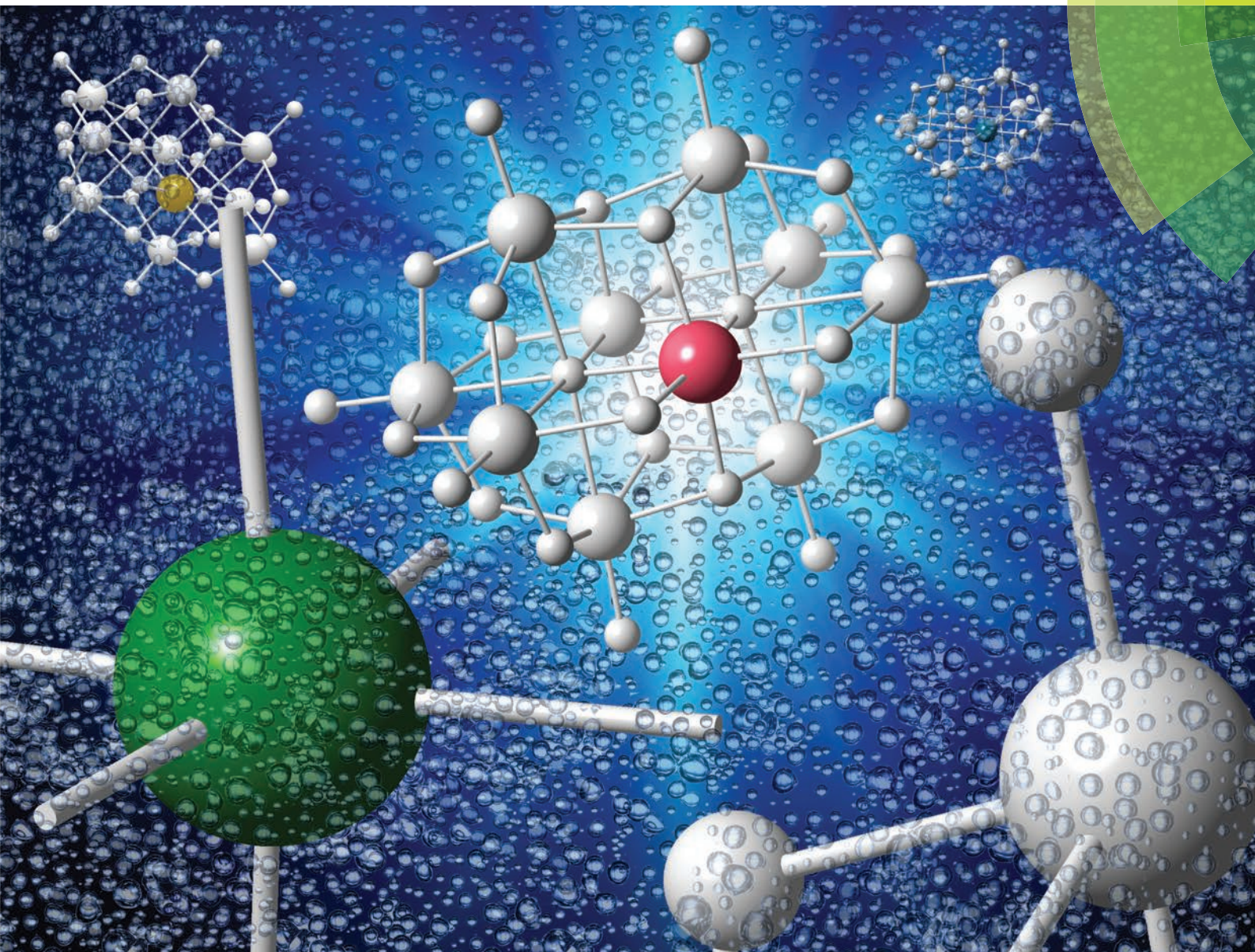


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Structure, stability and photocatalytic H₂ production by Cr-, Mn-, Fe-, Co-, and Ni-substituted decaniobate clusters†

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Here we report synthesis and characterization of early transition-metal(TM)-substituted decaniobates as a continuation of our previous report of tetramethylammonium (TMA) salt of FeNb₉ and NiNb₉: TMA₆[H₂Cr^{III}Nb₉O₂₈].14H₂O (**1**, CrNb₉), TMA₈[Mn^{III}Nb₉O₂₈].29H₂O (**2**, MnNb₉) and TMA₇[H₂Co^{II}Nb₉O₂₈].25H₂O (**3**, CoNb₉). Among the TM-substituted decaniobates, CoNb₉ or NiNb₉ exhibit a higher photocatalytic H₂ evolution activity in methanol–water mixtures than others.

