Inorganic Chemistry Hot Paper

International Edition: DOI: 10.1002/anie.201604670
German Edition: DOI: 10.1002/ange.201604670

Oxidation State 10 Exists

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Abstract: *In a recent paper, Wang et al. found an iridium-containing compound with a formal oxidation state of 9.*[5] *This is the highest oxidation state ever found in a stable compound. To learn if this is the highest chemical oxidation state possible, Kohn–Sham density functional theory was used to study various compounds, including* PdO_4^{2+}, PtO_4^{2+}, $PtO_3F_2^{2+}$, PtO_4OH^+, PtO_5, *and* PtO_4SH^+, *in which the metal has an oxidation state of 10. It was found that* PtO_4^{2+} *has a metastable state that is kinetically stable with a barrier height for decomposition of 31 kcal mol*$^{-1}$ *and a calculated lifetime of 0.9 years. All other compounds studied would readily decompose to lower oxidation states.*

The chemical physicist and spectroscopist, C. K. Jørgensen, famously declared, “One of the major goals of inorganic chemistry is to prepare compounds of elements in unusual oxidation states.”[1] As of 2009, the range of known oxidation states produced by chemical means was −4 to +8.[2,3] In 2010, Himmel et al. showed the existence of IrO_4^+ by electronic structure calculations;[4] they studied the stability of cationic species $[MO_4]^+$ (M = rhodium, iridium, meitneurium) and showed that IrO_4^+ is the only species that is stable to decomposition into MO_2^+ and O_2, or MO_2 and O_2^+. The existence of IrO_4^+ shows that oxidation state 9 exists. This was confirmed in 2014 by Wang et al. by time-of-flight photodissociation spectroscopy.[5] (As discussed previously,[2,4,6] good experimental Mössbauer isomer shift evidence already existed[7] for Ir^{IX} in 1969; Ref. [5] was the first to produce Ir^{IX} by chemical, as opposed to nuclear, means.) Pyykkö and Xu[8] reviewed the formal oxidation states of iridium and noted, “…for many new exotic species, prediction precedes production.” Herein, we pose the question: does oxidation state 10 exist? We predict that it does—in the species PtO_4^{2+}.

To answer the question posed in the first paragraph, we studied compounds containing palladium, platinum, and darmstadtium, which are located in the tenth column of the periodic table. We found that platinum is the element most likely to have an oxidation state of 10. In 2014, Srivastava and Misra studied compounds with the formula PdO_n ($n = 1$–5).[9] One of their conclusions is that palladium can bind stably to four oxygen atoms, indicating an oxidation state of palladium as high as 8. In the present paper, we studied the stability of six transition metal compounds (PdO_4^{2+}, PtO_4^{2+}, $PtO_3F_2^{2+}$, PtO_4OH^+, PtO_5, and PtO_4SH^+) of palladium and platinum that have a formal oxidation state of 10.

Reaction energies, enthalpies, and free energies were calculated (see methods in the Experimental Section) for the following reactions:

$$PdO_4^{2+} \rightarrow PdO_2^{2+} + O_2 \qquad \Delta H = -68.4\ \text{kcal mol}^{-1} \tag{1}$$

$$PtO_4^{2+} \rightarrow PtO_2^{2+} + O_2 \qquad \Delta H = 28.7\ \text{kcal mol}^{-1} \tag{2}$$

$$PtO_4^{2+} \rightarrow PtO_2^{+} + O_2^{+} \qquad \Delta H = -124.6\ \text{kcal mol}^{-1} \tag{3}$$

$$PtO_4^{2+} \rightarrow PtO_3^{+} + O^{+} \qquad \Delta H = 55.6\ \text{kcal mol}^{-1} \tag{4}$$

$$PtO_4^{2+} \rightarrow PtO_3^{2+} + O \qquad \Delta H = 83.2\ \text{kcal mol}^{-1} \tag{5}$$

$$PtO_4^{2+} \rightarrow PtO_3 + O^{2+} \qquad \Delta H = 627.5\ \text{kcal mol}^{-1} \tag{6}$$

$$PtO_3F_2^{2+} \rightarrow PtOF_2^{+} + O_2^{+} \qquad \Delta H = -217.4\ \text{kcal mol}^{-1} \tag{7}$$

$$PtO_4OH^{+} \rightarrow PtO_2OH^{+} + O_2 \qquad \Delta H = -94.8\ \text{kcal mol}^{-1} \tag{8}$$

$$PtO_4OH^{+} \rightarrow PtO_2OH + O_2^{+} \qquad \Delta H = -41.6\ \text{kcal mol}^{-1} \tag{9}$$

$$(PtO_4OH)^{+} \rightarrow PtO_5 + H^{+} \qquad \Delta H = 184.4\ \text{kcal mol}^{-1} \tag{10}$$

$$PtO_5 \rightarrow PtO_4 + O \qquad \Delta H = -9.2\ \text{kcal mol}^{-1} \tag{11}$$

$$PtO_5 \rightarrow PtO_3 + O_2 \qquad \Delta H = -93.7\ \text{kcal mol}^{-1} \tag{12}$$

$$PtO_4SH^{+} \rightarrow PtO_2SH^{+} + O_2 \qquad \Delta H = -99.6\ \text{kcal mol}^{-1} \tag{13}$$

