

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Two Rh^{III}-substituted polyoxoniobates and their base-induced transformation: [H₂RhNb₉O₂₈]⁶⁻ and [Rh₂(OH)₄Nb₁₀O₃₀]⁸⁻

Jung-Ho Son,^{*a} and Willam H. Casey^{a,b}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Two new rhodium-substituted polyoxoniobates, [H₂RhNb₉O₂₈]⁶⁻ (RhNb₉) and [Rh₂(OH)₄Nb₁₀O₃₀]⁸⁻ (Rh₂Nb₁₀) are reported. The two distinct Rh^{III}-substituted niobate clusters behave differently when the pH is raised with TMAOH: the Rh₂Nb₁₀ is stable until pH~12.7, but RhNb₉ dissociates to form RhNb₅ and RhNb₁₀, similar to some of our other metal-substituted niobates, such as the MNb₉ ions (M=Cr or Mn), which transform to MNb₁₀ 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.¹ In the polyoxoniobate system, a series of TM-substituted decaniobate-type [MNb₉O₂₈]^{x-} (MNb₉, M=Cr-Ni) have been synthesized recently² 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-coordinated (capped) hexaniobates (Nb₆).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, [H₂Pt^{IV}V₉O₂₈]⁵⁻ is known in the polyoxovanadate system.⁵

Here we report the synthesis, structure, characterization and photocatalytic H₂ evolution study of two Rh^{III}-substituted niobates. The two compounds reported here have the stoichiometry: [H₂RhNb₉O₂₈]⁶⁻ (RhNb₉) and [Rh₂(OH)₄Nb₁₀O₃₀]⁸⁻ (Rh₂Nb₁₀) as tetramethylammonium (TMA) salts. The structures of these clusters resemble those of two Cr^{III}-substituted niobates, [H₂CrNb₉O₂₈]⁶⁻ (CrNb₉) and [Cr₂(OH)₄Nb₁₂O₃₀]⁸⁻ (Cr₂Nb₁₀) that we previously described.^{2,6}

Substitution of Rh^{III} in the polyoxoniobate structure was challenging. Our previous methods employed for MNb₉ (M=Cr-Ni) generally showed low yield for rhodium substitution (less than 1 %).² The low yield might be a result from the notoriously 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 Rh⁰ 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 H₂O₂ was added (40 % and 7 % for Rh₂Nb₁₀ and RhNb₉, respectively). Hydrogen peroxide also might have helped to dissociate the rather stable Nb₆ or Nb₁₀ ions and facilitate the formation of Rh^{III}-substituted structures.⁸

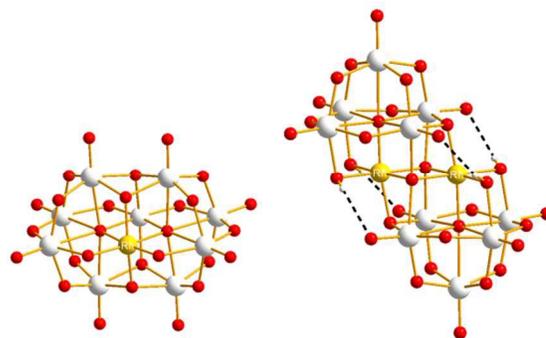


Fig. 1 Ball-and-stick model of RhNb₉ (left) and Rh₂Nb₁₀ (right) (Nb:gray, Rh:gold, O:red). Intramolecular hydrogen bonds are shown with dashed line in Rh₂Nb₁₀

The solution after hydrothermal reaction was typically a mixture of Nb₁₀, Nb₆, RhNb₉ and Rh₂Nb₁₀ 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 molecules. After washing with isopropanol, the product was extracted with ethanol. The ethanol extract was a mixture of Rh₂Nb₁₀ and Nb₆ ions, and the precipitate that remained after ethanol extraction was a mixture of Nb₁₀ and RhNb₉. The RhNb₉ was separated from Nb₁₀ by extraction with ethanol/methanol mixture. Mild heating of the ethanol extract for a few hours caused condensation of more soluble Nb₆ into less soluble Nb₁₀ precipitate. The ethanolic orange solution that remained after this heating step consisted of mostly Rh₂Nb₁₀. The crystalline products of Rh₂Nb₁₀ and RhNb₉ were obtained after solvent evaporation.

