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Mechanistic Role of H_2O and the Ligand in the Chemical Vapor Deposition of Cu, Cu_2O, CuO, and Cu_3N from Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II)

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The mechanism of chemical vapor deposition of Cu, Cu_2O, CuO, and Cu_3N from $Cu(hfacac)_2(H_2O)$ was studied by XRD, MS, FTIR, XPS, SIMS, and NMR techniques. The molecular structure of the precursor was established by a single-crystal X-ray diffraction experiment. Crystallographic data (−165 °C): triclinic space group $P\bar{1}$, $a = 9.402(3)$ Å, $b = 11.068(3)$ Å, $c = 7.958(2)$ Å, $\alpha = 105.71(2)°$, $\beta = 100.99(2)°$, $\gamma = 76.27(2)°$, $V = 767.31$ Å^3, $Z = 2$, $R = 0.0303$, $R_w = 0.0312$. In the presence of excess water in the process gas stream, a facile release of free Hhfacac ligand from the copper complex is activated by a proton transfer from coordinated water. Ligand-mediated reduction of the metal from Cu^{2+} to Cu^+ and from Cu^+ to Cu^0 oxidation states occurs in the absence of an external reducing agent at temperatures of 280 and 400 °C, respectively. Evidence for this ligand-mediated reduction is seen in the presence of the two major ligand-oxidation products (CF_3COOH and $CF_3C(OH)_2CH(OH)_2$) in the effluent from the deposition reaction. A labeling experiment using $H_2{}^{18}O$ proved that oxygen in copper oxide films deposited from $Cu(hfacac)_2$ onto insulating substrates is derived from water and not the hfacac ligand. As an example of benefits that can be derived from this mechanistic knowledge, we have also shown that replacing H_2O with NH_3 leads to the formation of Cu_3N.

Introduction

Copper(II) hexafluoroacetylacetonate **1**,[1–8] $Cu(hfacac)_2$, is being thoroughly studied as a precursor for the preparation of thin metallic[9] and oxide[10] films by chemical vapor deposition (CVD) techniques due to its reasonable volatility (a vapor pressure of 0.06 Torr at room temperature), low decomposition temperature, stability in air, low toxicity, and commercial availability.[11] Given the theoretical importance of both oxide and metallic copper films, there is a great need for detailed information regarding the chemical mechanisms of the deposition and the role played by ancillary ligands.

In the area of copper film preparation, it is generally agreed that the presence of hydrogen gas is necessary for a clean reduction of the precursor to the elemental metal under thermal[12–16] or plasma conditions.[17–21] However, some reports show that metallic copper can be obtained even in the absence of any external reductant using an inert gas.[22–24] This poses an interesting chemical question, namely, what is the reducing agent in these reactions?

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Another important issue is the role played by water in CVD using this class of precursors. The addition of H_2O or alcohols has been reported to be beneficial for deposition of metals from β-diketonate complexes. Decreased carbon contamination of the films and lower deposition temperatures have been observed in the presence of water. Furthermore, the addition of a small amount of H_2O to the H_2 carrier gas increases the copper growth rate from $Cu(hfacac)_2$.[23-31] On the other hand, adverse effects of water vapor observed at higher concentrations (above a certain critical level) include a loss of deposition selectivity[32-35] on metallic versus nonmetallic surfaces and the formation of copper oxide rather than metallic copper. This "detrimental" action of water can be utilized and turned into a functional method of copper oxide preparation[36,37] such as for cuprate-based superconductors[38] provided that we are able to rationalize the chemical mechanism behind these reactions.

In our present study, we investigate the role of the hfacac and water ligands in CVD reactions with $Cu(hfacac)_2$ in an attempt to elucidate the mechanism of their action. We limit our experiments to nonmetallic substrates[39] such as glass and silicon and to regimes with an excess of water in the system.

