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Polyoxometalates (2)

Platinum-Containing Polyoxometalates

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In the preceding correspondence, Hill and co-workers focus on three points. They draw attention to some perceived problems with our recent paper in this journal[1] reporting the isolation and structural characterization of $[H_2Pt^{IV}V_9O_{28}]^{5-}$ (**1**); they argue that an anion, α-$[SiW_{10}Pt^{IV}{}_2O_{40}]^{8-}$ (**2**), reported earlier[2] does not exist; and they reiterate their previously published arguments in support of the platinum oxo complex, $[O{=}Pt^{IV}(H_2O)(PW_9O_{34})_2]^{16-}$ (**3**),[3] and by implication similar Pd=O[4,5] and Au=O[6] polytungstate species, which we believe have not (yet) been unambiguously characterized and independently reproduced.

We can quickly dismiss the first point. Hill et al. agree that **1** is a confirmed new polyoxoanion, but they are concerned that we did not cite earlier papers on $[MoV_9O_{28}]^{5-}$ and both isomers of $[Mo_2V_8O_{28}]^{4-}$ as precedents for "transition metal substituted decavanadate derivatives". Although Hill et al. may choose to define Mo^{VI} as a heteroatom rather than as an addendum atom, most polyoxometalate chemists would not; in fact, based on the ^{51}V NMR spectra of those compounds, the molybdenum atoms occupy sites in the $M_{10}O_{28}$ framework that are clearly addenda (i.e. with terminal Mo−O bonds). We answer criticism of the crystallography of **1**, that is, the identification and location of the protons from a difference Fourier map, by reminding Hill et al. that direct identification of proton positions in polyvanadates (rather than polytungstates, which certainly do require neutron diffraction[7] for this purpose) is well-precedented. For example the 20-year-old paper by Day and Klemperer[8] on the structure of $[H_3V_{10}O_{28}]^{3-}$ does just this, also using data collected at room temperature. The Day–Klemperer structure reveals a hydrogen-bonded dimer in the solid state very similar to that found for **1**. Note that the quality of our structure is excellent, with no disordered crystal water molecules (rare in POM crystallography). This allowed us to refine all oxygen atoms anisotropically and to add hydrogen atoms in calculated positions to establish a complete hydrogen-bonding network. This was justified as it improved the overall refinement model (R-factor, esds, etc.) significantly. The standard SHELX programs allow hydrogen atoms to be added with the program XP and with position constraints and atomic displacement restraints to chemically sensible values controlled by the AFIX command. We wonder how Hill et al. found evidence that we just used HFIX to obtain hydrogen atom positions for water molecules. We agree that it is usually desirable to have equivalent reflections, but when the resultant structure is of very high quality and has no disorder, as is this case, the need for redundant data becomes moot. Clearly, the intrinsic data quality and importantly the quality of the numerical absorption correction are sufficiently good that even though this decavanadate was substituted by the "heavy atom" Pt^{IV}, hydrogen atoms on the hydroxy groups attached to the Pt^{IV} were not only observable but refinable.

In commenting on fractional protonation (e.g. 2.5) of one of several other platinum-substituted decavanadate species peripherally reported by us,[1] Hill et al. have overlooked the fact that the formulation reported here or indeed in any crystal structure is an average over the entire crystal. Stochastic disorder and/or presence of hydrogen atoms (or other atoms) on or close to special positions will inevitably lead to fractional occupancies. Fractional occupancy of a hydrogen atom site can be derived from bond valence sum (BVS) calculations,[9] provided metal–ligand (oxygen in this case) distances and numbers are precisely and accurately determined, which requires high quality diffraction data and crystal structure analysis.

