The Oxo Wall Prevails: Investigations of an Example of Pathological Science

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Transition metal oxo complexes are involved in, or believed to be involved in, many oxygen transfer reactions, such as those carried out by cytochrome P450 enzymes.[1-4] Terminal oxo complexes of the early transition metals are ubiquitous, and some are stable to concentrated acid solutions. However, there are very few reports of isolated terminal oxo complexes of the late transition metals.[5] In 1962, Ballhausen and Gray developed a molecular orbital diagram from the vanadyl ion, $VO(OH_2)_5^{2+}$, for tetragonal transition metal complexes containing a terminal oxo ligand. Based on this molecular orbital diagram, they proposed that terminal oxo ligands will not exist for transition metals with a d-electron count greater than five in a tetragonal ligand field. In fact, no tetragonal terminal oxo complexes or their isoelectronic imido analogs have been isolated for any transition metal from group 9 onwards. This phenomenon is referred to as the oxo wall.[5,6]

In 1993, Wilkinson et al. synthesized the first isolable late transition metal terminal oxo complex, $Ir(O)(mes)_3$.[7] The Ir atom in this d^4 Ir(V) complex is in a trigonal, not tetragonal, ligand field and therefore does not violate the oxo wall. Since then, there have been reports of a d^6 distorted square planar Pt(IV) oxo in 2008 and a d^8 linear Ni(II) imido complex in 2011.[8,9] None of these complexes violate the oxo wall.

Figure 1: The oxo wall divides group 8 and group 9.[13]

Between 2004 and 2007, Hill et al. reported the synthesis and characterization of air-stable Pt(IV) oxo, Pd(IV) oxo, and Au(III) oxo complexes, which were formulated as $K_7Na_9[Pt(O)(OH_2)(PW_9O_{34})_2]\cdot21.5H_2O$, $K_{10}Na_3[Pd(O)(OH)WO(OH_2)(PW_9O_{34})_2]$, $K_{15}H_2[Au(O)(OH_2)(PW_9O_{34})_2]\cdot25H_2O$, and $K_7H_2[Au(O)(OH_2)P_2W_{20}O_{70}]\cdot27H_2O$.[10-12] These complexes utilized clamshell polyoxotungstate ligands, placing the late transition metal in a tetragonal ligand field. All of these complexes violate the oxo wall. The authors used between nine and fifteen techniques to characterize these complexes and often performed duplicate or triplicate analyses to confirm their results.[10-12]

Earlier this year, Hill et al. retracted these papers and published a reinterpretation of the data they collected, explaining how the data had been misinterpreted. The authors reformulated the Pt(IV) and Au(III) complexes as their W(VI) analogs, and they proposed that the Pd(IV) complex contains a domed, square planar Pd(II) center without a terminal oxo or hydroxo ligand.[13]
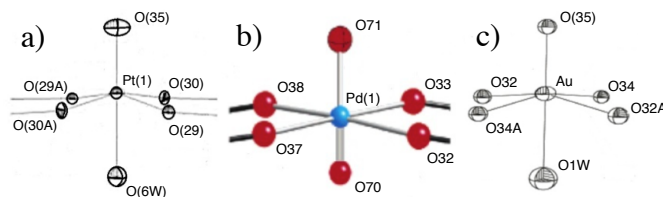

Figure 2: Local environments of a) Pt(IV) oxo complex,[10] b) Pd(IV) oxo complex,[11] and c) Au(III) oxo complexes.[12] The local environment of both Au(III) oxo complexes is nearly identical.

Hill et al. based their initial formulations mostly on the X-ray and neutron diffraction data. Errors in the data processing led the authors to believe these compounds were bona fide late transition metal oxo complexes. Upon investigating the parameters they used to initially process

the neutron diffraction data for the Pt(IV) complex, the authors discovered they had used a site occupancy of 0.50 for the Pt, although their originally published article claimed that the platinum atom had full occupancy. Half of the Pt scattering length (9.60 fm) is approximately the W scattering length (4.86 fm), which explains why the W atom actually present in the crystal could be successfully (though incorrectly) refined as a half Pt atom. The Pd(IV) complex suffered from disorder in which the Pd atom is replaced by two K atoms; this disorder was modeled incorrectly under the unwarranted assumption that a terminal oxo ligand was present. The Au(III) complexes were incorrectly refined with mixed (i.e. W and Au) occupancy at the "Au" sites, but Hill et al. now report that the data sets refine well if the site occupancy is assumed to be 100% W.[13] Hill et al. published new data in a retraction paper that support the new formulations of the complexes.[13] However, there are still discrepancies between this retraction paper and the original papers. If the data from the original papers are genuine and only the identities of the complexes were mistaken, then the data from the original papers should be consistent with the current formulations. In some cases (e.g. ^{17}O NMR studies and elemental analyses), they are not.

^{17}O NMR spectra were collected for the supposed Pd(IV) complex and its W(VI) analog. Peaks at δ 330 and 570 were assigned to Pd-OH and Pd=O, respectively, due to their absence in the ^{17}O NMR spectrum of the W(VI) analog.[11] ^{17}O NMR spectra were collected for both Au(III) complexes. A peak at δ 590 was assigned to Au=O for one complex and a peak at δ 605 was assigned to Au=O for the other complex based on the Pd=O chemical shift from the previous paper.[12] In the retraction paper, Hill et al. claim that the peak at δ 570 in the ^{17}O NMR spectrum of the Pd(IV) complex is due to $[PdPW_{11}O_{39}]^{5-}$, a suspected decomposition product. The origin of the peak at δ 330 is still unexplained.[13] The peaks at δ 590 and 605 in the ^{17}O NMR spectra of the Au(III) complexes are proposed to be due to $[PW_{11}O_{39}]^{7-}$, a decomposition product with Keggin-type structure.[13]
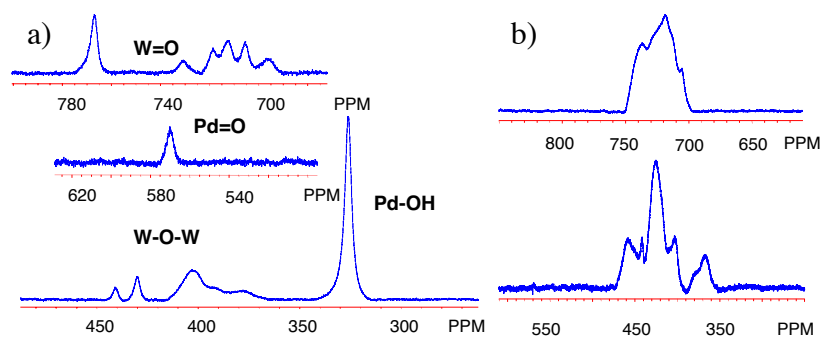

Figure 3: a) ^{17}O NMR spectrum of the palladium(IV) complex.
b) ^{17}O NMR spectrum of the tungsten(VI) analog.[11]

Hill et al. titrated the second Au(III) complex with PPh_3 to study oxygen transfer of the complex and observed the disappearance of the peak at δ 605 in the ^{17}O NMR spectrum.[12] In the retraction paper, they claim that the PPh_3 is actually reacting with $HAuCl_4$ and H_2O.[13] The reinterpretation does not attempt to explain the disappearance of the peak at δ 605 in the original paper. These are but a few of the inconsistencies between the original papers and the retraction paper.

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