The reaction enthalpies shown above were determined at 298.15 K; the reaction energies and Gibbs free energies are shown in Table S1 (Supporting Information). These results show that none of the six compounds is thermodynamically stable because they all have at least one decomposition reaction that gives negative ΔE, ΔH, and ΔG. In particular, PtO_4^{2+} can decompose into PtO_2^+ and O_2^+, $PtO_3F_2^{2+}$ can decompose into $PtOF_2^+$ and O_2^+, PtO_4OH^+ can decompose into PtO_2OH^+ and O_2, PtO_5 can decompose into PtO_3 and O_2, and PtO_4SH^+ can decompose into PtO_2SH^+ and O_2.

However, for PtO_4^{2+} all the possible reactions give positive reaction energies, enthalpies, and free energies except for reaction (3): $PtO_4^{2+} \rightarrow PtO_2^+ + O_2^+$. The energy profile and optimized structure of stationary points for reaction (3) are shown in Figure 1, which starts with the T_d structure. IrO_4^+ also has a T_d structure, for which the bond length is 1.689 Å and the PtO_4^{2+} bond length is 1.712 Å. These may be compared to standard values (all in Å):[10,11] Ir–O, 1.85; Pt–O, 1.86; Ir=O, 1.72; Pt=O, 1.69. On this basis, all the metal-oxo bonds in the T_d structures are double bonds. The T_d structure of PtO_4^{2+} decomposes through transition state TS1 into the C_{2v} structure; the O–O distance in the C_{2v} structure is 1.21 Å, essentially the same as the 1.21 Å distance in diatomic

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201604670.

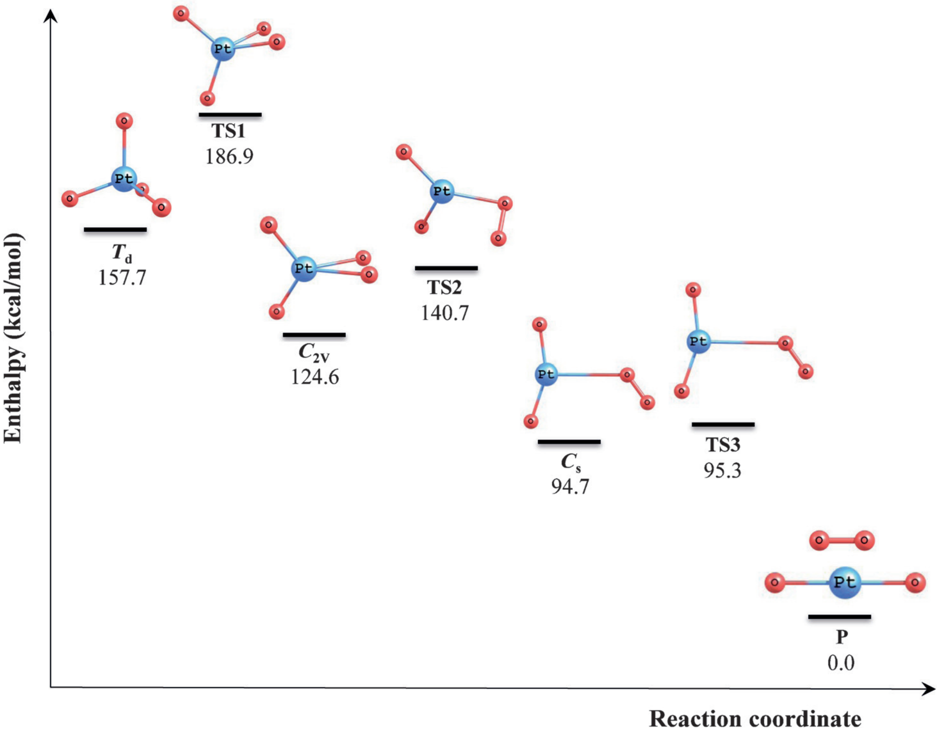

Figure 1. Enthalpy profile of reaction (3): $PtO_4^{2+} \rightarrow PtO_2^{+} + O_2^{+}$. The spin states for T_d, TS1, C_{2v}, TS2, C_s, and TS are all singlet. The spin states for O_2^{+} and PtO_2^{+} are doublet. P = products.

oxygen. The C_{2v} structure goes to the C_s structure through transition state TS2 and then through TS3 to the products PtO_2^{+} and O_2^{+}. The PtO_4^{2+} species is kinetically stable because it needs to go through a 30.7 kcal mol^{-1} energy barrier in the first step. We calculated an enthalpy of activation for this step of 29.2 kcal mol^{-1} and a free energy of activation of 27.6 kcal mol^{-1}. The transition state theory rate constant is 3.7×10^{-8} s^{-1}. This gives a unimolecular lifetime of 2.7×10^{7} seconds, which is 0.86 years. We conclude that PtO_4^{2+} is kinetically stable to decomposition.

