Communication

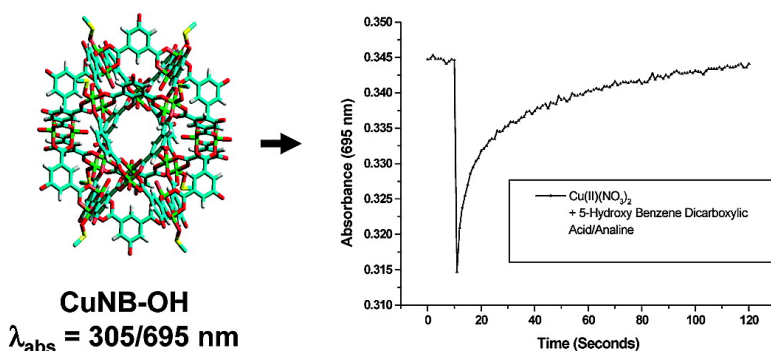# How Fast Do Metal Organic Polyhedra Form in Solution? Kinetics of [Cu(5-OH-bdc)L] Formation in Methanol

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CuNB-OH
λ_{abs} = 305/695 nm

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How Fast Do Metal Organic Polyhedra Form in Solution? Kinetics of [Cu$_2$(5-OH-bdc)$_2$L$_2$]$_{12}$ Formation in Methanol

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The faceted polyhedra, commonly referred to as nanoballs (NBs) represent a unique subset of metal−organic materials (MOMs) in that they are discrete structures thus allowing for the investigation of solution properties due to the high solubility in a variety of solvents.[1−8] In addition, the fact that these discrete structures are composed of M$_2$(RCO$_2$) type paddlewheel clusters (where M is a metal cation and RCO$_2$ is an organic carboxylic acid) allows for tunability in both dimensionality and function through variation in the structural properties of the organic ligand. With this in mind, a wide variety of NBs have been synthesized utilizing Cu^{2+} and 1,3 benzendicarboxylate ligands (bdc) due to the propensity for Cu^{2+} to form the paddle wheel geometry with carboxylate ligands. To date, CuNBs have been prepared with substituents at the 5-postion of the bdc that contain −NH$_2$, −*tert*-butyl, −NO$_2$, −SO$_3$, −OCH$_3$, −OH, −C$_{12}$H$_{25}$, −*o*-napthyl, and −*o*-benzyl.[9−11] These self-assembled CuNBs contain solvent molecules axially coordinated to the Cu ions on both the exterior and interior of the NB as well as relatively large molecular volumes (∼9 to ∼50 nm^3 depending upon the type of substitution on the aromatic ring).

A particularly interesting CuNB is the self-assembled [Cu$_2$(5-OH-bdc)$_2$L$_2$]$_{12}$ (where (5-OH-bdc)$^{2−}$ = 5-hydroxy benzene-1,3-dicarboxylate and L is a DMSO, methanol, or water) complex (CuNB-OH)(Figure 1).[12] CuNB-OH is readily soluble in methanol, can be easily prepared in high yields, and exhibits spectroscopic properties that allow for solution characterization.[12] Specifically, the optical spectrum of the CuNB-OH complex is dominated by ligand absorbance at 305 nm and a weaker Cu^{2+} to ligand charge transfer transition at ∼695 nm which are distinct from the absorption of either the free ligand (∼312 nm) or Cu^{2+}(NO$_3$)$_2$ (>750 nm) in methanol. Furthermore, previous fluorescence polarization studies indicate that CuNB-OH retains a spherical shape in solution.[12] The identification of unique optical signals associated with the CuNB-OH complex provides an avenue through which to explore not only the solution properties (including stability, reactivity, etc) but also the mechanism through which faceted polyhedra are formed. In this communication the kinetics of CuNB-OH formation are examined in methanol using rapid mixing techniques (stopped flow) together with transient absorption spectroscopy.

