SUPPLEMENTARY INFORMATION

Tetrapalladium-Containing Polyoxotungstate $[Pd^{II}_4(\alpha\text{-}P_2W_{15}O_{56})_2]^{16-}$: a Comparative Study

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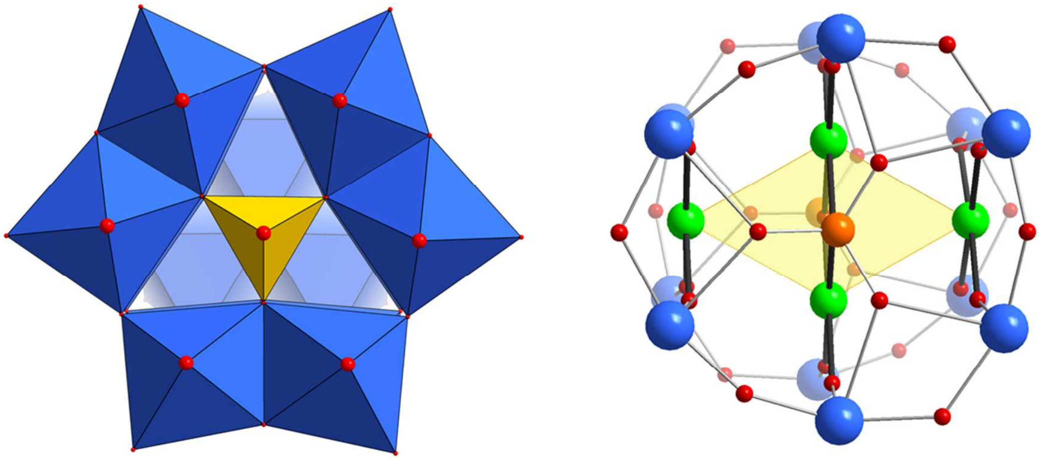

Figure S1. Left: View on the lacunary site of $\{P_2W_{15}\}$ (WO_6: blue octahedra, PO_4: yellow tetrahedra) with the nucleophilic oxygens of the vacant site highlighted as red spheres. Right: The rhombic Pd^{II}_4 core in **1**, (Pd: green spheres, the rhombus highlighted in transparent yellow) and the adjacent PW_6 belts (W: blue, P: orange, O: red), seen approx. along the main axis of **1**. Pd–O bonds are emphasized as bold lines, highlighting the coplanar arrangement of the four PdO_4 environments in **1**, all of which are perpendicular to the Pd_4 plane.

