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Communication

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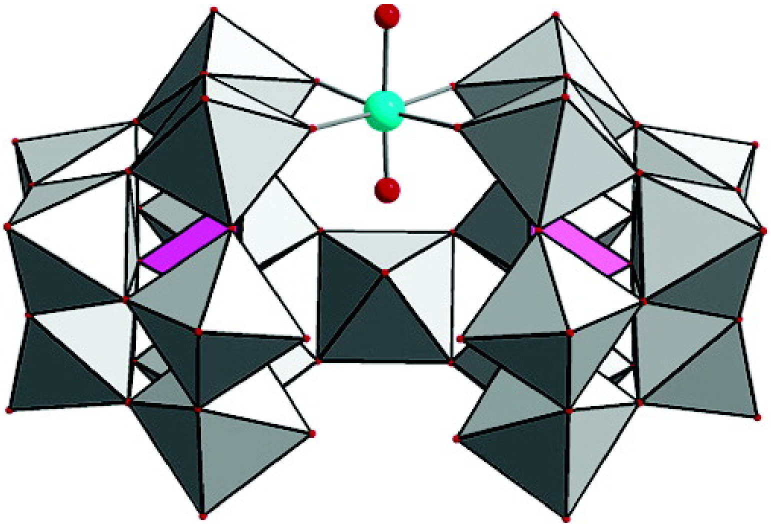

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A Palladium-Oxo Complex. Stabilization of This Proposed Catalytic Intermediate by an Encapsulating Polytungstate Ligand

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Terminal oxo complexes of the late-transition-metal elements have been proposed as possible intermediates for oxidations catalyzed by these elements and in technologies where these elements encounter O_2 or other oxidants. Despite considerable progress in late-transition-metal−ligand multiple bond chemistry,[1] no high d-electron count late-transition-metal-oxo complexes were known until the recently reported Pt-oxo complex $K_7Na_9[Pt^{IV}O(OH_2)(PW_9O_{34})_2]$ (**1**),[2] because high d-electron counts destabilize the metal-oxo unit.[3−6] Pt-oxo species may well be key intermediates in functioning automobile catalytic converters, fuel cell electrodes, and Pt catalysts for O_2-based green organic oxidations.[7] A Pd-oxo complex would also be unprecedented and relate to significant Pd-based catalytic chemistry and technology (supported Pd-based catalytic converters and oxidation catalysts).[7] We now report a very unique Pd-oxo compound, $K_{10}Na_3[Pd^{IV}O(OH)WO(OH_2)(PW_9O_{34})_2]$ (**2**). This complex, prepared by a route altered from that for **1**, has a structure quite distinct from that of **1**.

The reaction of Pd(II) (from $PdSO_4$) with $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ in 0.25 M sodium acetate/0.25 M acetic acid (pH = 4.9) yields the kinetically precipitated (with KCl) product $[Pd^{II}_3(PW_9O_{34})_2]^{12-}$. This complex undergoes a rapid, stepwise loss of Pd(II) in acidic media to form $[Pd^{II}WO(OH_2)(PW_9O_{34})_2]^{12-}$, based on ^{31}P and ^{183}W NMR studies performed by Knoth and co-workers on the Zn(II) analogue.[8] In the final step, Pd(II) is oxidized by O_2 to give the final product $K_{10}Na_3[Pd^{IV}O(OH)WO(OH_2)(PW_9O_{34})_2]$ (**2**).[9]

Crystallographic studies of **2** establish that the Pd center is coordinated by a tetradentate, clam shell-like polytungstate $[P_2W_{19}(OH_2)O_{69}]^{14-}$ ligand that defines a square equatorial plane (Figure 1).[10] A very short axial Pd═O bond is trans to a Pd−OH bond. The oxo moiety is located in a sterically protected cavity between two $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ units that are fused together by a single $[WO(OH_2)]^{4+}$ center. The Pd atom is displaced out of the O_4 equatorial plane (into the central cavity) by 0.10 Å.[11a] A total of 13 countercations were located by X-ray crystallography and confirmed by duplicate elemental analyses.[9] Anions other than **2** are clearly absent in the lattice (and the absence of Cl^- was confirmed by elemental analyses), consistent with the +4 oxidation state of Pd and an overall charge of −13 on the molecule. In addition, the diamagnetism of **2** (based on room-temperature magnetic susceptibility measurements and ^{31}P NMR) argues for a d^6 Pd(IV) and against a d^8 Pd(II) or d^4 Pd(VI) (for a local C_{4v} metal center).[12] There are two lines of evidence for OH^- as the ligand trans to the oxo unit. First, the 1.99(2) Å bond length is more consistent with a Pd−OH bond than Pd═O or Pd−OH_2 bonds. Second, elemental analyses and X-ray crystallography establish that the overall charge of the molecule is −13.[11b]

