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pH-dependent solution dynamics of a manganese(II) polyoxometalate, $[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$, and $[Mn(H_2O)_6]^{2+}$.[†]

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The aqueous reaction dynamics of the manganese(II)-functionalised Wells-Dawson polyoxometalate $[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ has been determined as a function of pH using variable temperature ^{17}O NMR, and compared with that of the well-studied monomeric manganese(II) hexa-aqua ion, $[Mn(H_2O)_6]^{2+}$. While the rate of aquo-ligand exchange on the hexa-aqua ion remains independent of pH in the range 3.2 – 6.0, the rate of water exchange of the polyoxometalate ion varies by a factor of fifteen, from $1.98 \cdot 10^7$ s^{-1} at pH 3.2 to $1.3 \cdot 10^6$ s^{-1} at pH 6.0. This decrease in rate of exchange correlates with the deprotonation of the polyoxometalate framework.

Metal oxides are important in many fields, for example as heterogeneous catalysts in industrial applications, as metal oxide clusters in enzymes, and in the form of minerals in nature, many of which are simple transition metal (hydr)oxides. As most of these are solids, one of the most important reactions that they undergo occur at the solid-solvent interface, for example in the form of interaction with water such as weathering or dissolution. Because it is often difficult to get information about reactions involving solids at a level of resolution that allows for site specific characterisation, a significant part of our knowledge about the reactivity of metal oxides and hydroxides comes from the use of discrete molecules as models.

One of the simplest classes of models is made up by the metal hexa-aqua ions, and the determination of water exchange rates on such as ions has been the subject of extensive literature.[1–4] However, ions with geminal water ligands do not adequately represent most mineral surfaces, where the aquo ligands are generally well separated, and it is thus desirable to use different ligands to modulate the coordination environment. In addition, as has been pointed out elsewhere, the literature lacks pH dependent data, even for the simplest metal aquo ions.[5]

Polyoxometalates (POMs), metal oxides comprising discrete oxide clusters of the group 5 and 6 metals in their highest oxidation states, are seeing a lot interest due to their potential in a wide range of fields, for example as catalysts, resins and drugs. They are also, however, of interest as molecular models for reactions involving water and minerals, but only the niobates have seen extensive use in this capacity and only to study the lability of framework oxygen atoms.[6–9] To the best of our knowledge, there are only two studies which have looked at the dynamics of water ligands bound to isolated metal centres in functionalised POMs. These studies looked at the water exchange reactions involving $[Co_4(H_2O)_2(B-\alpha-PW_9O_{34})_2]^{10-}$,[10,11] $\alpha\beta\beta\alpha$-$[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$,[10,11] and $[Co(H_2O)SiW_{11}O_{36}]^{6-}$,[11] using the paramagnetic nuclear magnetic resonance techniques described by Swift and Connick.[1,2,12]

We here introduce the first example of the ^{17}O NMR based[1,2] determination of the water exchange rate on a manganese(II)-functionalised POM, $Na_{15}H[\alpha\beta\beta\alpha$-$Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 70$ H_2O (see figure 1), as a function of temperature and pH, and also present the first study of pH dependent water exchange rates for the manganese(II) hexa-aqua ion. All experimental and theoretical details are provided as supporting information.

To determine the pH stability range of **1** the complex was titrated back and forth by alternating additions of acid and base. The pH stability range was found to be limited to pH 3–7 as hysteresis was observed outside this range, and a plot of the excess charge, z_e, vs pH constructed using equation S4 showed a two-proton protonation event, with a fitted pK_a of $4.4\pm0.0(2)$ (See figure 2A). UV/VIS spectroscopic data, which were acquired in the absence of background salt, likewise exhibited a pH-dependent behaviour in transitioning from a dark yellow to a paler yellow,