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Early transition-metal (TM) substituted Keggin-type polyoxometalates have been studied for decades because of their rich electrochemical, optical, magnetic and catalytic properties.¹ In group 5 polyoxometalate chemistry, decametate ions with *D*_{2v} symmetry, such as decavanadate and decaniobate (Nb₁₀) ions, are well known,² but TM-substituted decametates are rare, although Ti^{IV}-, Fe^{III}-, Ni^{II}-substituted decaniobates (henceforth denoted: FeNb₉ and NiNb₉, respectively) and Pt-substituted decavanadate have been synthesized.³ Herein we describe the synthesis of the Cr-, Mn-, and Co-substituted decaniobates, and examine the trend in the structural, magnetic, optical, and photocatalytic H₂-evolution properties of the TM-substituted decaniobates exhibit different stabilities and ease of synthesis that seem to be relatable to their structures. Moreover, the clusters show photocatalytic H₂-evolution, with Ni- and Co-substituted decaniobate ions being more active than other substituted decaniobates, although the molecules partly dissociate during irradiation into the corresponding MO_x and niobate. The results can aid the understanding of the factors governing the photocatalytic H₂-evolution properties of TM-doped metal oxides, including titanates,⁴ other niobates,⁵ and related polyoxoniobate systems.⁶

Isolation of tetramethylammonium (TMA) salts of Cr-, Mn- and Co-substituted decaniobates in this paper, TMA₆[H₂Cr^{III}-Nb₉O₂₈].14H₂O (**1**, CrNb₉), TMA₈[Mn^{III}Nb₉O₂₈].29H₂O (**2**, MnNb₉) and TMA₇[H₂Co^{II}Nb₉O₂₈].25H₂O (**3**, CoNb₉) was more challenging than our previously work on the Fe- and Ni-substituted decaniobates.^{3d} We noticed that in the chromium-substitution reaction, CrNb₉ coexisted with previously reported [Cr₂(OH)₄Nb₁₀O₃₀]⁸⁻ (Cr₂Nb₁₀) in most of the syntheses.⁷ These structurally distinct clusters were separable by taking advantage of their slightly different solubility. Firstly, TMA salt of Cr₂Nb₁₀ was extracted with ethanol, and remaining TMA salt of CrNb₉–Nb₁₀ mixture was extracted with ethanol–methanol to yield an extract of **1**. Crystallization of **2** and **3** were challenging because of the slow decomposition of MNb₉ (M = Mn or Co) to Nb₁₀ in the viscous liquid product. The color of the oily product changed from purple to brown (MnNb₉) and pink to blue (CoNb₉) during the crystallization attempt, concomitant with Nb₁₀ crystal formation. This observation suggests decomposition of MNb₉ cluster and oxidation of the corresponding released transition metal oxide (M = Mn or Co) by O₂ in air. However, we were able to isolate decent amount of MnNb₉ and CoNb₉ crystals (28 and 45% yields, respectively) by cooling the concentrated ethanolic solution after extraction. Decomposition of Mn- and Co-substituted decaniobate structures during storage was avoided by prompt filtration by washing with ethanol, followed by drying and storage *in vacuo*. On the other hand, Cr-, Fe- or Ni-substituted decaniobate ions did not decompose noticeably either during the long crystallization step in a viscous liquid product or upon storage in air.

Electrospray-ionization mass spectrometry (ESI-MS) was used to determine the identities of substituted decaniobates [Fig. 2]. The purified samples were dissolved in water for

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† Electronic supplementary information (ESI) available: ESI-MS and UV-Vis titration data, magnetism data, detailed H₂ evolution data with change of solution speciation by ESI-MS, UV-Vis, and TEM/EDS data of the colloids after irradiation. CCDC 990475, 990476 and 990477. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt02020k



ESI-MS analyses. ESI-MS of 1–3 shows peaks in the lower m/z region compared to Nb_{10} due to the substitution of one Nb^{V} site with an early TM of lower atomic mass than niobium. ESI-MS also indicates a single-site substitution, as was confirmed by X-ray crystallography (*vide infra*). We find no evidence of multiple site substitution, in spite of exploration of other reagent stoichiometries and/or different reaction temperatures.