The rate of development of the 695 nm absorption band (which is attributed to fully coordinated Cu^{2+} and thus formation of the CuNB-OH)[12] is monitored by mixing 5-hydroxy bdc (OH-bdc) and aniline (base required for deprotonation of the OH-bdc) in methanol (syringe 1) with Cu^{2+}(NO$_3$)$_2$ (syringe 2) in methanol in equimolar ratios. Figure 2 displays transient optical changes subsequent to mixing on a ∼110 s time scale (from the mixing point). The data display a biphasic decay back to the premix absorbance (due to the previous solution of fully formed CuNB-OH in the mixing cell) with lifetimes of $\tau_1 \approx 4.4 \pm 0.2$ s and $\tau_2 \approx 42 \pm 2$ s. Interestingly, 92% of the 695 nm absorbance is developed in <100 ms. The observed rates are also independent of the concentration of either Cu^{2+}(NO$_3$)$_2$ or OH-bdc (see Supporting Information). Examination
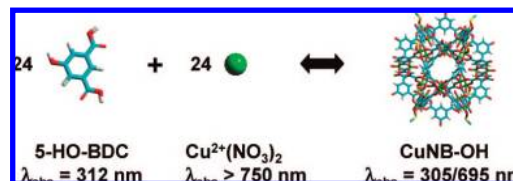

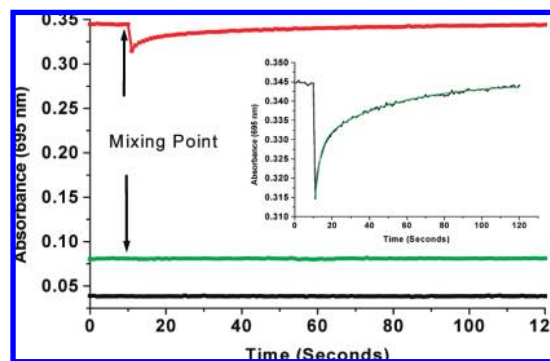**Figure 1.** Schematic illustrating CuNB-OH formation from OH-bdc and Cu^{2+}(NO$_3$)$_2$.

Figure 2. Stopped-flow/absorption spectroscopy associated with the mixing of OH-bdc/aniline+Cu^{2+}(NO$_3$)$_2$ vs Cu^{2+}(NO$_3$)$_2$ dilution (red) and OH-*p*-hydroxybenzoate/aniline+Cu^{2+}(NO$_3$)$_2$ vs Cu^{2+}(NO$_3$)$_2$ dilution (green). Cu^{2+}(NO$_3$)$_2$ dilution is shown in the black trace. Inset: Expansion of early mixing time data.

of the kinetics associated with formation of the molecular square building unit consisting of Cu$_2$(*p*-hydroxy benzoate)$_4$ which are unable to form the CuNB demonstrates that paddle wheel formation occurs on a time scale faster than the acquisition time presented in Figure 2 (∼100 ms per data point). Expansion of the kinetics to faster time scales reveals three additional kinetic phases (Figure 3). On time scales < ∼10−15 ms (mixing time), ∼22% of the absorbance at 695 nm is formed suggesting formation of a population of fully coordinated Cu^{2+} clusters on this time scale. This is consistent with kinetic data of Cu$_2$(*p*-hydroxy benzoate)$_4$, also obtained on the faster time scale, which indicates complete paddle wheel formation within the stopped-flow mixing time (<∼15 ms). The faster time kinetic phases observed subsequent to mixing of OH-bdc with Cu^{2+} have lifetimes (% contribution of the total absorbance change) of $\tau_3 = 310 \pm 4$ ms (20%), $\tau_4 = 26 \pm 0.1$ ms (49%), and $\tau_5 < 15$ ms (22%) with τ_3 and τ_4, again, being independent of the concentrations of OH-bdc and Cu^{2+}.

The observed kinetics can shed light onto the mechanism of formation for faceted polyhedra with possible relevance to a more general mechanism associated with MOM assembly. The kinetic results are consistent with one of two possible mechanistic pathways. It is clear from the lack of concentration dependence of the slower kinetic phases as well as the kinetic results of the model paddle wheel that the events occurring in <∼15 ms results in

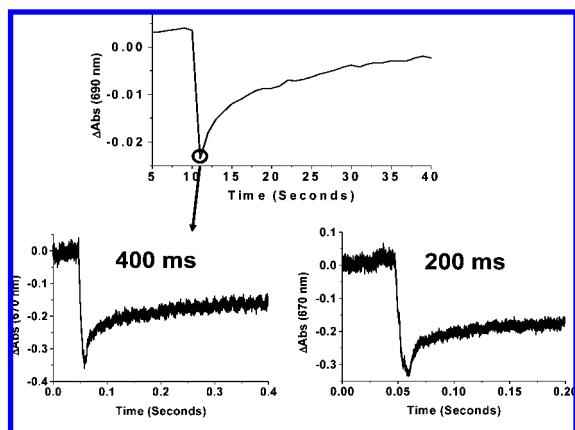**Figure 3.** Stopped-flow/absorption spectroscopy associated with the mixing of OH-bdc/aniline+$Cu^{2+}(NO_3)_2$ on faster time-scales.