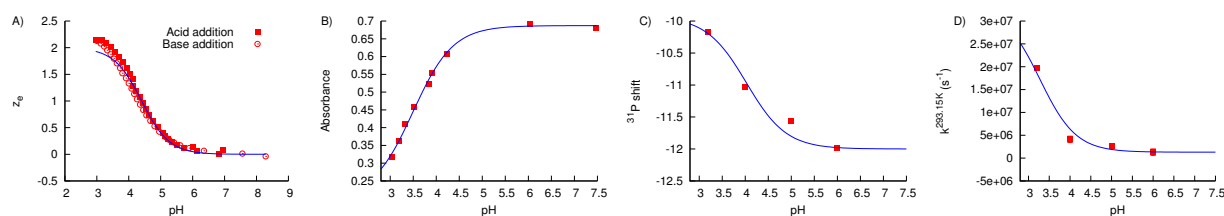*School of Chemistry, Monash University, Victoria, Australia. * E-mail: andy.ohlin@monash.edu*

Fig. 2 A) The excess charge (z_e) plot of **1** as a function of pH as the complex was titrated first with HClO$_4$ and then with NaOH. Acid addition is shown by filled squares and base addition is indicated using empty circles. The fitted line indicates the expected z_e for pK$_a$ 4.4±0.0(2). B) Absorbance at 400 nm as a function of pH. The fitted line indicates the change in absorbance with pH for pK$_a$ 3.5±0.1. C) ^{31}P NMR signal of distal phosphorus as a function of pH. The fitted line indicates the change in shift with a pK$_a$ 4.0±0.2. D) k$^{293.15K}$ as a function of pH. The fitted line is based on a simple protonation speciation model, with pK$_a$ *ca* 3.3±0.2.
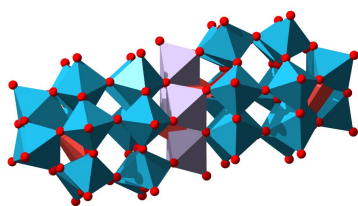

Fig. 1 Structure of αββα-[Mn$_4$(H$_2$O)$_2$(P$_2$W$_{15}$O$_{56}$)$_2$]$^{16-}$. Tungsten, oxygen, phosphorous and manganese atoms given in blue, red, orange and purple, respectively.

corresponding to weakened O-W CT,[13] on acidification, with a fitted pK$_a$ of 3.5±0.1 (fig. 2B). The ^{31}P NMR signal from the distal phosphorous centre in the ligand also showed a pH dependent behaviour with irreversible breakdown indicated below pH 3, with a pK$_a$ of 4.0±0.2 (fig. 2C). No protonation events were observed for the [Mn(H$_2$O)$_6$]$^{2+}$ ion in this range, in accordance with the reported pK$_a$ of 10.6.[14]

Note that these results differ somewhat from those of Ruhlmann *et al.*,[15] who found two pK$_a$s each for the Mn, Fe, Co, Cu, Zn and Cd derivatives of [M(II)$_4$(H$_2$O)$_2$(P$_2$W$_{15}$O$_{56}$)$_2$]$^{16-}$ at pH 3.2-3.6 and 5.0-5.6, and attributed them all to the aquo-ligands bound to the heterometal centres. We find it surprising that ions as different as Cu(II) (pK$_a$ of [Cu(H$_2$O)$_6$]2+ *ca* 7.3-8.0) and Mn(II) (pK$_a$ of [Mn(H$_2$O)$_6$]$^{2+}$ *ca* 10.6),[14] would exhibit such similar pK$_a$s solely by virtue of being complexed to the same ligand. Instead, the observed pK$_a$ is most likely associated with protonation of the polyoxotungstate ligands, as supported by the observation of two simultaneous protonation events which indicates that the two locii are identical but located distantly enough from one another that protonation at one of the sites does not affect the pK$_a$ of the other.