Structures of the substituted decaniobate clusters with Cr, Mn and Co substituents were determined by X-ray single crystallography. The results show that the substitution occurred exclusively at the central site of the decaniobate moiety, similar to other substituted decaniobate structures ($M = \text{Ti}, \text{Fe}, \text{Ni}$) [Fig. 1].³ Bond-valence sum (BVS) calculations of metal centres suggest the oxidation state of the metals as Cr^{III} (2.86 and 2.90), Mn^{III} (3.07) and Co^{II} (1.92) [Table S1†]. We note that some Mn^{IV} -included heteropolyniobate clusters have been reported previously.⁸ Numbers of TMA counteranions found in the crystal structures of 1–3 are 6, 8 and 7, respectively, and these numbers agree well with the elemental analysis results. Thus the formulae of the clusters in 1–3 can be expressed as $[\text{H}_2\text{Cr}^{\text{III}}\text{Nb}_9\text{O}_{28}]^{6-}$, $[\text{Mn}^{\text{III}}\text{Nb}_9\text{O}_{28}]^{8-}$ and $[\text{H}_2\text{Co}^{\text{II}}\text{Nb}_9\text{O}_{28}]^{7-}$, respectively. In the CrNb_9 structure, two protons are found on the two $\mu_2\text{-O}$ atoms between Cr and Nb. Protons were not found in the electron-density map of the CoNb_9 structure, but BVS calculation of the two $\mu_2\text{-O}$ bound to Co (0.983 and 1.013) suggests that two $\mu_2\text{-O}$ between Co and Nb are protonated, as in the CrNb_9 molecule. In MnNb_9 structure, BVS values of all Mn-bound oxygen atoms are higher than 1.5, supporting a conclusion that MnNb_9 is not protonated. While Cr^{III} and Co^{II} retained their oxidation state from the source reagent, Mn^{II} from the reagent was oxidized to Mn^{III} in the cluster, which might have happened in the hydrothermal synthesis condition.

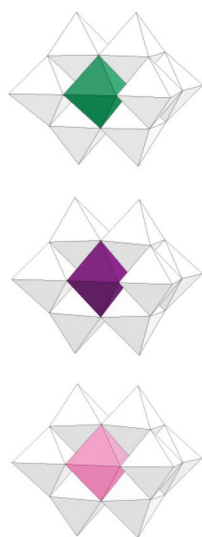


Fig. 1 Polyhedral model of MNb_9 clusters ($M = \text{Cr}^{\text{III}}, \text{Mn}^{\text{III}}$ and Co^{II} , from top to bottom) in 1–3 (white: Nb, green: Cr, purple: Mn, pink: Co).

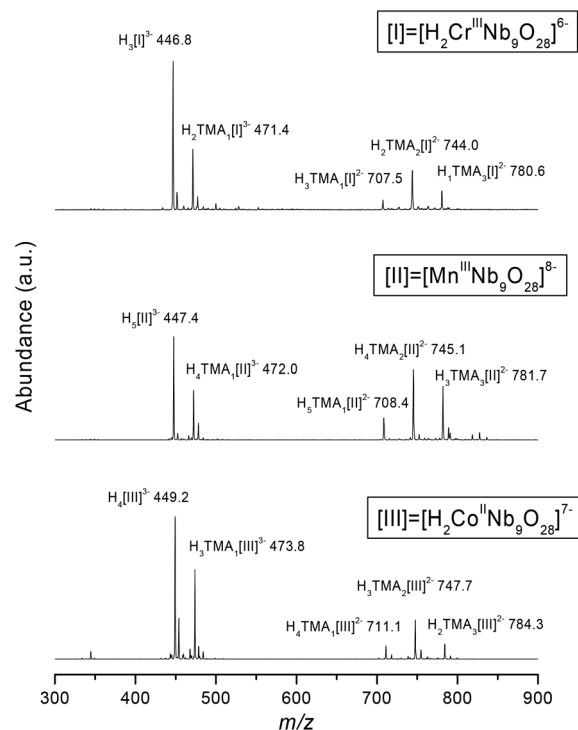


Fig. 2 ESI-MS of compounds 1–3 dissolved in water (from top to bottom).