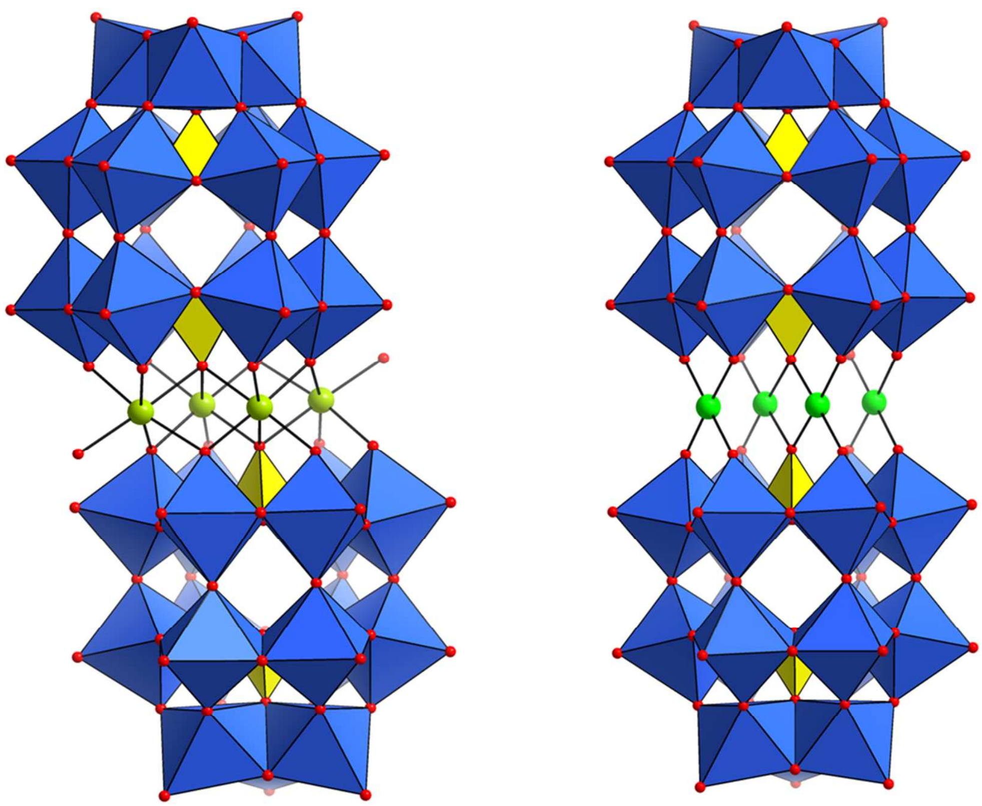

Figure S2. Comparison of *ββ*-$\{M_4(P_2W_{15})_2\}$ (left) and *anti*-$\{Pd_4(P_2W_{15})_2\}$ (right) structures. Color code: WO_6: blue octahedra; PO_4: yellow tetrahedra; M: yellow-green, Pd: green, O: red spheres.

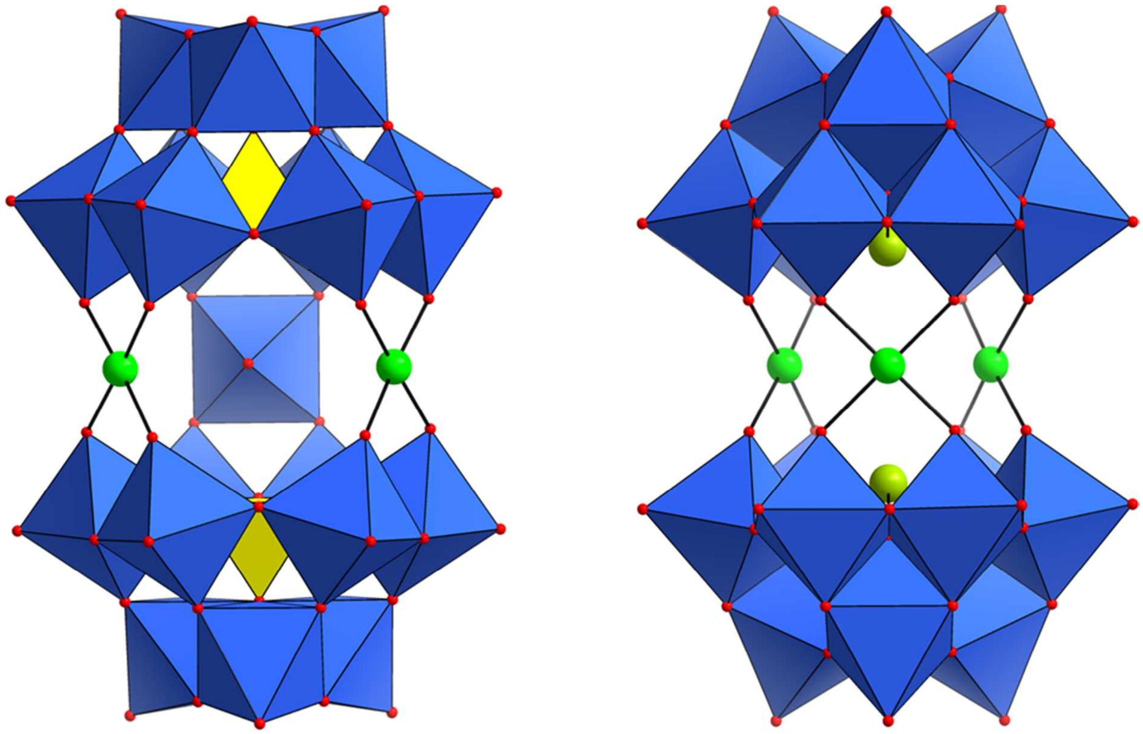

Figure S3. $[Pd_2(WO_2)(XW_9O_{34})_2]^{z-}$ (X = P^V, Si^{IV}) [1] (left) and $[Pd_3(XW_9O_{33})_2]^{z-}$ (X = As^{III}, Sb^{III}, Te^{IV}).[2] Color code as in Figure S2.

