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On Upper Limits of Oxidation-States in Chemistry

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Abstract: *The concept of oxidation state OS is based on the Lewis electron-pair picture, assigning all bonding electrons to the more electronegative element. It is useful for bookkeeping the electrons, predicting chemical trends and inspiring synthetic chemists. A survey of experimental and quantum-chemical data reveals a limit near +8 for the highest OS in stable neutral chemical compounds under ambient conditions. OS = +9 was observed for isolated* $[IrO_4]^+$ *cations in vacuum. The predicted existence of OS = +10 in a Pt compound is still to be verified experimentally. A high OS may involve the metal becoming electronegative and the* O^{-2} *ligands losing their closed-shell character as* O^{-1}.

The Utility of the Concept of Oxidation State (*OS*) is evident through its long history of more than two centuries.[1] The recently updated IUPAC definition basically reads:[2] Draw some reasonable Lewis (resonance) structure with one- and two-center electron pairs, then assign the two-center pairs as localized at the more electronegative atoms. The recipe can already be applied with a rather basic level of chemical knowledge, if elemental composition and atomic topology of the compounds are known. If additional data are available, various *partial atomic charges* can be assigned by various prescriptions.[3]

The highest *OS* of an element is usually limited by the maximum number of valence electrons, typically given by the group number *g* in the periodic table (modulo 10 on the right side). The few (*g*) valence electrons of electropositive elements from the left groups are easily "oxidized". Although the noble-gas cores are usually inert, the relatively soft cores of the heaviest left-group elements (such as Cs) may perhaps also be oxidized under extreme conditions, for instance at very high pressure.[4] Higher *OS* values are commonly obtained for elements of higher *g*, in particular for the heavier elements with comparatively low ionization energies.

Taking the 6th row of the periodic table as an example,*) compounds with *OS* = *g* are known for all groups up to *g* = 8, e.g. in the ionic solids $Na_4[Hf^{+4}O_4]$, $K_2[Ta^{+5}F_7]$, $Ca[W^{+6}O_4]$, $K[Re^{+7}O_4]$ and in the molecular solid $[Os^{+8}O_4]$. The case of *OS* = +8 is also known for the *g* = 18 element Xe, with $Ba_2[Xe^{+8}O_6]$ being a reasonably stable solid.[5] Recently the first case of *OS* = +9 was predicted,[6] namely $[Ir^{+9}O_4]^+$, and it was realized in the gas phase.[7] However, our attempts to synthesize Ir^{+9}-compounds in the bulk have failed so far, indicating that *OS* ≈ +9±1 may represent the borderland for chemical stability under ambient conditions, and for the stability of single molecules under exotic conditions.

Pyykkö[7c] has noted that often "prediction precedes production", and a previous paper[8] predicted *OS* = +10 for species $[Pt^{+10}O_4]^{2+}$ (Fig. 1-left) which was highlighted in various media.[9] Such predictions can be stimulating for bench chemistry, where they inspire the art of synthesis, for conceptual chemistry, where they help understanding periodic trends, and for characterizing non-Lewis structures, where they widen our picture of chemical bonding.

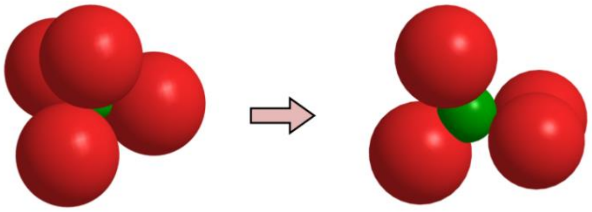

Figure 1. Space-filling calotte models of $[Pt{\cdot}4O]^{2+}$ (red: O^{-2}; green: Pt^{+q}). *Left:* Tetrahedral T_d-$[Pt^{+10}\,O^{-2}{}_4]^{2+}$. *Right:* C_{2v}-$[O^{-2}{}_2\,Pt^{+7}\,(O_2)^{-1}]^{2+}$. The O^{-2} ligands of T_d-$[PtO_4]^{2+}$ are all weakly overlapping. The right $(O_2)^{-1}$ ligand of the C_{2v} isomer is a superoxide unit.

Oxidation states of Pt from +4 to +10, corresponding to various geometric-electronic isomers of $[Pt{\cdot}4O]^{2+}$ (Scheme 1, Fig. 1 and Fig. S1 in the Supporting Information SI), had been obtained applying singlet spin-restricted density-functional approximations (DFAs).[8] Applying here higher-quality spin-unrestricted DFAs and multi-configuration wave-function (WF) approaches (Tables S1 and S2), we have qualitatively reproduced those findings.

