Metalation/demetalation strategies for magnetic molecules

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Chemical control of the magnetic properties of discrete (quasi-zerodimensional) and networked molecular magnets and networks implies the need for synthesis strategies that enable fine-tuning of the number and connectivity of spin centers in such molecules. Magnetically functionalized polyoxometalates are of particular interest in this context, as these systems combine structurally versatile and robust metal oxide-based fragments with a large variety and number of spin centers (3d and 4f ions). We developed a number of methods to control the number and connectivity of these spin centers for a family of polyoxotungstate clusters. The employed approach also allows the realization of unprecedented and highly anisotropic metal coordination geometries, in turn resulting in local magnetic anisotropy.

Polyoxometalates, i.e. the nanometer-sized condensation products of the early transition metal oxoanions in their high oxidation states, constitute a class of molecular metal oxide compounds that exhibit unmatched structural and chemical versatility. As these high-nuclearity cluster anions can be functionalized by a wide range of heterometal centers that can be integrated into the parental polyoxometalate (POM) structures, these systems represent ideal archetypes for highly tuneable molecular magnets.[1] Moreover, the high structural and redox stability common to polyoxometalates also allows depositing intact molecules onto surfaces as well as generating mixed-valent magnetic systems.

However, access to these systems is currently limited by a lack of understanding of the reaction mechanisms underlying the self-organized formation of such magnetically functionalized polyoxometalates. We target to systematically elucidate these mechanisms and focused on the solution chemistry of polyoxotungstate $\{\gamma\text{-}M_2\text{-}W_{12}E\}$ Keggin complexes (M = Mn(II), Cu(II), and Fe(III); E = Si(IV), Ge(IV),...). This choice is motivated by the solubility of these clusters not only in H_2O but also in organic solvents and by an interesting solvent-induced stereochemistry on the dinuclear M_2 unit in $\gamma\text{-}Fe_2$ complexes with implications for their electronic and magnetic properties: an "in-pocket" isomer (with the two Fe centers linked by two hydroxo bridges) observed in organic solvents and an "out-of-pocket" isomer (with the two Fe

centers linked by one hydroxo bridge and no longer bound to the central SiO_4 unit) present in aqueous solution, where these units oligomerize to e.g. form a trimer,

$$[(Fe_2(OH)_3(H_2O)_2)_3(\gamma-SiW_{10}O_{36})_3]^{15-} \quad \textbf{(1)}$$
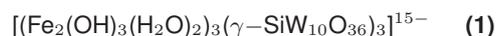
[2]. In the presence of acetate, an extensively used buffer component for aqueous solutions and also a versatile bridging ligand, a C_{2v}-symmetric acetate-bridged γ-di-iron(III) dimer,

$$[(Fe(OH)(OAc))_4(\gamma-SiW_{10}O_{36})_2]^{12-} \quad \textbf{(2)}$$

was found to form for a buffer concentration of 0.5 M CH_3COOH/CH_3COOK.[3] Probing the extent of ligand functionalization of γ-di-iron(III) complexes, we identified a higher buffer concentration (1 M), but otherwise identical synthetic conditions, to be crucial for the formation not of **(2)**, but of an unusual, open-shell diiron(III) derivative,

$$[(\beta-SiFe_2W_{10}O_{37}(OH))(\gamma-SiW_{10}O_{36})]^{13-} \quad \textbf{(3)}$$
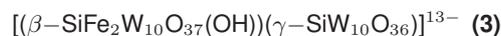
[4]. The structure of **(3)** (Fig. 1) reveals an asymmetric clam-shell-like arrangement of $\{\gamma\text{-}SiW_{10}\}$ and $\{\gamma\text{-}SiW_{10}Fe_2\}$ Keggin units connected by two Fe-O-W bridges acting as a 'hinge'. **(3)** also represents the first example of a polyoxometalate incorporating two different Baker-Figgis (rotational) isomers. The γ-Keggin unit in **(3)** incorporates two proximal ferric centers connected by a hydroxo ligand. As a result of the unusual connectivity of the two isomerically distinct units in **(3)**, the ferric centers have no terminal ligands and adopt distorted octahedral FeO_6 coordination environments with Fe-O bond lengths of 1.93–2.21 Å and *cis*-O-Fe-O bond angles of 77.6–99.2°. The structure of **(3)** is stabilized by an 8-coordinate K^+ cation located at the clam-shell opening created by the two polyanion subunits. The formation of **(3)** yielded several surprising findings:

- The facile incorporation of acetate ligands into the di-iron-POM framework observed in a 0.5 M CH_3COOH/CH_3COOK buffer is not observed at higher acetate concentrations.

- Instead of the expected structures based on "out-of-pocket" $\{\gamma\text{-}SiW_{10}Fe_2\}$ units, 1 M buffer solutions afford the formation of a lower-nuclearity Fe-POM.

