

**Slow Proton Exchange in Aqueous Solution. Consequences of  
Protonation and Hydration within the Central Cavity of Preyssler  
Anion Derivatives,  $[|M(H_2O)| \supset P_5W_{30}O_{110}]^{n-}$**

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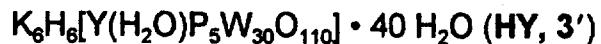
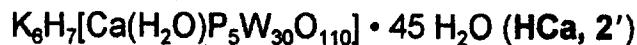
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**SUPPORTING INFORMATION**

**Table S1** Relative Intensities of -9.1- and +0.6-ppm P-NMR lines for  $[Eu(H_2O)P_5W_{30}O_{110}]^{12-}$  as a function of pH

**Table S2** Time-dependence of Relative Intensities of P-NMR lines of H/D Isotopomers of  $[Eu(H_2O)P_5W_{30}O_{110}]^{12-}$  at pD 3.6

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**Table S1** Relative Intensities of -9.1- and +0.6-ppm P-NMR lines for  $[\text{Eu}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$  as a function of pH

pH	Protonated form ( $\delta_p = -9.1$ )	Deprotonated form ( $\delta_p = +0.6$ )
2 M HCl	100	0
1 M HCl	98	2
0.5	95	5
0.73	92	8
0.81	85	15
1.5	7.5	92.5
1.74	1.5	98.5
2.84	0	100

**Table S2** Time-dependence of Relative Intensities of P-NMR lines of H/D Isotopomers of  $[\text{Eu}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$  at pD 3.6

Time (min)	$\text{H}_2\text{O}$ (0.64 ppm)	$\text{HDO}$ (0.51 ppm)	$\text{D}_2\text{O}$ (0.37 ppm)
10	65.1	28.3	6.6
40	34.1	40.1	25.8
70	17.7	32.7	49.6
100	11.0	26.1	62.9
130	4.3	17.7	78.0
160	2.4	13.8	83.8
240	1.5	7.7	90.8
280	1.5	7.7	90.8