

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

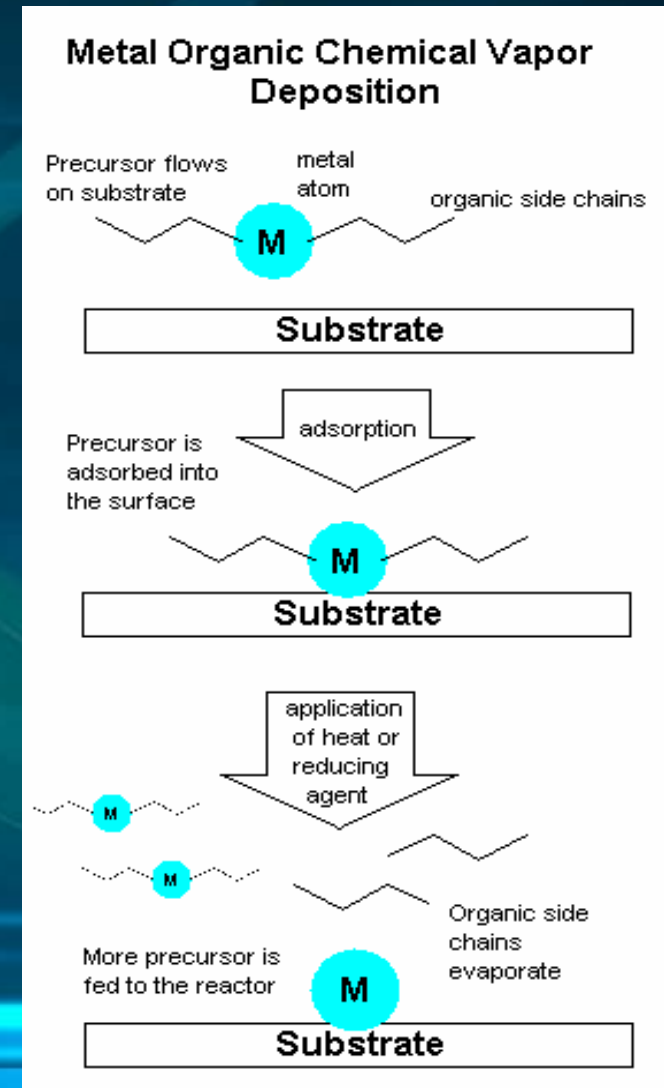
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REU-NSF Summer Program in UIC
August 4, 2005

Agenda

- Metal-Organic Chemical Vapor Deposition
- Purpose
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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.

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

Where :

\hbar = Planck's constant divided by 2π

m = mass of particle

V = potential energy of the particle

x = position

Ψ = 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

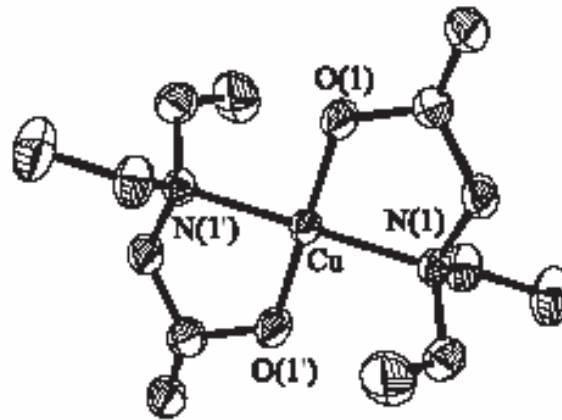
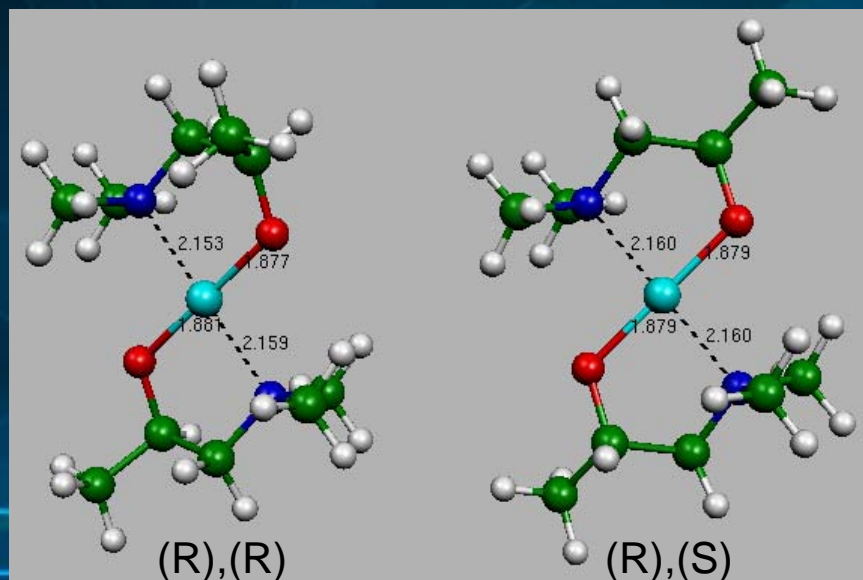


