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## Two Rh<sup>III</sup>-substituted polyoxoniobates and their base-induced transformation: [H<sub>2</sub>RhNb<sub>9</sub>O<sub>28</sub>]<sup>6-</sup> and [Rh<sub>2</sub>(OH)<sub>4</sub>Nb<sub>10</sub>O<sub>30</sub>]<sup>8-</sup>†

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Two new rhodium-substituted polyoxoniobates, [H<sub>2</sub>RhNb<sub>9</sub>O<sub>28</sub>]<sup>6-</sup> (RhNb<sub>9</sub>) and [Rh<sub>2</sub>(OH)<sub>4</sub>Nb<sub>10</sub>O<sub>30</sub>]<sup>8-</sup> (Rh<sub>2</sub>Nb<sub>10</sub>) are reported. The two distinct Rh<sup>III</sup>-substituted niobate clusters behave differently when the pH is raised with TMAOH: the Rh<sub>2</sub>Nb<sub>10</sub> is stable until pH ~ 12.7, but RhNb<sub>9</sub> dissociates to form RhNb<sub>5</sub> and RhNb<sub>10</sub>, similar to some of our other metal-substituted niobates, such as the MNb<sub>9</sub> ions (M = Cr or Mn), which transform to MNb<sub>10</sub> 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 polyoxomolybdates and -tungstates.<sup>1</sup> In the polyoxoniobate system, a series of TM-substituted decaniobate-type [MNb<sub>9</sub>O<sub>28</sub>]<sup>x-</sup> (MNb<sub>9</sub>, M = Cr–Ni) have been synthesized recently<sup>2</sup> and add to the Ti-, V- and Cu-substituted polyoxoniobates that were previously known.<sup>3</sup> 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)<sub>3</sub>-, CpRh- or Pt-coordinated (capped) hexaniobates (Nb<sub>6</sub>).<sup>4</sup> 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<sub>2</sub>Pt<sup>IV</sup>V<sub>9</sub>O<sub>28</sub>]<sup>5-</sup> is known in the polyoxovanadate system.<sup>5</sup>

Here we report the synthesis, structure, characterization and photocatalytic H<sub>2</sub> evolution study of two Rh<sup>III</sup>-substituted niobates. The two compounds reported here have the stoichiometry: [H<sub>2</sub>RhNb<sub>9</sub>O<sub>28</sub>]<sup>6-</sup> (RhNb<sub>9</sub>) and [Rh<sub>2</sub>(OH)<sub>4</sub>Nb<sub>10</sub>O<sub>30</sub>]<sup>8-</sup> (Rh<sub>2</sub>Nb<sub>10</sub>) as tetramethylammonium (TMA) salts (Fig. 1). The structures of these clusters resemble those of two

Cr<sup>III</sup>-substituted niobates, [H<sub>2</sub>CrNb<sub>9</sub>O<sub>28</sub>]<sup>6-</sup> (CrNb<sub>9</sub>) and [Cr<sub>2</sub>(OH)<sub>4</sub>Nb<sub>12</sub>O<sub>30</sub>]<sup>8-</sup> (Cr<sub>2</sub>Nb<sub>10</sub>) that we previously described.<sup>2,6</sup>

Substitution of Rh<sup>III</sup> in the polyoxoniobate structure was challenging. Our previous methods employed for MNb<sub>9</sub> (M = Cr–Ni) generally showed low yield for rhodium substitution (less than 1%).<sup>2</sup> The low yield might be a result from the notoriously slow reaction rate of ligand substitutions at the Rh<sup>III</sup> center.<sup>7</sup> When we attempted to circumvent the slow kinetics with temperature, we found that some Rh<sup>III</sup> was reduced to Rh<sup>0</sup> 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<sup>III</sup>. Correspondingly the yields were improved when H<sub>2</sub>O<sub>2</sub> was added (40% and 7% for Rh<sub>2</sub>Nb<sub>10</sub> and RhNb<sub>9</sub>, respectively). Hydrogen peroxide also might have helped to dissociate the rather stable Nb<sub>6</sub> or Nb<sub>10</sub> ions and facilitate the formation of Rh<sup>III</sup>-substituted structures.<sup>8</sup>