Enough of these MNb_9 structures are now available to compare the $M\text{-O}$ bond lengths [Fig. 3]. We find that the $M\text{-}\mu_6\text{-O}$ and $M\text{-}\mu_2\text{-O}$ lengths increase from Cr to Co then decrease slightly for the Ni-substituted molecule. This trend is similar to the Shannon's ionic radii of the TM ion series.⁹ We speculate that a discrepancy in this trend for MnNb_9 is due to the disordered central site with half occupancy of Nb in the structure of MnNb_9 . We point out that two axial *trans* $M\text{-}\mu_3\text{-O}$ bonds are asymmetric in Cr, Fe and Ni derivatives of the

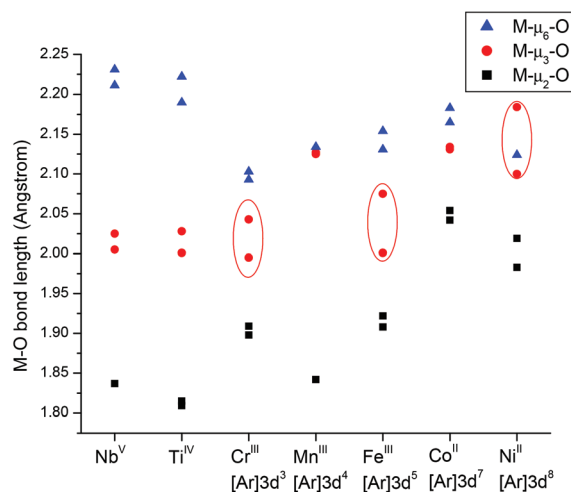


Fig. 3 The central $M\text{-O}$ bond lengths in decaniobate and TM-substituted decaniobates. X -axis shows corresponding central atoms and their electron configurations.



MNb₉, while those in Mn- and Co-substituted MNb₉ are more symmetric [Fig. 3]. Larger differences in the axial *trans* M-μ₃-O bond lengths are observed as the group number of the substituted metal increases. (The red stretched circles are shown the same size to better indicate how asymmetry increases as one moves to the right in Fig. 3.) We note that clusters with large asymmetry in the axial M-μ₃-O bonds have greater stability than clusters with symmetric M-μ₃-O bonds lengths: MnNb₉ and CoNb₉ slowly decomposed to Nb₁₀ in the viscous crude product, as described above. The correlation is interesting but inconclusive and but immediately suggests a useful computational study.

An ESI-MS titration of 2 mM solutions of each cluster was performed to compare the stabilities of the substituted decaniobates as a function of pH [Fig. S1–S3†]. The varying intensity of the strongest peak of each ESI-MS data (445–450 *m/z*) was plotted to evaluate the stability of each substituted decaniobate clusters according to pH [Fig. 4]. While 1–3 show similarly decreasing peak abundance above pH 11 in the base titration, which suggests decomposition, a different trend is evident in the acid titration. CoNb₉ forms a precipitate immediately upon adding a small amount of acid, as we have found previously in the titration of FeNb₉ and NiNb₉.^{3d} However, MnNb₉ and CrNb₉ did not readily precipitate by adding acid; titration of MnNb₉ and CrNb₉ with acid exhibited some buffering and significant precipitation only occurred below pH 5.3 and pH 4.7, respectively. Although the stabilities are broadly similar across the series [Fig. 4], the stability window in acidic region is CrNb₉ > MnNb₉ > Fe ≈ Co ≈ NiNb₉.