Fig. 1. Solid state structure of **1** showing 50 % probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and bond angles [$^\circ$]: Cu–O(1) 1.8667(17), Cu–N(1) 2.0684(19), O(1)–Cu–O(1') 180.00(15), O(1)–Cu–N(1) 93.30(8), O(1')–Cu–N(1) 86.70(8).

[From: Becker R, Devi A, et al. *Chem. Vap. Deposition*, 9, No.3, 2003, p. 150.]

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



Method: HF

Basis set:
LanL2DZ

Charge: 0

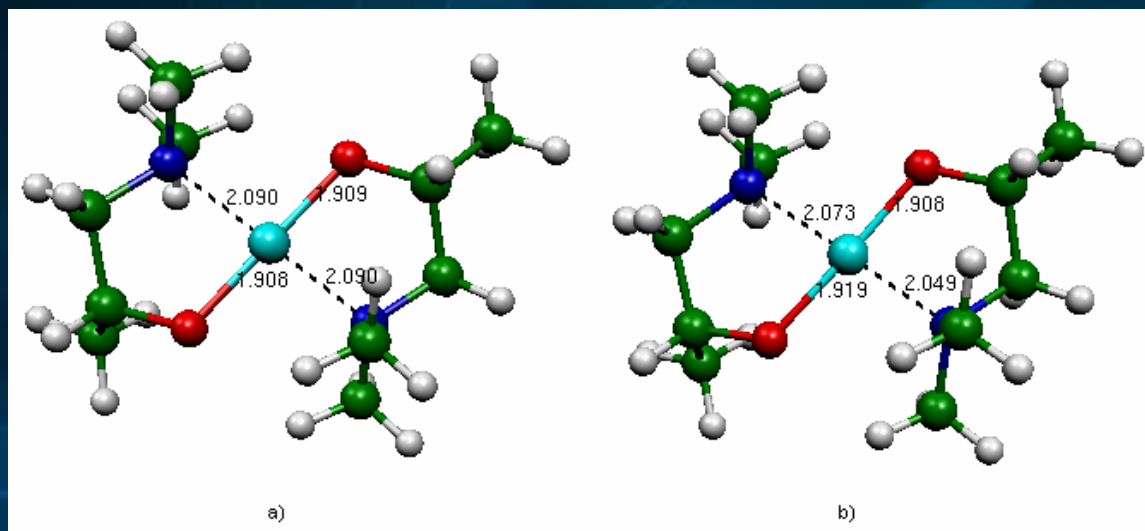
Multiplicity: 2

Dummy atom
used

Bonds \ Species	Experimental*	(R),(R) configuration	(R),(S) configuration
Cu-O1	1.8667	1.877	1.879
Cu-O2	1.8667	1.881	1.879
Cu-N1	2.0684	2.153	2.160
Cu-N2	2.0684	2.159	2.160

*Becker R, Devi A, et al. *Chem. Vap. Deposition*, 2003, 9, No. 3, p. 150.

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

Bonds \ Species	Species	Experimental*	Lower-level (HF Theory, LanL2DZ)	a) LanL2DZ basis set	b) Mixed basis set (3-21g for C, H; LanL2DZ for Cu, O, N)
Cu-O1		1.8667	1.877	1.909	1.908
Cu-O2		1.8667	1.881	1.908	1.919
Cu-N1		2.0684	2.153	2.090	2.049
Cu-N2		2.0684	2.159	2.090	2.073

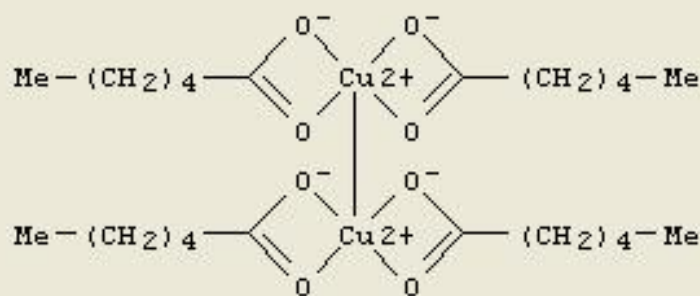
*Becker R, Devi A, et al. *Chem. Vap. Deposition*, 2003, 9, No. 3, p. 150.

