Polyoxometalates (1)

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Platinum-Containing Polyoxometalates**

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Lee, Kortz, and their co-workers recently reported a Pt-containing polyoxovanadate, $[H_2Pt^{IV}V_9O_{28}]^{5-}$, in this journal.[1] There are noteworthy features of this complex, and given the potential similarity of Pt- and other noble metal-containing polyoxometalates to a range of important metal-oxide supported noble-metal-based catalysts, electrodes, sensors, and other industrially significant materials, there is unquestionably interest in $[H_2Pt^{IV}V_9O_{28}]^{5-}$ and other Pt-containing polyoxometalates as possible tractable molecular representations of these materials. Nevertheless, there are some points many investigators will want to note. Lee, Kortz, and co-workers state: "Therefore, **1** $[[H_2Pt^{IV}V_9O_{28}]^{5-}]$ represents the first transition-metal-substituted decavanadate derivative…".[1] However, substituted decavanadates have been known for nearly two decades. See, for example, the work of Howarth, Pettersson, and co-workers on mono- and di-molybdopolyvanadates[2] or the study by Kamenar and colleagues on $[(CH_3)_4N]_4[H_2MoV_9O_{28}]Cl$.[3] Note that no $\{Mo_{10}O_{28}\}$ "decavanadate" analogue exists; in the Mo-substituted decavanadates (contrary to several other polyoxometalate structure types) the Mo sites thus do not constitute addenda sites but represent genuine substituents. In addition, other substituted decavanadate motifs exist: Sasaki, Pope, and co-workers, for example, refer to their complex, $[(MnV_{11}O_{31})_2O_2]^{10-}$, as "a manganese-substituted decavanadate" where "each half-unit may be dissected to reveal other familiar polyoxoanion structures, i.e., planar MnV_6O_{24} (Anderson) or MnV_9O_{28} (Mn-substituted decavanadate)".[4]

There are also some technical concerns regarding the work reported in Ref. [1]. Lee, Kortz, and co-workers claim that the hydrogen atoms (Hb7 and Hb8) on two of the oxygen atoms (Ob7 and Ob8) bound to Pt were "actually located in the difference Fourier map and refined with the O···H separations restrained to 0.85(10) Å." This is an unusual claim because hydrogen atoms on polyanion oxygen atoms bound to 5d metal centers (i.e. W or Pt) have seldom been located by X-ray analysis. The fact that the X-ray diffraction dataset was collected at high temperature ($T = 293$ K) makes this claim even more suspect. Without some independent confirmation of this claim, the community will be very skeptical about it. A single-crystal neutron diffraction study of this complex would provide such confirmation. We felt compelled to conduct a single-crystal neutron diffraction study of our terminal platinum oxo complex $[O{=}Pt^{IV}(H_2O)(PW_9O_{34})_2]^{16-}$ [5] for precisely this reason. Without such a study, knowledgeable colleagues would have rightly questioned whether that report involved a terminal platinum oxo or platinum hydroxo unit (i.e. whether there was a hydrogen on that critical oxygen atom or not). Another serious objection with regard to the crystallographic identification of hydrogen, however, is that Lee, Kortz, and co-workers state they "placed the H atoms of the water molecules in calculated positions." Of all the HFIX subroutines in SHELX, there is no command that will do this.[6]

In addition, Lee, Kortz, and co-workers report a R_{int} of "0.000" that indicates they did not collect any equivalent reflections in their data set; it is always better to have equivalent reflections, even in space group $P\bar{1}$. Moreover, they state "We also prepared derivatives of **1** with different degrees of protonation, such as $[H_xPt^{IV}V_9O_{28}]^{(7-x)-}$ ($x = 2.5$, 3, 4, 5), as shown by single-crystal X-ray analysis." How does the latter analysis show a protonation state of 2.5 in a single molecular unit? You can have fractional occupancies (such disorder, a common phenomenon, was not mentioned in the article), but you cannot have a fractional hydrogen.

Lee, Kortz, and co-workers, in reference [1] addressing our 2004 report[5] of a terminal platinum oxo compound, state we did not show ^{183}W or ^{195}Pt NMR spectra. However, these investigators do not explain why we did not report these spectra (the reason was that these investigations are not possible given the lability of the platinum oxo complex in solution), but more importantly Lee, Kortz, and co-workers fail to mention that this platinum oxo complex was characterized by 10 techniques including single-crystal neutron diffraction that confirmed a terminal platinum oxo and not a platinum hydroxo unit is present. Thus ^{183}W and ^{195}Pt NMR, the only techniques Lee, Kortz, and co-

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workers mentioned[1] in context with our 2004 terminal platinum oxo complex paper, were not needed to ascertain our reported findings in the latter paper.