The sets of *OS* values as well as the sets of partial atomic charges (of Pt and the four O) are coupled in the sense that each set sums up to 2 in each isomer. The inter-ligand distances *R*(O-O) vary systematically with the *OS*s of the Pt and O atoms; so we choose *R*(O-O) as abscissa in Fig. 2 for the $[Pt{\cdot}4O]^{2+}$ rearrangement reactions with *OS*s from Pt^{+4} to Pt^{+10}. There are three metastable molecular ions, formally

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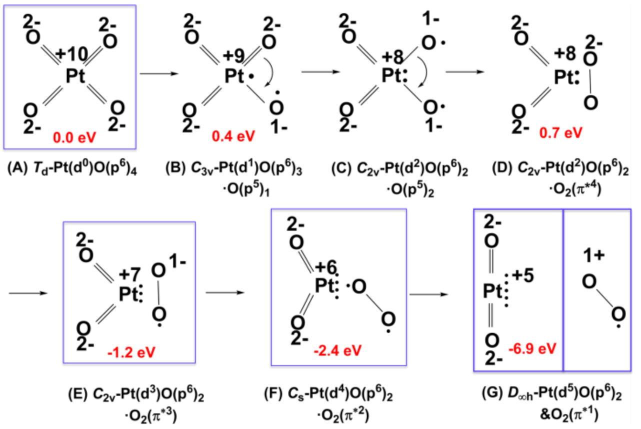
*) We write ±*q* for chemical oxidation states, and *q*± for realistic physical partial charges.

described as T_d-$[(O^{-2})_2\,Pt^{+10}\,(O^{-2})_2]^{2+}$, C_{2v}-$[(O^{-2})_2\,Pt^{+7}\,\eta^2\text{-}(O_2)^{-1}]^{2+}$ and C_s-$[(O^{-2})_2\,Pt^{+6}\,\eta^1\text{-}(O_2)^0]^{2+}$, and there are two stable separated mono-cations, $D_{\infty h}$-$[(O^{-2})_2\,Pt^{+5}]^{1+}$ & $(O_2)^{1+}$ (Table S3). The mono-cations are observable as building blocks of some crystalline materials.[10]



(A) T_d-Pt(d^0)O(p^6)$_4$

(B) C_{3v}-Pt(d^1)O(p^6)$_3$ ·O(p^5)$_1$

(C) C_{2v}-Pt(d^2)O(p^6)$_2$ ·O(p^5)$_2$

(D) C_{2v}-Pt(d^2)O(p^6)$_2$ ·O$_2$(π^{*4})

(E) C_{2v}-Pt(d^3)O(p^6)$_2$ ·O$_2$(π^{*3})

(F) C_s-Pt(d^4)O(p^6)$_2$ ·O$_2$(π^{*2})

(G) $D_{\infty h}$-Pt(d^5)O(p^6)$_2$ &O$_2$(π^{*1})

Scheme 1. Lewis structures (A) to (G) for various $[Pt{\cdot}4O]^{2+}$ species with *OS*(Pt) from +10 to +5 (for a more extended scheme see Fig. S6). Metastable molecules are in boxes. The energy (below the structures, in eV) goes from a local minimum (A) over an activation plateau to local minimum (E) and over further barriers to (F) and the stable separated fragments (G, bold boxes). The oxygen lone pairs were omitted for clarity.

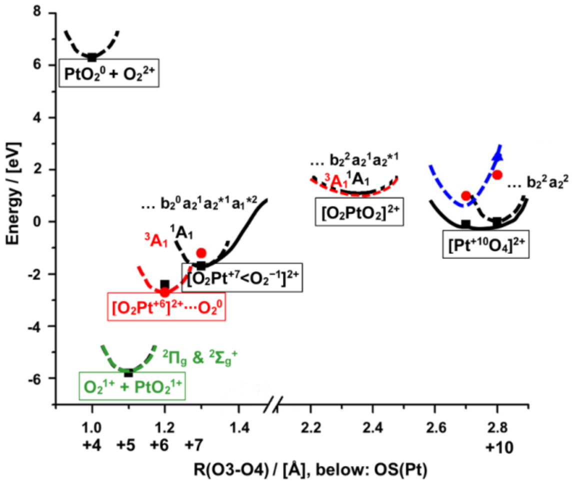


Figure 2. Sketch of isomerization energy curves (in eV) of $[Pt{\cdot}4O]^{2+}$ complexes with *OS*(Pt) = +4, +5, +6, +7 and +10, and various ligands/fragments (from left to right 2 O^{-2} ligands throughout, and separated fragments O_2^{2+}, O_2^{1+} or bound ligands O_2^{0}, O_2^{-1}, $2O^{-2}$). The upper abscissa scale is the O3−O4 distance in Å, and the lower scale labels *OS*(Pt). Dashed curves are from unrestricted single-determinant DFAs: black ~ ground-state singlet, blue ~ excited singlet, red ~ triplet, green ~ two doublets. Full curves are from multi-configuration calculations. The highest doubly and singly occupied MOs of the leading configuration are written in same order as in T_d-$[Pt^{+10}O_4]^{2+}$.