Total Energy Calculations in hartrees

Stereoisomer	Theory: HF Basis Set: LanL2DZ	Theory: B3LYP Basis Set: LanL2DZ	Theory: B3LYP Basis Set: Mixed (3-21G for C, H; LanL2DZ for Cu, O, N)
(R),(R)-copper(II)- dimethylamino-2- propoxide	-845.764067	-851.192803	-2286.204000
(R),(S)-copper(II)- dimethylamino-2- propoxide	-845.769537	-851.197425	-2286.407842
(S),(S)-copper(II)- dimethylamino-2- propoxide	-845.764070	-851.192862	-2286.395614

(1Eh = 27.211eV)

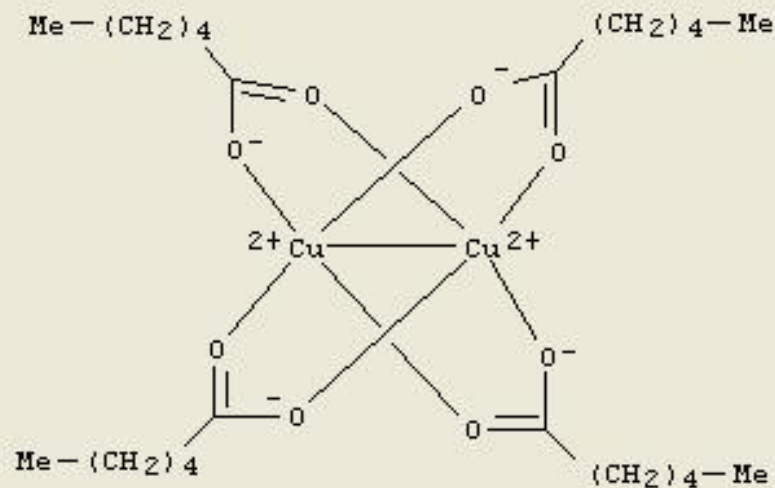
Case Study #2: Copper (II) hexanoate



Chelating bidentate

CA Index Name: Copper,
tetrakis(hexanoato-O,O')di-, (Cu-Cu) (9CI)

