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

By: Rivera-Montalvo, Alexis A.
University of Puerto Rico, Mayagüez Campus

For: REU-NSF Program
University of Illinois at Chicago
Advisor: Dr. Christos Takoudis
Date: August 3, 2005

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

Table of Contents

Page

List of Figures

Summary

Copper-containing organic molecules are being investigated as means of depositing copper films. Since the films deposited are very thin, we are interested in the reaction as it occurs at the atomic level. Therefore, we must be able to first simulate our precursor(s). In order to determine their viability as such, some calculations such as bond lengths and energies must be calculated. Using a computer program called Gaussian98[1], these can be calculated. First, a geometry optimization is performed. Then, using the optimized structure, the necessary calculations can be performed. The case studies are copper(II)dimethylamino-2-propoxide and copper(II) hexanoate. Copper(II) dimethylamino-2-propoxide has four different spatial arrangements due to its two chiral carbons. Since the molecule is symmetric, two of these spatial arrangements, namely (R),(S)-copper(II)dimethylamino-2-propoxide and (S),(R)-copper(II)dimethyl-amino-2-propoxide, are equivalent. All three spatial arrangements converged into an optimized structure. However, when analyzing the orbitals and bonds of copper(II)dimethylamino-2-propoxide, one of the nitrogen atoms does not have a sp^3 configuration like it should. This occurs in two structures of copper(II)dimethylamino-2-propoxide, specifically on the (R),(R)- and (R),(S)- configurations. The cause of the abnormality appears to be that the input file did not have a 180-degree angle between the copper atom and its bound oxygen. Gaussian98 seems to have trouble understanding these angles, and therefore a

---

[1] Gaussian 98, Revision A.11.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2002.

technique called a dummy atom was used. A dummy atom is a point of reference in space where the position of these atoms can be referred to so that the program does not register a 180-degree angle. These structures were run once more using different input files and basis sets. Using a more thorough theory, called B3LYP, and adding a dummy atom to the input structures, a symmetric geometry was achieved for all three different stereoisomers of copper(II)dimethylamino-2-propoxide. On the other hand, copper(II) hexanoate has not yielded an output yet, due to the lengthy calculations the program must do. Literature research proposes two different structures for copper(II) hexanoate, called the paddle-wheel and chelating bidentate structures. However, we will focus more on the chelating bidentate structure instead. This structure was also submitted to Gaussian98, but output could not be obtained because Gaussian98 could not converge into an optimized structure within its capabilities. As a possibility for future work in this matter, care should be taken when analyzing a large structure such as copper(II) hexanoate, by either simplifying the structure to obtain an optimized geometry, then slowly enlarging the structure and resubmitting it to arrive at a final converged structure; or by using a much simpler method and basis set to arrive at a favorable input structure that can later be resubmitted using a higher-level theory and larger basis set for a more accurate calculation.

Introduction

The microelectronics industry has developed an interest for the use of copper films as opposed to aluminum films, greatly in part by copper's higher conductivity and other properties[2]. A relatively low-cost option to making these copper films is the use of copper organic compounds to deposit said films. In order to do this, copper organic compounds are subjected to metal-organic chemical vapor deposition (MOCVD), a process in which the metals are deposited by breaking the bonds that tie the metal to the organic segments, causing the volatile organic segments to evaporate and leaving a relatively pure metal film. MOCVD can be carried out using a temperature gradient or by exposing the molecule to a reducing agent[2]. A simple schematic of the MOCVD process can be seen in Figure 1.

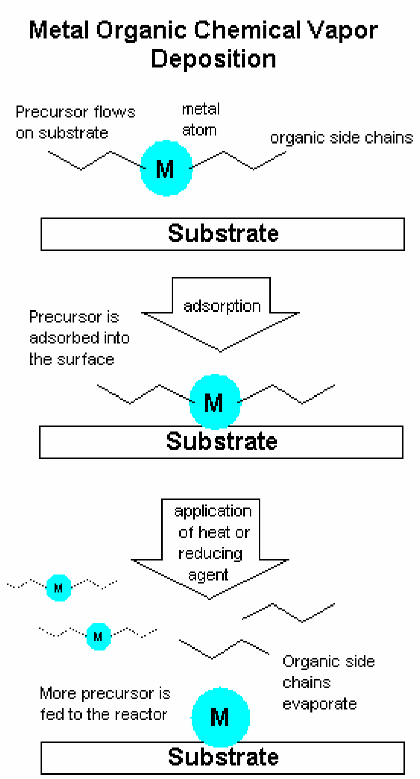


Figure 1. Schematic of the metal-organic chemical vapor deposition (MOCVD) process.

---

[2] Becker R, Devi, A, et al. *Chem. Vap. Deposition* **2003**, 9, No. 3, pp.149-156.

MOCVD yields a very thin film. Since this is the case, we are interested in knowing more about the reaction at the atomic level. In order to know what products the reaction would yield, an optimized geometric structure is needed. Also, the bond energies for all bonds of interest must be calculated. This is done to make sure we will have the desired product, because if other bonds break we might have a totally different product (for example, if there are any Cu-O bonds left unbroken, we might have cupric oxide CuO contamination instead of pure copper). Therefore, it is more favorable to simulate the reaction using quantum mechanical electronic structure calculations.

In order to simulate a molecule, every electron must be accounted for. Each electron, if alone, would be described using Schrödinger's time-independent equation. However, since a molecule may contain many electrons, and the surrounding electrons affect each other, this calculation is impractical, if not impossible. Therefore, several theories can be used to further simplify these calculations.

The Density Functional Theory (DFT) is a theory that substitutes the wave function in Schrödinger's equation for electronic density. This alone may not help, as electrons are in constant movement and the electron density in a point can change. However, there are other approximations that may help. One of such is the Local Density Approximation (LDA), which assumes that the electron density in one point varies so little it can be assumed constant. Another is the Generalized Gradient Approximation (GGA), which takes into consideration small changes in the local electron density. Using a density approximation with a DFT greatly simplifies calculation, since instead of calculating for every electron, the calculation is made throughout the structure in general.

The computer program used was Gaussian98. It is Unix-based, and uses Gaussian-type orbitals to simulate the molecules using DFT methods. In order to obtain output from this program, an input file must be created. This input file must contain an initial structure in the form of internal coordinates (referencing the position of an atom with respect to another instead of using a rectangular coordinate system), a DFT theory (there are many variations; some are more accurate than others, at the cost of speed of calculation) and a basis set. A basis set is a set of data which helps Gaussian98 to simulate the orbitals of a select group of atoms. Some basis sets, like 3-21g or 6-31g are fast, and include data to simulate various elements like carbon, hydrogen, oxygen and such; however, they might have some difficulty emulating transition metals like copper. A basis set like LanL2DZ can describe transition elements in a more accurate manner, while sacrificing speed in the calculation of simpler atoms. Taking this into consideration, in order to increase calculation time without risking accuracy, a mixed basis set can be used. A mixed basis set consists of using a certain basis set for some atoms, while using yet another basis set for another group of atoms in the same input file. In our case, which involves a copper atom in an organic molecule, it is important to correctly analyze the copper atom or atoms (with a basis set of LanL2DZ for example) while using a much simpler basis set to quickly and accurately describe the organic side chains in the molecule (for example, the 3-21g basis set). This would give us a calculation more accurate than the 3-21g basis set, yet at a faster rate than the calculation would take with LanL2DZ.

