The Characterization of Enviromentally Significant Oxidic and Sulfidic Metal Clusters using ESI FT-ICR MS

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Overview

Sulfidic and oxidic metal clusters were characterized using ESI-FT-ICR mass spectrometry.

Small metal clusters were observable in dilute solutions of cadmium nitrate and cadmium sulfide.

Systematic formation of metal sulfide clusters in dilute aqueous solutions was observed using ESI FT-ICR mass spectrometry.

Sulfur rich molecular species result from the addition of H_2S to dilute metal nitrate solutions.

Background

Research has shown that clusters are prevalent in the environment and are a possible building block in mineral formation (Wolthers et al., 2003). Environmentally, clusters can be defined as a quantum-sized particle or complex, which contains a discrete number of atoms in a molecule or ion that is small enough to behave as a dissolved species. The boundary between dissolved species and nanoparticulate solid has only recently been defined for FeS and ZnS and even still there appears to be overlap in the dimensions of aqueous clusters and nanoparticles (Luther and Rickard, 2005; Rozan et al. 2000). It is possible to have several clusters of different stoichiometries form into larger species, larger than the critical nucleus, before nanoparticle formation. Each cluster stoichiometry can have different physical chemical properties and reactivity due to their unique structural characteristics.

The chemical or molecular processes involved in the transformation of simple dissolved species to solid products are not as well understood. The Ostwald Step Rule step rule or "the rule of stages" postulates that the precipitate with the highest solubility (i.e., the least stable solid phase) will form first in a consecutive precipitation reaction. The precipitation sequence results because nucleation of a more soluble phase is kinetically favored over that of a less soluble phase due to the lower solid-solution interfacial tension of the more soluble phase. The classical interpretation of the Ostwald Step Rule is that the metastable phase forms first because it is more soluble than the stable phase. The formation of aqueous metal sulfide cluster complexes has been shown to provide an alternative mechanism for the Ostwald Step Rule (Luther and Rickard 2005).

The reaction between cadmium and sulfide has been monitored in solution electrochemically. Because CdS(aq) species are not electroactive themselves, titration experiments where performed in which sulfide was added to Cd(II) and vice versa. By measuring the decreasing peaks of unreacted sulfide or cadmium, a mole ratio can be estimated from the slopes of these titration curves. When Cd(II) is reacted with sulfide in the presence of an organic ligand (ethylenediamine and cysteine), the Cd:S ratio increases (i.e., electrochemically labile Cd is consumed with less added sulfide). This suggests that organic molecules can effectively "cap" metal sulfide clusters, preventing further particle growth and aggregation. Unfortunately, voltametry provides only limited, indirect information about metal sulfide clusters. It is our goal to reconcile the solution chemistry using ESI FT-ICR mass spectroscopy.

Methods

In order to investigate the nucleation and particle growth of metal clusters, we have begun to develop methods to isolated cluster species during stages of growth by encapsulating the metal clusters with a self-assembled monolayer such as 2-mercaptopyridine (**mpH**).

Solutions

A) 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ diluted 50/50 with MeOH.

B) 1.5 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ and 2-mercaptopyridine (1:1) diluted 50/50 with MeOH.

C) H_2S (g), produced by reaction between Na_2S and HCl, was bubbled through a 3 mM solution of $Cd(NO_3)_2 \cdot 4H_2O$ for ~10s followed by the addition of 2-mercaptopyridine (1:1) making the final concentration 1.5 mM. The reaction solution was then diluted 50/50 with MeOH.