Registry Number: 160895-94-3

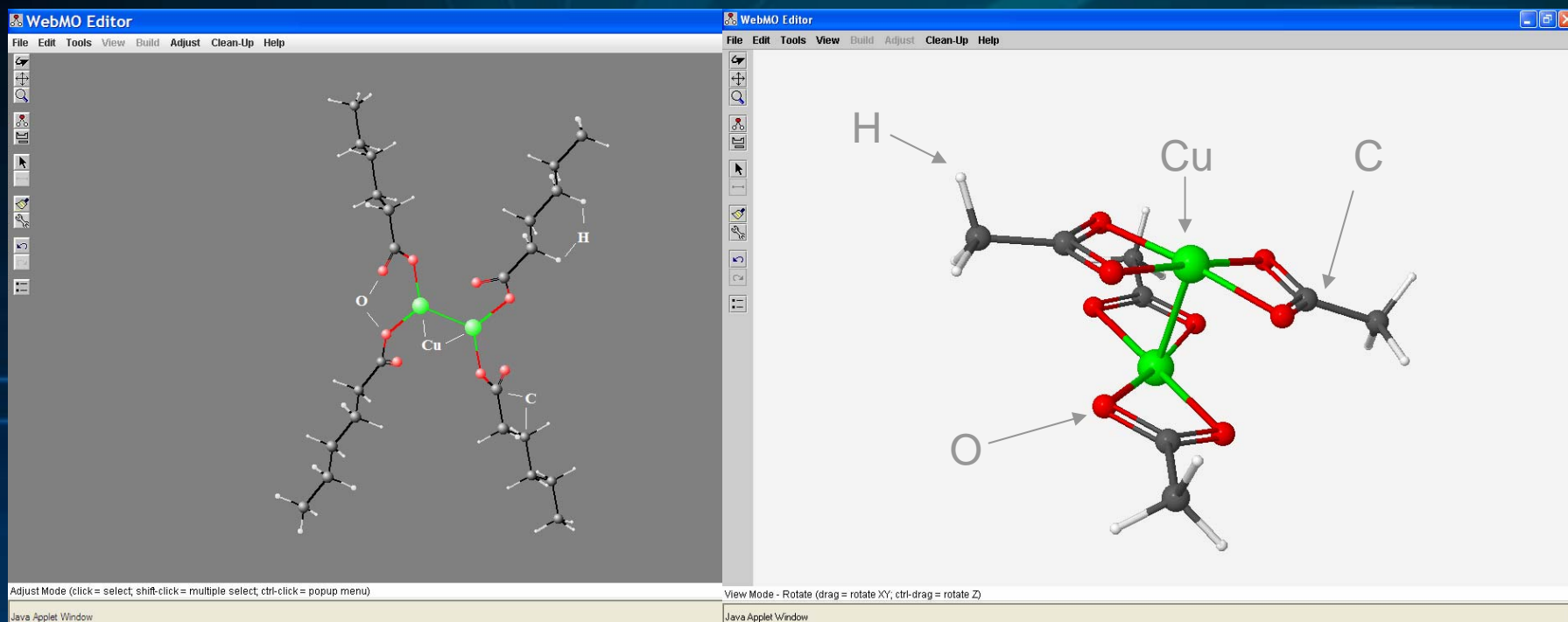


Paddle-wheel

CA Index Name: Copper, tetrakis[μ -
(hexanoato- κ O: κ O')]di-, (Cu-Cu)
(9CI)

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

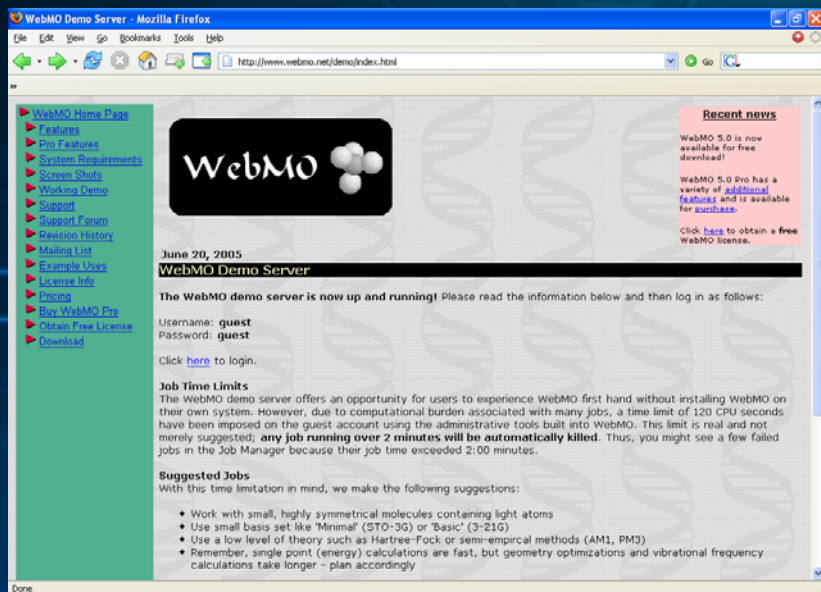
- A mixed basis set involves using a certain basis set to describe a group of atoms, while using a more specific basis set for other atoms. For example, you could instruct Gaussian98 to use the small 3-21g* basis set for H and C atoms, while using the larger LanL2DZ** basis set for simulating larger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

LanL2DZ is described in: P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82, 270 (1985).

Gaussian Input Files (cont.)

- Input files for Gaussian can be created using the user interface in WebMO (<http://www.webmo.net>)



The screenshot shows the WebMO Demo Server website. The page features a navigation menu on the left with links such as 'WebMO Home Page', 'Features', 'Pro Features', 'System Requirements', 'Screen Shots', 'Working Demo', 'Support', 'Support Forum', 'Revision History', 'Mailing List', 'Example Uses', 'License Info', 'Pricing', 'Buy WebMO Pro', 'Obtain Free License', and 'Download'. The main content area includes a 'WebMO' logo, a 'Recent news' section with a pink background, and a 'WebMO Demo Server' announcement dated June 20, 2005. The announcement states that the demo server is now up and running and provides login credentials: Username: guest, Password: guest. It also includes a 'Job Time Limits' section and 'Suggested Jobs' with a list of recommendations for users.