Once the input file is submitted, the program will carry out an extensive iterative procedure in which the program calculates the total energy in the system. Once the iteration is completed, the program calculates the new structure by displacing the atoms in the structure. The procedure is repeated until the atoms' displacement is small enough from one structure to the other, or if the energy change between the structures is not appreciable. At this time, Gaussian will perform any additional calculations, such as finding the vibrational frequencies, infrared spectra and others.

This project consists on simulating copper(II)-bound organic molecules that are proposed as possible precursors for copper films via MOCVD. First, this document will explain the tools used in the analysis (namely a computer program called Gaussian98 and others) and how the input files were created. Then, the output obtained is shown, explaining the differences between the output files and what these differences can mean. Finally, future work needed is also described, as well as any work being carried out currently.

Methodology

In this study, two copper(II) organic molecules are being studied. The first of the molecules is copper(II)dimethylamino-2-propoxide. Figure 2 shows a chemical structure for copper(II)dimethylaminopropoxide.

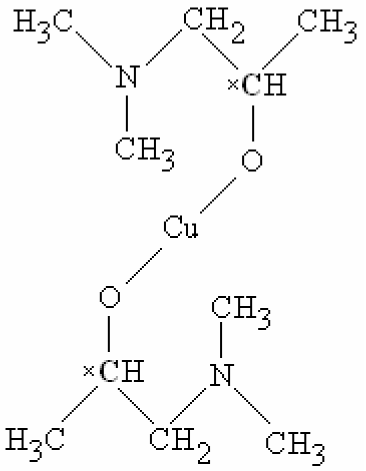


Figure 2. Structure of copper(II)dimethylamino-2-propoxide, where the x denotes a chiral carbon in the structure

Copper(II)dimethylamino-2-propoxide has two chiral carbons in its structure; that is, there are two carbons which have four different groups bound to them, so that the carbon has two possible spatial arrangements. A letter (R) denotes that, in a three-dimensional structure, if the hydrogen is the group facing back, the groups are ordered clockwise by priority (in this case, the order of priority of the groups bound to the chiral carbons in descending order is -OCu…, -CH_2N…, -CH_3). A letter (S) denotes that if the hydrogen faces back in a three-dimensional structure, the groups are ordered by priority counterclockwise. Therefore, for every chiral carbon in a structure, there are two different structures. Figure 3 describes how each chiral carbon is classified.

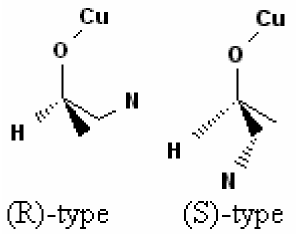


Figure 3. Two possible conformations in the chiral carbons of copper(II)dimethylamino-2-propoxide. Dotted lines indicate that the atom is facing inward; dark lines indicate that the group is facing outward.

This translates to a total of 2^N stereoisomers (compounds that differ only in the patial arrangement of their groups), where N denotes the number of chiral carbons in the molecule. This structure would have four different structures, but since the molecule is symmetric, it is easy to comprehend that the two structures would be equal to each other. If both chiral carbons have opposing denotations (one is (R), one is (S)), this results in one structure instead of two due to its symmetry. Therefore, there are three different structures to analyze: (R),(R)-copper(II)dimethylamino-2-propoxide, (R),(S)-copper(II)dimethylamino-2-propoxide (equal to (S),(R) due to symmetry) and (S),(S)-copper(II)dimethylamino-2-propoxide.

The second copper(II) film precursor being studied is copper(II) hexanoate. Figure 4 shows the structure under investigation.

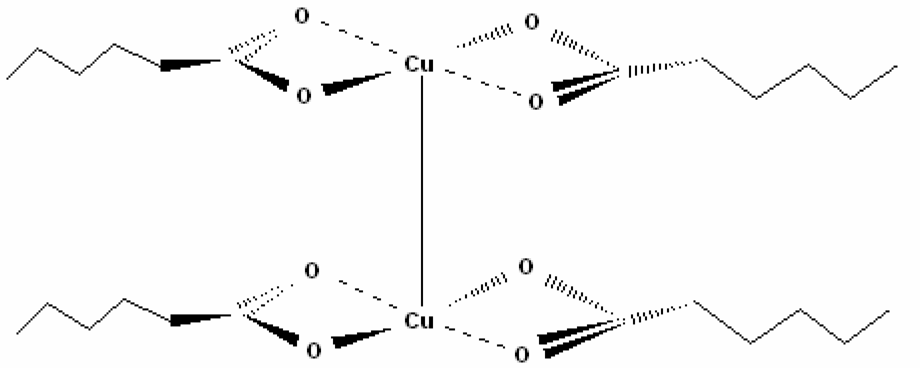


Figure 4. Structure of copper(II) hexanoate. Dotted lines are proposed bonds under investigation.

In order to make the input files, these structures were drawn using a user interface in WebMO[3]. In this website, the user-friendly interface allows you to make input files with relative ease, and run certain simple files. These structures were each drawn on the webpage, and the resulting input files were submitted. Each input file had its own DFT method and basis set, and the output obtained varied accordingly.

The method consisted of first creating an input file of the structure of interest with a low-level theory, such as Hartree-Fock theory (HF), and a small basis set (for example, STO-3G or 3-21G) and submitting the input file for geometry optimization (OPT) and vibrational frequency calculations (FREQ). Using the output from this first step, an input file was created and resubmitted for OPT and FREQ calculations using a larger basis set (such as LanL2DZ). Using the output for this second step, an input file was created and resubmitted for OPT and FREQ calculations using a higher-level theory (B3LYP, which is a density functional theory method) and different basis sets. This procedure can be repeated many times, either using a higher-level theory or a larger basis set.

---

[3] http://www.webmo.net

Results

The three structures of copper(II)dimethylamino-2-propoxide were run with Gaussian98 to find optimum geometries. The first set of data was run with the 3-21g basis set and using the Hartree-Fock (HF) method. However, none of the structures converged using this basis set. The basis set was changed to LanL2DZ to better represent the copper atom. Figure 5 shows a converged optimum structure for copper(II) dimethylamino-2-propoxide.