A purified sample of 1 has a lighter green color relative to the dark turquoise (bluish green) of [Cr₂Nb₁₀O₃₄]⁸⁻, both in solution and solid. Crystals of 2 are deep purple and those of 3 are violet. The UV-Vis spectra of 1–3 during titration with TMAOH solution are shown in Fig. S4–S6†. The solution of 1 shows absorption at 450 and 650 nm from ⁴A_{2g}(F)→⁴T_{1g}(F) and ⁴A_{2g}(F)→⁴T_{2g}(F) transitions, respectively [Fig. S4†].¹⁰ Different electronic transitions from light absorption are responsible for the slightly different colors of CrNb₉ and Cr₂Nb₁₀, as CrNb₉ is absorbing at 650 nm, while Cr₂Nb₁₀ shows absorption at

600 nm.⁷ During the titration of 1 with base, the two absorption maxima at 450 and 650 nm start to shift to 470 and 670 nm above pH 9 and a new absorption at 320 nm becomes evident. Titration coupled to ESI-MS indicated that significant decomposition only occurred above pH ~ 11 [Fig. 4 and Fig. S1†]. We thus suggest that the change of spectral profile of CrNb₉ above pH 9 is more likely due to deprotonation than decomposition, although this conclusion is speculative. A solution of 2 exhibits a broad absorption at 550 nm, which can be assigned to ⁵E_g→⁵T_{2g} transition of Mn^{III} [Fig. S5†].¹⁰ The natural pH attained by a 2 mM solution of 2 is relatively high (~10), compared to 1 (pH 6.7) and 3 (pH 8.6), indicating a higher proton affinity. During the base titration of 2, an isosbestic point was observed around pH 11. A solution of 3 shows absorption at 500 and 545 nm (⁴T_{1g}(F)→⁴T_{1g}(P) transition), which is a similar feature in the [Co(H₂O)₆]²⁺ ion [Fig. S6†].¹⁰ The spectra of CoNb₉ did not change significantly until pH ~ 12, which is similar to the behavior found in UV-Vis titrations of FeNb₉ and NiNb₉.^{3d}

The magnetic measurements satisfy the Curie law, as can be seen from the almost linear 1/χ_m vs. temperature plot of each compound [Fig. S7†]. Thus the compounds are paramagnetic, as is expected given that the clusters each contain a single isolated TM in otherwise diamagnetic niobate framework. The Curie constants derived by curve fitting χ_m vs. temperature plot are presented in Table S2.† Fig. 5 shows the effective magnetic moments (μ_{eff}) of the series as a function of temperature. The μ_{eff} values of each compound at their maxima are close to typical experimental μ_{eff} values for compounds with single corresponding TM ion in high-spin configuration (*i.e.* 3.8, 4.9, 5.9, 4.8, 3.2 for Cr^{III}, Mn^{III}, Fe^{III}, Co^{II}, Ni^{II}, respectively),¹¹ confirming the single-site substitution, the assigned oxidation states and high-spin states of the heterometals. However, the μ_{eff} values of all compounds slightly decrease with increasing temperature, which might be due to the spin disorder at higher temperatures. We note that FeNb₉ and CrNb₉ have maximum μ_{eff} around 7 K. On the other hand, NiNb₉, MnNb₉ and CoNb₉ show maxima at 20 K, 35 K and 120 K, respectively. The sharp decrease of μ_{eff} of Ni^{II} and Mn^{III}

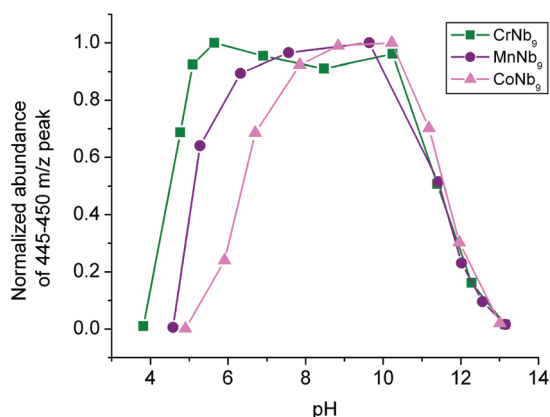


Fig. 4 Normalized peak intensity (strongest peak) in ESI-MS of 1–3 as a function of pH, based on Fig. S1–S3.†

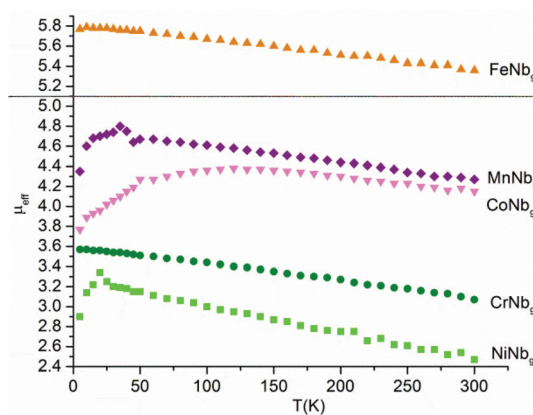


Fig. 5 μ_{eff} vs. temperature for TMA salts of TM-substituted decaniobates.