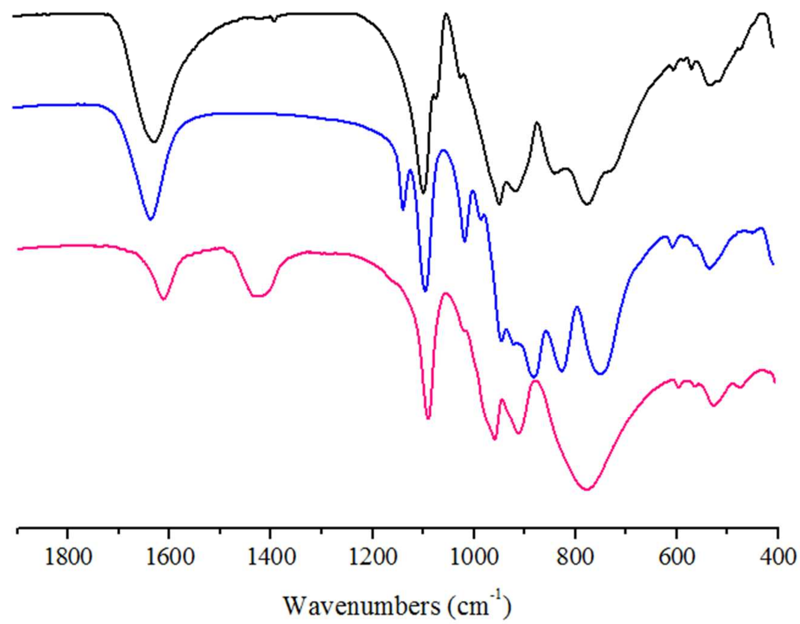

Figure S4. IR spectrum of **Na-1** (black) in comparison with the spectra of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ (blue) and $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$ (purple).

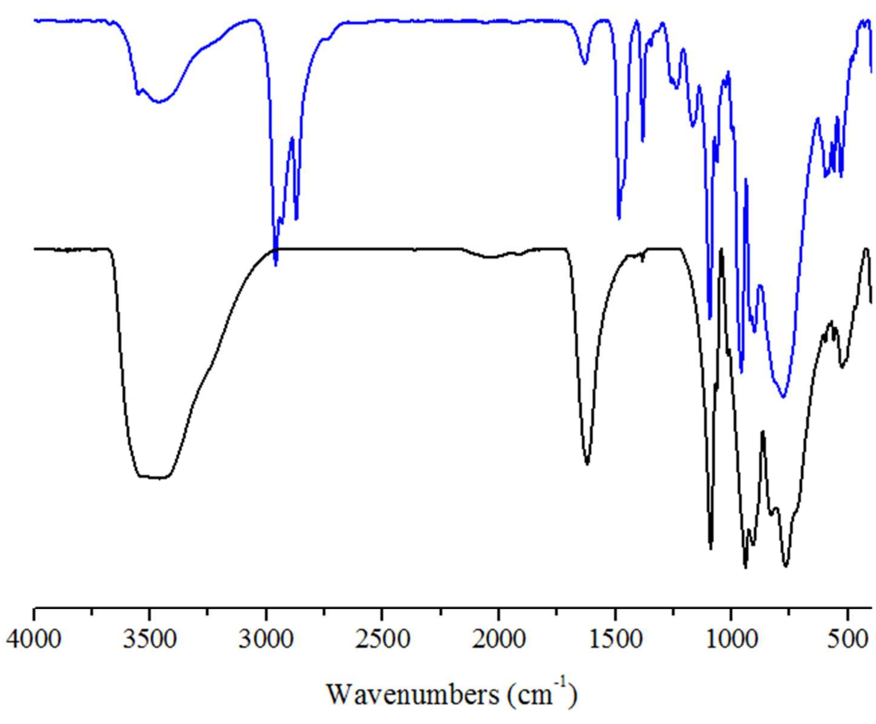

Figure S5. IR spectrum of **TBA-1** (blue) in comparison to the spectrum of **Na-1** (black).