The solution after hydrothermal reaction was typically a mixture of Nb<sub>10</sub>, Nb<sub>6</sub>, RhNb<sub>9</sub> and Rh<sub>2</sub>Nb<sub>10</sub> ions, as found by electrospray-ionization mass spectra (ESI-MS). We took advantage of the slightly different solubility of each compound to facilitate separation and purification of the Rh-substituted

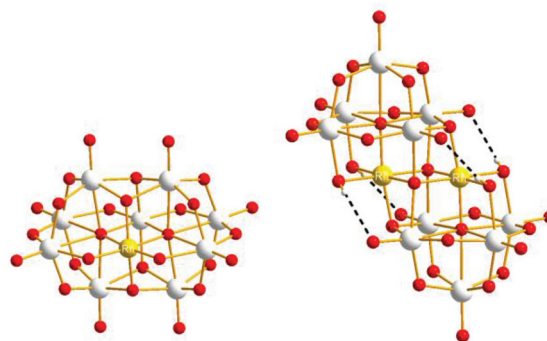


Fig. 1 Ball-and-stick model of RhNb<sub>9</sub> (left) and Rh<sub>2</sub>Nb<sub>10</sub> (right) (Nb: gray, Rh: gold, O: red). Intramolecular hydrogen bonds are shown with dashed line in Rh<sub>2</sub>Nb<sub>10</sub>.

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molecules. After washing with isopropanol, the product was extracted with ethanol. The ethanol extract was a mixture of  $\text{Rh}_2\text{Nb}_{10}$  and  $\text{Nb}_6$  ions, and the precipitate that remained after ethanol extraction was a mixture of  $\text{Nb}_{10}$  and  $\text{RhNb}_9$ . The  $\text{RhNb}_9$  was separated from  $\text{Nb}_{10}$  by extraction with ethanol/methanol mixture. Mild heating of the ethanol extract for a few hours caused condensation of more soluble  $\text{Nb}_6$  into less soluble  $\text{Nb}_{10}$  precipitate. The ethanolic orange solution that remained after this heating step consisted of mostly  $\text{Rh}_2\text{Nb}_{10}$ . The crystalline products of  $\text{Rh}_2\text{Nb}_{10}$  and  $\text{RhNb}_9$  were obtained after solvent evaporation.

In the crystal structure of  $\text{RhNb}_9$ ,  $\text{Rh}^{\text{III}}$  is substituted at the central metal site so that it does not possess a terminal oxo group, as we also observed in the  $\text{MNb}_9\text{O}_{28}$  ( $\text{M} = \text{Cr-Ni}$ ) series.<sup>2</sup> The  $\text{Rh}^{\text{III}}$  metal is disordered among the two central sites due to the centrosymmetry, and the sum of  $\text{Rh}^{\text{III}}$  occupancy in those two sites is 1.12, which agrees with stoichiometry of  $\text{RhNb}_9$ . Bond valence sum (BVS) calculation of the Rh site is (3.03), indicating the oxidation state of  $\text{Rh}^{\text{III}}$ . The BVS values of two  $\text{Rh}-\mu_2\text{-O}-\text{Nb}$  (1.37 and 1.38) are much lower than other bridging oxygen atoms, which suggest that those are protonated, similarly to the substituted  $\text{MNb}_9$  ( $\text{M} = \text{Cr-Ni}$ ).<sup>2</sup> The structure of  $\text{Rh}_2\text{Nb}_{10}$  is similar to  $\text{Cr}_2\text{Nb}_{10}$ , and it can be described as two  $\text{RhNb}_5$  Lindqvist-type clusters fused by two  $\mu_4\text{-O}$  atoms linking two  $\text{Rh}^{\text{III}}$  and two  $\mu_3\text{-O}$  atoms linking  $\text{Rh}^{\text{III}}$  and  $\text{Nb}^{\text{V}}$ . The oxidation state of rhodium in  $\text{Rh}_2\text{Nb}_{10}$  is also  $\text{Rh}^{\text{III}}$ , as determined by BVS calculation (2.95). The  $\text{Rh}-\text{O}$  bond lengths in  $\text{Rh}_2\text{Nb}_{10}$  are longer and more regular (2.0245(16)–2.0605(16) Å) than  $\text{Cr}-\text{O}$  bonds in  $\text{Cr}_2\text{Nb}_{10}$  (1.9428(13)–2.0131(12) Å). In the structure of  $\text{Rh}_2\text{Nb}_{10}$ , four protons are found on the four  $\text{Rh}-\mu_2\text{-O}-\text{Nb}$ , like in the structure of  $\text{Cr}_2\text{Nb}_{10}$ .<sup>6</sup> Those protons form intramolecular hydrogen bonds to the neighbouring  $\text{Nb}=\text{O}$  ( $\text{H}\cdots\text{O}$  distances of 2.309 and 2.386 Å). The ESI-MS spectra of the  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$  agree with their assigned stoichiometries (Fig. S1†).