compounds in the low-temperature region is known to be due to zero-field splitting.¹² The gradual decrease of μ_{eff} for the Co^{II}-substituted decaniobate at lower temperatures has been observed for other Co^{II} compounds, and is generally attributed to spin-orbit coupling.¹²

TM-doped polyoxometalate clusters have recently been shown to possess electrocatalytic properties for water oxidation.¹³ To test the ability of the niobate clusters to act as photocatalysts for H₂ evolution, irradiation tests were conducted. For the experiment, 50 mg of each compound was dissolved in mixed solution of methanol and water (50 mL, 20% v/v, methanol as sacrificial oxidant). Visible-light irradiation by using UV filter (cut-off wavelength <400 nm) on the sample solutions showed no appreciable H₂ evolution, indicating that the electron-hole pairs created by excitation of the TMs by visible light are not accessible for redox reactions on the cluster surface. However, irradiation with the full spectrum of the Xe lamp produced significant amounts of H₂. NiNb₉ and CoNb₉ showed ~4 times higher H₂ evolution than Nb₁₀ [Fig. S8†]. FeNb₉, MnNb₉ and CrNb₉ showed similar or lower activity than Nb₁₀. ESI-MS of the solutions after irradiation indicated that a significant amount of each cluster had decomposed to hexaniobate and Nb₁₀ during irradiation. To explain the nature of active photocatalyst, we carried out H₂-evolution experiments using higher cluster concentrations.

When the H₂-evolution experiment was performed with four-times higher cluster concentration (*i.e.* with 0.2 g of sample in 50 mL MeOH-water, 20% v/v; 1.6 to 2.0 mM), similar trends were found, with NiNb₉ (217 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and CoNb₉ (214 $\mu\text{mol g}^{-1} \text{h}^{-1}$) showing higher H₂-evolution activity than the other clusters, which was generally similar or lower than Nb₁₀ (59 $\mu\text{mol g}^{-1} \text{h}^{-1}$) [Fig. 6]. The non-linearly increasing H₂-evolution rate of both NiNb₉ and CoNb₉ suggests formation of photocatalytically active forms from consumption or dissociation of original cluster. The color of the solutions changed after irradiation [Fig. S9†] and the solution exhibited scattering of laser light by colloids. Overall absorbance in UV-Vis spectra of the solutions increased after irradiation,

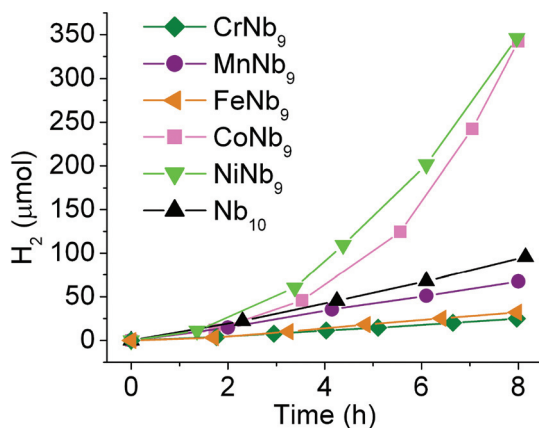


Fig. 6 H₂-evolution upon Xe-lamp irradiation of 0.2 g of TM-substituted decaniobate TMA salts in 50 mL MeOH-H₂O solution (20% v/v).

