conditions. Whether or not the surface deposition of carbon is important to the enhanced reactivity remains an open question. Further work is under way to clarify this matter.

The effects of ultrasound on the reactivity of Cu metal as a stoichiometric reagent have been documented in the literature in two cases: the Ullmann coupling\textsuperscript{(23)} (where \(\text{C}_6\text{H}_4\text{(NO}_2\text{)}\text{ is o-nitrophenyl)}

\[
\text{NO}_2 + 2 \text{Cu} \rightarrow \text{NO}_2 \text{NO}_2 + 2 \text{CuI}
\]

and the reaction of Cu with salicylaniline to form uncharacterized copper complexes.\textsuperscript{(20)} In the former case, substantial rate enhancements (as large as 64-fold) are reported when the entire reaction mixture is irradiated with ultrasound. This synthetically important rate increase was postulated to arise from multiple possible effects, including particle size reduction and surface cleaning. In addition, ultrasound has been used to enhance\textsuperscript{(21,22)} the reduction of Cu salts by alkali metals to form highly reactive copper dispersion.\textsuperscript{(23)}

To determine the effect of ultrasound on the reactivity of the copper powder, we choose to use the Ullmann coupling reaction as a kinetic probe. To this end, we irradiated a slurry of the copper powder in the absence of substrate (2-iodonitrobenzene) and then examined the rate of coupling upon addition of substrate. As shown in Figure 3, we find substantial rate enhancements upon ultrasonic pretreatment of the Cu powder. The induction period observed in the absence of ultrasound complicates a quantitative comparison of rates. At early stages of the reaction, pretreatment of Cu powder with ultrasound can increase rates more than 50-fold, while at later stages the rate increase is 10-fold. The effectiveness of pretreatment demonstrates that ultrasound produces an irreversible change in the Cu powder (i.e., the removal of the oxide coating), even in the absence of substrate. Enhanced mass transport is not responsible for the sonochemical improvements.

In conclusion, ultrasonic irradiation of Cu powder removes the passivating oxide coating, induces significant surface damage, and enhances the reactivity of Cu powder. Interparticle collisions driven by shock waves are probably the causative event.

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**Chemical Vapor Deposition of Copper and Copper Oxide Thin Films from Copper(I) tert-Butoxide**

Patrick M. Jeffries and Gregory S. Girolami*

School of Chemical Sciences and Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

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The low-temperature deposition of thin-film materials from molecular transition-metal precursors is an area of rapidly growing interest.\textsuperscript{(14)} We now describe the deposition of copper-containing films from copper(I) tert-butoxide tetramer, \([\text{Cu}(\text{O-t-Bu})_4]\), which was chosen because it is one of the more volatile molecular derivatives of copper known. These results are related to efforts directed toward the chemical vapor deposition of thin films of the

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(7) Although the vapor pressure of [Cu(O-t-Bu)]\textsubscript{4} has not been measured, it sublimes readily at 100 °C and 10\textsuperscript{-4} Torr. (a) Tauda, T.; Hashimoto, T.; Soga, T. J. Am. Chem. Soc. 1972, 94, 655-659. (b) Greier, T.; Weiss, E. Chem. Ber. 1978, 110, 3142-3146.
Films of metallic copper have previously been vapor deposited by evaporation from the bulk metal, by thermal decomposition of copper(I) and copper(II) halides, and by various techniques from 1,1,1-trifluoro-2,4-pentanedionato (tfa) or 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfa) complexes of copper(II). For example, thermal decomposition of Cu(tfa)₃ or Cu(hfa)₂H₂O, or argon/hydrogen and laser photothermal decomposition of Cu(hfa); some of these methods result in appreciable fluoride contaminants in the deposits; a volatile copper precursor free of halogen or halogen-containing ligands is accordingly of interest. 

[Cu(O-t-Bu)₄], which is a white air-sensitive solid, is introduced into a Pyrex vacuum system via a break-seal ampule after the system has been baked out and evacuated to a base pressure of 10⁻⁶ Torr. The precursor sublimes slowly at a pressure of 10⁻⁵ Torr from a reservoir that is heated to 100 °C by an oil bath. The precursor travels via 5-cm diameter glass tubing into the deposition zone, which is maintained at a constant temperature of 400 °C by a tube furnace. The glass tubing leading to the deposition chamber is warmed to 100 °C with heating tape to prevent the precursor from condensing before reaching the hot zone.

Chemical vapor deposition (CVD) from [Cu(O-t-Bu)₄] yields thin films of copper metal on a variety of substrates, including borosilicate glass, silicon, KBr, quartz, aluminium, and graphite. No appreciable differences in the film morphology as a function of substrate were noted. The films are approximately 1.5 μm thick and are polycrystalline; they exhibit sharp X-ray powder diffraction profiles characteristic of bulk copper. Auger analysis confirms the presence of copper, indicates that the films contain approximately 5% oxygen, and shows that carbon is essentially absent (<1%). Scanning electron microscopy (SEM) indicates that the films are uniform and featureless. Mass spectrometric analysis of the gaseous byproducts exiting the hot zone reveals that tert-butyl alcohol is the only species present. This suggests a decomposition mechanism involving cleavage of the Cu-O bonds to produce tert-butoxy radicals, which subsequently abstract hydrogen atoms from surface-bound hydroxyl groups on the surrounding glass chamber.