The situation with **2** is less well-resolved at present. That Hill et al. were apparently only able to isolate a salt of α-$[SiW_{11}O_{39}]^{8-}$ following the reported synthesis procedure for **2** does not prove that **2** or another Pt^{IV}-containing Keggin anion does not exist. We, for example, following the exact published synthetic procedure, have been unable to reproduce Hill's Pd^{IV} complex $K_{10}Na_3$-$[Pd^{IV}O(OH)WO(OH_2)(PW_9O_{34})_2]$;[4,5]

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does this mean that it does not exist?[10] Anion **2**, which would be important as another example of a complex containing $Pt^{IV}=O$, should at least have been cited in the paper reporting the existence of **3**.[4,5]

As described above, Hill et al. argue that they have been unable to confirm the existence of Lee's **2** but that **3** has been characterized by ten different techniques. It must be asked how many of these techniques are *independently* sufficient to confirm the presence of $Pt^{IV}=O$? The bulk of the argument must be based on unambiguous crystallography. For this reason, we decided to closely investigate the crystallographic refinements of Hill's Pt-POM, using their original XRD files (.ins and .hkl). We have found that the same structure refines even slightly better when platinum is replaced by tungsten. Furthermore, we have used disorder models of octahedral W^{VI} and square-planar Pt^{II} (Hill et al. performed the synthesis with a Pt^{II} precursor). We conclude that several occupancy models exist which are all as good (or even better) than what is proposed by Hill et al. However, none of the other nine techniques used by Hill et al. and, moreover, not all of them together, prove the existence of a $Pt^{IV}=O$ moiety in the polyanion. With some of these techniques (e.g. neutron diffraction) Hill et al. did not explore the nature of the addenda site (which is the most crucial and key to the problem), but rather the coordinated ligands (O versus OH versus H_2O). The nature of these coordinated ligands does not prove if the addenda site is platinum or tungsten (or a mixture thereof). No pre-edge and K-edge X-ray absorption spectroscopy was reported, which would have provided crucial information on the oxidation state of the platinum species.

Two possible reasons are given for non-observation of ^{195}Pt NMR signals for **3**: decomposition of **3** in solution or a "highly-distorted" platinum coordination sphere. However, if **3** decomposes in solution as suggested, then the platinum ion is no longer in a "low-symmetry environment" and hence one should be able to observe a ^{195}Pt NMR signal. The chemical shift of this signal would also be diagnostic for the presence of Pt^{II} versus Pt^{IV}. The same arguments as above also apply for ^{183}W NMR. ^{195}Pt and ^{183}W NMR are independent structural techniques which would allow establishing Hill's proposed structure (in particular, the $Pt^{IV}=O$ unit). To date, none of the other experimental techniques alone or in combination provides such evidence.

In summary, Hill et al. have been unable to reproduce the Pt^{IV} oxo Keggin ion **2** reported by some of us in 2003.[2] On the other hand, some of us have been unable to reproduce the Pd^{IV} oxo ion $[Pd^{IV}O(OH)WO(OH_2)(PW_9O_{34})_2]^{13-}$ reported by Hill and coworkers in 2005.[4,5,10]

The exceptionally well-ordered **1**, ostensibly the primary target of the preceding correspondence, is crystallographically unequivocally a Pt^{IV}–OH species. Criticism not only of the novelty of this compound as the first transition-metal-substituted decavanadate species but also of the crystallographic methodology is unfounded.

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[10] The jury is still out on this question. Our group has tried numerous times to reproduce the synthesis of this compound. The main conclusions of our efforts over the last two and a half years are: 1) No experiment following the published procedure ever resulted in a pure product, but rather in at least two to three major products in the solid state for each reaction; 2) In total, we identified five different crystalline forms; 3) We were able to perform single-crystal XRD analysis for four of them; 4) We discovered that all structures exhibited modest to serious crystallographic disorder, which, however, could be modeled and refined without any need for an "octahedral Pd^{IV}" model (see also the Supporting Information of ref. [3], page 4); and 5) One of the structures was clearly $[P_2W_{19}O_{69}(OH_2)]^{14-}$, in spite of the crystals being colored. We conclude that there is no real evidence yet for the existence of the palladium oxo compound, $K_{10}Na_3[Pd^{IV}O(OH)WO(OH_2)(PW_9O_{34})_2]$.