which is also consistent with the formation of metal-oxide colloids upon irradiation [Fig. S10†]. ESI-MS indicated that a large portion of the MNb₉ clusters in solutions decomposed after irradiation to hexaniobate and Nb₁₀, but some MNb₉ still remained [Fig. S11†]. Similarly, we observed photodecomposition of the Te-substituted Lindqvist-type niobate clusters into hexaniobate and metallic tellurium nanowires, which showed high H₂-evolution activity.¹⁴ High H₂-evolution activity from NiNb₉ is not surprising, since Ni-doped K₄Nb₆O₁₇ showed much higher H₂-evolution activity compared to other early TM- (from Cr to Cu) doped K₄Nb₆O₁₇.⁵ The high H₂-evolution activity of Ni-loaded K₄Nb₆O₁₇ was attributed to segregated NiO nanoparticles on K₄Nb₆O₁₇ sheets.¹⁵ Thus the high activity of NiNb₉ could similarly be attributed to formation of Ni⁰ or NiO_x particles and their interaction with niobates. Niobate will generate electron-hole pairs upon UV light irradiation¹⁶ and Ni⁰/NiO_x particle will reduce protons, producing H₂. We note that whether Ni⁰, or NiO_x, or both, are the active cocatalyst is controversial; we cannot contribute to this discussion here.¹⁷

Upon irradiation, CoNb₉ solutions exhibited H₂-evolution curves that were similar to NiNb₉ solution [Fig. 6]. ESI-MS spectrum after irradiation indicated that a solution of CoNb₉ is still dominated by the CoNb₉ ion, but the UV-Vis spectra had changed, indicating some decomposition [Fig. S10 and S11†]. The appreciable activity of CoNb₉ in photocatalytic H₂-evolution is interesting because Co-doped K₄Nb₆O₁₇ showed much lower H₂-evolution activity compared to Ni-doped K₄Nb₆O₁₇.⁵ Hill *et al.* remarked that the distinction between homogeneous and heterogeneous catalysis is elusive for their Co-doped polyoxotungstate catalytic systems, and that is certainly also true here for the substituted niobates.¹⁸

The H₂-evolution activity of the cluster solution depends on pH. A large amount of light grey precipitate formed after irradiating the NiNb₉ solution when the pH was lowered before irradiation, and this solution showed enhanced H₂-evolution activity upon irradiation, with a distinct nonlinear curve (986 $\mu\text{mol g}^{-1} \text{h}^{-1}$) [Fig. S12†]. No clusters remained in the solution after irradiation, as indicated by ESI-MS. The pH after irradiation was 5.8, much lower than natural pH of a solution formed from freshly dissolved solid, and is instead consistent with extensive hydrolysis reactions upon irradiation, leading to proton release and precipitation. Transmission-electron microscopy (TEM) images of the precipitate showed agglomerated nanoparticles (<10 nm), and the composition is about Ni : Nb = 1 : 8.7, as determined by energy-dispersive X-ray spectroscopy (EDS) [Fig. S13†], which is close to the cluster composition. This result suggests that the nanoparticles are composed of NiO_x and NbO_x, but phase distinction was not possible due to resolution limit. Powder X-ray diffraction of this precipitate indicated no crystallinity. One hypothesis is that, by forcing precipitation at low pH, the NiNb₉ system exhibited a higher H₂-evolution because the colloids were catalytic. Interestingly, CoNb₉ exhibited an opposite trend [Fig. S12†]. The H₂-evolution activity of CoNb₉ was nearly lost after precipitate formed by lowering the pH, which suggests



that H₂ evolution in CoNb₉ solution may be from cluster ions and not the colloids.

Conclusions

Early TM-substituted (from group 6 to 10) decaniobate ions have differences in their solid-state structure that can be related to their stability and properties. The range of widely varying stabilities of the clusters is a key challenge in the synthesis and purification of this series of polyoxoniobates. We suggest that the higher H₂-evolution activity from the Ni- and Co-substituted decaniobate ions arises *via* separate heterogeneous (Ni) and homogeneous (Co) routes, but in any case is only evident during UV irradiation. Their increased activity is attributed to cocatalysis from the photodecomposition products, most likely as Ni⁰ and Ni oxide, and Co hydroxide, with amorphous Nb₂O₅ or with the niobate cluster in solution. CoNb₉ is interesting because a relatively larger amount of the cluster ions survive irradiation.

Experimental details

Synthesis of 1 (CCDC 990475)

Hydrous niobium oxide (5 g, 80% w/w) was mixed with 0.89 g of CrCl₃·6H₂O in a 23 mL capacity PTFE-lined autoclave and 5.5 g of TMAOH·6H₂O was added. The mixture was reacted at 110 °C for 4 days. Reaction mixture solution was washed with isopropanol in a plastic centrifuge tube (50 mL) several times until the sticky product remained. The product was extracted with ethanol until extract was nearly colorless. Ethanol extract was discarded and remaining green precipitate was extracted with methanol–ethanol (*ca.* 1 : 1) solution. Crystalline product was obtained after evaporation. Yield = 1.9 g (28%). Elemental analysis Found: C 14.34, H 5.19, N 4.06, Cr 2.34, Nb 38.40. Calcd for C₂₄H₁₀₂N₆CrNb₉O₄₂: C 14.15, H 5.05, N 4.13, Cr 2.56, Nb 41.09.

