Prediction of the pK_a's of Aqueous Metal Ion +2 Complexes

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Aqueous metal ions play an important role in many areas of chemistry. The acidities of $[Be(H_2O)_4]^{2+}$, $[M(H_2O)_6]^{2+}$, M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, and $[M(H_2O)_n]^{2+}$, M = Ca^{2+} and Sr^{2+}, n = 7 and 8, complexes have been predicted using density functional theory, second-order Møller−Plesset perturbation theory (MP2), and coupled cluster CCSD(T) theory in the gas phase. pK_a's in aqueous solution were predicted by using self-consistent reaction field (SCRF) calculations with different solvation models. The most common binding motif of the majority of the metal +2 complexes is coordination number (CN) 6, with each hexaaquo cluster having reasonably high symmetry for the best arrangement of the water molecules in the first solvation shell. Be^{2+} is tetracoordinated, but a second solvation shell of 8 waters is needed to predict the pK_a. The Ca^{2+} and Sr^{2+} aquo clusters have a coordination number of 7 or 8 as found in terms of the energy of the reaction $M(H_2O)_7^{2+} + H_2O \rightarrow M(H_2O)_8^{2+}$ and the pK_a values. The calculated geometries are in reasonable agreement with experiment. The SCRF calculations with the conductor-like screening model (COSMO), and the conductor polarized continuum model (CPCM) using COSMO-RS radii, consistently agree best with experiment at the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ levels of theory. The CCSD(T) level provides the most accurate pK_a's, and the MP2 level also provides reliable predictions. Our predictions were used to elucidate the properties of metal +2 ion complexes. The pK_a predictions provide confirmation of the size of the first solvation shell sizes. The calculations show that it is still difficult to predict pK_a's using this cluster/implicit solvent approach to better than 1 pK_a unit. This work is sponsored by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.