These results establish that metallic films can be deposited from a molecular alkoxide precursor; we have previously shown that metallic palladium and platinum thin films may be grown by CVD from organometallic precursors such as the allyl compounds Pd(C₂H₅)₂ and Pt(C₂H₅)₂. Some of these methods result in appreciable fluoride contaminants in the deposits; a volatile copper precursor free of halogen or halogen-containing ligands is accordingly of interest. 


Figure 1. Scanning electron micrograph of Cu₂O deposit at 15 kV showing whisker formation.
butyl alcohol changes. The peaks at 31 and 59 mass units, which are the most intense peaks in the spectrum of unlabeled tert-butyl alcohol, decrease in intensity; correspondingly, the peaks at 32 and 60 mass units increase in intensity. The mass 31 and 59 species have been ascribed to the hydroxyl-containing ions $\text{CH}_2\text{O}H^+$ and $\text{C}_3\text{H}_6\text{O}H^+$, respectively,
and therefore the $\text{D}_2\text{O}$ experiment clearly suggests that tert-butyl alcohol specifically labeled at the hydroxyl site is formed. Although we cannot present rule out the possibility that H/D exchange with $\text{D}_2\text{O}$ occurs after the formation of unlabeled tert-butyl alcohol during CVD, the data are most consistent with a mechanism involving direct hydrolysis of [Cu(O-t-Bu)$_2$]. This study represents the first chemical vapor deposition of pure copper(II) oxide, although a chemical vapor transport method has been reported previously.17

Further work will be directed toward the use of carrier gases such as hydrogen and oxygen, which would respectively reduce the level of contaminants in the copper film and promote the formation of CuO. Depositions conducted in the presence of $\text{H}_2\text{O}$ are being investigated to determine unambiguously the source of oxygen in the Cu$_2$O deposits.

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Hydrogen-Bond Directed Co-crystallization as a Tool for Designing Acentric Organic Solids

Margaret C. Etter* and Gayle M. Frankenbach

Chemistry Department, University of Minnesota
Minneapolis, Minnesota 55455

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One of the dilemmas facing chemists trying to make useful organic nonlinear optical materials is that they have exquisite control over designing individual molecules but practically no control over designing molecular packing patterns in solid-state materials. Since even-order nonlinear optical properties (such as second harmonic generation) occur only in acyclic materials1 and since the magnitude of the effect depends strongly on relative orientations of molecular and crystallographic axes,2 progress in this field requires that new useful solid-state design tools be developed. Despite notable advances in understanding the molecular basis of organic crystal growth processes,3 there are still no general synthetic tools available for controlling the structures of molecular aggregates or crystals. We have shown previously how hydrogen-bond interactions in organic compounds can be used to direct formation of aggregate structures with predictable connectivity patterns and, in some cases, with predictable symmetry.4 In this paper we demonstrate how these concepts can be applied to the design and preparation of acentric organic crystals, exemplified by the structure of a 1:1 cocrystalline complex of 4-aminobenzoic acid (4-ABA) and 3,5-dinitrobenzoic acid (3,5-DNBA). I

Any single hydrogen bond is inherently acentric when the hydrogen atom is covalently bonded to one electronegative atom, $X$, and associated with another atom, $Y (X \neq Y)$:

$$\text{Y} \cdots \text{HX}$$

If the donor, $X$, and acceptor, $Y$, groups are on the same molecule and positioned so that hydrogen-bonded chains form, these chains will necessarily be acentric, as shown:

$$\cdots \text{HX} \cdots \text{Y} \cdots \text{HX} \cdots \text{Y} \cdots$$

Acentric one-dimensional aggregates such as this are the common packing patterns for nitroanilines and isographic analogues.6c Two-dimensional acentric aggregates, of which squaric acid is a prototype,5 can be designed in a similar fashion with multiple donor and acceptor sites, as shown in 3.

The same principles of molecular organization can be applied to the design of cocrystals. For example, if Y and HX are on different molecules and intermolecular bonding between them is of the type $\text{Y} \cdots \text{HX}$, this results in a heterodimer. Likewise, two different carboxylic acids substituted with Y and HX

Figure 1. Photograph of a typical crystal of I (approximately 0.5 cm along the longest edge). On the right is a schematic diagram of the crystal showing Miller index assignments of the prominent faces.

*To whom correspondence should be addressed at 78 Kolthoff Hall, Department of Chemistry, 207 Pleasant St. S. E., University of Minnesota, Minneapolis, Minnesota 55455.