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Metal Oxo Complexes

NMR Spectra of Terminal Oxo Gold and Platinum Complexes: Relativistic DFT Predictions**

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Transition metals that have a high d-electron count do not easily form terminal oxo complexes, as the metal valence electrons tend to repel those of the oxo ligand. Indeed, until recently, very few such complexes (of Ir^V, Fe^{IV}, and Re^I) were known.[1] Complexes with late-transition and post-transition elements such as Pd, Pt, and Au are proposed to be reactive intermediates in oxidation reactions catalyzed by noble metals. After some inconclusive studies were reported by other research groups,[2] Lee et al. reported the crystal structure of the polyoxometalate (POM) α-$[SiPt_2W_{10}O_{40}]^{8-}$,[3] for which terminal oxo Pt=O bonds were claimed, although positional disorder did not allow for an accurate location of the Pt atoms.

Hill and co-workers have reported Pt^{IV},[4] Pd^{IV},[5] and Au^{III} [6] oxo POMs. The bonding arrangements of Pt, Pd, and Au in the solid state were similar, and feature a linear $[O{=}M{-}OH_2]^{n+}$ moiety embedded in the polyoxotungstate framework with a relatively short (1.6–1.8 Å) M=O bond and a longer (2.0–2.3 Å) M−OH_2 bond. Lee, Kortz, and coworkers provided crystal structures for $[PtM_6O_{24}]^{8-}$ (M = Mo, W)[7] and $[H_2PtV_9O_{28}]^{5-}$,[8] where no Pt-oxo bond was claimed.

Shortly thereafter, the two research groups challenged each other's contentions on the characterization of the respective structures by NMR spectroscopy.[9] Thus, whereas the ^{51}V and ^{195}Pt NMR spectra of $[H_2PtV_9O_{28}]^{5-}$ were consistent with the crystal structure, in the case of oxo Pd, Pt, and Au POMs, the ^{183}W and ^{195}Pt NMR spectra failed to yield any information.[4–6] For the Pd and Au complexes, ^{31}P and ^{17}O NMR spectra were obtained. However, the ^{31}P NMR signals span a narrow range of frequencies and their use for structure elucidation is questionable.

Milstein and co-workers reported a pincer-type Pt^{IV}-oxo complex,[10,11] the ^{195}Pt NMR spectrum of which was consistent with the proposed structure. However, the lack of any reference data calls for some caution; furthermore, a crystal structure be could not be obtained.

Both studies[6,10] indicate a diverse reactivity with facile oxygen transfer to other substrates. However, terminal oxo POMs cannot be characterized in solution by using established NMR techniques. Heteronuclear magnetic resonance is often fraught with technical difficulties: 1) without prior knowledge, it may be difficult to locate the signals of interest; 2) for ^{195}Pt and ^{183}W NMR spectroscopy, chemical shift anisotropy (CSA) may lead to broad lines,[12–14] but is well-documented only for ^{195}Pt. Thus, there seem to be unexplained features that render NMR spectroscopic characterization elusive.

Numerous studies have demonstrated the capability to predict the NMR properties of heavy-atom nuclei by means of relativistic density functional theory.[15–21] Herein, we present computational results that concern the electronic structure of terminal oxo Pt and Au complexes and their ^{17}O, ^{195}Pt, and ^{183}W NMR spectra.

We have investigated Kortz's Pt decavanadate $[H_2PtV_9O_{28}]^{5-}$ (PtV9);[8] Milstein's pincer complex $[Pt(O){-}PCN]^+$ (PtO−PCN), where PCN is the tridentate ligand $C_6H_3[CH_2P(tBu)_2](CH_2)_2N(CH_3)_2$;[10] Hill's terminal oxo POM $[P_2W_{20}O_{70}Au(O)(OH_2)_3]^{9-}$ (P2W20Au),[6] its lacunary ligand $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ (P2W20),[22] and the isostructural $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ (P2W21)[23] (Figure 1 and Scheme 1).

We firstly computed the HOMO–LUMO gaps (ΔE; HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) at the spin-orbit (ZSO) level, since for P2W20Au, self-consistent field (SCF) convergence could not be achieved in calculations at the scalar level (ZSC), owing to the extremely small ΔE value (see below). On the other hand, inclusion of spin-orbit coupling is associated with a lower orbital symmetry, which allows for a greater flexibility in the SCF.