We note that PtO_4^{2+} is isoelectronic with IrO_4^{+} and the commodity chemical OsO_4. The orbitals of PtO_4^{2+} are very similar to those of IrO_4^{+}, as illustrated in Figure 2 for the highest occupied molecular orbital (HOMO) and in the Supporting Information for additional orbitals. However, the orbital energies are quite different, as would be expected from the differing net charges. For example, the HOMO orbital energy of IrO_4^{+} is −16.3 eV, whereas that of PtO_4^{2+} is −23.6 eV.

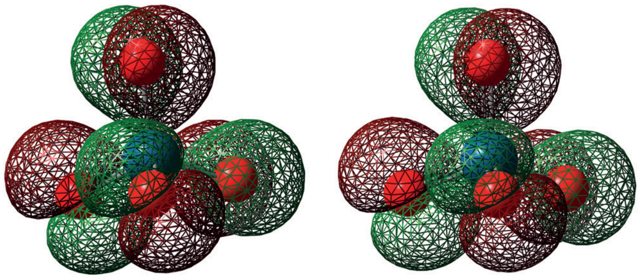

Figure 2. HOMO of IrO_4^{+} (left) and PtO_4^{2+} (right).

To understand the charge distribution in the compounds with a high oxidation state, we calculated partial atomic charges on the metal by both CM5[12] and Hirshfeld[13,14] charge analysis. The results for the T_d structure are in Table 1. For both IrO_4^{+} and PtO_4^{2+}, the T_d structure gives the highest positive charge on the metal. The CM5 charge of the metal is higher than the Hirshfeld charge for all three structures (T_d, C_{2v}, and C_s). The charge difference between PtO_4^{2+} and IrO_4^{+} is significant in that platinum has a charge about 0.2 atomic units higher than iridium. In Table 2 we also compared the dipole moments of the polar structures, as calculated by CM5 charges, Hirshfeld charges, and the DFT density. As we can see, the Hirshfeld dipole moment is closer to the DFT dipole moment than the CM5 dipole moment. Thus, the Hirshfeld charges give the best estimate of the partial atomic charges in these molecules.

Table 1: Hirshfeld Charges and CM5 Charges of T_d structures of IrO_4^{+} and PtO_4^{2+}.

	IrO_4^{+}		PtO_4^{2+}	
Metal center	CM5	Hirshfeld	CM5	Hirshfeld
Platinum/iridium	1.63	1.01	1.85	1.28
Oxygen	−0.16	0.00	0.04	0.18

Table 2: Hirshfeld, CM5, and density dipole moments (in Debye units) of the polar structures of PtO_4^{2+} and IrO_4^{+}.

Dipole moment	CM5	Hirshfeld	Density
IrO_4^{+} (C_{2v})	2.16	1.95	2.00
PtO_4^{2+} (C_{2v})	1.55	1.56	1.98
IrO_4^{+} (C_s)	0.38	0.65	0.71
PtO_4^{2+} (C_s)	8.19	7.82	7.57

In summary, we predict that oxidation state 10 exists in the T_d structure of PtO_4^{2+}. The energy profile shows that in order to decompose, PtO_4^{2+} needs to pass a high barrier—so high that the lifetime is calculated to be 0.86 years. Compared to the previously found highest oxidation state (oxidation number 9 in IrO_4^{+}), PtO_4^{2+} shows a similar charge distribution and electron densities, but the partial atomic charge on the metal is about 0.2 units higher.

Experimental Section

Methods

The method employed involves electronic structure calculations by Kohn–Sham density functional theory (DFT) with the M06-L exchange-correlation functional,[15] the aug-cc-pVTZ basis set[16] for H, O, and F, the aug-cc-pV(T+d)Z basis set[17] for S, and the aug-cc-pVTZ-PP basis set[18,19] for palladium, iridium, and platinum. The M06-L functional has been well-validated for transition-metal energetics.[20] Calculated Born–Oppenheimer energies of reactions (ΔE) were converted into enthalpies of reaction (ΔH) and free energies of reaction (ΔG) by the rigid-rotator, quasiharmonic-oscillator-approximation with a vibrational scale factor[21] of 0.980. We used the same functional, basis sets, and vibrational approximation to calculate the enthalpy of activation, and we used conventional transition state theory[22] to calculate the unimolecular rate constant k for one reaction; the unimolecular lifetime is $1/k$. All calculations are for thermally equilibrated gas-phase species at 298.15 K and 1 bar. Gaussian 09[23] software was used for all the electronic structure calculations.

Acknowledgements

We thank C. Cramer, W. Gladfelter, D. Leopold, and I. Tonks for feedback on the manuscript. This work was supported as part of the Inorganometallic Catalyst Design Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0012702.

Keywords: density functional calculation · formal oxidation state · oxidation state · platinum tetroxide dication

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9004–9006
Angew. Chem. **2016**, *128*, 9150–9152

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Received: May 13, 2016