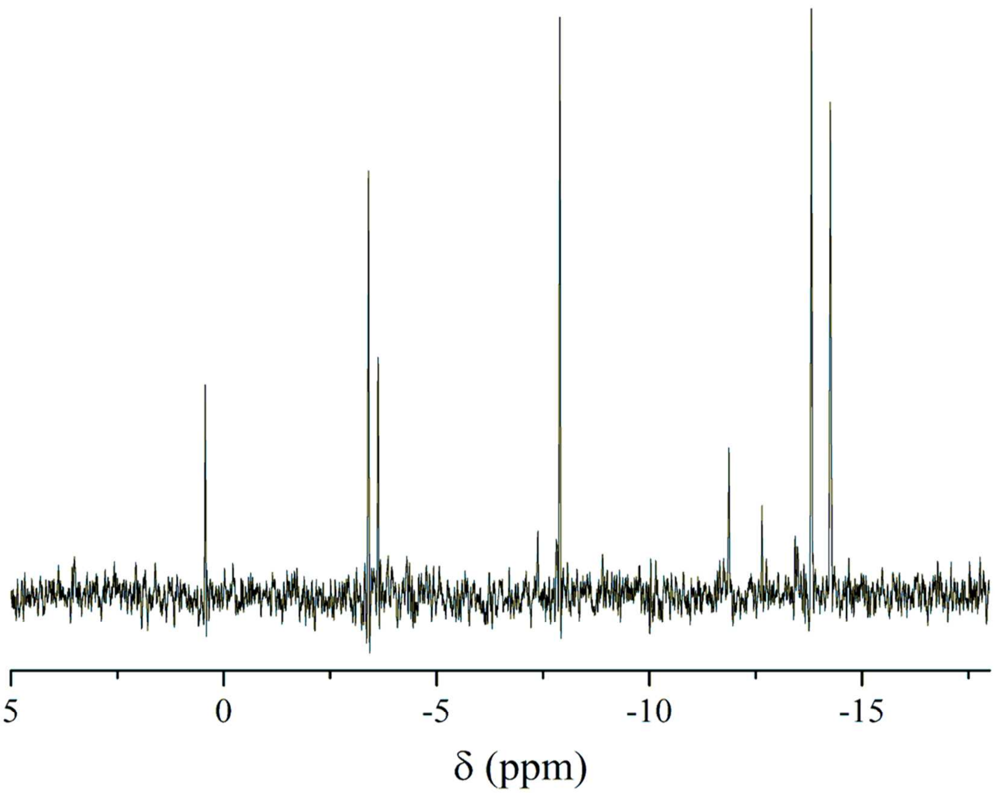

Figure S6. Room temperature ^{31}P NMR spectrum of the Pd^{II} / $\{P_2W_{15}\}$ / 0.5 M CH_3COONa reaction mixture.

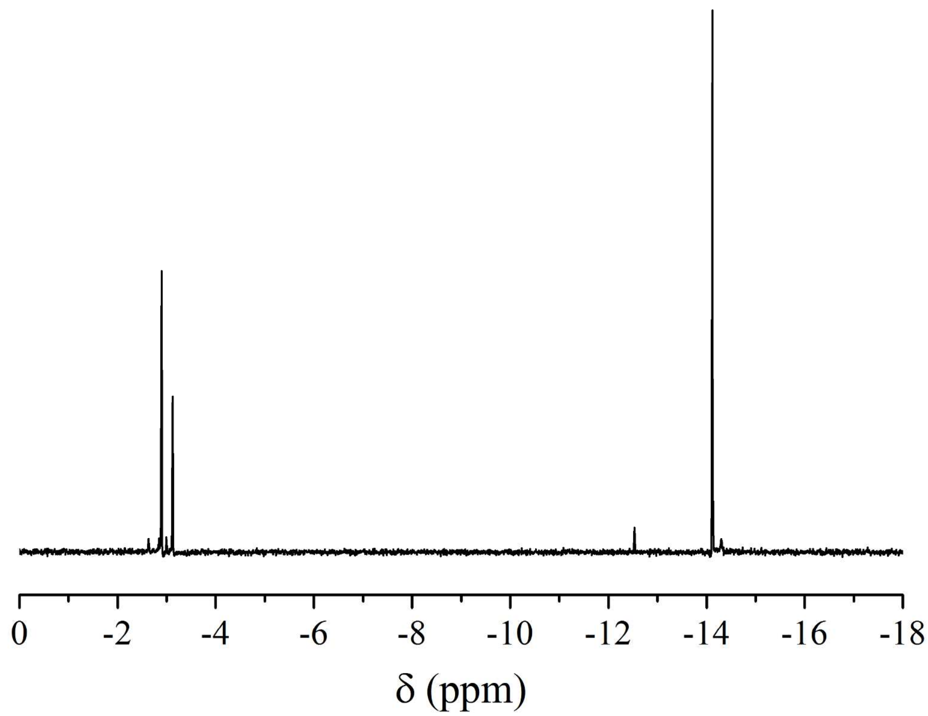

Figure S7. ^{31}P NMR spectrum of **Na-1** redissolved in H_2O / D_2O at 278 K.