In the crystal structure of RhNb₉, 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 MNb₉O₂₈ (M=Cr-Ni) series.²² above 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 $\text{Rh}-\mu_2\text{-O}-\text{Nb}$ (1.37 and 1.38) are much lower than other bridging oxygen atoms, which suggest that those are protonated, similarly to the substituted MNb_9 ($\text{M}=\text{Cr}-\text{Ni}$).² 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 RhNb_5 Lindqvist-type clusters fused by two $\mu_4\text{-O}$ atoms linking two Rh^{III} and two $\mu_3\text{-O}$ atoms linking Rh^{III} and Nb^{V} . The oxidation state of rhodium in $\text{Rh}_2\text{Nb}_{10}$ is also Rh^{III} , as determined by BVS calculation (2.95). The Rh-O bond lengths in $\text{Rh}_2\text{Nb}_{10}$ are longer and more regular (2.0245(16)-2.0605(16) Å) than Cr-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 $\text{Cr}_2\text{Nb}_{10}$.⁶ 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 RhNb_9 and $\text{Rh}_2\text{Nb}_{10}$ agree with their assigned stoichiometries (Fig. S1).

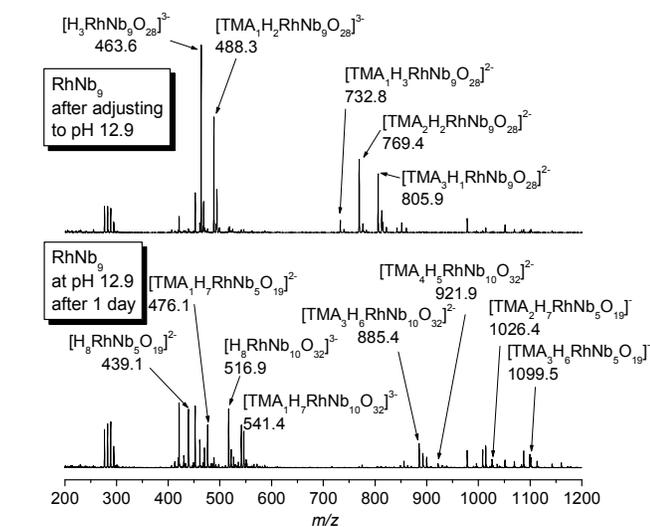
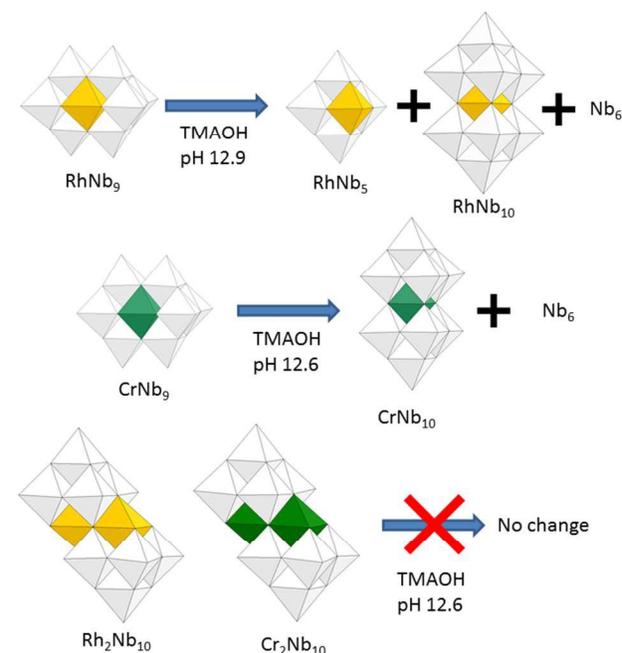


Fig. 2 Change of ESI-MS spectra of RhNb_9 when the solution pH was adjusted to 12.9.