Synthesis of 2 (CCDC 990476)

Hydrous niobium oxide (5 g, 80% w/w) was mixed with 0.66 g of MnCl₂·4H₂O in a 23 mL capacity PTFE-lined autoclave and 5.5 g of TMAOH·6H₂O was added. The mixture was reacted at 110 °C for 4 days. Reaction mixture solution was washed with isopropanol in a plastic centrifuge tube (50 mL) several times until the sticky product remained. The product was extracted with ethanol (*ca.* 200 mL). The ethanolic solution was concentrated to less than 50 mL by using rotary evaporator and kept in a freezer. Dark purple rod-like crystals formed. The product crystals were quickly filtered on a frit and washed with minimum amount of ethanol, and dried *in vacuo*. Yield = 2.3 g (28%). Elemental analysis Found: C 15.39, H 5.99, N 4.41, Mn 2.19, Nb 34.10. Calcd for C₃₂H₁₅₄N₈MnNb₉O₅₇: C 15.65, H 6.32, N 4.56, Mn 2.24, Nb 34.07.

Synthesis of 3 (CCDC 990477)

Hydrous niobium oxide (5 g, 80% w/w) was mixed with 0.8 g of CoCl₂·6H₂O in a 23 mL capacity PTFE-lined autoclave and 5.5 g of TMAOH·6H₂O was added. The mixture was reacted at 110 °C for 4 days. Reaction mixture solution was washed with isopropanol in a plastic centrifuge tube (50 mL) several times until the sticky product remained. The product was extracted with ethanol (*ca.* 200 mL). The ethanolic solution was concentrated to less than 50 mL by using rotary evaporator and kept in a freezer. Pale violet needle-like crystals formed were quickly filtered on a frit and washed with minimum amount of ethanol and dried *in vacuo*. Yield = 3.5 g (45%). Elemental analysis Found: C 14.53, H 6.01, N 4.44, Co 2.50, Nb 34.30. Calcd for C₂₈H₁₃₆N₇CoNb₉O₅₃: C 14.52, H 5.92, N 4.24, Co 2.55, Nb 36.14.

Crystal data

(1) CCDC 990475. C₂₄H₉₃N₆Cr_{1.03}Nb_{8.98}O_{42.44}, *M* = 2032.17, monoclinic, *a* = 16.6016(8), *b* = 17.2436(8), *c* = 24.0263(11) Å, β = 106.121(1)°, *U* = 6607.6(5) Å³, *T* = 93 K, space group *P*2₁/*n* (no. 14), *Z* = 4, 66308 reflections measured, 13 488 unique (*R*_{int} = 0.0218) which were used in all calculations. The final *wR*(*F*²) was 0.0656 (all data). (2) CCDC 990476. C_{33.60}H₆₀N₈Mn_{1.04}Nb_{8.96}O_{56.90}, *M* = 2376.48, monoclinic, *a* = 22.846(6), *b* = 13.767(4), *c* = 17.970(5) Å, β = 129.353(4)°, *U* = 4370(2) Å³, *T* = 93 K, space group *C*2/*m* (no. 12), *Z* = 2, 23936 reflections measured, 5199 unique (*R*_{int} = 0.0138) which were used in all calculations. The final *wR*(*F*²) was 0.1285 (all data). (3) CCDC 990477. C₂₈H₇₂N₇CoNb₉O₅₃, *M* = 2250.05, monoclinic, *a* = 25.543(2), *b* = 13.8124(12), *c* = 23.383(2) Å, β = 104.026(1)°, *U* = 8003.9(12) Å³, *T* = 88 K, space group *P*2₁/*c* (no. 14), *Z* = 4, 126087 reflections measured, 24 416 unique (*R*_{int} = 0.0315) which were used in all calculations. The final *wR*(*F*²) was 0.1700 (all data).

Acknowledgements

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