Lee, Kortz, and co-workers,[1] while placing considerable emphasis on the ^{195}Pt NMR spectroscopic characterization of $[H_2Pt^{IV}V_9O_{28}]^{5-}$ (and on the absence of such a spectrum in our *Science* paper Ref. [5]), do not note the inherent limitations of ^{195}Pt NMR spectroscopy, a topic of potential value to other investigators in this area, namely that such spectra are usually only observed for highly symmetric Pt^{II} and Pt^{IV} environments. Lee, Kortz, and co-workers note that the Pt site in $[H_2Pt^{IV}V_9O_{28}]^{5-}$ is highly symmetrical, but the connection between the Pt coordination geometry and the observance of a ^{195}Pt NMR resonance signal is not made. Unfortunately, key references noting this limitation of ^{195}Pt NMR are missing;[7–9] Tourné et al. note "the ^{195}Pt NMR signal [in $[WZnPt_2(ZnW_9O_{34})_2]^{12-}$] is considerably broadened and difficult to observe".[9] Furthermore, Lee, Kortz, and co-workers speculate that there should be "strain" at the Pt site of the $M_{10}O_{28}$ structure. They may want to note that Nyman et al. rationalized this very impact of metal-ion substitution in the decavandate structure (specifically the energetics of two Ti^{4+} centers substituted in isostructural $Nb_{10}O_{28}$).[10]

Far more importantly, Lee, Kortz, and co-workers make several statements with far-reaching implications in putting their work into the context of previous research on late-transition-metal-containing polyoxometalates, quoting: "In 2003 the Lee group also reported on the Pt^{IV}-containing Keggin ion α-$[SiPt^{IV}{}_2W_{10}O_{40}]^{8-}$, which represents the first late-transition-metal oxo complex. In 2004 Hill and co-workers reported the Pt^{IV}-containing Knoth-type tungstophosphate dimer $[O{=}Pt^{IV}(H_2O)(PW_9O_{34})_2]^{16-}$, but no ^{183}W or ^{195}Pt NMR spectra were shown." We use the adverb "importantly" because terminal oxo compounds of the late-transition-metal elements, including Pt, were unknown prior to the recent research despite many attempts since the 1960s to produce them.[5,12–14] Furthermore, terminal metal oxo species exhibit the only multiple noble-metal–oxygen bonds and such species should not exist based on electronic structure arguments.[5,13,14] In contrast, the Pt center in $[H_2Pt^{IV}V_9O_{28}]^{5-}$ reported in Ref. [1] is a conventional and well-precedented coordination environment for Pt with all single bonds to oxygen.

There are five strong indicators that the first putative terminal platinum oxo compound reported by Lee and coworkers in 2003 in *Acta Crystallogr. Sect. C*[11] (cited as reference [12] in reference [1]) the (guanidinium)$_8$ salt of "α-$[SiPt^{IV}{}_2W_{10}O_{40}]^{8-}$" (henceforth $\{SiPt_2W_{10}\}$) almost certainly represents an incorrect assignment and is actually the guanidinium salt of α-$[SiW_{11}O_{39}]^{8-}$ ($\{SiW_{11}\}$). First, the infrared spectra of the crystalline guanidinium salts of $\{SiPt_2W_{10}\}$ prepared using the exact published procedure of Lee et al.,[11] and $\{SiW_{11}\}$ are identical (Figure 1 a). In addition, the peaks of $\{SiW_{11}\}$ [992(s), 940(s), 868(s), 794(s), 725(s), 520(s)] are almost identical to the values reported by Lee et al. for $\{SiPt_2W_{10}\}$ [994(s), 938(s), 871(s), 794(s), 727(s), 520(s)].[11] Second, the infrared spectrum of (guanidinium)$_4[SiW_{12}O_{40}]$ (Figure 1 b), a complex far closer in symmetry and consequently in vibrational spectroscopic features to the supposed $\{SiPt_2W_{10}\}$ than to $\{SiW_{11}\}$, is dramatically different. Third, the eight guanidinium countercations reported by Lee et al. are fully consistent with (guanidinium)$_8$-$[SiW_{11}O_{39}]$. Fourth, the energy-dispersive X-ray-fluorescence (EDXRF) elemental analysis data provided by Lee et al. for Pt and W are not adequate to determine a Pt to W ratio.[15] Indeed, their elemental analysis (EA) data for C, N, and H only (no EA data for Si, Pt, and W were reported by Lee et al.) are closer to the values calculated for (guanidinium)$_8[SiW_{11}O_{39}]\cdot 2\,H_2O$ than