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 $\text{Rh}_2\text{Nb}_{10}$ 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 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 $[\text{H}_2\text{Mn}^{\text{IV}}\text{Nb}_{10}\text{O}_{32}]^{8-}$ (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 \cdot 5 H_2O to each aqueous solution containing 30 mg of MNb_9 ($\text{M}=\text{Ti}, \text{Cr}-\text{Ni}$) 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 a long period of time, like $\text{Rh}_2\text{Nb}_{10}$ (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. The color of MnNb_9 solution changed from purple to brown with time, suggesting oxidation of Mn^{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 MnNb_5 or CrNb_5 was not detectable, which suggests that they are unstable. Other MNb_9 clusters ($\text{M}=\text{Fe}-\text{Ni}$) 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} ($\text{M}=\text{Rh}^{\text{III}}$ 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, $\text{Rh}_2\text{Nb}_{10}$ was evident in the ESI-MS spectra until pH 4.0, and RhNb_9 was stable until pH 4.5, 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 $\text{Rh}_2\text{Nb}_{10}$ ($4<\text{pH}<13$) is similar to $\text{Cr}_2\text{Nb}_{10}$.⁶ The RhNb_9 exhibited a wider stability range ($4.5<\text{pH}<12$) than other MNb_9 clusters ($\text{M}=\text{Cr}-\text{Ni}$) in general.



Scheme 1 Base-induced transformation of MNb_9 and M_2Nb_{10} ($\text{M}=\text{Rh}, \text{Cr}$)

The UV-Vis spectra of 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 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 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 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 Rh^{III} .¹⁰ The RhNb_9 and $\text{Rh}_2\text{Nb}_{10}$ clusters were also characterized by using FT-IR (Fig. S11). 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 RhNb_9 is similar to those of MNb_9 , which reflect their structural similarity.

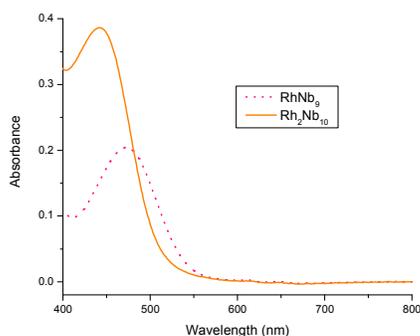


Fig. 3 UV-Vis spectra of 2 mM solution of $\text{Rh}_2\text{Nb}_{10}$ and RhNb_9 without background electrolyte

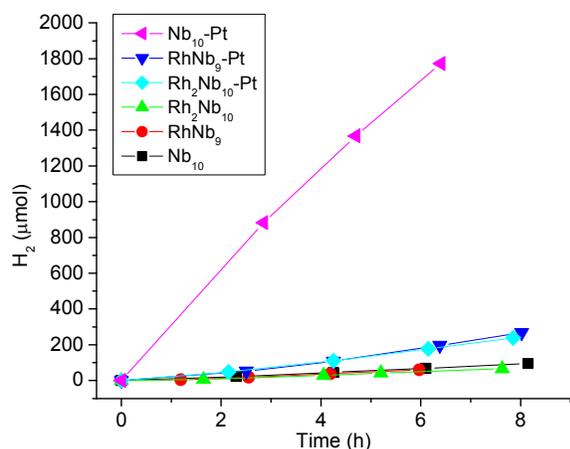


Fig. 4 Comparison of H_2 -evolution activity from the methanol/water solutions (20% v/v) of RhNb_9 , $\text{Rh}_2\text{Nb}_{10}$ and Nb_{10} , with and without H_2PtCl_6

