

Coordination Chemistry of Xenon

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Literature Seminar

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Situated on the far side of the periodic table, the chemical inertness of the noble gases has led to their widespread applications ranging from gas-discharge lamps and ion engines for space travel to medical applications including as MRI contrast agents and radiotherapy.¹ Though all practical applications of the noble gases center around Xe (0), understanding the reactivity and bonding of xenon in higher oxidation states is fundamental to investigating chemistry at the far end of the periodic table.

The reactivity of the noble gases, in particular xenon, was first uncovered when Bartlett, who had previously prepared dioxygenyl hexafluoroplatinate (V) (O_2PtF_6), noted similar ionization energies for molecular oxygen and atomic xenon (a difference of 0.1 eV).² Mixing of xenon with PtF_6 vapor led to the formation of an orange-yellow solid led to the synthesis of the first noble gas compound, xenon hexafluoroplatinate (V) (XePtF_6).

The chemistry of xenon has evolved significantly since its' discovery to include an assortment of xenon fluorides, oxides, oxyfluorides, organoxenon³, and metalloxenon compounds such as the tetraxenoaurate (II) cation (Figure 1).⁴ These species have weak covalent bonding between Xe and the oxygen/fluorine moieties.⁵ The chemistry of xenon is dominated by the 2+, 4+, and 6+ oxidation states, though Xe (VIII) compounds are known in the form of perxenates and xenon tetroxide. These primarily ionic species, particularly the oxides, oxyfluorides, and fluorides, serve as precursors to noncovalent adducts of xenon.

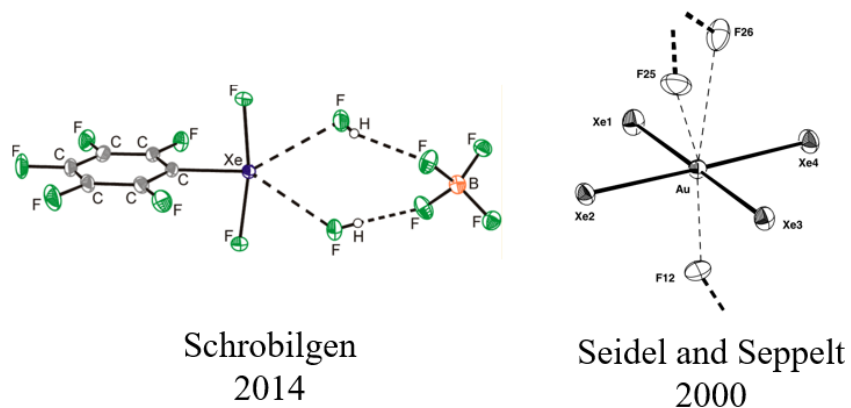


Figure 1. Organoxenon and metalloxenon species

Recent work has led to the preparation of xenon adducts with noncovalently interacting ligands such as acetonitrile^{6a, 6b}, ketones^{6c}, sulfoxides^{6c}, and crown ethers^{6d} (Figure 2) capable of weakly coordinating to xenon salts to afford stable species at room temperature. The stability of

these adducts is dependent on the resilience of the ligands to oxidation, precluding species such as alcohols (which are oxidized to CO and H₂O) and sulfur from acting as electron donors under ambient conditions.^{6d} This interaction primarily occurs through a σ -hole interaction. The aforementioned noncovalent interactions are due to a proposed nondirectional σ -hole interaction known as an “aerogen bond” (Figure 3).⁷ Bauzá and Frontera calculated the molecular electrostatic potential surface (MEPS) using MP2/aug-cc-pVTZ for XeF₂O and XeO₃, which indicated the presence of an electropositive region situated near the lone pair of Xe capable of accepting electron density but note that this is less directional than hydrogen bonding.

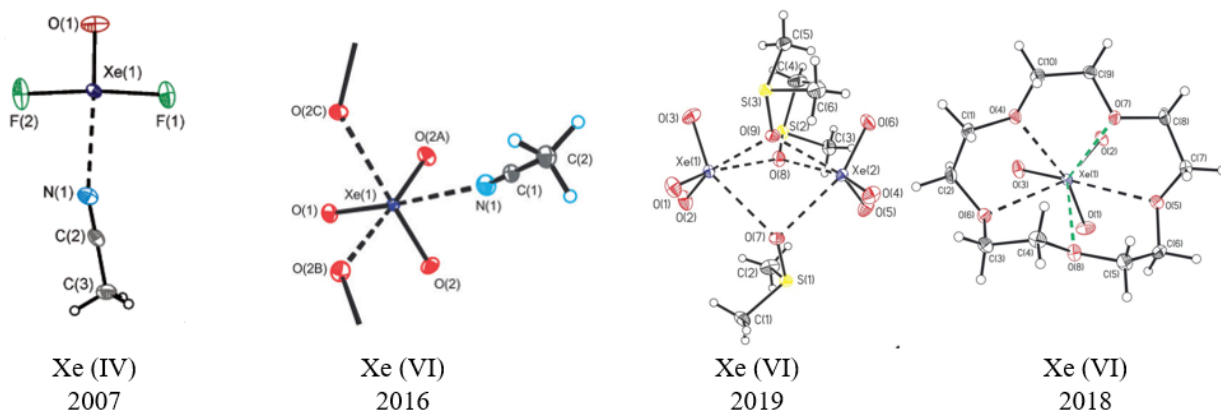


Figure 2. Noncovalently coordination compounds with Xe (IV) and (VI) prepared by Schrobilgen and coworkers^{6a-d}

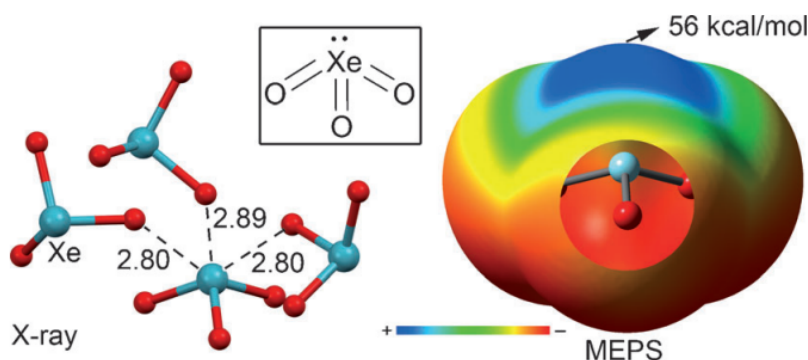


Figure 3. Calculated MEP surface of XeO₃ with σ -hole (blue)⁷

Traditional xenon chemistry, which has employed the use of covalently bound and charged ligands for coordination to xenon, has evolved in recent years to reveal a host of noncovalently bound neutral species bonding through a σ -hole interaction. More recent work has led to the preparation of a XeO₃ complex with 15-crown-5, the first instance of polydentate coordination to a xenon atom. Challenges moving forward include the limitations imposed by the oxidation potential of xenon cations, particularly Xe (IV) and (VI), on the scope of potential ligands for these types of compounds. Further, the shock sensitivity and reactivity of these species likely limits their applications and consigns these species principally to the realm of basic science.

References

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