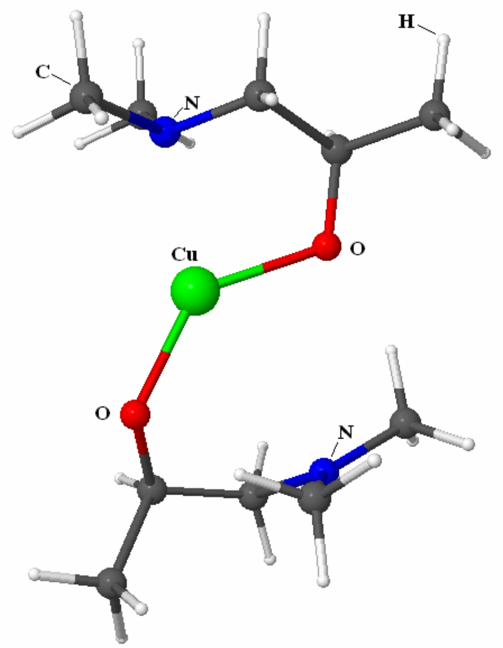


Figure 5. Optimized structure of (R),(R)-copper(II)dimethylamino-2-propoxide using the HF method and the LanL2DZ basis set

The same procedure was performed for the other two configurations of (R),(R)-copper(II)dimethylamino-2-propoxide. Following this, another (R),(R)-copper(II) dimethylamino-2-propoxide structure was run, but using a mixed basis set. The basis set for carbon, oxygen, nitrogen and hydrogen atoms was 3-21g, and only the copper atom was treated with the LanL2DZ basis set. Figure 6 shows the result of this calculation.

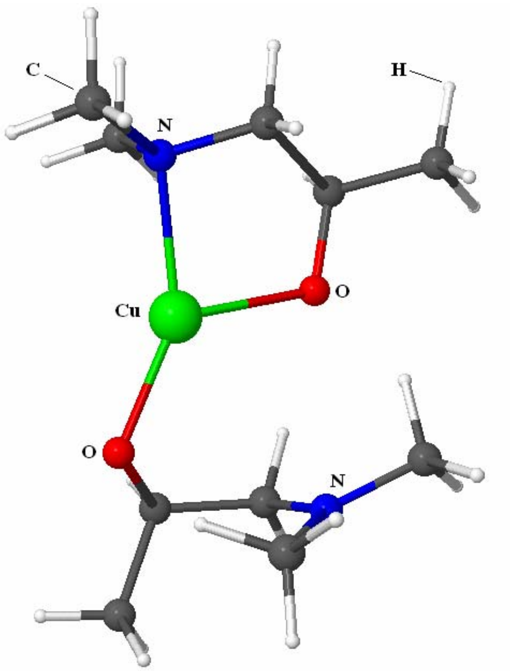


Figure 6. Optimized geometry for (R),(R)-copper(II)dimethylamino-2-propoxide using the HF theory and a mixed basis set (3-21g for all atoms except copper, LanL2DZ for copper)

Using an extra keyword, the input structures were run once more (with HF theory and LanL2DZ basis set) to calculate the electron orbitals in the structure in order to analyze the output. Figure 7 shows the output obtained for (R),(R)-copper(II) dimethylamino-2-propoxide.

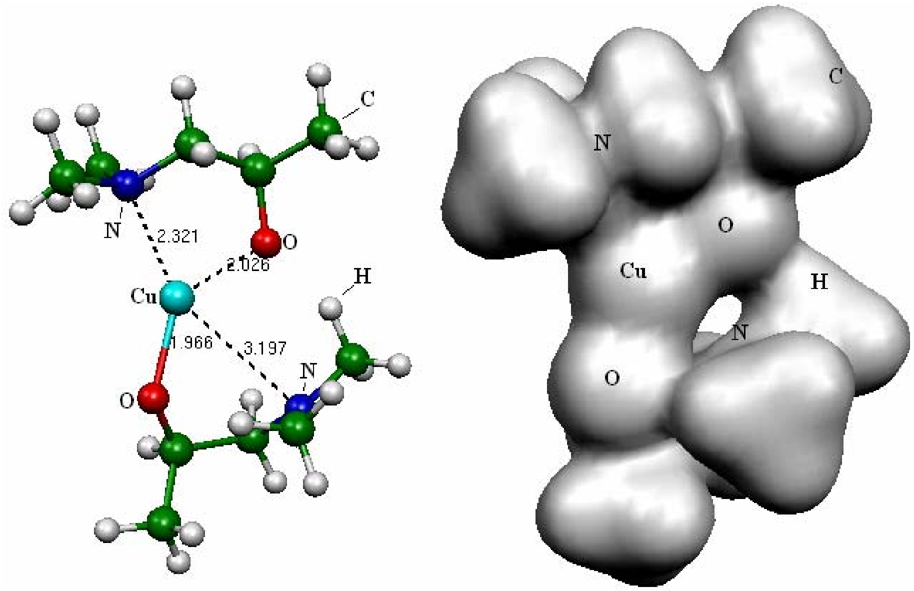


Figure 7. Output obtained for electronic density calculation of (R),(R)-copper(II)dimethylamino-2-propoxide

Another electron density calculation shows the unoccupied orbitals of the atoms in the structure. This analysis was performed on two structures: (R),(R)-copper(II) dimethylamino-2-propoxide and (R),(S)-copper(II) dimethylamino-2-propoxide. Figure 8 shows this analysis on a side-by-side comparison.

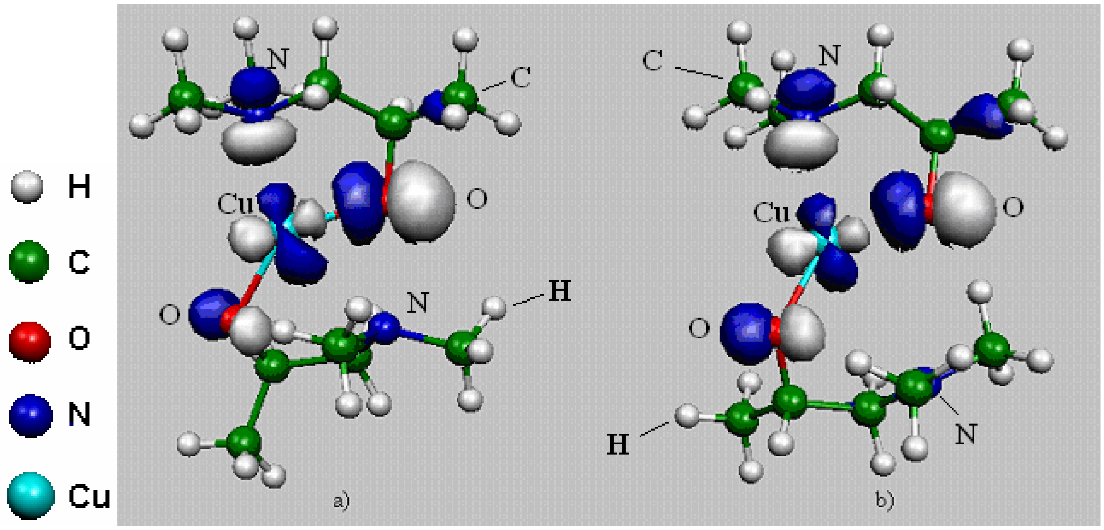


Figure 8. Optimized structures with electronic orbitals for a) (R),(R)-copper(II)dimethylamino-2-propoxide, and b) (R),(S)-copper(II)dimethylamino-2-propoxide using HF theory and the LanL2DZ basis set

After encountering this angle between the copper and oxygen atoms, a dummy atom was placed in the input file, so that Gaussian98 would not have trouble achieving a 180-degree angle that appears in the literature. Using this dummy atom, and using HF theory and the LanL2DZ basis set, a symmetric geometry was achieved with all three stereoisomers of copper(II)dimethylamino-2-propoxide. Figure 9 shows two of the output structures.

