2$RhNb$_9$O$_{28}$]$^{6-}$ (RhNb$_9$) and [Rh$_2$(OH)$_4$Nb$_{10}$O$_{30}$]$^{8-}$ (Rh$_2$Nb$_{10}$) are reported. The two distinct Rh^{III}-substituted niobate clusters behave differently when the pH is raised with TMAOH: the Rh$_2$Nb$_{10}$ is stable until pH ∼ 12.7, but RhNb$_9$ dissociates to form RhNb$_5$ and RhNb$_{10}$, similar to some of our other metal-substituted niobates, such as the MNb$_9$ ions (M = Cr or Mn), which transform to MNb$_{10}$ when the solution pH is raised.

Transition-metal (TM) – substituted polyoxometalates are an important class of materials. The TM-substitution can add catalytic function to the cluster and the polyoxometalate framework adds great redox properties, especially for polyoxo-molybdates and -tungstates.[1] In the polyoxoniobate system, a series of TM-substituted decaniobate-type [MNb$_9$O$_{28}$]$^{x-}$ (MNb$_9$, M = Cr–Ni) have been synthesized recently[2] and add to the Ti-, V- and Cu-substituted polyoxoniobates that were previously known.[3] In these studies, the substitution is limited to the early transition metals. For the heavier transition metals, there have been structures reported for Re(CO)$_3$-, CpRh- or Pt-co-ordinated (capped) hexaniobates (Nb$_6$).[4] However, substitution of 2nd- or 3rd-row transition metals in the polyoxoniobates as atoms internal to the structure, rather than as capping atoms, has not yet been reported to our knowledge, although among the group V polyoxometalates, [H$_2$Pt^{IV}V$_9$O$_{28}$]$^{5-}$ is known in the polyoxovanadate system.[5]

Here we report the synthesis, structure, characterization and photocatalytic H$_2$ evolution study of two Rh^{III}-substituted niobates. The two compounds reported here have the stoichio-metry: [H$_2$RhNb$_9$O$_{28}$]$^{6-}$ (RhNb$_9$) and [Rh$_2$(OH)$_4$Nb$_{10}$O$_{30}$]$^{8-}$ (Rh$_2$Nb$_{10}$) as tetramethylammonium (TMA) salts (Fig. 1). The structures of these clusters resemble those of two

Cr^{III}-substituted niobates, [H$_2$CrNb$_9$O$_{28}$]$^{6-}$ (CrNb$_9$) and [Cr$_2$(OH)$_4$Nb$_{12}$O$_{30}$]$^{8-}$ (Cr$_2$Nb$_{10}$) that we previously described.[2,6]

Substitution of Rh^{III} in the polyoxoniobate structure was challenging. Our previous methods employed for MNb$_9$ (M = Cr–Ni) generally showed low yield for rhodium substitution (less than 1%).[2] The low yield might be a result from the notor-iously slow reaction rate of ligand substitutions at the Rh^{III} center.[7] When we attempted to circumvent the slow kinetics with temperature, we found that some Rh^{III} was reduced to Rh^0 as a gray or black powder mixed with the crude product at the hydrothermal reaction conditions when the temperature was higher than 120 °C. In order to solve this problem, we added hydrogen peroxide in the reaction mixture to prevent reduction of Rh^{III}. Correspondingly the yields were improved when H$_2$O$_2$ was added (40% and 7% for Rh$_2$Nb$_{10}$ and RhNb$_9$, respectively). Hydrogen peroxide also might have helped to dis-sociate the rather stable Nb$_6$ or Nb$_{10}$ ions and facilitate the for-mation of Rh^{III}-substituted structures.[8]

The solution after hydrothermal reaction was typically a mixture of Nb$_{10}$, Nb$_6$, RhNb$_9$ and Rh$_2$Nb$_{10}$ ions, as found by electrospray-ionization mass spectra (ESI-MS). We took advan-tage of the slightly different solubility of each compound to facilitate separation and purification of the Rh-substituted
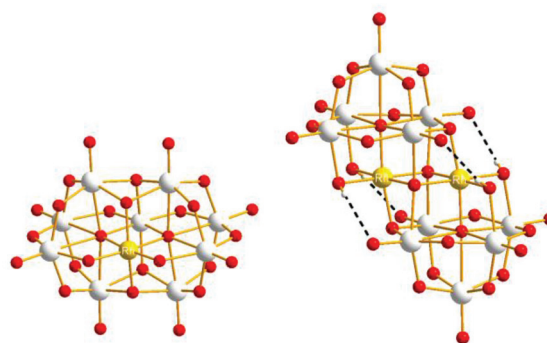
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Fig. 1 Ball-and-stick model of RhNb$_9$ (left) and Rh$_2$Nb$_{10}$ (right) (Nb: gray, Rh: gold, O: red). Intramolecular hydrogen bonds are shown with dashed line in Rh$_2$Nb$_{10}$.