PtV9, P2W21, and P2W20 have $\Delta E = 1.5$–2.0 eV; most POMs have $\Delta E = 2$–3 eV.[24,25] For PtO–PCN, ΔE is substantially smaller (0.40 eV); however, the complex is prepared in the presence of donor molecules (water, acetone),[10] which may bind to Pt ($\Delta E = -5.0$ and -5.5 kcal mol^{-1}, respectively, without vibrational corrections). In such adducts, ΔE rises to 1.1–1.2 eV.[26] For P2W20Au, ΔE is only 0.03 eV.

In PtV9, the HOMO is localized over the PtO_6 unit, and the LUMO delocalized over the entire framework, with hardly any contribution from Pt. PtO−PCN features both frontier molecular orbitals (FMOs) localized on the Pt=O bond. However, in solvent-coordinated species, the LUMO becomes strongly delocalized onto the solvent. In P2W20Au both FMOs are largely localized on the Au=O fragment and W(3i) (Figure 2 and S1 in the Supporting Information).

The extremely small ΔE value implies very low-lying excited states and a facile switch between nucleophilic and

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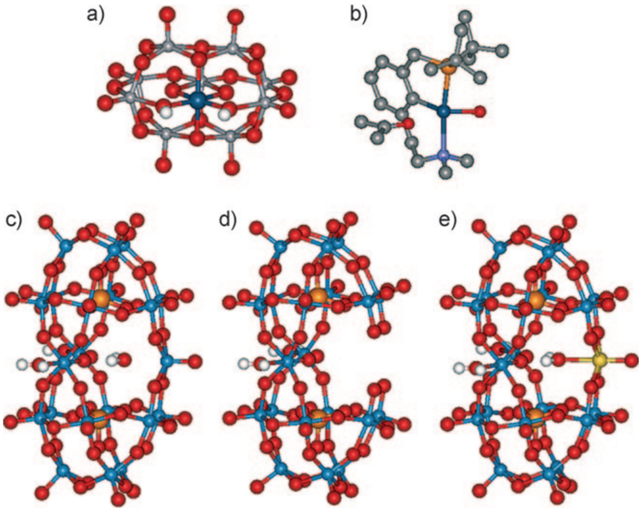
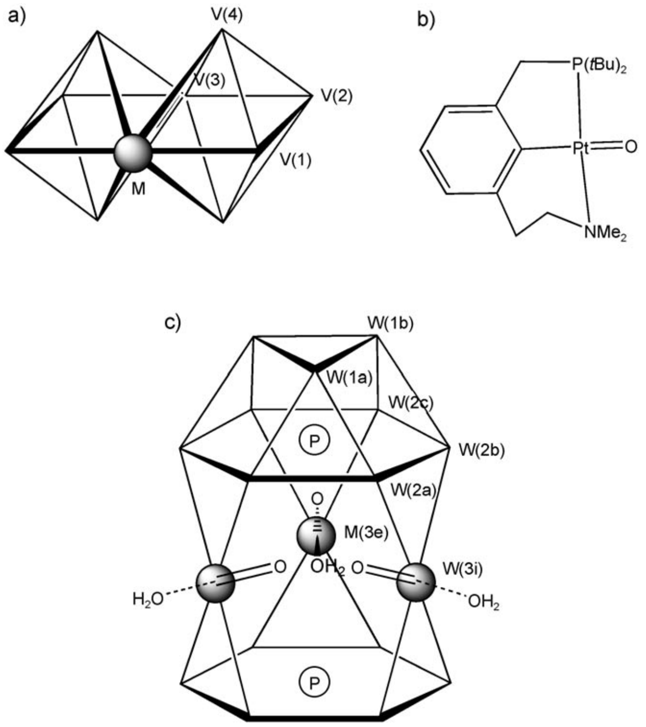


Figure 1. Ball-and-stick representations of a) $[H_2PtV_9O_{28}]^{5-}$; b) $[Pt(O)(Me_2CO)-PCN]^+$; c) $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$; d) $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$; e) $[P_2W_{20}O_{70}Au(O)(OH_2)_3]^{9-}$. Au yellow, Pt dark blue, W cyan, V light gray, P orange, O red, N blue, C gray, H white. In (b) hydrogen atoms are omitted for clarity; the optimized Pt=O distance is 1.83 Å with any donor molecule (compare with 1.81 Å in Ref. [10]).



Scheme 1. Structures of a) PtV9; b) PtO–PCN; c) P2W20M (lower part omitted for clarity); M(3e) is W (P2W21), absent (P2W20), or Au (P2W20Au).

electrophilic traits, and accounts for their high and diverse reactivity and difficulty in synthesis and storage.[4–6,10] Apparently, reversible solvent coordination may stabilize PtO–PCN without hindering its reactivity, whereas no such balance is possible for P2W20Au.