The rates of exchange of the aquo ligands in [Mn(H$_2$O)$_6$]$^{2+}$ and **1** were determined as a function of temperature and pH (see table 1). We took a two-fold approach to calculating the activation parameters: the first approach, method 1, was to calculate the parameters by focussing only on the region where $\frac{1}{T_{2p}} \approx P_m k_m$,[12] and the second approach, method 2, involved fitting the data using equation 1,[1] which is applicable for manganese species with negligible signal shift and a long T$_{1e}$. The chief weaknesses with the first approach is the difficulty in objectively delimiting the linear region, and, more significantly, that $\frac{1}{T_{2p}}$ is approximate to, but

not exactly equal to, $P_m k_m$. The consequence is that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are somewhat underestimated.

As T$_{1e}$ and A/h are covariant, and eq. 1 gets progressively decoupled from T$_{1e}$ as it is increased, we used the value of $1.25 \cdot 10^{-8} s$ by Ducommun *et al.* for the hexa-aqua ion rather than fitting it.[4] However, a value of $5.25 \cdot 10^{-8}$s was chosen for **1** via fitting, as there is no literature value available. See supporting information for details.

$$\frac{1}{T_{2p}} = \frac{P_m}{\frac{1}{k_m} + \frac{1}{B\left(\frac{A}{h}\right)^2}\left(\frac{1}{T_{1e}} + k_m\right)} \tag{1}$$

The rates of exchange are calculated by the difference in linewidth at 293.15 K using eq. S16. The width of ^{17}O NMR signals are well determined and fitted such that the errors in rates are almost negligible. As seen from the rate data, the exchange of aquo-ligand on the manganese hexa-aqua ion is insensitive to pH, as would be expected from the known pK$_a$ of *ca* 10.6.[14] The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are consistently lower for method 1 than 2, as would be expected from not accounting for the contribution of $\frac{A}{h}$ and T$_{1e}$. For method 2, activation parameters and $\frac{A}{h}$ are consistent with the literature.

In contrast, the rates of water exchange involving complex **1** depend strongly on pH, with a fifteen-fold increase in rate moving from pH 6.0 to pH 3.2. The change in rates with pH is consistent with the pK$_a$s determined from potentiometric titration and UV/VIS measurements, and a very crude pK$_a$ of 3.3±0.3 was obtained by fitting the rates against a simple speciation model (fig. 2D). Looking at the data from method 2, the $\Delta H^{\ddagger}$ increases somewhat with pH, whereas $\Delta S^{\ddagger}$ is constant to within error, with the exception of at pH 6.0.

It is important to note that whereas the values of absolute rates and the activation parameters vary with the method chosen to fit the data, the same trends are observed. Whereas the values from method 2 agrees better with literature – as this is the approach taken in previous studies – it is troubling that the choice of T$_{1e}$, contrary to the common perception, has a very large influence on the determined $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and A/h values for 10^{-9}<T$_{1e}$<10^{-7}s, as shown in figures S11-S12. This is a particular problem for species such as Mn(II) where the $\Delta\omega_m$ is too small to aid in the independent determination of A/h, and where the temperature stability region is limited, as in the case of **1**.

Table 1 Kinetic and rate parameters of water-exchange in [Mn(H₂O)₆]²⁺ and **1** calculated from temperature dependent ¹⁷O NMR spectroscopy at different pH