molecules. After washing with isopropanol, the product was extracted with ethanol. The ethanol extract was a mixture of Rh_2Nb_{10} and Nb_6 ions, and the precipitate that remained after ethanol extraction was a mixture of Nb_{10} and $RhNb_9$. The $RhNb_9$ was separated from Nb_{10} by extraction with ethanol/methanol mixture. Mild heating of the ethanol extract for a few hours caused condensation of more soluble Nb_6 into less soluble Nb_{10} precipitate. The ethanolic orange solution that remained after this heating step consisted of mostly Rh_2Nb_{10}. The crystalline products of Rh_2Nb_{10} and $RhNb_9$ were obtained after solvent evaporation.

In the crystal structure of $RhNb_9$, Rh^{III} is substituted at the central metal site so that it does not possess a terminal oxo group, as we also observed in the MNb_9O_{28} (M = Cr–Ni) series.[2] The Rh^{III} metal is disordered among the two central sites due to the centrosymmetry, and the sum of Rh^{III} occupancy in those two sites is 1.12, which agrees with stoichiometry of $RhNb_9$. Bond valence sum (BVS) calculation of the Rh site is (3.03), indicating the oxidation state of Rh^{III}. The BVS values of two $Rh–\mu_2-O–Nb$ (1.37 and 1.38) are much lower than other bridging oxygen atoms, which suggest that those are protonated, similarly to the substituted MNb_9 (M = Cr–Ni).[2] The structure of Rh_2Nb_{10} is similar to Cr_2Nb_{10}, and it can be described as two $RhNb_5$ Lindqvist-type clusters fused by two μ_4-O atoms linking two Rh^{III} and two μ_3-O atoms linking Rh^{III} and Nb^V. The oxidation state of rhodium in Rh_2Nb_{10} is also Rh^{III}, as determined by BVS calculation (2.95). The Rh–O bond lengths in Rh_2Nb_{10} are longer and more regular (2.0245(16)–2.0605(16) Å) than Cr–O bonds in Cr_2Nb_{10} (1.9428(13)–2.0131(12) Å). In the structure of Rh_2Nb_{10}, four protons are found on the four $Rh–\mu_2-O–Nb$, like in the structure of Cr_2Nb_{10}.[6] Those protons form intramolecular hydrogen bonds to the neighbouring Nb=O (H⋯O distances of 2.309 and 2.386 Å). The ESI-MS spectra of the $RhNb_9$ and Rh_2Nb_{10} agree with their assigned stoichiometries (Fig. S1†).

The pH-dependent stability of the Rh^{III}-substituted niobate clusters were studied by using ESI-MS. When titrated with TMAOH, the golden yellow color of Rh_2Nb_{10} solution did not change until highly basic conditions (pH ~ 12.9, Fig. S2†), and most of the Rh_2Nb_{10} clusters remained intact for months at this strongly basic condition, as checked by ESI-MS (Fig. S3†). When the solution of $RhNb_9$ was titrated with TMAOH to this condition, the solution color slowly changed from orange to faint yellow overnight (Fig. S2†). The ESI-MS spectra of the solution after one day (Fig. 2) indicated dissociation of $RhNb_9$ to $RhNb_5$ and Nb_6. Also, formation of a new $RhNb_{10}$ was detectable via ESI-MS, which could have formed by self-assembly of dissociated fragments (Fig. 2). It is most likely that this $RhNb_{10}$ would have a similar structure of previously reported $[H_2Mn^{IV}Nb_{10}O_{32}]^{8-}$ ($MnNb_{10}$), in view of their similar ESI-MS pattern.[9] This observation spurred us to further investigate other TM-substituted polyoxoniobate clusters. We added 50 mg of TMAOH·5H₂O to each aqueous solution containing 30 mg of MNb_9 (M = Ti, Cr–Ni) and Cr_2Nb_{10} clusters to make pH ~ 12.6 and monitored the solution by using ESI-MS (Fig. S4–S10†). The Cr_2Nb_{10} clusters were stable at this pH for