The pH-dependent stability of the  $\text{Rh}^{\text{III}}$ -substituted niobate clusters was studied by using ESI-MS. When titrated with TMAOH, the golden yellow color of  $\text{Rh}_2\text{Nb}_{10}$  solution did not change until highly basic conditions ( $\text{pH} \sim 12.9$ , Fig. S2†), and most of the  $\text{Rh}_2\text{Nb}_{10}$  clusters remained intact for months at this strongly basic condition, as checked by ESI-MS (Fig. S3†). When the solution of  $\text{RhNb}_9$  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  $\text{RhNb}_9$  to  $\text{RhNb}_5$  and  $\text{Nb}_6$ . Also, formation of a new  $\text{RhNb}_{10}$  was detectable *via* ESI-MS, which could have formed by self-assembly of dissociated fragments (Fig. 2). It is most likely that this  $\text{RhNb}_{10}$  would have a similar structure of previously reported  $[\text{H}_2\text{Mn}^{\text{IV}}\text{Nb}_{10}\text{O}_{32}]^{8-}$  ( $\text{MnNb}_{10}$ ), in view of their similar ESI-MS pattern.<sup>9</sup> This observation spurred us to further investigate other TM-substituted polyoxoniobate clusters. We added 50 mg of TMAOH·5H<sub>2</sub>O to each aqueous solution containing 30 mg of  $\text{MNb}_9$  ( $\text{M} = \text{Ti, Cr-Ni}$ ) and  $\text{Cr}_2\text{Nb}_{10}$  clusters to make  $\text{pH} \sim 12.6$  and monitored the solution by using ESI-MS (Fig. S4–S10†). The  $\text{Cr}_2\text{Nb}_{10}$  clusters were stable at this pH for

