

What Determines the Binding Parameters of Mercury?

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Objective

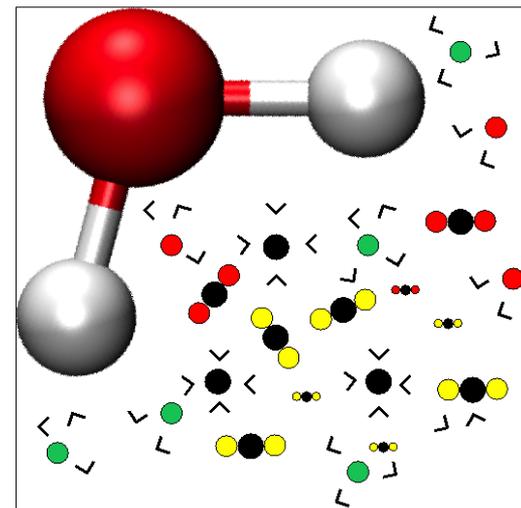
- To understand why mercury (Hg) interacts so strongly with thiols, which are the dominant ligands to oxidize Hg in many ecosystems.

New Science

- Quantum chemical calculations are used to dissect the relative binding free energies for a series of inorganic anion complexes of Hg^{2+} .
- Comparing Hg^{2+} -ligand interactions in the gaseous and aqueous phases reveals that differences in interactions with a few, local water molecules lead to a clear periodic trend within the chalcogenide and halide groups and result in the well-known experimentally observed preference of Hg^{2+} for “soft” ligands such as thiols.

Significance

- Defining the factors that determine the relative affinities of different ligands for Hg^{2+} is critical to understanding its speciation, transformation, and bioaccumulation in the environment. Our approach establishes a basis for understanding Hg speciation in the biosphere.



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Mercury occurs largely as the oxidized, mercuric ion, Hg^{2+} , which is often bound tightly to thiol ligands. Quantifying the factors that determine the affinities of thiols and other diverse partners for Hg^{2+} is central to understanding biotic and abiotic Hg speciation and trafficking in the environment. To furnish a theoretical basis for Hg^{2+} speciation, we used density functional theory (DFT) to calculate aqueous binding free energies for a series of environmentally relevant chalcogenide (OH^- , SH^- , SeH^-) and halide (F^- , Cl^- , and Br^-) ligands. The results reveal a surprising increase in the local interaction strength between Hg^{2+} and two negatively charged ligands with increasing hardness of the ligands. Differences in proton affinities and interactions with a very small number of local water molecules recover the experimentally well-known increasing affinity of Hg^{2+} for softer ligands, which is consistent with Hard and Soft Acids and Bases concepts. The analytical framework and systematic treatment of hydration provides a molecular explanation of the experimentally observed, robust preference of Hg^{2+} for soft ligands such as thiols. This approach is applicable to interactions of organomercurials and other metal cations with inorganic and organic anionic ligands including cysteine and selenocysteine, which are essential to living organisms.

Riccardi, D., H-B. Guo, J.M. Parks, B. Gu, A.O. Summers, S.M. Miller, L. Liang, and J.C. Smith. 2013. Why mercury prefers soft ligands. *The Journal of Physical Chemistry Letters* 4:2317-2322 (doi: 10.1021/jz401075b).