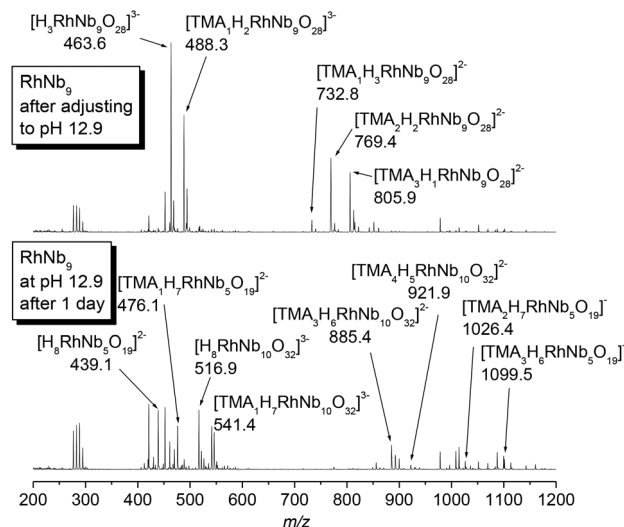**Fig. 2** Change of ESI-MS spectra of $RhNb_9$ when the solution pH was adjusted to 12.9.

a long period of time, like Rh_2Nb_{10} (Fig. S4†). The $TiNb_9$, $CrNb_9$ and $MnNb_9$ clusters changed in a few days at this high-pH condition. Some Ti_2Nb_8 clusters,[3a,c,d] formed after a week when the pH of $TiNb_9$ was increased (Fig. S5†). Considerable amount of $CrNb_{10}$ formed after a few days from the $CrNb_9$ solution at high pH (Fig. S6†). This result shows that Cr^{III}- and Rh^{III}-substituted polyoxoniobates are not only structurally similar, but also transform via similar pathways at high pH (Scheme 1). The color of $MnNb_9$ solution changed from purple
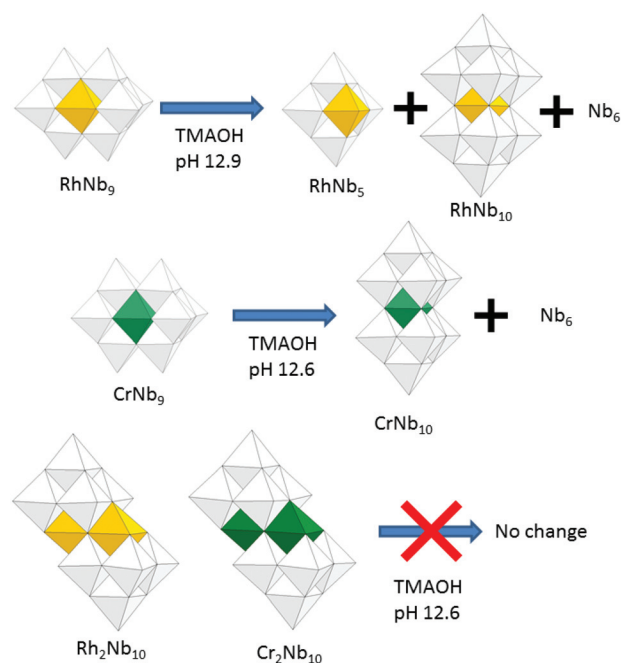
Scheme 1 Base-induced transformation of MNb_9 and M_2Nb_{10} (M = Rh, Cr).

to brown with time, suggesting oxidation of Mn^{III}, and ESI-MS spectra after 19 days showed formation of small amount of $Mn^{IV}Nb_{10}$ (Fig. S7†). However, species such as $MnNb_5$ or $CrNb_5$ was not detectable, which suggests that they are unstable. Other MNb_9 clusters (M=Fe–Ni) were relatively stable at the high pH, but small amount of Nb_6 as a decomposition product was detected (Fig. S8–S10†). Thus M_2Nb_{10} (M = Rh^{III} or Cr^{III}) seems to be more stable than MNb_9 at high pH. This higher stability of M_2Nb_{10} is partly attributable to the existence of intramolecular hydrogen bonds, which hold the structure together, perhaps making it less susceptible to base hydrolysis.