Experimental Section

Procedures and Materials. The deposition reactions were carried out in a hot-wall horizontal Pyrex tube reactor (o.d. 26 mm) heated by a Lindberg 55035 resistance furnace (Figure 1). The reactor was cleaned before every run with diluted HNO_3, a 10% solution of HF, and the detergent solution, then flushed with deionized water, ethanol, and acetone, and dried in an oven. Glass and silicon slides (25 × 16 × 1 mm) used as substrates were cleaned[40] by boiling HNO_3, then sonicated in a warm detergent solution for 20 min, and flushed with deionized water, ethanol, and acetone. The slides were kept in an oven at 110 °C before loading them in a removable Pyrex "sleeve" (o.d. 20 mm), which was then inserted into the CVD reactor. The temperature of the hot zone (length 30 cm) was measured by a built-in thermocouple calibrated by an external thermocouple and appeared to be stable to ±1 °C of the reading. The temperature gradient at 400 °C was 5 °C/cm at the halfway distance between the center of the hot zone and its end. Before every run, the system was pumped for several hours to a base pressure of ~10 mTorr at the hot-zone temperature of 300 °C to remove adsorbed moisture and impurities and then flushed with a particular carrier gas for 10 min. A known amount of the precursor **1** (typically 1.8–2.5 g) was loaded in an evaporator cup, heated with a heating tape to 70–90 °C,[12] and sublimed[41] through an inlet manifold into the CVD reactor. The inlet manifold was kept at 120–130 °C to prevent condensation of the precursor. The carrier gas flow was controlled by a mass flow controller of MKS Instruments, Model 1159B. The pressure in the system was measured by a Pirani gauge of K. J. Lesker Co., Model 902002, in the range 0–2000 mTorr. Water vapors were introduced at a rate of 5 ± 1 or 20 ± 2 mL of liquid H_2O/h from an evaporation flask kept at 20–25 or 30–40 °C, respectively, and equipped with a magnetic stirrer. Water was degassed by three freeze–pump–thaw cycles or by 30-min stripping with argon.

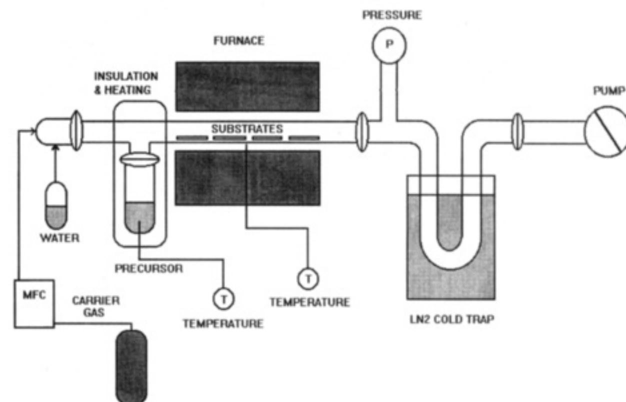

Figure 1. Experimental setup for the CVD studies on $\mathbf{1}\cdot H_2O$.

A typical CVD experiment was carried out for 4 h to ensure a sufficient thickness of the film for characterization. After deposition, the system was left to cool to room temperature under vacuum. Volatile components, collected downstream from the substrates in a liquid nitrogen cooled trap, were vacuum-transferred to a 5 mm NMR tube for characterization. A deuterated solvent was added and the tube was flame sealed. NMR spectra were measured directly when D_2O was used as a reactant.

Carrier gases, supplied by Air Products, (Ar, H_2, O_2, NH_3), were of anhydrous and high-purity grades and were used without further treatment. $Cu(hfacac)_2(H_2O)$ was purchased from Aldrich and used as received for reactions with water vapors. Dark blue crystalline anhydrous $Cu(hfacac)_2$ was prepared by a slow double sublimation of the hydrate at 60–70 °C at 10^{-2} Torr, mp 98–99 °C.[6] Both MS and IR spectra agreed with literature data. The bands of OH stretching vibrations were absent in the latter. Anhydrous $Cu(hfacac)_2$ was handled in a He-filled drybox. CuO (99.99%), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, and 1,1,1,5,5,5-hexafluoro-2,2,4,4-pentanetetrol were purchased from Aldrich and used as received. Water enriched in ^{18}O (53.97%) was purchased from Swan Chemical Inc.