Instrumentation: Analysis was done using a 7T Bruker Apex-70Qe FT-ICR mass spectrometer. CID experiments were done in the source region of the spectrometer by adjusting the potential used to bring the ions into the accumulation hexapole.
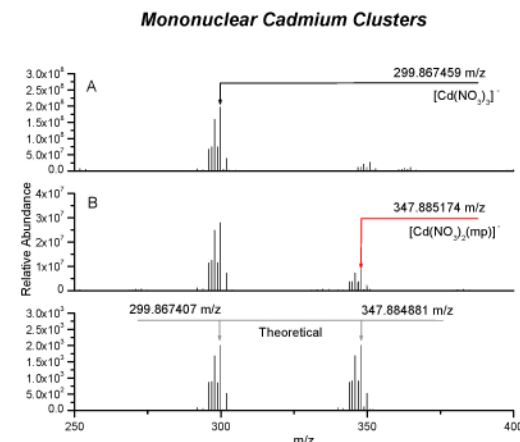
Experimental Results & Discussion

Mononuclear Cadmium Clusters

Figure 1: ESI-FTMS spectra of the Cd_1 cluster region for solutions A and B with comparison to theoretical isotopic distributions and isotopic m/z.

Mononuclear Cadmium Clusters (Figure 1)

■ Reaction of $Cd(NO_3)_2$ with 2-mercaptopyridine (**mpH**) results in the formation of $[Cd(NO_3)_2(mp)]^-$.

■ Comparisons between theoretical and observed isotopic distributions and accurate masses (±2ppm) were used to determine cluster stoichiometry.

□ _Example_: Mass accuracy is within 0.173 ppm and 0.842 ppm for $[Cd(NO_3)_3]^-$ and $[Cd(NO_3)_2(mp)]^-$ respectively.
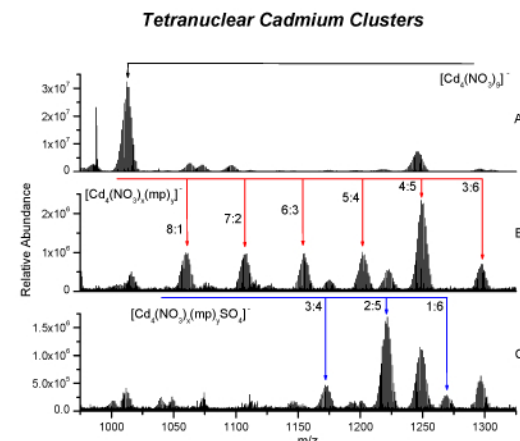
Tetranuclear Cadmium Clusters

Figure 4: ESI-FTMS spectra of the Cd_4 cluster region for solutions A, B and C.
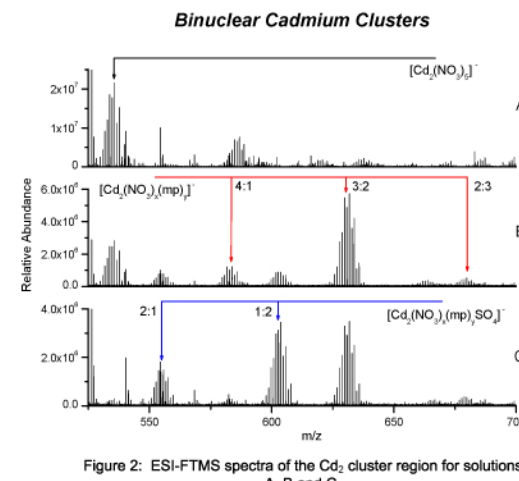
Binuclear Cadmium Clusters

Figure 2: ESI-FTMS spectra of the Cd_2 cluster region for solutions A, B and C.

Polynuclear (2-5) Cadmium Clusters (Figures 2-5)

■ Reaction of $Cd(NO_3)_2$ with 2-mercaptopyridine (**mpH**) results in the formation of clusters of the type $[Cd_n(NO_3)_x(mp)_y]^-$ in which x+y = n+1.

■ Introduction of H_2S (g) to the solution results in the formation of metal sulfides which are oxidized to form cadmium sulfate clusters.