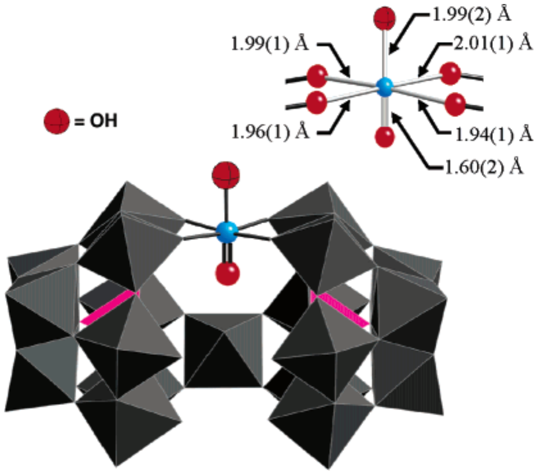

Figure 1. Combination polyhedral/ball-and-stick representation of **2**. The WO_6 and PO_4 polyhedra are shown in gray and pink, respectively. The Pd and O atoms are shown in light blue and red, respectively. The bond distances given are for the 173 K data set and are slightly different for the 30 and 90 K data (see Table S2 in the SI for details).

Three data sets of **2** (collected at 30, 90, and 173 K) indicate that the Pd═O bond length is 1.60−1.63 ± 0.03 Å.[10] The final R values for $I > 2\sigma(I)$ are in close agreement with those for which all intensities are considered, and there is no positional disorder (including O═Pd−OH/OH−Pd═O disorder). However, the oxo and hydroxo ligands coordinated to Pd could only be refined at 50% occupancy (rather than the customary 100%).[13a]

The unprecedented and controversial nature of the title claim, a Pd-oxo unit,[13b] combined with the uncertainty from the collective X-ray structures argue strongly that an independent unequivocal structural method is needed to assess the Pd-oxo distance. This is true despite the fact that ^{31}P NMR and elemental analysis data suggest that only **2** is present in the unit cell. In this context, we provide Pd *K*-edge extended X-ray absorption fine structure (EXAFS)[14a] data that address both the crystallographic disorder and the unusually short Pd═O bond distance.

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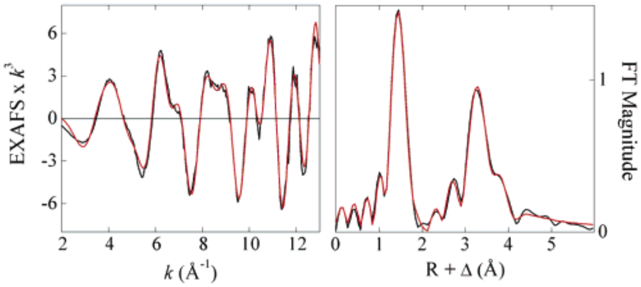

Figure 2. Pd *K*-edge EXAFS spectra (left) and the corresponding nonphase shift corrected Fourier transform magnitudes (right) for **2**: black line, experimental data; red line, best fit.

The k^3-weighted EXAFS data for **2** and the corresponding Fourier transform are shown in Figure 2. Theoretical phase and amplitude parameters for the fit were generated by FEFF,[14b] using the crystallographic parameters of **2** for the initial model. The best fit is obtained with five Pd−O bond distances of 1.96 ± 0.03 Å and one Pd−O bond distance of 1.68 ± 0.03 Å (see Table S3 in the SI). Therefore, the EXAFS data support the crystallographic conclusions (i.e., a Pd−O bond distance of 1.60−1.63 ± 0.03 Å) within experimental error, despite the disorder (occupancy) problems that adversely affect the precision of the X-ray diffraction results.