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Table 1. Crystallographic Data for 1·H_2O

formula	$CuC_{10}H_4O_5F_{12}$
fw	495.67
a (Å)	9.402(3)
b (Å)	11.068(3)
c (Å)	7.958(2)
α (deg)	105.71(2)
β (deg)	100.99(2)
γ (deg)	76.27(2)
V (Å^3)	767.31
Z	2
space group	$P\bar{1}$ (No. 2)
T(°C)	−165
λ (Å)	0.710 69
d_{calcd} (g cm^{-3})	2.145
μ (cm^{-1})	15.815
R(*F*)	0.0303
$R_w(F)$	0.0312
GOF	1.820

Physical Measurements. ^1H (500.138 MHz) and ^{13}C (125.759 MHz) NMR spectra were recorded on a Bruker AM500 instrument and were referenced to the corresponding TMS and DSS signals in organic solvents and D_2O, respectively. ^{19}F (339.721 MHz) NMR spectra were taken on a Nicolet NT360 instrument and referenced to the signal of CF_3COOH in a particular solvent (D_2O, CD_2Cl_2) at −78.5 ppm. Deuterated solvents were used as an internal lock. IR spectra were acquired on a Nicolet 510P FTIR spectrometer (4000–400 cm^{-1}) in KBr pellets. X-ray powder diffraction studies (XRD) were performed on a Scintag XDS 2000 powder diffractometer equipped with a Cu source (λ = 1.540 60 Å). X-ray photoelectron spectra (XPS) were measured on a PHI Model 548 system equipped with a nonmonochromated Mg source operated at 400 W. The pressure in the vacuum chamber was less than 5 × 10^{-9} Torr. The pass energy was set to 25 eV, and binding energies were referenced to the Au $4f_{7/2}$ line at 83.8 eV. Mass spectra were run on a Kratos MS-80RFA high-resolution instrument using EI mode at 30 and 80 eV and CI mode with NH_3 and CH_4 ionizing gases. The masses are reported for the most abundant isotope present. Secondary ion mass spectra (SIMS) were acquired on a PHI model SIMS II instrument with Ar^+ primary beam at 5 kV. The positive ion signal from 2 × 2 mm area was gated to 50% to avoid edge effects.

Mass Spectroscopy Data for 1·H_2O. LR MS (EI, 30 eV) *m/z* (ion, rel intensity) 747 ([Cu_2(hfacac)$_3$]$^+$, 12), 678 ([Cu_2(hfacac)$_3$ −CF_3]$^+$, 3), 540 ([Cu_2(hfacac)$_2$]$^+$, 45), 477 ([M − H_2O]$^+$, 35), 408 ([M − H_2O − CF_3]$^+$, 65), 339 ([M − H_2O − 2CF_3]$^+$, 45), 251 ([Cu(hfacac) − F]$^+$, 10), 201 ([Cu(hfacac) − CF_3]$^+$, 100), 139([Hhfacac − CF_3]$^+$, 7), 91 (5), 69 (CF_3^+ and $C_3O_2H^+$, 30). LR MS (EI, 80 eV) *m/z* (ion, rel intensity) 540 ([Cu_2(hfacac)$_2$]$^+$, 10), 477 ([M − H_2O]$^+$, 30), 408 ([M − H_2O − CF_3]$^+$, 65), 339 ([M − H_2O − 2CF_3]$^+$, 40), 201 ([Cu(hfacac) − CF_3]$^+$, 100), 139 ([Hhfacac − CF_3]$^+$, 7), 63 (Cu^+, 20). HR MS (EI, 30 eV) calcd for $C_{10}H_2O_4F_{12}{}^{63}Cu_2$, [$Cu_2$(hfacac)$_2$]$^+$, *m/z* 539.8310; found 539.8334. LR MS (DCI, NH_3) *m/z* (ion, rel intensity) 477 ([M − H_2O]$^+$, 45), 408 ([M − H_2O − CF_3]$^+$, 70), 339 ([M − H_2O − 2CF_3]$^+$, 50), 287 ([Cu(hfacac)NH_3]$^+$, 95), 218 ([Cu(hfacac)NH_3 − CF_3]$^+$, 30), 201 ([Cu(hfacac) − CF_3]$^+$, 100), 139 ([Hhfacac − CF_3]$^+$, 15), 97 ($Cu(NH_3)_2^+$, 50), 80 ($Cu(NH_3)^+$, 10). LR MS (DCI, CH_4) *m/z* (ion, rel intensity) 540 ([Cu_2(hfacac)$_2$]$^+$, 5), 477 ([M − H_2O]$^+$, 45), 458 ([M − H_2O − F]$^+$, 8), 408 ([M − H_2O − CF_3]$^+$, 60), 339 ([M − H_2O − 2CF_3]$^+$, 48), 201 ([Cu(hfacac) − CF_3]$^+$, 100), 139([Hhfacac − CF_3]$^+$, 7), 82 (CuF^+, 32), 69 (CF_3^+ and $C_3O_2H^+$, 35).