The obtained barriers to decay of the metastable species are lower than originally anticipated,[8] owing to strong electron correlation (Figs. S2 and S3). In particular, the tetrahedral $^1A_1$ closed-shell ground configuration of $[Pt^{+10}O^{-2}{}_4]^{2+}$ obtained by various DFAs has a weight of less than 50% in multi-configuration WF approaches (Figs. S4 and S5). This Pt^{+10} species becomes weakly dynamic pseudo-Jahn-Teller C_{2v}-deformed due to mixing in of further configurations and will undergo large-amplitude vibrations around the average T_d structure. With a free energy of activation of only 10-15 kcal/mol (Table S4), it will quickly decay at room temperature (lifetimes around 10^{-5} - 10^{-2} s), but if producible with very low internal energy might become observable at sufficiently tuned and cryogenic conditions (lifetimes at liquid N_2 possibly $>10^{15}$ s).

The peculiar type of bonding of $[PtO_4]^{+2}$ with significant population of the formally empty valence shell of the $Pt(5d^0)^{+10}$ central ion and covalent interactions between the slightly overlapping oxygen anions with no longer closed O-2p shells is highlighted by the localized MO picture in Figs. 3 and S3.

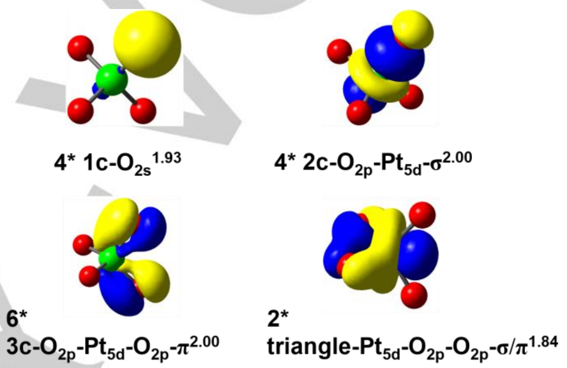


Figure 3. Boldyrev-localized[14] Kohn-Sham orbitals of T_d-$[PtO_4]^{2+}$ (values of blue and yellow contours = ±0.04 au). Green ball: Pt-core; four red balls: O-cores. *Top, left*: one of the four O-2s 1-center lone pairs with a small contribution from O-2p and the other atoms; *right:* one of the four Pt-O 2-center σ-bonds with comparable Pt-5d and O-2p contributions. *Bottom, left*: one of six O-Pt-O 3-center π-bonds at each tetrahedral edge with 12% Pt-5d contribution; *right:* one of two -O-O-Pt- triangle σ-bonds with 75% Pt-5d contribution.

Experimental evidence of fluoro, oxo and peroxo compounds of platinum in the bulk showed formal Pt^{+5} and Pt^{+6} species such as in $[(O_2)^{+1}\,Pt^{+5}\,F_6]$ and $[Pt^{+6}\,F_6]$.[15,10c] Fielicke and coworkers[16] generated argon-coordinated platinum oxide cations by pulsed-laser platinum vaporization into an argon gas phase, into which di-oxygen was injected. The species were studied by mass spectrometry and infrared photodissociation spectroscopy and were identified as superoxide complexes of $Ar_2\,[Pt^{+2}\,(O_2)^{-1}]^{1+}$ cations with typical superoxide stretching vibrations around 1200 cm^{-1} (Fig. S7). In similar experiments, an oxygen-richer $[PtO_4]^{1+}$ could be obtained. We identified it as $Ar_2\,[(O_2)^0\,Pt^{+2}\,(O_2)^{-1}]^{1+}$, where the two O_2 moieties show the typical stretching vibrations of superoxide $(O_2)^{-1}$ and dioxygen $(O_2)^0$ ligands at 1184 and 1500 cm^{-1}. Accordingly, the *OS* of Pt is only +2.

