Solvents and Weakly Coordinating Anions as Stabilizers for Transition-Metal Nanoclusters

L.S. Ott[S] and R.G. Finke[C]
Department of Chemistry, Colorado State University, Fort Collins, CO, U.S.A.
rfinke@lamar.colostate.edu

The literature contains a wide variety of claimed transition-metal nanocluster stabilizing agents, these agents intended to arrest the kinetically stable nanoclusters from agglomerating to their thermodynamic minimum of bulk metal. There are even several claims of "solvent-only" stabilization of the coordinatively unsaturated, electrophilic nanoclusters. However, "solvent-only" stabilization does not fall under either of the two precedented modes of nanocluster stabilization, electrostatic or steric. Hence, the nature of the stabilizing entity is unclear for these prior literature reports. Complicating this confusion are two frequent problem in the area of transition-metal nanocluster stabilization: (i) the compositionally ill-defined nature of the nanoclusters, and (ii) the authors failing to consider potentially stabilizing entities present in the reaction solution (such as halides, alcohols, and weakly coordinating anions). Herein we present a systematic investigation into the contributions to the stabilization of prototype Ir(0)n nanoclusters in the presence of the traditionally weakly coordinating anion BF_4^- in five different solvents. Each nanocluster system studied herein is ranked by 5 criteria developed in 2002 developed to evaluate the formation and stabilization of transition-metal nanoclusters. Multiple alternative hypotheses are tested to determine the true nature of the stabilizing entity. Additionally, the accuracy of DLVO theory of colloidal stability is probed, both with BF_4^- and with the strongly coordinating $P_2W_{15}Nb_3O_629^-$ anion. Overall, we find that the predictions of DLVO theory apply to even weakly coordinating anions, and that the combination said weakly coordinating anion and a high dielectric constant solvent yields surprisingly stable nanoclusters.