WebMO

Recent news

WebMO 5.0 is now available for free download!

WebMO 5.0 Pro has a variety of additional features, and is available for purchase.

Click [here](#) to obtain a free WebMO license.

June 20, 2005
WebMO Demo Server

The WebMO demo server is now up and running! Please read the information below and then log in as follows:

Username: **guest**
Password: **guest**

Click [here](#) to login.

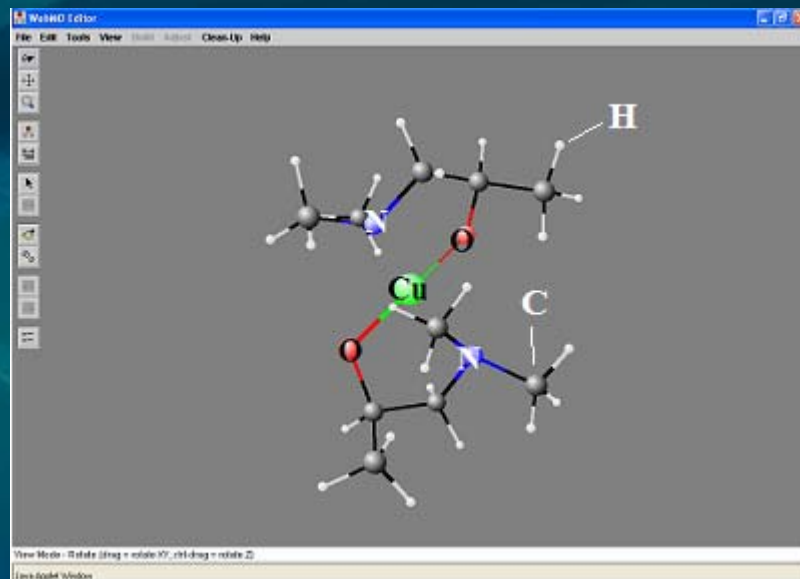
Job Time Limits

The WebMO demo server offers an opportunity for users to experience WebMO first hand without installing WebMO on their own system. However, due to computational burden associated with many jobs, a time limit of 120 CPU seconds have been imposed on the guest account using the administrative tools built into WebMO. This limit is real and not merely suggested; **any job running over 2 minutes will be automatically killed**. Thus, you might see a few failed jobs in the Job Manager because their job time exceeded 2:00 minutes.

