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Highlights

Oxidation States

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The Formal Oxidation States of Iridium Now Run from −III to +IX**

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After much effort, Wang et al.[1] were able to observe the Ir^{+IX} species IrO_4^+ and its argon complexes in the gas phase by infrared spectroscopy. With a solid species[2] containing Ir^{-III}, there are thirteen possible formal oxidation states of iridium. New, well-established oxidation states in chemistry are rarer than new elements. For instance, the element E117 was reported quite recently[3] after E118, while compounds in the previously highest established oxidation state, +VIII, such as OsO_4 and XeO_4 have been known for decades. Examples of elements in the next positive oxidation state of +IX had remained elusive until the very recent report by Wang et al.[1] On the anionic side, of interest for the present discussion, a series of formally $5d^{10}6s^2$ systems is known. In addition to cesium auride, CsAu, the bulk Cs_2Pt was reported by the group of Jansen.[4] The possibility of Pt^{-II}, formally another $5d^{10}6s^2$ system, had been evoked before.[5,6] Indeed, for many new exotic species, prediction precedes production.[7] The next steps after Au^{-I} and Pt^{-II} would be Ir^{-III} and Os^{-IV}. Indeed, the solid $Na_3[Ir^{-III}(CO)_3]$ has been reported.[2] We observe that $9+3+6=18$: This compound obeys the 18-electron rule. For the interpretation of that rule, see reference [8]. For some reviews also covering negative oxidation states of metals, see references [9] and [10]. A further aspect is relativity: As discussed in a review,[11] about half of the electron affinity of the gold atom comes from relativistic effects.

The formal oxidation states are defined at the ionic limit and their importance is in rationalizing redox reactions. In the IUPAC definition of these formal oxidation states, F and/or O are thus assigned an oxidation state of −I and −II, respectively, and the other oxidation states follow by simple arithmetic. The bonding electron pairs are assigned to the more electronegative atom, corresponding to the ionic limit. Please note that the actual charge of an atom, as measured by population analysis, can be very different from its oxidation state. In the work of Wang et al.,[1] the calculated natural atomic charge of Ir in $[(Ir^{+IX})O_4]^+$ was +1.47, although the formal oxidation state of Ir can be clearly assigned as +IX.

What is the evidence for $[(Ir^{+IX})O_4]^+$? As a preliminary step, Gong et al.[12] produced the neutral IrO_4 in a matrix and showed that it is a tetrahedral, $5d^1$ system. Both for this neutral molecule and for the cation, a possible alternative are side-on peroxide structures. These side-on structures could be identified by comparing the observed IR frequencies against ab initio calculations.

The IrO_4^+ molecular ion was predicted by Himmel et al.[13] It was now experimentally produced by a pulsed laser vaporization/supersonic expansion method and studied by IR photodissociation spectroscopy in the 850–1600 cm^{-1} range. Mass spectra were observed both for the bare cation and for the argon-tagged species $[IrO_4]^+{\cdot}Ar_n$ (see Figure 1). These complexes could be photodissociated. The photodissociation spectra, including oxygen isotope substitution studies, gave evidence for both side-on O_2 complexes and the tetrahedral IrO_4^+ complexes, the latter being more stable. The $[(\eta^2\text{-}O_2)Ir^{+VII}O_2]^+$ species moreover shows the missing oxidation state Ir^{VII}. The highest-energy calculated isomer

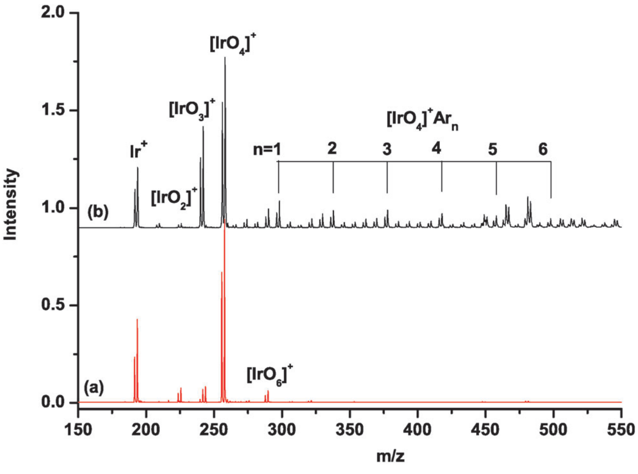

Figure 1. Mass spectra for the argon-tagged iridium oxide species. Reprinted from reference[1] with permission from Macmillan Publishers Ltd.

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was $[(\eta^1\text{-}O_2)Ir^{+VI}O_2]^+$. High-level ab initio calculations at both CCSD(T) and CASPT2 levels were used. Mass spectra of the argon-tagged complexes are shown in Figure 1.

This work is a result of close cooperation between experiments and theory, showing how this interaction benefits both sides. The experiments confirmed theoretical predictions made much earlier.[13] Modern quantum chemistry predicts IR frequencies with errors of only 20–30 cm^{-1}, which greatly helped the assignment. The computations also made predictions about the site of Ar on $[(Ir^{+IX})O_4]^+$, which could not be determined by the experiments yet. Further attempts were made[1] to synthesize Ir^{IX} compounds as bulk fluoroantimonates, but so far without success.

In conclusion, iridium now has thirteen possible oxidation states, ranging from −III to +IX. Of them, only −II has not yet been observed.[14]

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