formation of the paddle wheel and possibly larger assemblies. One possible pathway for the subsequent assembly of square paddle wheel building units into CuNB-OH which may account for the longer lifetime processes involves the diffusion limited linking of the building units, dimers of the building units, trimers, etc. Utilizing a Stoke's Einstein analysis (which assumes the building units sweep out a spherical volume), the diffusion coefficients ($D = k_B T/6\pi r\eta$ where k_B is Boltzman's constant, T is the temperature, r is the radius of the building unit, and η is the viscocity) and diffusional rates ($k_d = 4\pi N_A(r_A + r_B)(D_A + D_B)$ where $r_A + r_B$ is the reaction distance between two building units and N_A is Avagadro's number) can be estimated based upon the dimensions of each fragment. Using this analysis and a radius of 8.6 Å for the building unit and a methanol viscosity at 298 K of $5.84e^{-7}$ m²/s, the k_d values are <15 ms regardless of unit dimensions (as $D_A + D_B$ decreases, ($r_A + r_B$) increases).[13] This would suggest that both the building units and larger fragments all form within the mixing time of <15 ms.

The longer time processes must then be associated with activation controlled isomerization of existing fragments followed by subsequent fragment condensation, which will be referred to as the FIC mechanism (Fragment Isomerization Condensation). There are two potential pathways (outlined in Figure 4) through which the FIC mechanism would be consistent with the observed kinetics. The FIC-A mechanism will be described as a simultaneous isomerization/condensation process. Within this mechanism, large fragments are formed in <15 ms with a variety of lengths/conformations. Within this distribution, certain fragment types undergo isomerization and condense with other specific fragments to directly form the fully assembled CuNB-OH. The FIC-B mechanism involves *sequential* isomerization−condensation processes in which a small fraction of the fragments (formed during the first ~15 ms) isomerizes and link, forming a new distribution of larger fragments. As the concentration of these new fragments increases, they also undergo isomerization/linakge with either existing fragments or with other newly formed fragments. This process continues (four isomerization/condensation steps would account for the observed rates) until the complete CuNB-OH complex is formed.
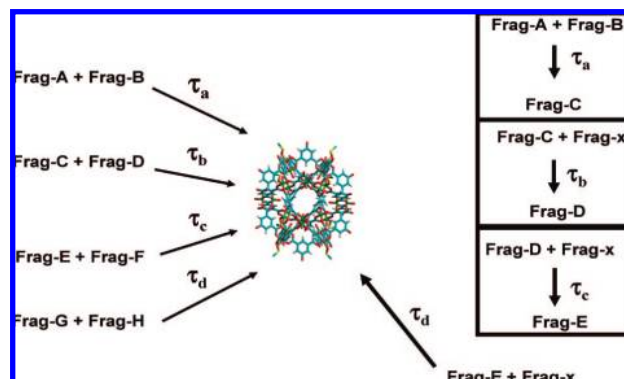

Figure 4. Diagram illustrating two possible pathways within the Fragment Isomerization Condensation (FIC) mechanism for CuNB-OH formation.

To date studies concerning the mechanism through which MOMs are formed have been limited to probing the relationship between reaction conditions (such as temperature, pH, water content, etc.) and the type of structure formed.[14,15] However, one recent study has examined the stability of Cu^{2+}-pyrogallol[4]arene nanocapsules (CuPgCn) in methanol.[16] Based upon equilibrium MALDI-TOF studies, it was concluded that Cu^{2+} rapidly binds to the PgCn followed by capsule formation. These results are consistent with the observations presented here in which the Cu^{2+} square building units assemble in <15 ms. Thus, <10 ms building unit assembly may be a common feature of discrete MOM formation.

Supporting Information Available: Additional kinetics traces, curve fitting analysis, and experimental details. This information is available free of charge via the Internet at http://pubs.acs.org.

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