When titrated with acid, Rh_2Nb_{10} was evident in the ESI-MS spectra until pH 4.0, and $RhNb_9$ was stable until pH 4.5 (Fig. S11 and S12†), although we recognize that the kinetics of dissociation may be suppressed by inclusion of the Rh^{III}. Both solutions formed hydrous niobium-oxide precipitate below those pH values, which could form without dissociating the structures. On the other hand, we note that the stability window of Rh_2Nb_{10} (4 < pH < 13) is similar to Cr_2Nb_{10}.[6] The $RhNb_9$ exhibited a wider stability range (4.5 < pH < 12) than other MNb_9 clusters (M = Cr–Ni) in general.

The UV-Vis spectra of $RhNb_9$ and Rh_2Nb_{10} are shown in Fig. 3. The Rh_2Nb_{10} shows about twice the absorption of visible light relative to the $RhNb_9$ ion, as expected from the stoichiometry of the clusters. The absorption band of Rh_2Nb_{10} (440 nm) is more blue shifted compared to that of $RhNb_9$ (475 nm), which is responsible for the slightly different colors of the solutions of Rh_2Nb_{10} (golden yellow) and $RhNb_9$ (orange-red). These absorption bands correspond to $^1A_{1g}$ to $^1T_{1g}$ or $^1T_{2g}$ transition of Rh^{III}.[10] The $RhNb_9$ and Rh_2Nb_{10} clusters were also characterized by using FT-IR (Fig. S13†). The FT-IR spectrum of Rh_2Nb_{10} show similar feature to that of Cr_2Nb_{10} and that of $RhNb_9$ is similar to those of MNb_9, which reflect their structural similarity.

TM-substituted polyoxometalates, including polyoxoniobates, have recently been actively studied for use in the water-splitting reaction to generate H_2 and/or O_2 for energy applications.[11] We studied H_2 evolution from $RhNb_9$ and Rh_2Nb_{10}
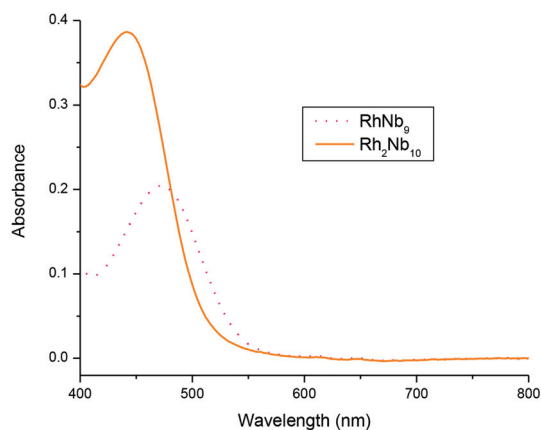

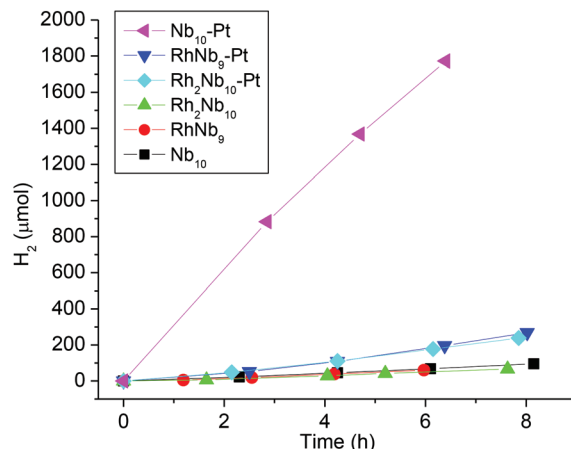**Fig. 4** Comparison of H_2-evolution activity from the methanol/water solutions (20% v/v) of $RhNb_9$, Rh_2Nb_{10} and Nb_{10}, with and without H_2PtCl_6.