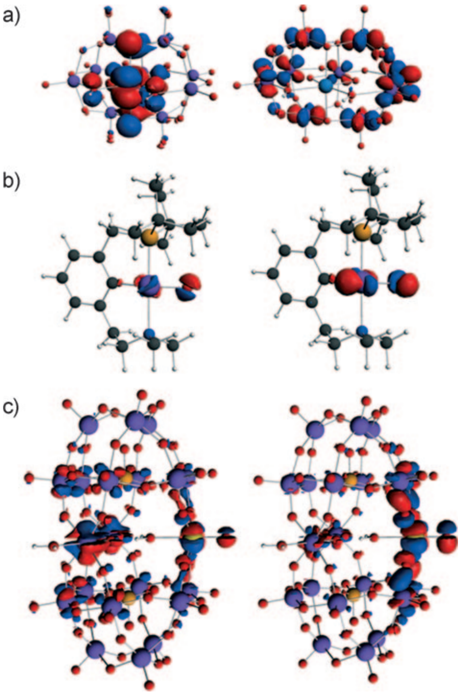


Figure 2. HOMO (left) and LUMO (right) of a) PtV9; b) PtO-PCN; c) P2W20Au.

The entire known range of ^{195}Pt chemical shifts was successfully modeled by calculations at the spin-orbit (ZSO) level (Figure 3 and Table S2 in the Supporting Information). The signal of "naked" PtO–PCN deviates from the correlation line by some 4000 ppm; however, when water or acetone are coordinated to Pt, the calculated shift fits with the correlation, and the computed $^1J(\mathrm{Pt,P}) = 2600–2800$ Hz matches the experimental value (2686 Hz). Similar major solvation effects are known in ^{195}Pt NMR.[19]

The structure of PtV9 (C_{2v}) exhibits three distinct Pt–O bonds (1.982, 2.023, and 2.071 Å), which are consistent with

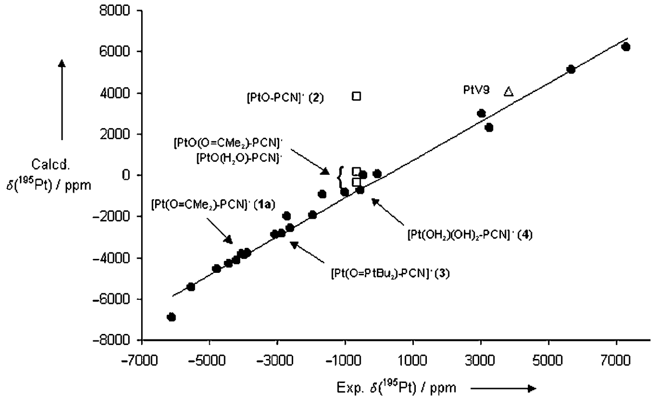


Figure 3. Correlation between experimental and calculated ^{195}Pt NMR chemical shifts. Filled circles: shifts of calibration compounds (see Supporting Information for details). Empty squares: PtO–PCN with molecules coordinated to Pt. Empty triangle: PtV9. Pt pincer complexes are described as in Ref. [10].

those of the optimized structure (1.987, 2.072, and 2.086 Å). The ^{195}Pt chemical shift of PtV9 also fits with the correlation of Figure 3, thus confirming the proposed assignment, as do the $\delta(^{51}V)$ shifts.[27] Thus, the DFT level adopted is effective at predicting the NMR spectrum of terminal oxo species as closed-shell singlet states.

Geometry optimization of P2W20Au resulted in detachment of $[O{=}Au\text{-}OH_2]^+$ from the POM framework. This behavior may be due to the absence of solvation, which is known to be an important factor in modeling POM geometry and properties,[17] and is expected to be even more important in the Au^{III} system, where the charge density is higher. All attempts at including solvation failed owing to major SCF convergence problems, and (unlike PtO–PCN), the coordination shell of Au is already filled. Hence, we assumed the available experimental structure, and computed NMR properties at the ZSO/FC level.

$\delta(^{183}W)$ of P2W21 and P2W20 (Table S9a in the Supporting Information) are typical (mostly around $\delta = -100$ ppm) with small CSA; indeed, narrow well-resolved signals were reported. Thus, this structural motif is not, in itself, related to unusual ^{183}W NMR spectra. For P2W21, most ^{17}O signals of bridging (O_b) and terminal (O_t) oxygen atoms fall into their typical regions[28] (Table S5 and Figure S4 in the Supporting Information).