Single-Crystal X-ray Diffraction Study of 1·H_2O. Green crystals of 1·H_2O were grown by slow vacuum sublimation at 40–45 °C. A well-formed crystal (0.25 × 0.30 × 0.40 mm) was affixed to a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −165 °C for characterization and data collection.[42] Pertinent data are presented in Table 1. A systematic search of a limited hemisphere of reciprocal space located a set of data with no symmetry or systematic absences corresponding to a triclinic space group. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice. Data were corrected for Lorentz and polarization terms, and equivalent data averaged. The structure was solved by direct methods (MULTAN78) and Fourier techniques. Hydrogen atoms were located in a difference map phased on the non-hydrogen atoms and were included as isotropic contributors in the final cycles of least squares.

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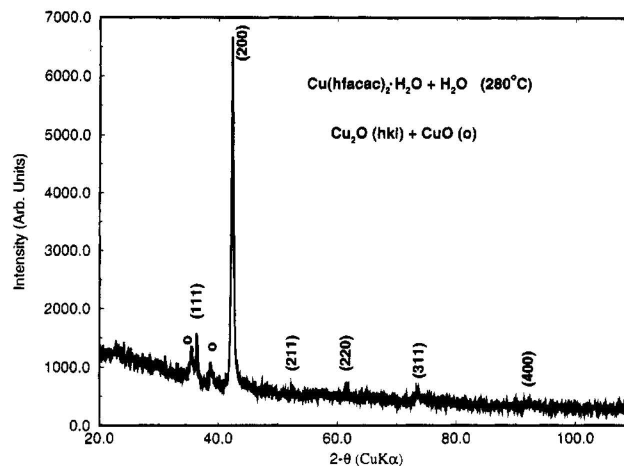


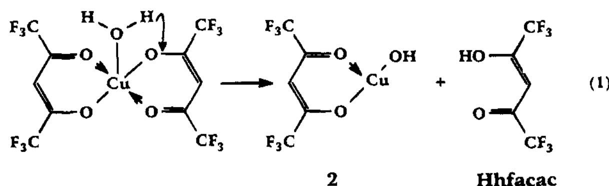
Figure 2. XRD pattern of the Cu_2O/CuO film from the reaction of 1·H_2O with H_2O at 280 °C.

Results and Discussion

Reaction of 1 with H_2. This reaction was carried out at 280, 400, and 500 °C with the hydrogen flow rate of 20 mL/min and a total pressure of 720 mTorr. The molar ratio of Cu:H_2 was approximately 1:120. No apparent decomposition of the precursor occurred at either 280 or 400 °C and dark blue crystals of Cu(hfacac)$_2$ condensed beyond the hot zone. At 500 °C, a dark brown film was formed on the substrates. This film was insoluble in HNO_3 and consisted of carbonaceous solids. A small amount of a white solid (0.03 g) condensed beyond the hot zone and was examined by IR and ^1H NMR spectroscopies. Bands of CF_3, C=O, and CH groups were identified in the IR spectrum, but the spectrum differed from those of Cu(hfacac)$_2$ and $CF_3C(OH)_2CH_2C(OH)_2CF_3$. Only one broad signal (δ 5.40; $\Delta v_{1/2}$ = 24 Hz) was observed in the ^1H NMR spectrum in CD_3CN. These results compare well with previous results from our laboratory, where an adduct Cu(hfacac)$_2$(THF) gave only carbonaceous deposits under CVD conditions. Our explanation, as will be elaborated further below, is based on the essential role of proton bearing ligands such as H_2O and NH_3 to promote a ligand release by a proton-transfer reaction in the absence of a metal surface.

