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Theoretical studies on the formation of mercury complexes in solution and the dissolution and reactions of cinnabar

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ABSTRACT

Expanding upon our previous studies of the properties of Au complexes, we present calculations for several Hg^{2+} species in aqueous solution and for molecular models for cinnabar. Hydration effects are treated with a combination of "supermolecule" calculations containing several explicit water molecules and polarizable continuum calculations. We focus upon the following problems: (1) calculation of the stabilities of HgL_2, L = F^-, Cl^-, OH^-, SH^-, and CN^- and $HgCl_n^{2-n}$ n = 1–4; (2) development of a molecular model for cinnabar of the form $Hg_3S_2(SH)_2$; and (3) dissolution or adsorption reactions using this cinnabar model. The absolute and relative formation enthalpies of the HgL_2 species can be satisfactorily reproduced at the Hartree-Fock plus Moller-Plesset second order correlation correction level using relativistic effective core potential basis sets if the hydration of neutral HgL_2 is explicitly taken into account. Evaluating the energetics for the series of complexes $HgCl_n^{2-n}$ is more difficult, because great accuracy is needed in the large hydration energies and some of the species are highly nonspherical. The $Hg_3S_2(SH)_2$ species shows an equilibrium structure very much like that in cinnabar. The relative energetics for dissolution of cinnabar by H_2O, H_2S, SH^-, and SH^- + elemental S are correctly reproduced using this model molecule. Calculations on Hg_3S_2ClI provide a model for understanding the adsorption of I^- ions on cinnabar surfaces in the presence of Cl^-.