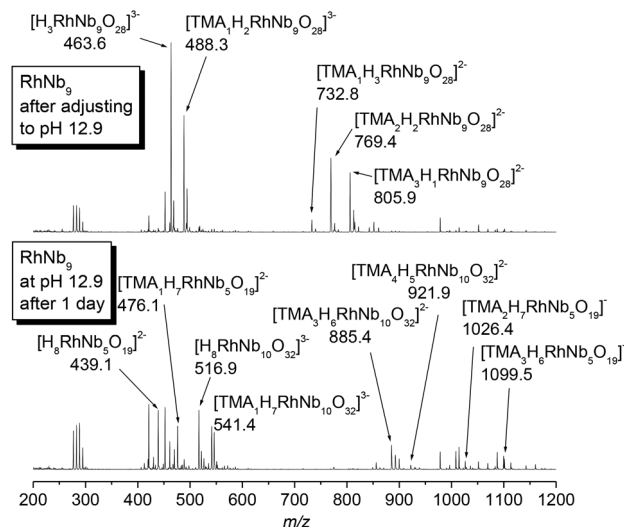
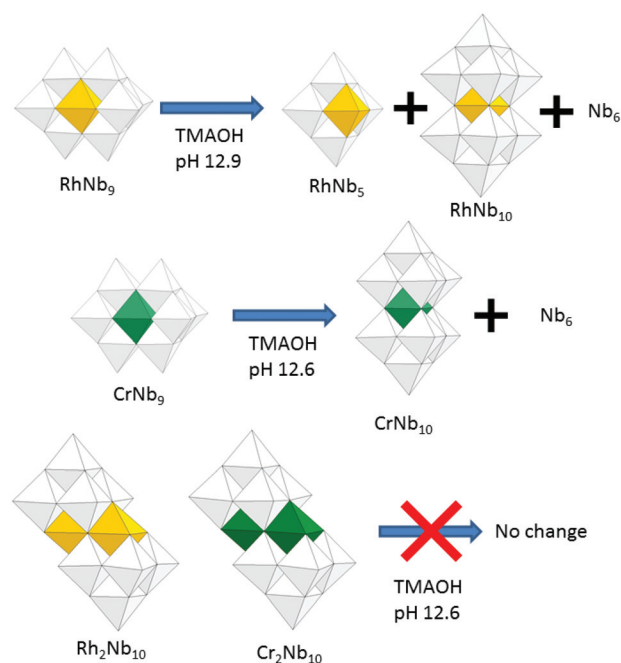


Fig. 2 Change of ESI-MS spectra of  $\text{RhNb}_9$  when the solution pH was adjusted to 12.9.

a long period of time, like  $\text{Rh}_2\text{Nb}_{10}$  (Fig. S4†). The  $\text{TiNb}_9$ ,  $\text{CrNb}_9$  and  $\text{MnNb}_9$  clusters changed in a few days at this high-pH condition. Some  $\text{Ti}_2\text{Nb}_8$  clusters,<sup>3a,c,d</sup> formed after a week when the pH of  $\text{TiNb}_9$  was increased (Fig. S5†). Considerable amount of  $\text{CrNb}_{10}$  formed after a few days from the  $\text{CrNb}_9$  solution at high pH (Fig. S6†). This result shows that  $\text{Cr}^{\text{III}}$ - and  $\text{Rh}^{\text{III}}$ -substituted polyoxoniobates are not only structurally similar, but also transform *via* similar pathways at high pH (Scheme 1). The color of  $\text{MnNb}_9$  solution changed from purple



Scheme 1 Base-induced transformation of  $\text{MNb}_9$  and  $\text{M}_2\text{Nb}_{10}$  ( $\text{M} = \text{Rh, Cr}$ ).



to brown with time, suggesting oxidation of  $\text{Mn}^{\text{III}}$ , and ESI-MS spectra after 19 days showed formation of small amount of  $\text{Mn}^{\text{IV}}\text{Nb}_{10}$  (Fig. S7†). However, species such as  $\text{MnNb}_5$  or  $\text{CrNb}_5$  was not detectable, which suggests that they are unstable. Other  $\text{MNb}_9$  clusters ( $\text{M}=\text{Fe-Ni}$ ) were relatively stable at the high pH, but small amount of  $\text{Nb}_6$  as a decomposition product was detected (Fig. S8–S10†). Thus  $\text{M}_2\text{Nb}_{10}$  ( $\text{M}=\text{Rh}^{\text{III}}$  or  $\text{Cr}^{\text{III}}$ ) seems to be more stable than  $\text{MNb}_9$  at high pH. This higher stability of  $\text{M}_2\text{Nb}_{10}$  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,  $\text{Rh}_2\text{Nb}_{10}$  was evident in the ESI-MS spectra until pH 4.0, and  $\text{RhNb}_9$  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  $\text{Rh}^{\text{III}}$ . 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  $\text{Rh}_2\text{Nb}_{10}$  ( $4 < \text{pH} < 13$ ) is similar to  $\text{Cr}_2\text{Nb}_{10}$ .<sup>6</sup> The  $\text{RhNb}_9$  exhibited a wider stability range ( $4.5 < \text{pH} < 12$ ) than other  $\text{MNb}_9$  clusters ( $\text{M}=\text{Cr-Ni}$ ) in general.

