



	<b>Experiment title:</b> Molecular domino: nanoscale positioning of transition metals during self-assembly	<b>Experiment number:</b> CH 3203
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**Report:**

Abstract

A previously non-discovered chromate stabilized  $PW_{10}Cr_x$  species was identified as the key intermediate in the quantitative conversion of Keggin-type  $PW_{12}O_{40}^{3-}$  heteropolyacid into the  $[KP_2W_{20}O_{72}]^{13-}$  polyoxometalate. Though the formation of  $PW_{10}$  containing crystals has previously been reported by a selected number of authors, concrete evidence for monomeric  $PW_{10}$  species stabilized in aqueous solution has not been established. Upon addition of  $H_3PW_{12}O_{40}$  to an aqueous solution of  $K_2CrO_4$ , the hydrolysis of  $PW_{12}$  in a chromate environment induces the formation of a chromate stabilized  $PW_{10}$  species. A detailed analysis of the formation mechanism of  $K_{13}[KP_2W_{20}O_{72}]$  is presented. Substantial evidence for the existence the  $PW_{10}Cr_x$  species was obtained using  $^{183}W$  NMR,  $^{31}P$  NMR, EXAFS, SAXS and EPR spectroscopy.

Conclusion

In conclusion, a new and simple one pot synthesis route was discovered to directly form the dilacunary  $PW_{10}O_{xy}$  species, stabilized with chromate. Upon hydrolysis of  $PW_{12}O_{40}^{3-}$  heteropolyacid in an alkaline aqueous solution of chromate anions, gradual conversion of  $PW_{11}$  into a different species can be observed. While the  $^{183}W$  NMR and EXAFS provide evidence for the presence of chromate stabilized  $PW_{10}$  units, SAXS indisputably narrows the candidate species down to a monomeric  $PW_{10}Cr_x$  unit. At room temperature the initial formation of this  $PW_{10}Cr_x$  allows for the quantitative conversion of  $PW_{12}O_{40}^{3-}$  into  $K_{13}[KP_2W_{20}O_{72}] \cdot 24H_2O$  crystals, hereby opening up simple route towards  $PW_{10}$  containing products such as  $PW_{10}V_2O_{40}$  or  $[(PW_{10}Ti_2O_{38})_2O_2]^{10-}$  that are relevant to practical applications.

Reference: Chromate-Mediated One-Step Quantitative Transformation of  $PW_{12}$  into  $PW_{10}$  Polyoxometalates.

S. R. Bajpe, E. Breynaert, K. Robeyns, K. Houthoofd, G. Absillis, D. Mustafa1, T. N. Parac-Vogt, J. A. Martens1 and C. E. A. Kirschhock, 2012, 24, 3852–3858.