Reaction of 1·H_2O with Water. To examine the influence of water on the nature of deposition products at low temperature, the CVD reaction was carried out at 280 °C with the molar ratio of Cu:H_2O of approximately 1:100. Water was deoxygenated before the reaction. A uniform, smooth gray-blue deposit was formed on glass and silicon substrates. Its XRD pattern is shown in Figure 2. The major component of the film is Cu_2O with a small amount of CuO. The intensities of the (111), (220), and (311) lines are unusually weak, while the (200) diffraction peak becomes the strongest

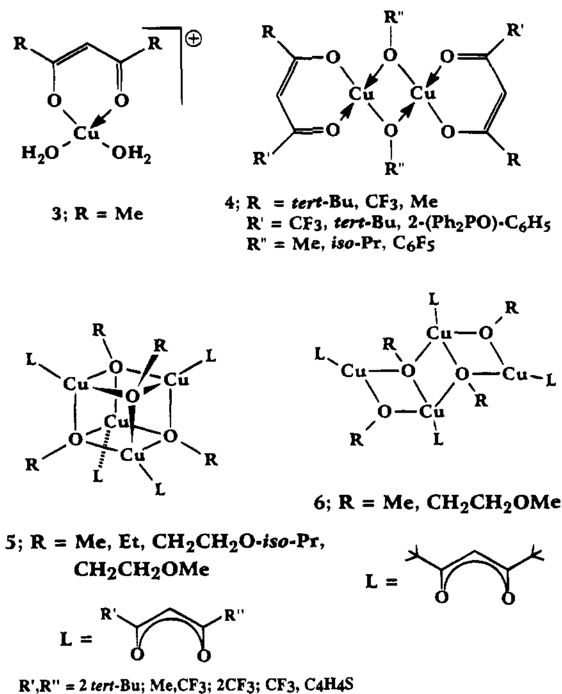
in this spectrum, thus attesting to a preferential orientation of the Cu_2O film. The elemental composition of the film, established by XPS, was 74 at. % of copper, 26 at. % of oxygen. No carbon or fluorine was observed in the sample above the detection limit of 1.5 at. %. As the difference between Cu $2p_{3/2}$ binding energies in Cu_2O and Cu[43] is below the resolution of the instrument, it was impossible to decide whether the excess of Cu over O is caused by an oxygen deficiency in the Cu_2O or by the presence of metallic Cu in a sufficiently disordered state to escape detection in the XRD. The considerably lower decomposition temperature as compared to the preceeding experiment is a strong indication that water plays an important role in facilitating the ligand removal from $Cu(hfacac)_2$. A stepwise intramolecular proton transfer according to reaction 1 can

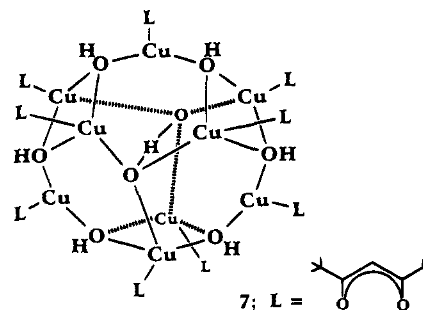


be envisioned. The species **2** can be stabilized either by coordination of another molecule of H_2O, thus forming a monomeric structure similar to the crystallographically characterized complex **3**,[44] or more importantly by an oligomerization to species analogous to a dimer, **4**,[45,46] tetramers, **5**,[46,47] **6**,[46,48] and a nonamer, **7**[48] (Chart 1). The second intramolecular proton transfer in species similar to **2**–**7** is sufficient to liberate the remaining Hhfacac molecules and form CuO. This process presumably constitutes a minor pathway because the observed amount of CuO was small. The major process must involve reduction of Cu^{2+} to Cu_2O, and we are therefore confronted with the need to find a mechanism through which the Cu site can be reduced during the deposition even in the absence of an explicit reducing agent.