The UV-Vis spectra of  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$  are shown in Fig. 3. The  $\text{Rh}_2\text{Nb}_{10}$  shows about twice the absorption of visible light relative to the  $\text{RhNb}_9$  ion, as expected from the stoichiometry of the clusters. The absorption band of  $\text{Rh}_2\text{Nb}_{10}$  (440 nm) is more blue shifted compared to that of  $\text{RhNb}_9$  (475 nm), which is responsible for the slightly different colors of the solutions of  $\text{Rh}_2\text{Nb}_{10}$  (golden yellow) and  $\text{RhNb}_9$  (orange-red). These absorption bands correspond to  $^1\text{A}_{1g}$  to  $^1\text{T}_{1g}$  or  $^1\text{T}_{2g}$  transition of  $\text{Rh}^{\text{III}}$ .<sup>10</sup> The  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$  clusters were also characterized by using FT-IR (Fig. S13†). The FT-IR spectrum of  $\text{Rh}_2\text{Nb}_{10}$  show similar feature to that of  $\text{Cr}_2\text{Nb}_{10}$  and that of  $\text{RhNb}_9$  is similar to those of  $\text{MNb}_9$ , which reflect their structural similarity.

TM-substituted polyoxometalates, including polyoxoniobates, have recently been actively studied for use in the water-splitting reaction to generate  $\text{H}_2$  and/or  $\text{O}_2$  for energy applications.<sup>11</sup> We studied  $\text{H}_2$  evolution from  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$

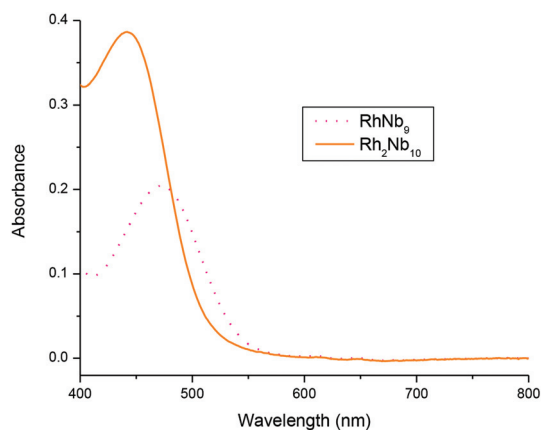


Fig. 3 UV-Vis spectra of 2 mM solution of  $\text{Rh}_2\text{Nb}_{10}$  and  $\text{RhNb}_9$  without background electrolyte.

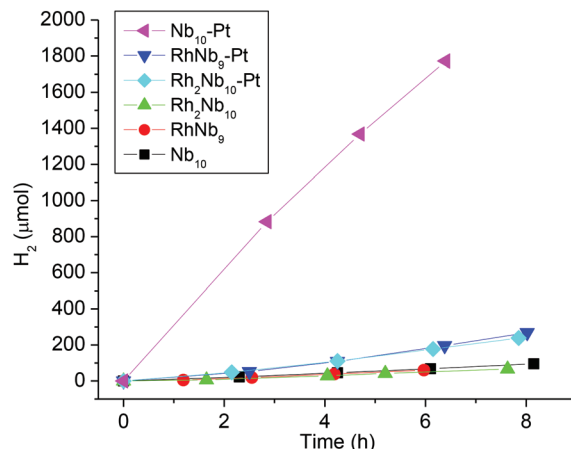


Fig. 4 Comparison of  $\text{H}_2$ -evolution activity from the methanol/water solutions (20% v/v) of  $\text{RhNb}_9$ ,  $\text{Rh}_2\text{Nb}_{10}$  and  $\text{Nb}_{10}$ , with and without  $\text{H}_2\text{PtCl}_6$ .