■ Increasing abundance of sulfidic cadmium clusters associated with diminished cadmium nitrate signal along with the systematic displacement of nitrate with sulfidic species suggest that ESI is sampling the products of sequential solution processes.
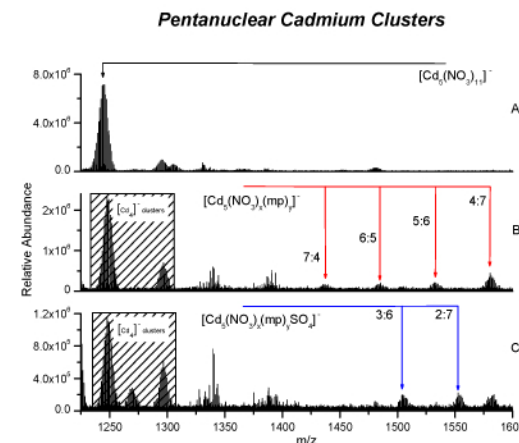
Pentanuclear Cadmium Clusters

Figure 5: ESI-FTMS spectra of the Cd_5 cluster region for solutions A, B and C.
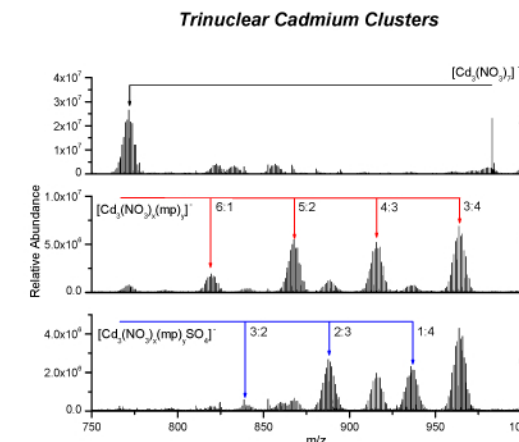
Trinuclear Cadmium Clusters

Figure 3: ESI-FTMS spectra of the Cd_3 cluster region for solutions A, B and C.

CID of Cationic Cadmium Clusters (Figure 6)

■ Pyridal functionality allows for protonation resulting in the formation of cations such as $[Cd(mp)_3+2H]^+$.

■ Collision Induced Dissociation (CID) experiments show multiple neutral losses of 2-mercaptopyridine (**mpH**).
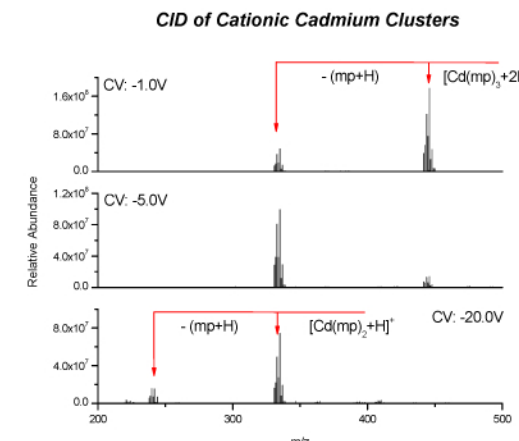
CID of Cationic Cadmium Clusters

Figure 6: ESI FT-MS CID spectra of $[Cd(mp)_3+2H]^+$ at collision potentials of -1.0V, -5.0V and -20.0V.

Conclusions

■ Small $Cd_n(NO_3)_{2n+1}$ clusters appear in dilute $Cd(NO_3)_2$ solutions. These clusters are precursers to the formation of an ionic solid.

■ Treating dilute $Cd(NO_3)_2$ solutions with 2-mercaptopyridine gives successive substitutions of _mp_ for NO_3 in observed clusters. These clusters are intermediate to the formation of stable $Cd_n(mp)_y$ species (eg: n= 4 Dance, Choy, and Scudder 1984).

■ Treating dilute $Cd(NO_3)_2$ solutions with H_2S then mpH produces clusters in which a sulfate replaces two nitrates giving $Cd_n(NO_3)_x(mp)_ySO_4$ clusters. These clusters are oxidized forms of sulfur rich molecular species $Cd_n(mp)_y(S)z$ (eg: n= 8, 10, 17, 32 Lover et al. 1997).

Future Experiemnts

■ Pursue further characterization of cationic sufidic metal clusters.

■ Characterize other metal systems (M=Zn, Co, Fe)

■ Probe the effects of concentration on cluster formation.

■ Vary counter ions and sulfide ligands.

Aknowledgements

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