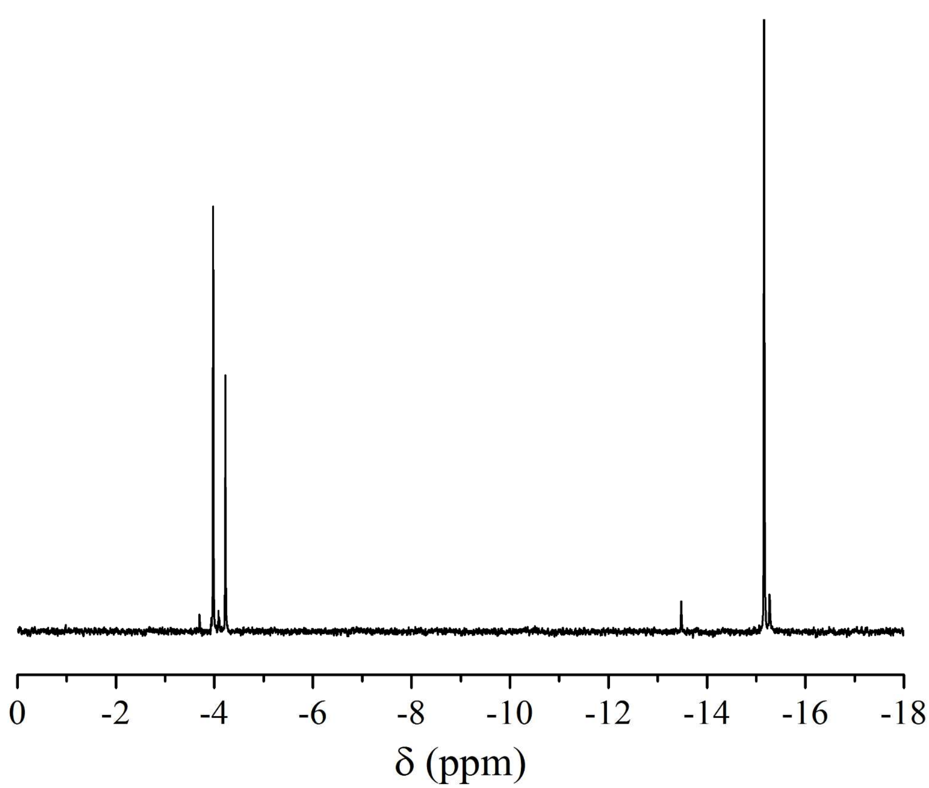

Figure S8. ^{31}P NMR spectrum of **Na-1** redissolved in H_2O / D_2O at 353 K.