ions as a continuation of our previous  $\text{H}_2$ -evolution study of the  $\text{MNb}_9$  ions ( $\text{M}=\text{Cr-Ni}$ ). When irradiated with visible light, similarly to the  $\text{MNb}_9$  ions, neither  $\text{RhNb}_9$  nor  $\text{Rh}_2\text{Nb}_{10}$  solutions (20% v/v methanol/water) evolved  $\text{H}_2$ . Methanol was used as a sacrificial oxidant. The solution did not evolve  $\text{H}_2$  without methanol. When a full spectrum from Xe lamp (without UV filter) was employed, however,  $\text{H}_2$  evolution was observed (50  $\mu\text{mol g}^{-1} \text{h}^{-1}$  and 43  $\mu\text{mol g}^{-1} \text{h}^{-1}$ , for  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$ , Fig. 4). After irradiation, the originally orange-red or yellow solution of  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$  turned greenish brown with small amount of colloids, which probably indicate partial reduction of  $\text{Rh}^{\text{III}}$  to  $\text{Rh}^0$ . We have found such colloids in our previous work and are not surprised by them.<sup>2</sup> The  $\text{Rh}^{\text{II}}$  is known to exhibit a green color.<sup>10</sup> We do not know the amount of  $\text{Rh}^{\text{III}}$  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  $\text{Rh}_2\text{Nb}_{10}$  before and after the irradiation also did not change considerably, but absorption of  $\text{RhNb}_9$  solution increased after irradiation, undoubtedly due to the presence of the colloids mentioned above (Fig. S16 and S17†). In the previous  $\text{H}_2$  evolution study of the  $\text{MNb}_9$  ions ( $\text{M}=\text{Cr-Ni}$ ),<sup>2</sup> we found that a significant amount of  $\text{MNb}_9$  decomposed into  $\text{Nb}_6$  and  $\text{Nb}_{10}$ , with corresponding changes in the UV-Vis spectrum due to the colloid formation. Among them, formation of colloids from  $\text{NiNb}_9$  and  $\text{CoNb}_9$  positively affected  $\text{H}_2$  evolution, while colloid formation from other  $\text{MNb}_9$  ( $\text{M}=\text{Cr-Fe}$ ) did not increase the amount of  $\text{H}_2$  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  $\text{Nb}_6$  and  $\text{Nb}_{10}$  decomposition products after irradiation in the present  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$  suggests that these rhodium  $\text{RhNb}_9$  and  $\text{Rh}_2\text{Nb}_{10}$  clusters are more stable, perhaps only kinetically so, under the irradiation of intense light when compared to  $\text{MNb}_9$  ( $\text{M}=\text{Cr-Ni}$ ). We also compared



H<sub>2</sub>-evolution activity of the clusters when H<sub>2</sub>PtCl<sub>6</sub> was added as a cocatalyst. In the existence of Pt, Nb<sub>10</sub> solution showed ~20 fold increase in the H<sub>2</sub> evolution (1385 μmol g<sup>-1</sup> h<sup>-1</sup>) and amount of precipitate was negligible, but H<sub>2</sub> evolution from RhNb<sub>9</sub> and Rh<sub>2</sub>Nb<sub>10</sub> after adding H<sub>2</sub>PtCl<sub>6</sub> showed only about 3 fold increases (167 and 152 μmol g<sup>-1</sup> h<sup>-1</sup>, 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<sub>2</sub> evolution, but we did not attempt to characterize it further. The different precipitation behavior of Nb<sub>10</sub> and RhNb<sub>9</sub>/Rh<sub>2</sub>Nb<sub>10</sub> after photocatalytic reaction might be due to their different stabilities upon addition of acidic H<sub>2</sub>PtCl<sub>6</sub>. And the lower H<sub>2</sub> evolution activity of RhNb<sub>9</sub>/Rh<sub>2</sub>Nb<sub>10</sub> compared to Nb<sub>10</sub> 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<sub>9</sub> to RhNb<sub>5</sub> and RhNb<sub>10</sub> 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<sub>9</sub> and CrNb<sub>9</sub> 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<sup>III</sup>-substituted polyoxoniobates discussed here are important because these can serve as feedstock to make even more TM-substituted polyoxoniobates, such as RhNb<sub>5</sub> which might have terminal Rh–OH groups.

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