

Investigation of New Iridium Oxidation States by Matrix-Isolation Spectroscopy and Quantum-Chemical Calculations

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Matrix-isolation experiments in both argon and krypton matrixes clearly show IR absorptions that are consistent with the formation of a true iridium tetraoxide, Ir^{VIII}O₄, with d¹ configuration. This is supported by accurate quantum-chemical calculations e.g. CCSD(T), which indicate the tetraoxide to be the most stable isomer, albeit with a more shallow potential-energy surface for rearrangements than computed for the analogous OsO₄. Construction of Born-Haber cycles shows why IrO₄ could not be observed as bulk solid under conditions where OsO₄ is well known. IrO₄ is much less stable than OsO₄ under comparable conditions but may be stabilized in low-temperature matrices. As the Jahn-Teller distorted tetrahedral IrO₄ is undoubtedly a proper d¹ system, the new oxidation state Ir^{VIII} has thus been established.^[1]

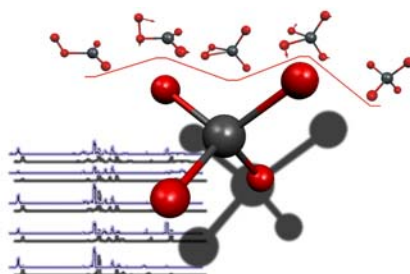


Figure 1: Iridium tetraoxide

This new oxidation state of iridium is after the recent preparation of HgF₄^[2] the second new oxidation state which was discovered in the last two years by matrix-isolation spectroscopy. Quantum-chemical calculations have predicted that there is still hope for further discoveries of new high-valent species and oxidation states.^[3-5]

Literatur:

[1] Y. Gong, M. Zhou, M. Kaupp, S. Riedel, *Angew. Chem. Int. Ed.* **2009**, *48*, 7879. [2] X. Wang, L. Andrews, S. Riedel, M. Kaupp, *Angew. Chem. Int. Ed.* **2007**, *46*, 8371. [3] S. Riedel, M. Kaupp, *Angew. Chem. Int. Ed.* **2006**, *45*, 3708. [4] S. Riedel, M. Kaupp, *Coord. Chem. Rev.* **2009**, *253*, 606. [5] D. Himmel, C. Knapp, M. Patzschke, S. Riedel, *ChemPhysChem*, **2010**, *11*, 865.