pH	$k_m^{293.15\ a}$ [$10^7 s^{-1}$]	$\Delta H^{\ddagger}$ [kJ· mol^{-1}]	$\Delta S^{\ddagger}$ [J· mol^{-1} K^{-1}]	A/h [MHz]	Reference
[Mn(OH₂)₆]²⁺					
3.2	1.34±0.02 (1.22±0.02)	35±1 (30±1)	13±4 (-6±4)	6.17±0.06	
4.0	1.65±0.02 (1.21±0.02)	37.9±1.0 (31±2)	22±3 (-4±5)	6.15±0.05	
5.0	1.38±0.02 (1.25±0.02)	35±1 (29±2)	11±4 (-11±7)	6.17±0.06	
6.0	1.86±0.02 (1.31±0.02)	33±1 (26±3)	7±5 (-20±11)	6.15±0.07	
1[b]	3.1	33.9	12.1	9.2	Swift et al.[1,2]
1-2[c]	2.1±1.7	32.9±1.3	5.7±5.0	5.3±0.5	Ducommun et al.[4]
3	2.2±0.6	32.2±0.4	3.8±1.7	5.4±0.3	Zetter et al.[16]
4.3	2.7±6.2	36.8±4.2	20.9±12.6	4.4	Grant et al.[3]
1					
3.2	1.98±0.01 (1.16±0.01)	28.1±0.8 (19±2)	-10±3 (-44±9)	3.06±0.01	
4.0	0.41±0.00 (0.38±0.00)	30±1 (20.6±0.9)	-14±4 (-49±3)	1.44 ±0.01	
5.0	0.27±0.00 (0.18±0.00)	31±2 (25±2)	-15±8 (-41±7)	1.05±0.02	
6.0	0.13±0.00 (0.11±0.00)	44±4 (41±2)	21±14 (12±7)	1.04±0.02	

Activation parameters were obtained using equation 1 (method 2). Values in parentheses were obtained by fitting only the linear region (method 1; eq. S12). ^{a}Calculated from difference in line-width at 293.15 K with and without paramagnetic ion (method 1: eq. S12; method 2: eq. S16). ^{b}[HClO₄] given as 0.1 M. ^{c}[HClO₄] given as 0.06-0.1 m.

The cause of the increase in rates of exchange with pH is not immediately clear. As discussed, the locus of protonation is very unlikely to be an aquo-ligand, but is instead on the polyoxotungstate ligand. Whether the locus is close to the Mn-OH₂ moiety and affecting the solvent shell near the aquo-ligand, or farther away and causing a change in rates solely via the decrease in charge on the polyoxotungstate ligand, is difficult to resolve. However, the observation that the pH-driven change in rates is accompanied by a change in the magnitude of the O-W charge transfer suggests the latter. It should also be noted that there are likely many protonation states of similar energies, rendering protons effectively delocalised over the ligand. An intriguing observation is the lack of pH dependence of the rates for the cobalt(II) analogue of 1, [Co₄(H₂O)₂(P₂W₁₅O₅₆)₂]¹⁶⁻,[10] in spite of the similar protonation behaviour. Without a more systematic study of the entire series of transition metal substituted clusters it is difficult to know how well the observations for monomeric aqua species in terms of associative and dissociative mechanisms translate to these highly substituted systems.[17]

Finally, it is important to note that the pK$_a$ is associated with the labilisation of **1**. Below pH 3.0, ³¹P NMR, potentiometric titrimetry and UV/VIS data all show decomposition of the molecule. However, the reversible z$_e$-plot shows unequivocally that the molecule is intact in the pH range (3.2-6.0) where the dynamic NMR study was executed, and the rate data shows that the rate of exchange of the bound water ligands increases at least fifteen-fold as the pH approaches the pK$_a$. The increase in rate can thus not be due to release of Mn(II). This behaviour, where sites in a molecule become labile to exchange as the pH is approaching the unstable regime, has recently also been demonstrated for a uranyl peroxohydroxide cluster.[18]

Conclusions

In conclusion, this study provides the results of the first pH dependent study of the exchange involving the manganese hexaaqua ion and confirmed that it is pH independent, and presents the first rate data for a manganese-containing POM. We have also re-interpreted the previously pK$_a$ values for **1**. Significantly, we have demonstrated that even protonation events that are not directly associated with bound aquo-ligands can have dramatic impacts on the lability of such ligands. These observations are important when considering the reactivity of extended metal-oxide surfaces where the reactivity of a site on one type of crystal face or kink site may have regional or global effects, and affect the reactivity of neighbouring but different types of sites.

Acknowledgements

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The NMR-determined pH-dependent water-ligand exchange rates of a Mn(II)-polyoxometalate varies by more than an order of magnitude, in contrast with those of the hexa-aqua ion.