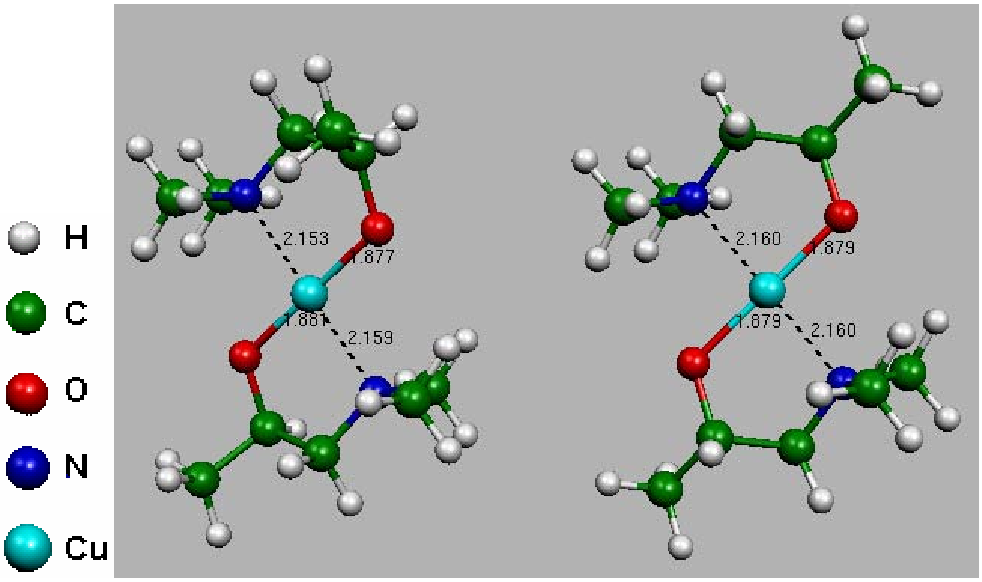


Figure 9. Optimized geometries for (R),(R)-copper(II)dimethylamino-2-propoxide (at left) and (R),(S)-copper(II)dimethylamino-2-propoxide (at right). Bond lengths are in angstroms (1Å = 10^{-10}m).

Afterwards, the ouput from this step was submitted as an input file using the B3LYP theory and the LanL2DZ basis set. Also, the same output was resubmitted to Gaussian98 using the B3LYP method and a mixed basis set, which was composed of the 3-21G basis set for carbon and hydrogen atoms; and the LanL2DZ basis set for copper, nitrogen and oxygen atoms. Figure 10 shows a comparison for the bond lengths of interest in the (R),(R)-copper(II)dimethylamino-2-propoxide stereoisomer.

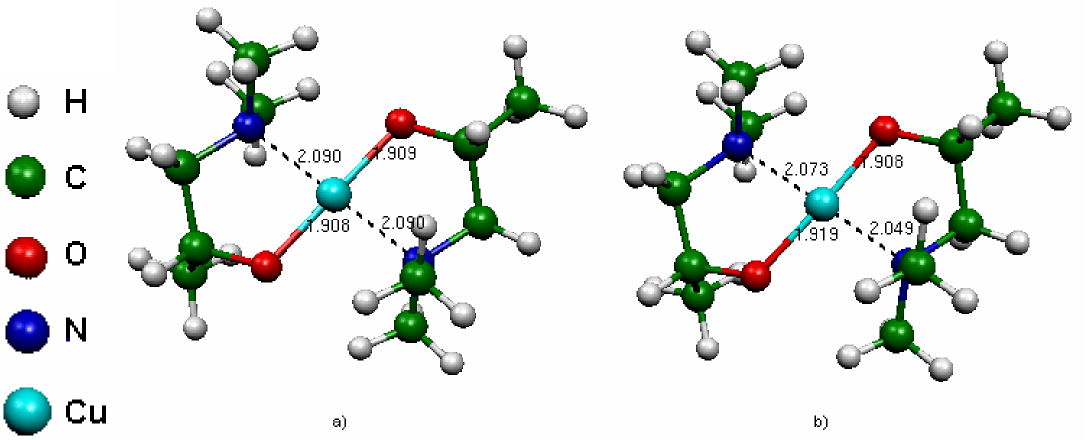


Figure 10. Optimum geometries and bond lengths of interest in Å for (R),(R)-copper(II)dimethylamino-2-propoxide using the B3LYP method and; a) LanL2DZ basis set, b) Mixed basis set (3-21G for C and H, LanL2DZ for Cu, O and N)

Table 1 shows the tabulated results for (R),(R)-copper(II)dimethylamino-2-propoxide.

Table 1. Interatomic distances of interest for (R),(R)-copper(II)dimethylamino-2-propoxide, in Å.

Species Bonds	Experimental[4]	a) LanL2DZ basis set	b) Mixed basis set
Cu-O1	1.8667	1.909	1.908
Cu-O2	1.8667	1.908	1.919
Cu-N1	2.0684	2.090	2.049
Cu-N2	2.0684	2.090	2.073

The copper(II) hexanoate molecule has been submitted to Gaussian98 many times; however its bulky structure does not allow Gaussian98 to find a suitable geometry for it. A simpler version of the core of copper(II) hexanoate was run in which the side chains were shortened to hydrogen atoms or methyl groups, but still Gaussian98 encountered problems. Therefore there is not current output for that molecule.

---

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

Analysis

When looking at the optimized structure of (R),(R)-copper(II) dimethylamino-2-propoxide, there are various particular details that one can see. First of all, when copper binds to two atoms, its geometry is supposed to be linear, yet we see an angle in the bonds. When running this same input molecule with a mixed basis set, the output suggests there is a bond between one of the nitrogens with the copper as well, which would explain why the angle was formed: when copper binds to three elements, it adopts planar triangular geometry.

Another detail to observe seems to be that the nitrogen opposed to the bonding one adopts planar geometry. A nitrogen atom bound to three atoms should have a pseudo-tetrahedral structure induced by its free electron pair. However, this does not seem to occur. However, this does not appear when the dummy atom was used, indicating perhaps that the inability of Gaussian98 to handle 180-degree angles might have affected this calculation.

After calculating the optimized geometries using the dummy atom and HF theory with the LanL2DZ basis set, we can see that the bond lengths approach those found in the literature, with exception to the Cu-N bonds. When these structures were run using the B3LYP method, however, these Cu-N bonds came closer to the bond lengths found experimentally via X-ray diffraction. When using a mixed basis set, these bond lengths were much more accurate with respect to those found experimentally.