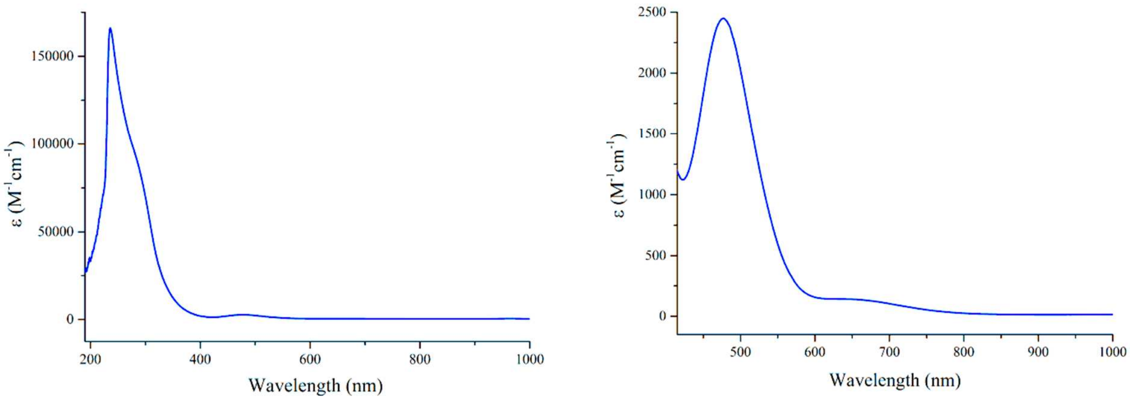

Figure S9. UV/Vis/NIR spectra of **Na-1** redissolved in 0.5 M CH_3COONa (pH 4.3). Right: enlargement of the visible spectral range.

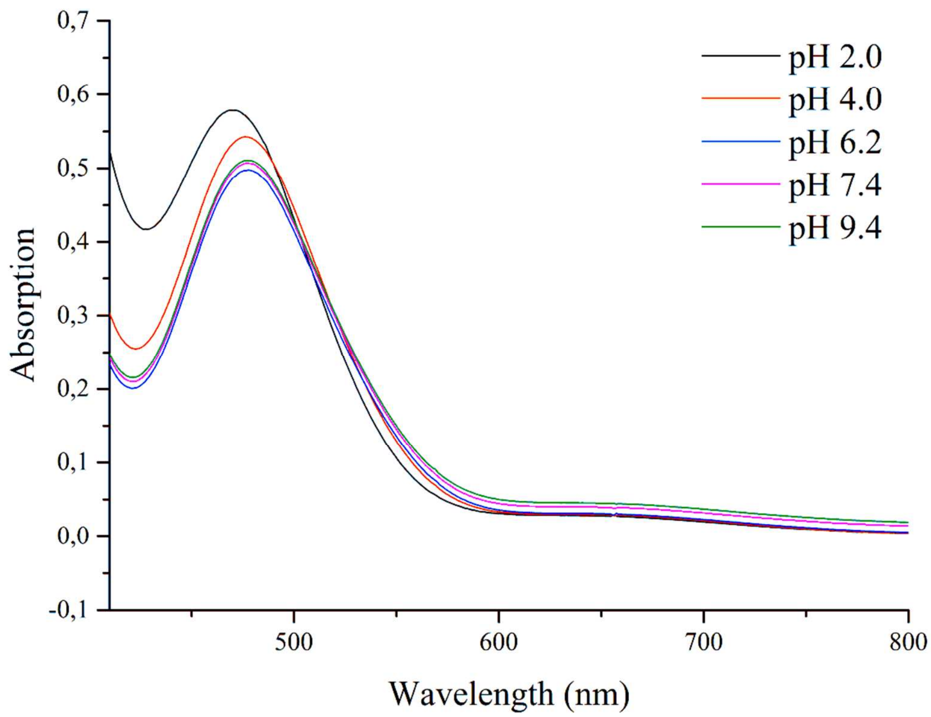

Figure S10. Absorption spectra of 2.1×10^{-4} M **Na-1** solutions in 1 M CH_3COOH (pH 2.0) and 1M CH_3COONa (pH 4.0 – 9.4) in the visible spectral range at room temperature.

References

1. (a) Villanneau, R.; Renaudineau, S.; Herson, P.; Boubekeur, K.; Thouvenot, R.; Proust, A. *Eur. J. Inorg. Chem*. **2009**, 479-488; (b) Bi, L.-H.; Kortz, U.; Keita, B.; Nadjo, L.; Borrmann, H. *Inorg. Chem*. **2004**, *43*, 8367-8372.

2. (a) Krebs, B.; Droste, E.; Piepenbrink M. in *Polyoxometalate Chemistry. From Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A. Eds.; Kluwer, Dordrecht, **2001**, pp. 89 – 99; (b) Bi, L.-H.; Reicke, M.; Kortz, U.; Keita, B.; Nadjo, L.; Clark, R. J. *Inorg. Chem*. **2004**, *43*, 3915-3920; (c) Bi, L.-H.; Kortz, U.; Keita, B.; Nadjo, L.; Daniels, L. *Eur. J. Inorg. Chem*. **2005**, 3034-3041; (d) J. Gao, J. Yan, S. Beeg, D.-L. Long, L. Cronin, *Angew. Chem. Int. Ed*. **2012**, *51*, 3373-3376.