Molecular simulation of copper(II)-bound organic compounds for use in metal-organic chemical vapor deposition (MOCVD) of copper films

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Agenda

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Metal-Organic Chemical Vapor Deposition

- The microelectronics industry is gaining interest in copper films as opposed to aluminum films.
- Organic copper compounds are proposed as precursors for depositing copper films via a process called metal-organic chemical vapor deposition (MOCVD).
Purpose

• Since we are interested in deposition of thin films, we want to be able to simulate the reaction at the atomic level.

• To do this, we must accurately calculate:
  – Optimum geometries of our reactant(s)
  – Bond energies
  – Transition structures
Molecular Simulations

- These could be obtained from quantum mechanical electronic structure calculations.
- Quantum mechanics is a fundamental description of matter at the atomic scale.
- We can predict material properties from the calculation of interaction of electrons.

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x)\Psi(x) = E\Psi(x)\]

Where:

- \(\hbar\) = Planck's constant divided by \(2\pi\)
- \(m\) = mass of particle
- \(V\) = potential energy of the particle
- \(x\) = position
- \(\Psi\) = the wave function
- \(E\) = total energy
Computer Program Used

- Gaussian98 is a quantum mechanical software package.
- Given an input file, Gaussian98 can calculate optimum geometry, vibrational frequencies, total energy, transition structure, etc.
Gaussian Input Files

• In order to find what we need in Gaussian98, the following six inputs must be specified:
  – Structure (in internal or Cartesian coordinates)
  – Model theory (such as DFT*, HF** or a hybrid)
  – Basis set (helps Gaussian represent these atoms in its calculations)
  – Keywords (types of calculations; OPT for geometry optimization, FREQ for vibrational frequencies, etc.)
  – Multiplicity of the molecule (multiplicity = number of unpaired electrons in the structure + 1)
  – Charge of the molecule

*DFT – Density Functional Theory, uses electronic density instead of the wave function as the fundamental variable in the Schrödinger equation.

**HF – Hartree-Fock Theory, does not take electron correlation into consideration.
Methodology

• Run an initial geometry optimization:
  – Low-level theory (method and basis set)
  – Simplified structure (removing hydrocarbon chains)
  – Build structure (adding hydrocarbon chains)

• Re-run the optimized structure from the previous calculation:
  – Higher-level theory
Case Study #1: Copper (II) dimethylamino-2-propoxide

Fig. 1. Solid state structure of 1 showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cu–O(1) 1.8667(17), Cu–N(1) 2.0684(19), O(1)–Cu–O(1') 180.00(15), O(1)–Cu–N(1) 93.30(8), O(1')–Cu–N(1) 86.70(8).

Interatomic distances of interest in Å for stereoisomers of copper(II) dimethylamino-2-propoxide

Method: HF
Basis set: LanL2DZ
Charge: 0
Multiplicity: 2
Dummy atom used

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Species</th>
<th>Experimental*</th>
<th>(R),(R) configuration</th>
<th>(R),(S) configuration</th>
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<td>1.879</td>
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Interatomic distances of interest in Å for (R),(R)-copper(II) dimethylamino-2-propoxide using higher-level theory

Method: B3LYP
Multiplicity: 2
Charge: 0
Dummy atom used

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<th>Bonds</th>
<th>Species</th>
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<th>Lower-level (HF Theory, LanL2DZ)</th>
<th>a) LanL2DZ basis set</th>
<th>b) Mixed basis set (3-21g for C, H; LanL2DZ for Cu, O, N)</th>
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Total Energy Calculations in hartrees

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<td>(R),(R)-copper(II)-dimethylamino-2-propoxide</td>
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</tbody>
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(1Eh = 27.211eV)
Case Study #2: Copper (II) hexanoate

Chelating bidentate

CA Index Name: Copper, tetrakis(hexanoato-O,O')di-, (Cu-Cu) (9Cl)
Registry Number: 160895-94-3