Copper(II) hexanoate simulations did not converge, possibly because of the large structure it has, or its complexity. Running these simulations in smaller basis sets and simpler methods might give a more accurate input file to work with.

Conclusions

According to the data and the analysis performed, there is a strong possibility of a bond between one of the nitrogens in the copper(II)dimethylamino-2-propoxide structures and the central copper atom. Also, the data suggests that the electron pair of nitrogen is delocalized in a ring-like structure held together by a hydrogen bond between the dimethylamino group in one side of the molecule and the propoxide group in the opposing side of the molecule. A plausible explanation for the orbital found in one of the carbon atoms in all structures is still not known, yet it is proposed that the delocalized lone electron pair of the planar dimethylamino group might have caused it. It is also apparent that there is no bonding between one of the nitrogens in the structure and the copper atom. There is currently no data for copper(II) hexanoate. As for future research, the structures will be run in Gaussian with a more rigorous method (called B3YLP) and the LanL2DZ basis set. Secondly, the bond lengths between copper and its surrounding atoms will be calculated to figure out the reaction energy needed to deposit the copper film. Also, a simplified copper(II) hexanoate analogous structure will be run in Gaussian, hoping to eventually reach an optimized structure for copper(II) hexanoate. This is necessary to find the bond lengths associated with depositing copper using this precursor.

Appendix

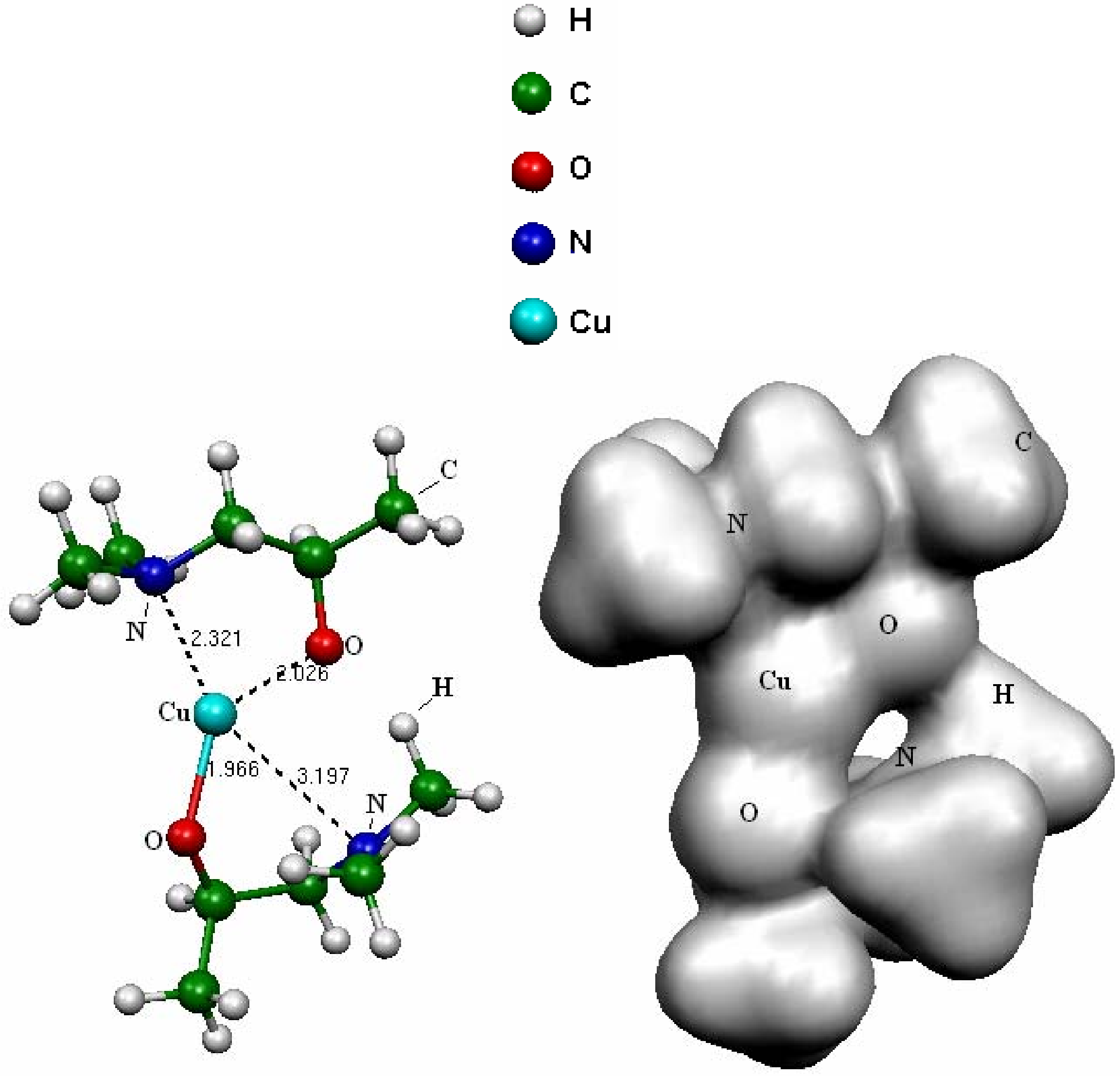
Raw input data for (R),(R)-copper(II)dimethylamino-2-propoxide with the Hartree-Fock method and the LanL2DZ basis set

```
#P HF/LanL2DZ OPT FREQ POP=regular GFPrint

Cu(II)dimethyl amino propoxide (1st config)

0 2
C
O 1 B1
Cu 2 B2 1 A1
O 3 B3 2 A2 1 D1
C 4 B4 3 A3 2 D2
C 5 B5 4 A4 3 D3
N 6 B6 5 A5 4 D4
C 7 B7 6 A6 5 D5
H 8 B8 7 A7 6 D6
C 1 B9 2 A8 3 D7
N 10 B10 1 A9 2 D8
C 11 B11 10 A10 1 D9
H 12 B12 11 A11 10 D10
C 11 B13 10 A12 1 D11
H 14 B14 11 A13 10 D12
C 7 B15 6 A14 5 D13
H 16 B16 7 A15 6 D14
C 1 B17 2 A16 3 D15
H 18 B18 1 A17 2 D16
C 5 B19 4 A18 3 D17
H 20 B20 5 A19 4 D18
H 1 B21 2 A20 3 D19
H 5 B22 4 A21 3 D20
H 10 B23 1 A22 2 D21
H 10 B24 1 A23 2 D22
H 6 B25 5 A24 4 D23
H 6 B26 5 A25 4 D24
H 12 B27 11 A26 10 D25
H 12 B28 11 A27 10 D26
H 14 B29 11 A28 10 D27
H 14 B30 11 A29 10 D28
H 8 B31 7 A30 6 D29
H 8 B32 7 A31 6 D30
H 16 B33 7 A32 6 D31
H 16 B34 7 A33 6 D32
H 18 B35 1 A34 2 D33
H 18 B36 1 A35 2 D34
H 20 B37 5 A36 4 D35
H 20 B38 5 A37 4 D36

B7 1.5200000
B8 1.0900000
B9 1.5400006
A10 109.47120
A11 109.47122
```

```
A12 109.47124
A13 109.47126
A14 109.47122
A15 109.47123
B10 1.5199999
A16 109.47123
B11 1.5200005
A17 109.47122
B12 1.0900002
A18 109.47122
D1 -177.7725
B13 1.5199995
A19 109.47122
D2 -47.26152
B14 1.0900003
D3 44.775596
B15 1.5200006
D4 30.981664
B16 1.0899998
D5 34.417817
B17 1.5400000
D6 -168.0918
B18 1.0899996
D7 27.759309
B19 1.5400000
D8 -53.40949
D9 162.20847
D10 -175.2626
D11 -77.79154
D12 -62.12876
D13 154.41780
D14 -148.1912
D15 147.75934
D16 62.201791
D17 164.77564
D18 -54.34168
D19 -92.24066
A20 109.47119
A21 109.47119
A22 109.47122
A23 109.47116
A24 109.47120
A25 109.47127
B20 1.0899997
A26 109.47122
B21 1.0900006
A27 109.47118
B22 1.0900004
A28 109.47126
B23 1.0899996
A29 109.47122
B24 1.0899997
B25 1.0900003
B26 1.0900001
B27 1.0899996
B28 1.0899998
B29 1.0899999
```

```
D20 -75.22441
D21 -173.4095
D22 66.590502
D23 150.98166
D24 -89.01830
D25 64.737438
D26 -55.26259
D27 177.87123
D28 57.871260
D29 71.908284
A30 109.47123
A31 109.47125
A32 109.47122
A33 109.47119
A34 109.47123
A35 109.47120
B30 1.0900001
A36 109.47124
B31 1.0900006
A37 109.47122
B32 1.0899992
B33 1.0899996
B34 1.0900002
B35 1.0899994
B36 1.0900001
B37 1.0899994
B38 1.0900001
D30 -48.09177
D31 91.808786
D32 -28.19123
D33 -57.79826
D34 -177.7982
D35 -174.3418
D36 65.658277
A1 109.47122
A2 135.07714
A3 109.47119
A4 109.47125
A5 109.47120
A6 109.47121
A7 109.47121
A8 109.47124
A9 109.47120
B1 1.5000000
B2 1.9300003
B3 1.9299998
B4 1.5000003
B5 1.5399996
B6 1.5200002
```