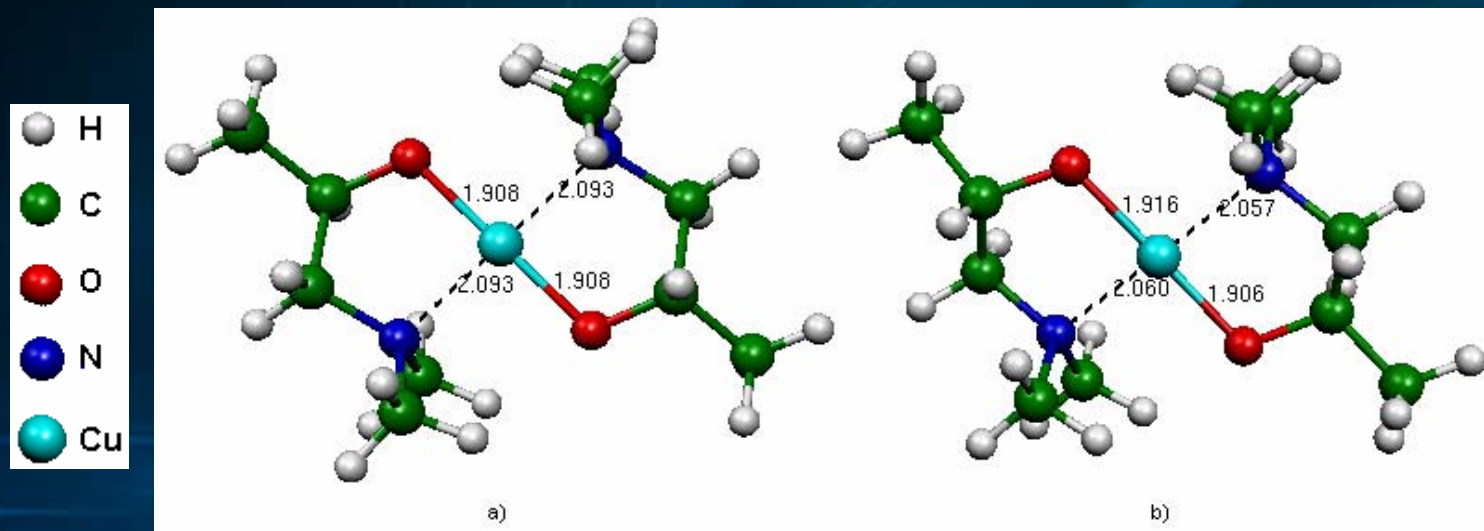
Suggested Jobs

With this time limitation in mind, we make the following suggestions:

- Work with small, highly symmetrical molecules containing light atoms
- Use small basis set like 'Minimal' (STO-3G) or 'Basic' (3-21G)
- Use a low level of theory such as Hartree-Fock or semi-empirical methods (AM1, PM3)
- Remember, single point (energy) calculations are fast, but geometry optimizations and vibrational frequency calculations take longer - plan accordingly



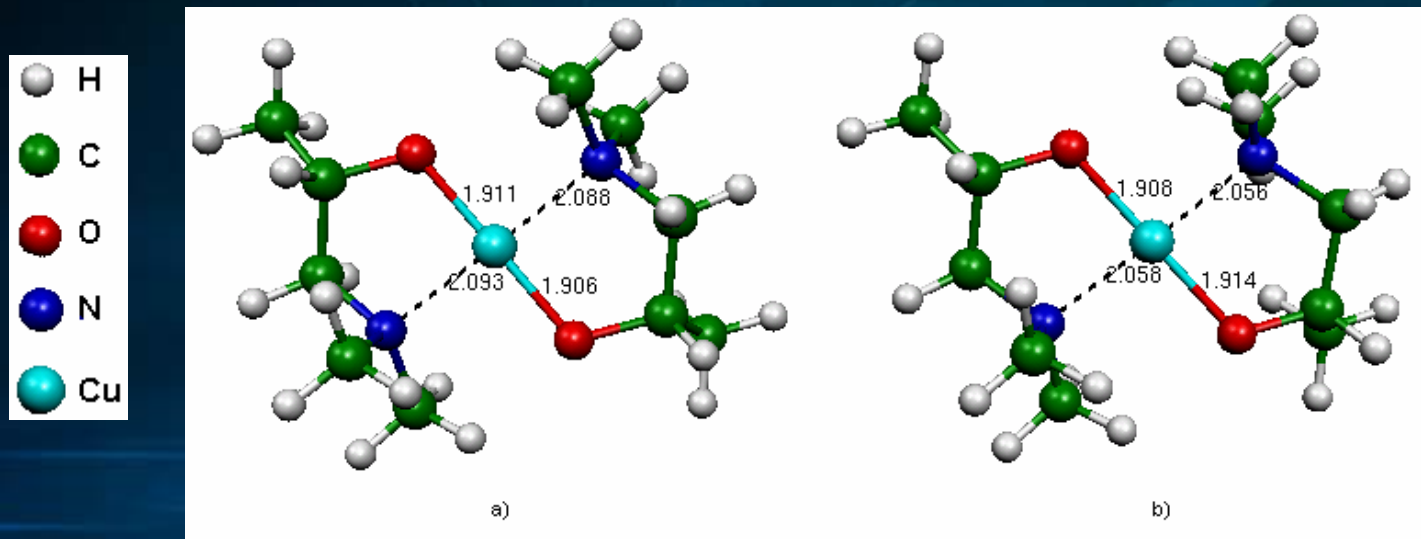
Interatomic distances of interest in Å for (R),(S)-copper(II) dimethylamino-2-propoxide using B3LYP method



Bonds	Species	Experimental*	a) LanL2DZ basis set	b) Mixed basis set (3-21g for C, H; LanL2DZ for Cu, O, N)
	Cu-O1	1.8667	1.908	1.916
	Cu-O2	1.8667	1.906	1.906
	Cu-N1	2.0684	2.093	2.057
	Cu-N2	2.0684	2.093	2.060

*Becker R, Devi A, et al. *Chem. Vap. Deposition*, 2003, 9, No. 3, p. 150.

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



Bonds \ Species	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

*Becker R, Devi A, et al. *Chem. Vap. Deposition*, 2003, 9, No. 3, p. 150.

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.