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 $\text{Rh}_2\text{Nb}_{10}$ ions as a continuation of our previous H_2 -evolution study of the MNb_9 ions ($\text{M}=\text{Cr-Ni}$). When irradiated with visible light, similarly to the MNb_9 ions, neither RhNb_9 nor $\text{Rh}_2\text{Nb}_{10}$ 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 ($50 \mu\text{mol g}^{-1} \text{h}^{-1}$ and $43 \mu\text{mol g}^{-1} \text{h}^{-1}$, for RhNb_9 and $\text{Rh}_2\text{Nb}_{10}$, Fig. 4). After irradiation, the originally orange-red or yellow solution of RhNb_9 and $\text{Rh}_2\text{Nb}_{10}$ 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 S12 and S13). The UV-Vis spectra of $\text{Rh}_2\text{Nb}_{10}$ 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 S14 and S15). In the previous H_2 evolution study of the MNb_9 ions ($\text{M}=\text{Cr-Ni}$),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 ($\text{M}=\text{Cr-Fe}$) 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 after irradiation in the present RhNb_9 and $\text{Rh}_2\text{Nb}_{10}$ suggests that these rhodium 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 MNb_9 ($\text{M}=\text{Cr-Ni}$). We also compared 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 ($1385 \mu\text{mol g}^{-1} \text{h}^{-1}$) and amount of precipitate was negligible, but H_2 evolution from RhNb_9 and $\text{Rh}_2\text{Nb}_{10}$ after adding H_2PtCl_6 showed only about 3 fold increases (167 and $152 \mu\text{mol g}^{-1} \text{h}^{-1}$, 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 $\text{RhNb}_9/\text{Rh}_2\text{Nb}_{10}$ 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 $\text{RhNb}_9/\text{Rh}_2\text{Nb}_{10}$ 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 S12 and S13).

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.

We thank Jiarui Wang and Prof. Frank E. Osterloh for H_2 evolution measurement. This work was supported by an NSF CCI

grant through the Center for Sustainable Materials Chemistry, number CHE-1102637.

Notes and references

^a Dr. J.-H. Son, Department of Chemistry, University of California, Davis
5 One Shields Ave. Davis, CA 95616, USA. E-mail: junghoson@gmail.com

^b Prof. W. H. Casey, Department of Chemistry, Department of Earth and Planetary Sciences, University of California, Davis, One Shields Ave. Davis, CA 95616, USA.

† Electronic Supplementary Information (ESI) available: Experimental
10 details, ESI-MS, FT-IR, UV-Vis data. See DOI: 10.1039/b000000x/

- ¹ a) L. C. W. Baker, V. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, L. L. Koh, *J. Am. Chem. Soc.* **1966**, *88*, 2329; b) L. C. W. Baker, J. S. Figgis, *J. Am. Chem. Soc.* **1970**, *92*, 3794-3797; c) T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.* **1973**, 341-346; d) C. L. Hill, R. B. Brown Jr., *J. Am. Chem. Soc.* **1986**, *108*, 536-538; e) M. Faraj, C. L. Hill, *J. Chem. Soc. Chem. Commun.* **1987**, 1487-1489; f) J. Hu, R. C. Burns, *J. Mol. Catal. A: Chemical* **2002**, *184*, 451-464; g) J.-H. Choi, J. K. Kim, D. R. Park, T. H. Kang, J. H. Song, I. K. Song, *J. Mol. Catal. A: Chemical* **2013**, *371*, 111-117.
- ² a) J.-H. Son, J. Wang, W. H. Casey, *Dalton Trans.*, **2014**, *43*, 17928-17933. b) J.-H. Son, C. A. Ohlin, W. H. Casey, *Dalton Trans.*, **2013**, *42*, 7529-7533.
- ³ a) M. Nyman, L. J. Criscenti, F. Bonhomme, M. A. Rodriguez, R. T. Cygan, *J. Solid State Chem.* **2003**, *176*, 111-119; b) C. A. Ohlin, E. M. Villa, J. C. Fettinger, W. H. Casey, *Dalton Trans.* **2009**, 2677-2678; c) E. M. Villa, C. A. Ohlin, J. R. Rustad, W. H. Casey, *J. Am. Chem. Soc.*, **2009**, *131*(45), 16488-16492; d) E. M. Villa, C. A. Ohlin, W. H. Casey, *J. Am. Chem. Soc.*, **2010**, *132*(4), 5264-5272; e) G. Guo, Y. Xu, J. Cao, C. Hu, *Chem. Commun.*, **2011**, *47*, 9411-9413; f) P. Huang, C. Qin, X.-L. Wang, C.-Y. Sun, G.-S. Yang, K.-Z. Shao, Y.-Q. Jiao, K. Zhou, Z.-M. Su, *Chem. Commun.*, **2012**, *48*, 103-105; g) J.-H. Son, C. A. Ohlin, E. C. Larson, P. Yu, W. H. Casey, *Eur. J. Inorg. Chem.*, **2013**, 1748-1753. h) Y.-T. Zhang, P.