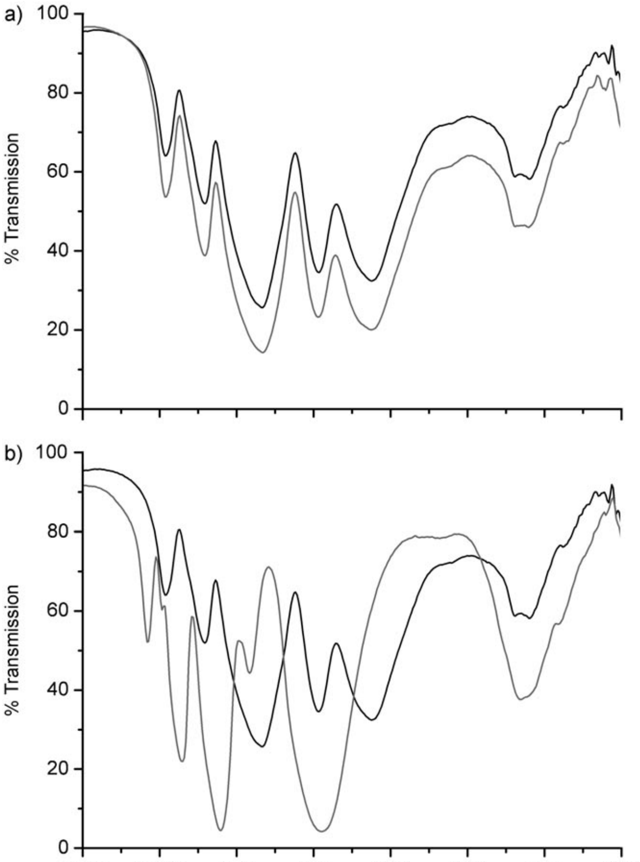

Figure 1. Comparison of IR spectra in the range relevant to metal oxygen vibrational modes. The black line is the spectrum of the material produced by following the published synthesis in *Acta Crystallogr. Sect. C*.[11] In (a) the gray line is authentic (guanidinium)$_8[SiW_{11}O_{39}]$; in (b) the gray line is authentic (guanidinium)$_4[SiW_{12}O_{40}]$ as prepared by literature methods.[16]

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those calculated for (guanidinium)$_8$[$SiPt_2W_{10}O_{40}$]·2H_2O. Fifth, the exact synthesis procedure of Lee et al.[11] results in a very weakly colored compound; whereas, the platinum oxo polytungstate, $[O{=}Pt^{IV}(H_2O)(PW_9O_{34})_2]^{16-}$, is darkly colored as mandated by the electronic transitions in such a complex.[5]

In summary, our $[O{=}Pt^{IV}(H_2O)(PW_9O_{34})_2]^{16-}$[5] is the only genuine terminal platinum oxo complex reported to date (although a second example by Milstein's group has just been reported online).[17] Unlike {$SiPt_2W_{10}$},[11] our $[O{=}Pt^{IV}(H_2O)(PW_9O_{34})_2]^{16-}$[5] species was characterized by 10 different techniques and used neutron diffraction in addition to X-ray diffraction to confirm both the Pt coordination polyhedron and the lack of hydrogen on the platinum oxo oxygen atom. Our group has used 10, 15, and 17 techniques in reporting the first terminal oxo complexes of Pt, Pd and Au, respectively,[5,13,14] making these some of the most thoroughly and carefully studied complexes in the literature. This thoroughness was necessary for our late-transition metal oxo compounds because such compounds have resisted major synthetic efforts for years and defy simple explanation based on accepted bonding paradigms. Thus reports of such complexes require a commensurately compelling set of experiments to prove their existence and verification by other groups is helpful.[18] Given the possible relevance of these compounds to industrially useful materials including, but not limited to, catalysts, polyoxometalates containing Pt and other noble metals, including those reported by the Lee and Kortz groups, are and will be of considerable consequent interest.

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[15] There are two reasons for this: 1) The weighted average for their L-shell electrons differs by 1.0 keV for alpha and 1.3 keV for beta excitations. Given that the average width of the peaks at baseline is almost always over 1 keV for both solid and liquid samples, it is unlikely the two signals could be properly resolved for quantitative purposes; and 2) Lee et al. used a calibration curve spanning a 50000 ppm range. This is well beyond the linear range for these elements (a typical value is 1000 ppm but can be as high 10000 ppm with very well behaved samples and using a helium purge).

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