Finally, ^{17}O NMR experiments run on an enriched[15a] sample of **2** suggest the solid-state structure is maintained in solution. Two peaks at 330 and 570 ppm (relative to D_2O at 0 ppm) are attributable to the hydroxo and oxo ligands of Pd, respectively. The two peaks are assigned based on the established correlation between downfield chemical shift and oxygen π-bond order[15a] and the fact that they are not observed in the isostructural complex $[(WO(OH_2))_2(PW_9O_{34})_2]^{10-}$ (see Figure S4 in the SI).[15b]

In conclusion, a long-proposed but previously unknown Pd-oxo unit has now been prepared and fully characterized. An important implication of the isolation and characterization of a second structural family of high d-electron count late-transition-metal-oxo complexes is that **1** and **2** are not unique but rather are the first two members of a previously unrecognized class of coordination complexes.

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Supporting Information Available: CIF for **2** (combined for data collected at 30, 90, and 173 K), synthesis and spectroscopic data, Pd *K*-edge EXAFS data and interpretation, CASSCF calculations and electrochemistry (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Analytical data: IR (2% KBr pellet, 1200−400 cm^{-1}): 1089 (m, sh), 1076 (s), 1018 (s), 945 (m), 921 (m), 783 (m), 700 (m), 594 (m), 521 (m), 445 (w), and 413 (w). ^{31}P NMR (5 mM solution in D_2O): −11.7 ppm ($\Delta\nu_{1/2} = 7$ Hz). See the SI for electronic absorption data. Anal. Calcd for **2**: K, 7.03; Na, 1.24; P, 1.11; Pd, 1.91; W, 62.8. Found (average): Cl, <0.01; K, 6.92; Na, 1.25; P, 1.15; Pd, 1.91; W, 62.6. [MW = 5565 g/mol].

(10) Crystal data for **2**: Triclinic space group $P\bar{1}$, dark red efflorescent crystal with $a = 11.8734(15)$ Å, $b = 17.225(2)$ Å, $c = 22.814(3)$ Å, $\alpha = 90.536(2)°$, $\beta = 103.247(2)°$, and $\gamma = 108.671(2)$ Å, and $Z = 2$ (173 K data set). The data were collected on a Bruker D8 SMART APEX CCD sealed-tube diffractometer with Mo Kα (0.71073 Å) radiation ($T = 173(2)$ K, 90(2) K, and 30(2) K). At final convergence R1 = 5.71% and GOF = 1.202 based on 21 214 reflections with $F_o > 2\sigma F_o$ (for the 173 K structure). The final R1 (GOF) values for the 90 K and the 30 K structures were 7.83% (1.026) and 5.80% (1.083), respectively, based on 19 071 reflections for the 90 K structure and 20 284 reflections for the 30 K structure. See Table S1 (in the SI) for more information.

(11) (a) There is crowding around the Pd═O unit from O69 (a terminal oxo (from W19) located 2.57 Å from O70) and K10 (a countercation located 2.35 Å from O70). See Figure S1 for the numbering scheme. (b) Additional evidence for OH^- as the ligand trans to the oxo unit is provided by titration studies; see Figure S2 in the SI.

(12) Cyclic voltammetry data are included in the SI. A reduction peak potential for **2** is observed at $E_{pc} = -0.47$ V (versus SCE), a value substantially more negative than that observed for Pd(II) alone (i.e., a solution prepared from $PdSO_4$) ($E_{pc} = -0.28$ V versus SCE). In addition, **2** also displays a larger current intensity (at equal concentrations) than Pd(II) alone. This is attributed to the larger number of electrons involved in its reduction (relative to Pd(II)). The number of electrons involved in the exhaustive reduction of the Pd center in **2** (at −0.45 V versus SCE) and in Pd(II) alone (at −0.32 V versus SCE) was determined by controlled potential coulometry and confirmed to be four and two, respectively.

(13) (a) Refinement of the oxo and hydroxo ligands of Pd at 50% occupancy could imply that there is a mixture of four-coordinate Pd(II) and six-coordinate Pd(IV), but all other data suggest the sample is chemically homogeneous. (b) A reviewer states: "Such extraordinary claims require extraordinary evidence." We concur.

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