Output structure for (R),(R)-copper(II)dimethylamino-2-propoxide with the Hartree-Fock method and the LanL2DZ basis set



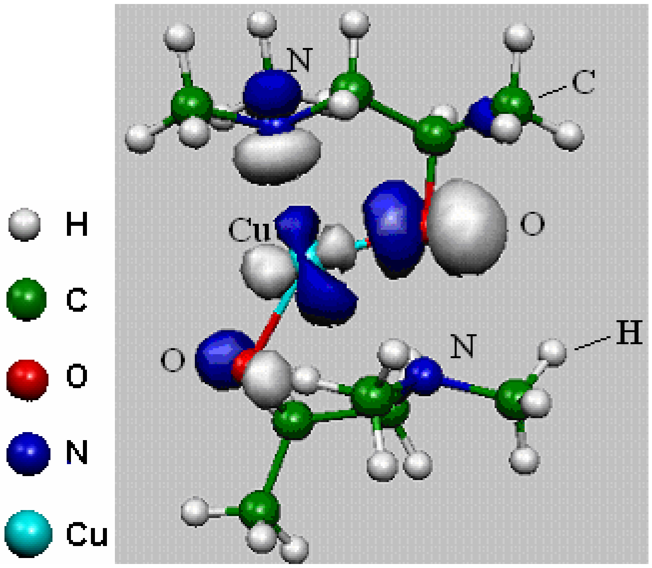
Raw input data for (R),(R)-copper(II)dimethylamino-2-propoxide with the Hartree-Fock method and a mixed basis set

```
#N HF/3-21G ExtraBasis OPT FREQ

Cu(II)-dimethyl amino propoxide

0 2
 C
 O                     1    B1
 Cu                    2    B2       1    A1
 O                     3    B3       2    A2       1    D1       0
 C                     4    B4       3    A3       2    D2       0
 C                     5    B5       4    A4       3    D3       0
 N                     6    B6       5    A5       4    D4       0
 C                     7    B7       6    A6       5    D5       0
 H                     8    B8       7    A7       6    D6       0
 C                     1    B9       2    A8       3    D7       0
 N                     10   B10      1    A9       2    D8       0
 C                     11   B11      10   A10      1    D9       0
 H                     12   B12      11   A11      10   D10      0
 C                     11   B13      10   A12      1    D11      0
 H                     14   B14      11   A13      10   D12      0
 C                     7    B15      6    A14      5    D13      0
 H                     16   B16      7    A15      6    D14      0
 C                     1    B17      2    A16      3    D15      0
 H                     18   B18      1    A17      2    D16      0
 C                     5    B19      4    A18      3    D17      0
 H                     20   B20      5    A19      4    D18      0
 H                     1    B21      2    A20      3    D19      0
 H                     5    B22      4    A21      3    D20      0
 H                     10   B23      1    A22      2    D21      0
 H                     10   B24      1    A23      2    D22      0
 H                     6    B25      5    A24      4    D23      0
 H                     6    B26      5    A25      4    D24      0
 H                     12   B27      11   A26      10   D25      0
 H                     12   B28      11   A27      10   D26      0
 H                     14   B29      11   A28      10   D27      0
 H                     14   B30      11   A29      10   D28      0
 H                     8    B31      7    A30      6    D29      0
 H                     8    B32      7    A31      6    D30      0
 H                     16   B33      7    A32      6    D31      0
 H                     16   B34      7    A33      6    D32      0
 H                     18   B35      1    A34      2    D33      0
 H                     18   B36      1    A35      2    D34      0
 H                     20   B37      5    A36      4    D35      0
 H                     20   B38      5    A37      4    D36      0
       Variables:
  B7                     1.52
  B8                     1.09
  B9                     1.54
  A10                  109.47122
```

```
A11                 109.47122
A12                 109.47122
A13                 109.47122
A14                 109.47122
A15                 109.47122
B10                   1.52
A16                 109.47122
B11                   1.52
A17                 109.47122
B12                   1.09
A18                 109.47122
D1                 -177.7725
B13                   1.52
A19                 109.47122
D2                  -47.26153
B14                   1.09
D3                   44.77563
B15                   1.52
D4                   30.98166
B16                   1.09
D5                   34.41783
B17                   1.54
D6                 -168.0917
B18                   1.09
D7                   27.75933
B19                   1.54
D8                  -53.40952
D9                  162.20849
D10                -175.2626
D11                 -77.79151
D12                 -62.12878
D13                 154.41783
D14                -148.1912
D15                 147.75933
D16                  62.20177
D17                 164.77563
D18                 -54.34166
D19                 -92.24067
A20                 109.47122
A21                 109.47122
A22                 109.47122
A23                 109.47122
A24                 109.47122
A25                 109.47122
B20                   1.09
A26                 109.47122
B21                   1.09
A27                 109.47122
B22                   1.09
A28                 109.47122
B23                   1.09
A29                 109.47122
B24                   1.09
B25                   1.09
B26                   1.09
B27                   1.09
B28                   1.09
```

```
  B29                   1.09
  D20                 -75.22437
  D21                -173.4095
  D22                  66.59048
  D23                 150.98166
  D24                 -89.01834
  D25                  64.73743
  D26                 -55.26257
  D27                 177.87122
  D28                  57.87122
  D29                  71.90827
  A30                 109.47122
  A31                 109.47122
  A32                 109.47122
  A33                 109.47122
  A34                 109.47122
  A35                 109.47122
  B30                   1.09
  A36                 109.47122
  B31                   1.09
  A37                 109.47122
  B32                   1.09
  B33                   1.09
  B34                   1.09
  B35                   1.09
  B36                   1.09
  B37                   1.09
  B38                   1.09
  D30                 -48.09173
  D31                  91.80878
  D32                 -28.19122
  D33                 -57.79823
  D34                -177.7982
  D35                -174.3417
  D36                  65.65834
  A1                  109.47122
  A2                  135.07714
  A3                  109.47122
  A4                  109.47122
  A5                  109.47122
  A6                  109.47122
  A7                  109.47122
  A8                  109.47122
  A9                  109.47122
  B1                    1.5
  B2                    1.93
  B3                    1.93
  B4                    1.5
  B5                    1.54
  B6                    1.52

3 0
LanL2DZ
****
```