- Huang, C. Qin, L.-K. Yan, B.-Q. Song, Z.-X. Yang, K.-Z. Shao, Z.-M. Su, *Dalton Trans.*, **2014**, *43*, 9847-9850; i) P. Huang, E.-L. Zhou, X.-L. Wang, C.-Y. Sun, H.-N. Wang, Y. Xing, K.-Z. Shao, Z.-M. Su, *CrystEngComm*, **2014**, *16*, 9582-9585; j) J.-Y. Niu, G. Chen, J.-W. Zhao, P.-T. Ma, S.-Z. Li, J.-P. Wang, M.-X. Li, Y. Bai, B.-S. Ji, *Chem. Eur. J.*, **2010**, *16*, 7082-7086.
- ⁴ a) A. V. Besserguenev, M. H. Dickman, M. T. Pope, *Inorg. Chem.*, **2001**, *40*(11), 2582-2586. b) P. A. Abramov, M. N. Sokolov, A. V. Virovets, S. Floquet, M. Haouas, F. Taulelle, E. Cadot, C. Vicent, V. P. Fedin, *Dalton Trans.*, **2015**, *44*(5), 2234-2239. c) P. A. Abramov, C. Vicent, N. B. Kompankov, A. L. Gushchin and M. N. Sokolov, *Chem. Commun.*, **2015**, *51*, 4021-4023
- ⁵ U. Lee, H.-C. Joo, K.-M. Park, S.S. Mal, U. Kortz, B. Keita, L. Nadjo, *Angew. Chem., Int. Ed.* **2008**, *47*, 793-796;
- ⁶ J.-H. Son, C. A. Ohlin, W. H. Casey, *Dalton Trans.* **2012**, *41*, 12674-12677.
- ⁷ a) J. S. Loring, J. Rosenqvist, W. H. Casey, *J. Colloid Interface Sci.*, **2004**, *274*(1), 142-149. b) J. R. Houston, P. Yu, W. H. Casey, *Inorg. Chem.*, **2005**, *44*(14), 5176-5182.
- ⁸ C. A. Ohlin, E. M. Villa, J. Fettinger, W. H. Casey, **2008**, *47*, 8251-8254.
- ⁹ J.-H. Son, W. H. Casey, *Dalton Trans.*, **2013**, *42*, 13339-13342.
- ¹⁰ F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th Ed. Wiley-Interscience: New York, **1999**.
- ¹¹ a) Z. Zhang, Q. Lin, D. Kurunthu, T. Wu, F. Zuo, S.-T. Zheng, C. J. Bardeen, X. Bu, P. Feng, *J. Am. Chem. Soc.* **2011**, *133*, 6934-6937; b) P. Huang, C. Qin, Z.-M. Su, Y. Xing, X.-L. Wang, K.-Z. Shao, Y.-Q. Lan, E.-B. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 14004-14010; c) Z.-L. Wang, H.-Q. Tan, W.-L. Chen, Y.-G. Li, E.-B. Wang, *Dalton Trans.* **2012**, *41*, 9882-9884. d) J.-H. Son, J. Wang, F. E. Osterloh, P. Yu, W. H. Casey, *Chem. Commun.* **2014**, *50*, 836-838. e) H. Lv, J. Song, H. Zhu, Y. V. Geletii, J. Bacsa, C. Zhao, T. Lian, D. G. Musaev, C. L. Hill, *J. Catal.* **2013**, *307*, 48-54. f) H. Lv, W. Guo, K. Wu, Y. V. Geletii, Z. Chen, S. M. Lauinger, J. Bacsa, D. G. Musaev, T. Lian, C. L. Hill, *J. Am. Chem. Soc.* **2014**, *136*, 14015-14018..