One plausible explanation for this pronounced buffer

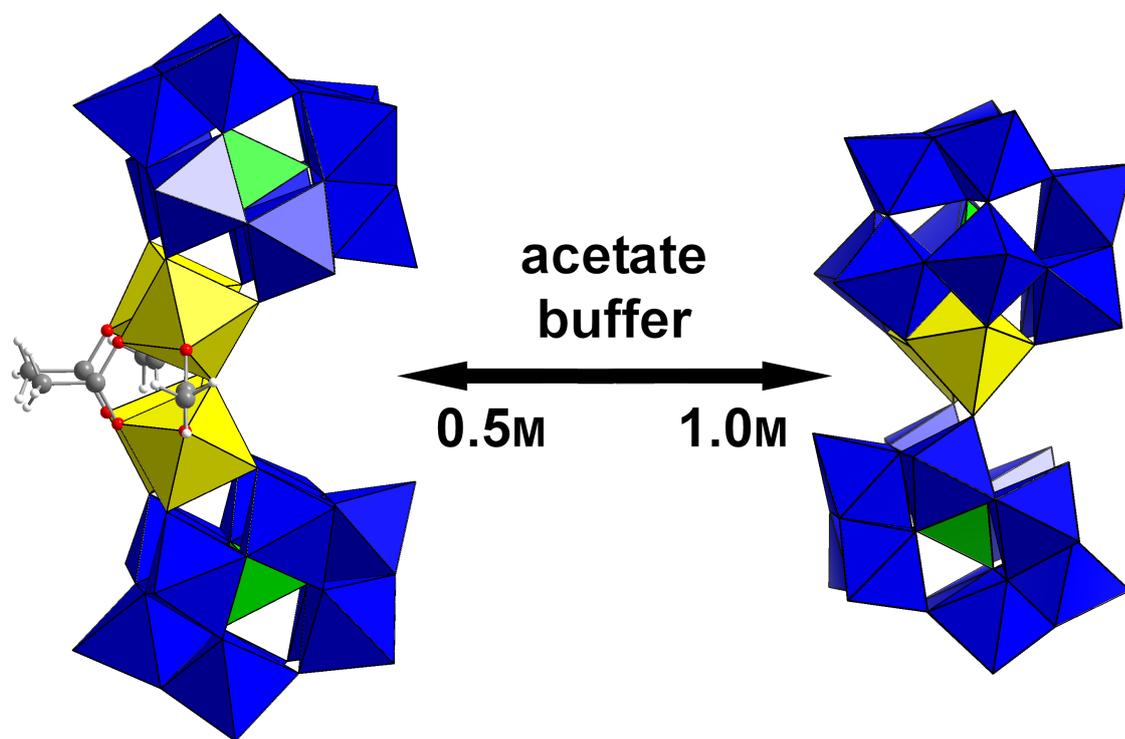FIG. 1: *Schematic metalation/demetalation reactions in aqueous solution originating from {γ-Fe$_2$W$_{10}$Si} Keggin-based structures. The concentration of acetate surprisingly represents one critical reaction parameter. W: blue, Fe: yellow, Si: green polyhedra, acetate as ball-and-stick.*

concentration effect is that in stronger buffer solutions the acetate ligands bind stronger to the ferric centers, competing with the polytungstate ligands and thermodynamically removing the Fe cations from their polytungstate coordination environment (POM demetalation). Indeed, the reaction solution from which **(3)** was isolated produces red crystals after ca. 2 weeks which were crystallographically identified as the classical tri-ferric oxo/acetato complex,

$$[Fe_3(\mu-O)(H_2O)_3(CH_3COO)_6]^+ \qquad \textbf{(4)}$$
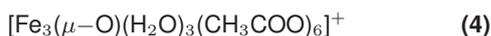
The effect of acetate on demetalation of diiron-POMs is also evidenced when the ratio of Fe(III) to [γ-SiW$_{10}$O$_{36}$]$^{8-}$ is increased (4:1 versus 2:1 used in the preparation of **(3)**). Under these conditions, **(4)** becomes the main reaction product, and no Fe-containing POMs can be obtained.

Compound **(3)** shows pronounced intramolecular antiferromagnetic exchange between the two s = 5/2 Fe(III) centers, mediated primarily by the single μ-hydroxo ligand and the O-Si-O pathway present in the γ-di-iron Keggin fragment and resulting in a singlet ground state. The low-field magnetic dc susceptibility data are very well reproduced by an isotropic spin-only Heisenberg model: employing a spin-only model for an s-5/2 dimer using a spin Hamiltonian of the type **H** = $-J$S$_1$·S$_2$, we obtain a fit for J/k_B = −44.2 K and g_{iso} = 2.01. Given the Fe-O(H)-Fe angle of 139.6° of the dominant exchange pathway, this value of J is higher than comparable interactions in similar compounds (ca. −30 K in **(1)**)[2] and thus indicates a significant contribution of the O-Si-O bridge to the antiferromagnetic coupling.

In summary, the unexpected and critical effect of acetate concentration on the formation of {SiW$_{10}$Fe$_2$}-type derivatives, a finding so far unrecognized for any other class of magnetically functionalized polyoxometalates. While the extent of acetate-driven functionalization of {SiW$_{10}$Fe$_2$} derivatives is limited to dilute acetate solutions, higher acetate concentrations lead to partial de-metalation and subsequent formation of a di-iron tungstosilicate derivative. This synthetic control by carboxylate/polytungstate ligand competition constitutes a potentially attractive approach that is currently expanded to other multi-metal polyoxometalate systems.

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