New gas-phase experiments here on Pt^{2+} ions reacting with oxygen-donating molecules reveal the following(Table S5):

$$Pt^{2+} + 1\text{-}2\ O_2^{0} \rightarrow Pt^{1+},\ PtO^{1+},\ PtO_2^{1+} + O_2^{1+}, \tag{1a}$$

$$Pt^{2+} + 1\text{-}3\ N_2O^{0} \rightarrow Pt^{1+},\ PtO^{1+},\ PtO_2^{1+} + N_2O^{1+} + 0\text{-}2\ N_2 \tag{1b}$$

These results indicate that even in low oxidation states, Pt atoms rather than O atoms prefer accepting electrons. Reaction (1b) is particularly remarkable, since N_2O is a favorable O-atom donor with a low dissociation energy of only 1.73 eV for $N_2O \rightarrow N_2 + O$, while that of $O_2 \rightarrow 2O$ is much larger, 5.16 eV. These facts can be rationalized by the increase of ionization potentials both with increasing nuclear charge and with ionization stage, favoring lower oxidation states of Pt as a general tendency.

We also irradiated iridium metal, which just precedes Pt in the periodic table, by a pulsed-laser beam under excess of oxygen and identified the product molecules by infrared photodissociation spectroscopy as singlet T_d-$[Ir^{+9}O_4]^{1+}$ cations in the gas phase, which are isoelectronic with T_d-$[Pt^{+10}O_4]^{2+}$.[7] Related neutral molecule $[Ir^{+8}O_4]^0$ had been discovered under cryogenic conditions in rare gas matrices.[17] It had then been predicted on quantum-chemical basis that the $[IrO_4]^+$ cation could be stabilized in bulk quantities by weakly coordinating anions (WCA) such as $[SbF_6]^{1-}$ and even better by bigger WCAs.[6] However our attempts at bulk synthesis have not succeeded so far, and the attempt to create $[PtO_4](WCA)_2$ appears futile.

Our four final conclusions are:

(1) The present calculations show that Pt^{+10} in PtO_4^{2+}, albeit being metastable at very low temperatures, is even less stable than Ir^{+9} in IrO_4^+, which was so far only found as single cations in the gas phase.

(2) For isolated atoms in the gas phase (i.e. in physical vacuum), *OS* and cationic charge are only limited by the total electron number. Ligated cations of very high *OS* in chemical compounds, however, oxidize the ligands by spontaneous self-reduction. The analysis of the empirical atomic ionization potentials (to be discussed elsewhere) supports a rule that *OS* around +8 is an upper limit for compounds in condensed phases under ambient conditions.

(3) The change of *OS* occurs either through an adiabatic polarization of the ligand orbitals toward the metal's valence shell, or by electron transfer from filled to empty orbitals localized on the ligand or the metal cation. In many cases, single-configuration Lewis pair pictures are adequate while, e.g., in cases isoelectronic to $[Pt^{+10}O_4]^{2+}$ such as $[Mn^{+7}O_4]^{1-}$,[11] $[Fe^{+8}O_4]^0$,[12] or $[Ir^{+9}O_4]^{1+}$,[7] the single-configuration picture breaks down with break-up of electron pairs and the formation of multi-configuration types of bonding. The present case throws light on the "inverted ligand field" situation recently reviewed by Hoffmann et al.[13] as well as on recent discussions of the so-called correlated charge-shift bonding.[18]

(4) The present investigations highlight the abundance of different electronic structures that are representable, or not, by some Lewis structure. With the joint development of experimental and theoretical chemistry, the classical repertoire of chemical symbolism and of classificatory concepts needs continuous extension.

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Conflict of interest

The authors declare no conflicts of interest.

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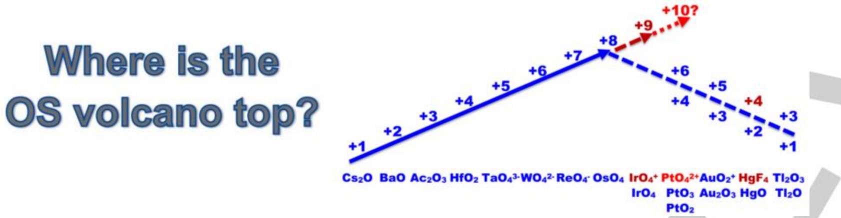

The Highest Oxidation-State (OS) of elements in compounds is not only limited by the number and by the ionization energies of their valence electrons, but also by the properties of their ligands. With spontaneous ligand oxidation, radical character in an ‘inverted ligand field’ and strongly correlated multi-center bonds are formed. A joint theoretical-experimental case study of PtO_4^{2+} isomers reveals a maximum OS near +8 for elements in chemical compounds under ambient conditions.

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