ions as a continuation of our previous H_2-evolution study of the MNb_9 ions (M = Cr–Ni). When irradiated with visible light, similarly to the MNb_9 ions, neither $RhNb_9$ nor Rh_2Nb_{10} solutions (20% v/v methanol/water) evolved H_2. Methanol was used as a sacrificial oxidant. The solution did not evolve H_2 without methanol. When a full spectrum from Xe lamp (without UV filter) was employed, however, H_2 evolution was observed (50 μmol g^{-1} h^{-1} and 43 μmol g^{-1} h^{-1}, for $RhNb_9$ and Rh_2Nb_{10}, Fig. 4). After irradiation, the originally orange-red or yellow solution of $RhNb_9$ and Rh_2Nb_{10} turned greenish brown with small amount of colloids, which probably indicate partial reduction of Rh^{III} to Rh^0. We have found such colloids in our previous work and are not surprised by them.[2] The Rh^{II} is known to exhibit a green color.[10] We do not know the amount of Rh^{III} that has been reduced, but comparison of the peak intensities in ESI-MS spectra of the solution before and after irradiation indicated that most of the clusters remained intact (Fig. S14 and S15†). The UV-Vis spectra of Rh_2Nb_{10} before and after the irradiation also did not change considerably, but absorption of $RhNb_9$ solution increased after irradiation, undoubtedly due to the presence of the colloids mentioned above (Fig. S16 and S17†). In the previous H_2 evolution study of the MNb_9 ions (M = Cr–Ni),[2] we found that a significant amount of MNb_9 decomposed into Nb_6 and Nb_{10}, with corresponding changes in the UV-Vis spectrum due to the colloid formation. Among them, formation of colloids from $NiNb_9$ and $CoNb_9$ positively affected H_2 evolution, while colloid formation from other MNb_9 (M = Cr–Fe) did not increase the amount of H_2 evolution. In our previous work we have found that the colloids were mixed TM–niobium oxide and they were amorphous, as determined by XRD, TEM and EDX. The relative lack of Nb_6 and Nb_{10} decomposition products s after irradiation in the present $RhNb_9$ and Rh_2Nb_{10} suggests that these rhodium $RhNb_9$ and Rh_2Nb_{10} clusters are more stable, perhaps only kinetically so, under the irradiation of intense light when compared to MNb_9 (M = Cr–Ni). We also compared

Fig. 3 UV-Vis spectra of 2 mM solution of Rh_2Nb_{10} and $RhNb_9$ without background electrolyte.

H_2-evolution activity of the clusters when H_2PtCl_6 was added as a cocatalyst. In the existence of Pt, Nb_{10} solution showed ~20 fold increase in the H_2 evolution (1385 µmol g^{-1} h^{-1}) and amount of precipitate was negligible, but H_2 evolution from $RhNb_9$ and Rh_2Nb_{10} after adding H_2PtCl_6 showed only about 3 fold increases (167 and 152 µmol g^{-1} h^{-1}, respectively) and conspicuous gray-black precipitate formed in the solution (Fig. 4). This presumed Pt–Rh–NbOx precipitate must be responsible for the slight increase of the H_2 evolution, but we did not attempt to characterize it further. The different precipitation behavior of Nb_{10} and $RhNb_9/Rh_2Nb_{10}$ after photocatalytic reaction might be due to their different stabilities upon addition of acidic H_2PtCl_6. And the lower H_2 evolution activity of $RhNb_9/Rh_2Nb_{10}$ compared to Nb_{10} is likely due to the reduced amount of dissolved clusters in solution caused by precipitation, as seen in ESI-MS (Fig. S14 and S15†).

Conclusions

Two types of new rhodium-substituted polyoxoniobates were synthesized and isolated. The evidences of base-promoted transformation of $RhNb_9$ to $RhNb_5$ and $RhNb_{10}$ suggest a new synthetic strategy for new polyoxoniobates. Such a reaction can be a useful post-synthetic pathway for new polyoxoniobates, instead of commonly employed hydrothermal reaction in the polyoxoniobate chemistry. The transformation of $MnNb_9$ and $CrNb_9$ at high pH shows that the stabilities of each TM-substituted decaniobate are different, even if they form similar dissociation products at high pH. The Rh^{III}-substituted polyoxoniobates discussed here are important because these can serve as feedstock to make even more TM-substituted polyoxoniobates, such as $RhNb_5$ which might have terminal Rh–OH groups.

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