Paddle-wheel

CA Index Name: Copper, tetrakis[µ-(hexanoato-κO:κO')]di-, (Cu-Cu) (9Cl)
Registry Number: 24594-06-7
Input file for copper(II) hexanoate
Copper(II) hexanoate

• Why didn’t the structure converge?
  – Long side chains
  – Large molecule
  – Transition metals (Cu)

• How could calculations be performed?
  – Using a simpler method first
  – Simplifying the structure
Conclusions

- Simulations show good agreement with experimental structure of copper(II)dimethylamino-2-propoxide. Nitrogen lone pairs form a dative bonding with copper.
- Dummy atoms required to adequately represent the O-Cu-O linear bond.
- Compared to experimental values for bond lengths, low-level theory yielded more accurate Cu-O bond lengths, and higher-level theory yielded more accurate Cu-N bond lengths.
Future Work

• Using the optimized structures of the precursors, the bond energies and transition structures must be calculated.

• For copper(II) hexanoate, simplifying the input structure and increasing the model theory, and using larger basis set for the Cu atoms might help achieve convergence.
Acknowledgements

• NSF EEC-0453432 Grant, Novel Materials and Processing in Chemical and Biomedical Engineering (Director C.G. Takoudis).
• NSF CTS-0533499 & 0434201 GOALI: Atomic-scale Investigation of High Dielectric Constant Thin Films Using In Situ and Other Techniques, (Director C.G. Takoudis)
• Dr. Christos Takoudis, UIC
• Javier Rosado, UIC
Questions
Simplifying the Schrödinger Equation

• There are two leading methods for solving the Schrödinger equation.

• In Hartree-Fock (HF) method, each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons.*

• In Density Functional Theory (DFT) method, the electron density is used instead of the wave function as the fundamental variable in the Schrödinger equation.

*http://vergil.chemistry.gatech.edu/notes/hf-intro/hf-intro.pdf
Basis Sets

• 3-21G - The valence functions are split into one basis function with two gaussian-type orbitals (GTOs), and one with only one GTO. (This is the "two one" part of the nomenclature.) The core consists of three primitive GTOs contracted into one basis function.
Basis Sets (cont.)

- LanL2DZ – it is a double-zeta basis set (DZ); every member of a minimal basis set is replaced by two functions. In this way both core and valence orbitals are scaled in size. For some heavier atoms, double zeta basis sets may have slightly less than double the number of minimal basis set orbitals. Care must be taken when naming these basis sets, since their names don’t accurately describe its function like for 3-21g.
Using mixed basis sets

• A mixed basis set involves using a certain basis set to describe a group of atoms, while using a more specific basis set for other atoms. For example, you could instruct Gaussian98 to use the small 3-21g* basis set for H and C atoms, while using the larger LanL2DZ** basis set for simulating larger atoms, like transition metals.

*3-21g is described in: J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. 102, 939 (1980).

Gaussian Input Files (cont.)

- Input files for Gaussian can be created using the user interface in WebMO (http://www.webmo.net)
Interatomic distances of interest in Å for (R),(S)-copper(II) dimethylamino-2-propoxide using B3LYP method

<table>
<thead>
<tr>
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</tbody>
</table>

Interatomic distances of interest in Å for (S),(S)-copper(II) dimethylamino-2-propoxide using B3LYP method

**Species** | **Experimental** | **a) LanL2DZ basis set** | **b) Mixed basis set (3-21g for C, H; LanL2DZ for Cu, O, N)**
--- | --- | --- | ---
Cu-O1 | 1.8667 | 1.911 | 1.908
Cu-O2 | 1.8667 | 1.906 | 1.914
Cu-N1 | 2.0684 | 2.088 | 2.056
Cu-N2 | 2.0684 | 2.093 | 2.058

Dummy atoms

- Since Gaussian98 has trouble dealing with 180° angles, if an input file contains a 180° angle in its structure, Gaussian will terminate.
- To eliminate this, a dummy atom is used. This is just a point of reference so that Gaussian can refer the positions of the atoms in question to the dummy atom, and therefore Gaussian does not recognize the 180° angle.