Output structure for (R),(R)-copper(II)dimethylamino-2-propoxide with the Hartree-Fock method and a mixed basis set



Input for copper(II) hexanoate with Hartree-Fock method and the 3-21g basis set

```
#N HF/3-21G OPT FREQ

Cu-h Trial

0 1
C
C 1 B1
O 2 B2 1 A1
Cu 3 B3 2 A2 1 D1
Cu 4 B4 3 A3 2 D2
O 5 B5 4 A4 3 D3
C 6 B6 5 A5 4 D4
O 7 B7 6 A6 5 D5
O 2 B8 3 A7 4 D6
C 1 B9 2 A8 3 D7
C 10 B10 1 A9 2 D8
C 11 B11 10 A10 1 D9
C 12 B12 11 A11 10 D10
H 13 B13 12 A12 11 D11
C 7 B14 6 A13 5 D12
C 15 B15 7 A14 6 D13
C 16 B16 15 A15 7 D14
C 17 B17 16 A16 15 D15
C 18 B18 17 A17 16 D16
H 19 B19 18 A18 17 D17
H 1 B20 2 A19 3 D18
H 1 B21 2 A20 3 D19
H 10 B22 1 A21 2 D20
H 10 B23 1 A22 2 D21
H 11 B24 10 A23 1 D22
H 11 B25 10 A24 1 D23
H 12 B26 11 A25 10 D24
H 12 B27 11 A26 10 D25
H 13 B28 12 A27 11 D26
H 13 B29 12 A28 11 D27
H 15 B30 7 A29 6 D28
H 15 B31 7 A30 6 D29
H 16 B32 15 A31 7 D30
H 16 B33 15 A32 7 D31
H 17 B34 16 A33 15 D32
H 17 B35 16 A34 15 D33
H 18 B36 17 A35 16 D34
H 18 B37 17 A36 16 D35
H 19 B38 18 A37 17 D36
H 19 B39 18 A38 17 D37
O 4 B40 5 A39 6 D38
C 41 B41 4 A40 5 D39
O 42 B42 41 A41 4 D40
C 42 B43 41 A42 4 D41
C 44 B44 42 A43 41 D42
C 45 B45 44 A44 42 D43
C 46 B46 45 A45 44 D44
C 47 B47 46 A46 45 D45
```

```
H 48 B48 47 A47 46 D46
H 44 B49 42 A48 41 D47
H 44 B50 42 A49 41 D48
H 45 B51 44 A50 42 D49
H 45 B52 44 A51 42 D50
H 46 B53 45 A52 44 D51
H 46 B54 45 A53 44 D52
H 47 B55 46 A54 45 D53
H 47 B56 46 A55 45 D54
H 48 B57 47 A56 46 D55
H 48 B58 47 A57 46 D56
O 5 B59 4 A58 3 D57
C 60 B60 5 A59 4 D58
O 61 B61 60 A60 5 D59
C 61 B62 60 A61 5 D60
C 63 B63 61 A62 60 D61
C 64 B64 63 A63 61 D62
C 65 B65 64 A64 63 D63
C 66 B66 65 A65 64 D64
H 67 B67 66 A66 65 D65
H 63 B68 61 A67 60 D66
H 63 B69 61 A68 60 D67
H 64 B70 63 A69 61 D68
H 64 B71 63 A70 61 D69
H 65 B72 64 A71 63 D70
H 65 B73 64 A72 63 D71
H 66 B74 65 A73 64 D72
H 66 B75 65 A74 64 D73
H 67 B76 66 A75 65 D74
H 67 B77 66 A76 65 D75

B50 1.0900000
B51 1.0900000
B52 1.0900000
B53 1.0900000
B54 1.0900000
B55 1.0900000
B56 1.0900000
D50 -60.00000
B57 1.0900000
D51 -60.00000
B58 1.0900000
D52 60.000000
B59 1.9300000
D53 59.999999
D54 -60.00000
D55 -68.81894
D56 171.18106
D57 -37.03210
D58 -71.65270
D59 13.084433
B60 1.5000000
B61 1.2750000
B62 1.5400000
B63 1.5400000
B64 1.5400000
B65 1.5400000
```