^{183}W spectra of P2W20Au are extremely unusual: W(3i) and W(2c)-O_b-Au fall at $\delta = -1200$ and 1100 ppm, respectively. W(2a) and W(2b) have fairly standard shifts ($\delta = -330$, -470 ppm), and the farthest atom, W(1a,b), has a normal shift value. Moreover, the CSAs of W(3i) and W(2b-c) (Table S7 in the Supporting Information) are 10-times larger; assuming a rotational correlation time τ_c of 1.3 ns, line widths may reach 300 Hz for W(3i). Detection of such broad signals at unusual frequencies is impossible with conventional acquisition parameters.

Experimental ^{17}O NMR spectra[6] feature an isolated signal ($\delta \approx 600$ ppm), which was suggested to be the Au=O oxygen atom. Calculations predict some ^{17}O NMR signals to be extremely deshielded: Au-O_b-W(2c) at $\delta = 9500$ ppm (1.6 kHz width) and Au=O at $\delta = 3035$ ppm (6 kHz width; Tables S9–S11 in the Supporting Information); W(1b)-O_b-W(2c), Au-OH_2, and W(3i)=O at $\delta = 1445$, 1189, and 1087 ppm, respectively. The O_b and O_t signals are spread over the entire $\delta = 200$–700 ppm range (Figure 4c and Figure S8 in the Supporting Information). Thus, the signal at $\delta = 600$ ppm cannot be assigned to Au=O; indeed, this signal will be extremely difficult to detect because of its very large width. Overall, the experimental spectrum may still be consistent with the proposed structure, although most informative signals lie outside the explored region.

In conclusion, the electronic structure of terminal oxo Au and Pt complexes is characterized by an extremely small HOMO–LUMO gap; both orbitals are localized on an M=O fragment, consistent with their involvement through the noble-metal moiety as electrophiles or nucleophiles. However, the interaction between the M=O core and the pincer or polyoxotungstate framework seems very weak and strongly effected by intermolecular interactions. NMR spectra of P2W20Au exhibit uncommon resonance frequencies and wide lines that account for the failure to detect ^{183}W signals, and render ^{17}O NMR spectra inconclusive.

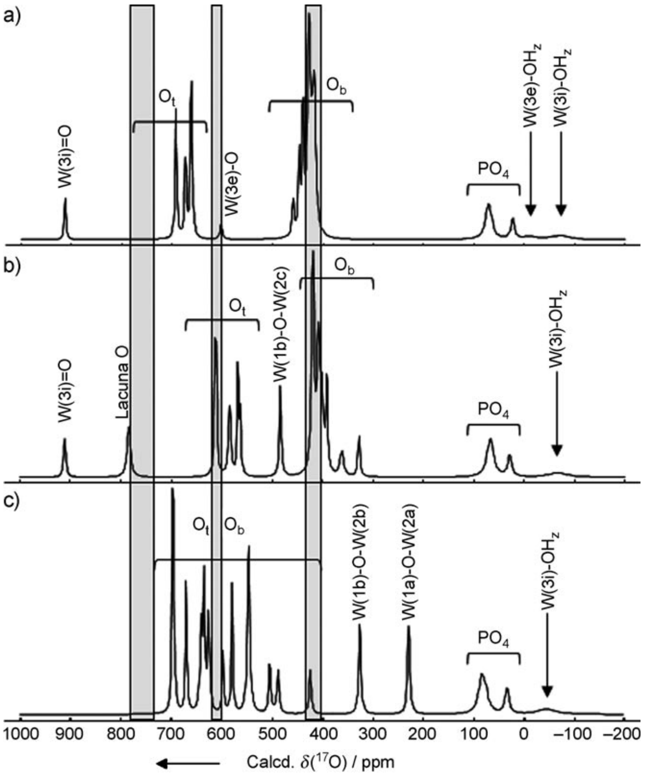


Figure 4. Calculated ^{17}O NMR spectra (shielded region) of a) P2W21; b) P2W20; c) P2W20Au. Shaded bars indicate experimental shift ranges.[6]

Experimental Section

All calculations were carried out using DFT including relativistic effects by means of the two-component zero-order regular approximation (ZORA), at the scalar (ZSC), or spin-orbit (ZSO) levels, with the Becke 88-Perdew 86 (BP) functional. The basis sets were of double- and triple-zeta quality, singly or doubly polarized Slater functions, with flexible (AE) or frozen (FC) cores. Methods are detailed in the Supporting Information.

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