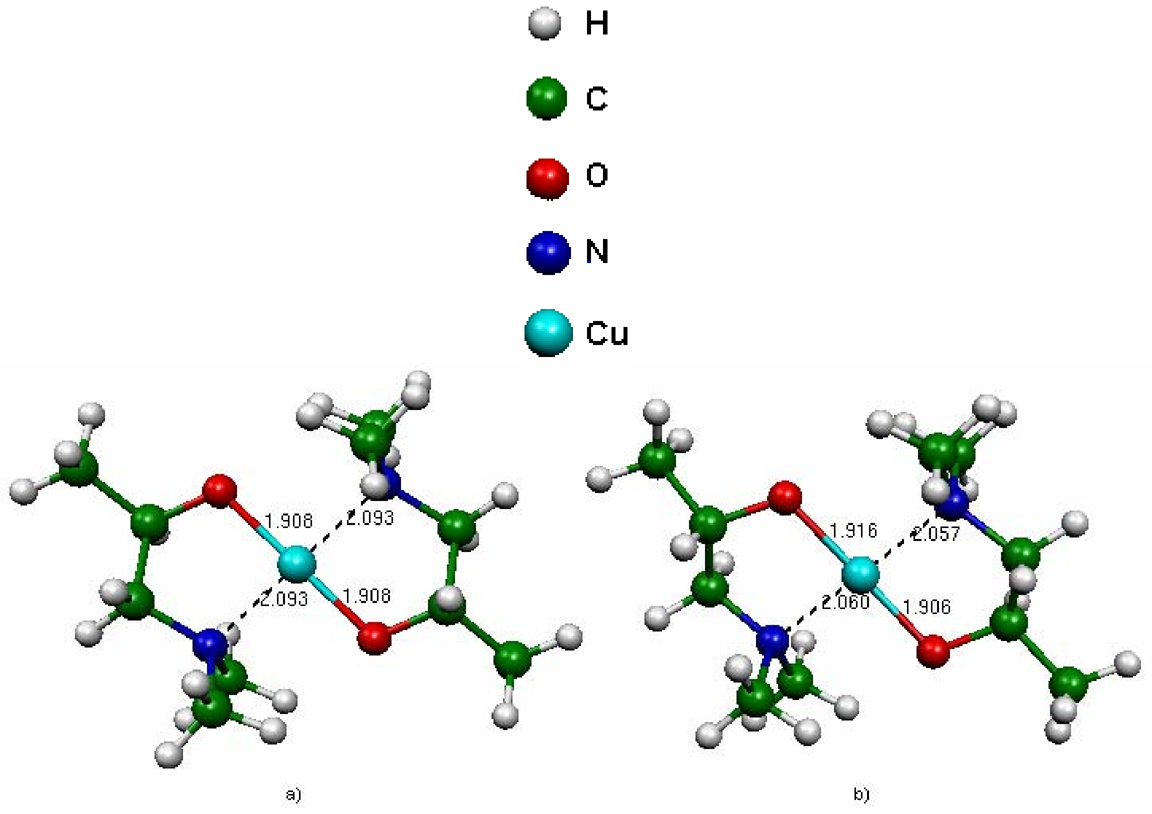
```
B66 1.5400000
D60 -166.9156
B67 1.0900000
D61 -180.0000
B68 1.0900000
D62 180.00000
B69 1.0900000
D63 180.00000
D64 180.00000
D65 155.50557
D66 -59.99977
D67 60.000000
D68 60.000000
D69 -60.00000
B70 1.0900000
B71 1.0900000
A10 109.47122
B72 1.0900000
A11 109.47122
B73 1.0900000
A12 109.47122
B74 1.0900000
A13 120.00000
B75 1.0900000
A14 109.47122
B76 1.0900000
A15 109.47122
D70 59.999999
B77 1.0900000
A16 109.47122
D71 -60.00000
A17 109.47122
D72 59.999999
A18 109.47122
D73 -60.00000
A19 109.47122
D74 35.505568
D75 -84.49443
A20 109.47122
A21 109.47122
A22 109.47122
A23 109.47122
A24 109.47122
A25 109.47122
A26 109.47122
A27 109.47122
A28 109.47122
A29 109.47078
A30 109.47122
A31 109.47122
A32 109.47122
A33 109.47122
A34 109.47122
A35 109.47122
A36 109.47122
A37 109.47122
A38 109.47122
```

```
A39 120.00000
A1 120.00000
A2 109.47122
A3 120.00000
A4 120.00000
A5 109.47122
A6 120.00000
A7 120.00000
A8 109.47122
A9 109.47122
A40 109.47122
A41 120.00000
A42 120.00000
A43 109.47122
A44 109.47122
A45 109.47122
A46 109.47122
A47 109.47122
A48 109.47112
A49 109.47122
B1 1.5400000
B2 1.5000000
B3 1.9300000
B4 2.4000000
B5 1.9300000
B6 1.5000000
B7 1.2750000
B8 1.2750000
B9 1.5400000
A50 109.47122
A51 109.47122
A52 109.47122
A53 109.47122
A54 109.47122
A55 109.47122
A56 109.47122
A57 109.47199
A58 120.00000
A59 109.47122
A60 120.00000
A61 120.00000
A62 109.47122
A63 109.47122
A64 109.47122
A65 109.47122
A66 109.47122
A67 109.47109
A68 109.47122
A69 109.47122
D1 162.74633
D2 -15.64370
D3 142.96790
D4 -58.11038
D5 -12.01705
D6 -17.25367
D7 153.46269
D8 -176.7801
```

```
D9 180.00000
A70 109.47122
A71 109.47122
A72 109.47122
A73 109.47122
A74 109.47122
A75 109.47122
A76 109.47122
B10 1.5400000
B11 1.5400000
B12 1.5400000
B13 1.0900000
B14 1.5400000
B15 1.5400000
B16 1.5400000
D10 178.96830
B17 1.5400000
D11 146.07541
B18 1.5400000
D12 167.98295
B19 1.0900000
D13 176.78122
D14 -140.6562
D15 -180.0000
D16 180.00000
D17 39.291237
D18 -86.53730
D19 33.462694
B20 1.0900000
B21 1.0900000
B22 1.0900000
B23 1.0900000
B24 1.0900000
B25 1.0900000
B26 1.0900000
D20 -56.78009
B27 1.0900000
D21 63.219912
B28 1.0900000
D22 -60.00000
B29 1.0900000
D23 60.000000
D24 -61.03170
D25 58.968303
D26 26.075412
D27 -93.92459
D28 -63.21798
D29 56.781222
B30 1.0900000
B31 1.0900000
B32 1.0900000
B33 1.0900000
B34 1.0900000
B35 1.0900000
B36 1.0900000
D30 99.343815
B37 1.0900000
```

```
D31 -20.65618
B38 1.0900000
D32 -60.00000
B39 1.0900000
D33 60.000000
D34 60.000000
D35 -60.00000
D36 -80.70876
D37 159.29124
D38 -37.03210
D39 33.748360
B40 1.9300000
B41 1.5000000
B42 1.2750000
B43 1.5400000
B44 1.5400000
B45 1.5400000
B46 1.5400000
D40 -3.579415
B47 1.5400000
D41 176.42058
B48 1.0900000
D42 -180.0000
B49 1.0900000
D43 180.00000
D44 -180.0000
D45 180.00000
D46 51.181058
D47 -59.99981
D48 60.000001
D49 60.000000
```

Output for (R),(S)-copper(II)dimethylamino-2-propoxide using B3LYP theory and a) LanL2DZ basis set and b) Mixed basis set (3-21g for C and H atoms; LanL2DZ for Cu, O and N atoms)



a)

b)

Output for (S),(S)-copper(II)dimethylamino-2-propoxide using B3LYPtheory and a) LanL2DZ basis set and b) Mixed basis set (3-21g for C and H atoms; LanL2DZ for Cu, O and N atoms)