Stepwise building processes such as those described above, where molecular monomeric precursors are converted through oligomeric intermediates to infinite solid-state structures are well-known in other systems.[49] We note that a major consequence of the proposed mechanism is that the oxygen in oxide films is derived from water not the hfacac ligand, and below we present evidence that this is indeed seen in our experiments. We have also seen evidence for oligomerization of $Cu(hfacac)_2$ in the gas phase (mass spectroscopy, EI at 30 eV). Using high source pressures to allow for bimolecular collisions, peaks at 540, 678, and 747 were observed (see Experimental Section). Their masses and isotopic

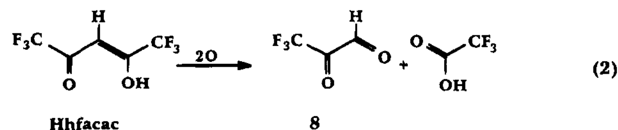
Chart 1

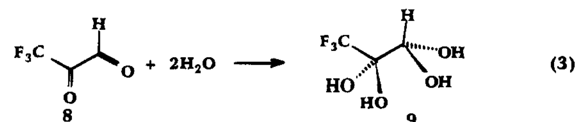




patterns imply the formation of Cu_2 dimers. Previously reported EI mass spectra of this compound at 80 eV contained $[Cu(hfacac)_2]^+$ as its highest mass.[8]

Given the absence of any external reducing agent in this study, the observed reduction of Cu^{2+} to Cu^{1+} (i.e., formation of Cu_2O) can only be accomplished at the expense of ligand oxidation in the sense of eq 2. To confirm this hypothesis, the condensate from a downstream liquid nitrogen trap was analyzed, and the anticipated product of such a redox reaction, trifluoroacetic acid (pH = 2), was identified by ^{13}C and ^{19}F NMR





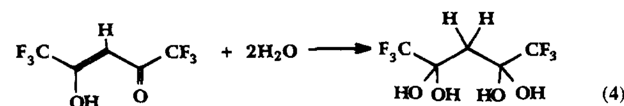


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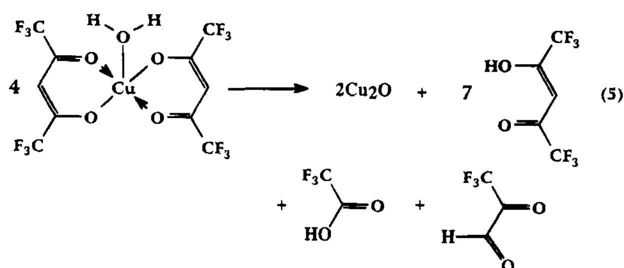
Table 2. ^{1}H, ^{13}C, and ^{19}F NMR Data[a] for the Compounds Found in the Volatiles from CVD Reactions

compound	CF3 δ(^{13}C)	CF3 δ(^{19}F)	CO δ(^{13}C)	C(OH) δ(^{13}C)	C(OH) δ(^{1}H)	CHn δ(^{13}C)	CHn δ(^{1}H)
CF_3COOH	116.8q $^{1}J_{CF}$ = 292	−78.5	163.0q $^{2}J_{CF}$ = 35		11.28[b]		
9	no[e]	−84.5	no	no		no	5.15
10(tetrol)	122.5q $^{1}J_{CF}$ = 287	−89.9		93.8q $^{2}J_{CF}$ = 33	5.97s[c]	34.5s	2.19s[c] $^{1}J_{CH}$ = 131[d]
Hhfacac[b]	117.4q $^{1}J_{CF}$ = 281	−79.5	177.2q $^{2}J_{CF}$ = 39	177.2q $^{2}J_{CF}$ = 39	12.89s	94.7s	6.42s $^{1}J_{CH}$ = 175[d]
$CF_3C(OH)_2CD_3$	125.7q $^{1}J_{CF}$ = 292	−88.5		95.4q $^{2}J_{CF}$ = 29		23.8 $^{1}J_{CD}$ = 19	

[a] Chemical shifts in ppm, coupling constants in hertz; all spectra were measured in D_2O unless otherwise stated. [b] Dichloromethane-d_2. [c] Acetonitrile-d_3. [d] ^{13}C satellites. [e] no = not observed.

spectroscopies. The other expected ligand oxidation product trifluoropyruvaldehyde, **8**, is known to undergo a reaction with H_2O in the aqueous solution forming the geminal diol **9** (eq 3). ^{1}H and ^{19}F NMR signals consistent with the species **9**[50] were also observed. Unfortunately, a low concentration of the ligand-oxidation products prevented a more precise characterization of **9** by ^{13}C NMR spectroscopy. Pertinent NMR data on which our assignments are based are gathered in Table 2.

The NMR spectra of the condensate also revealed signals for tetrol **10**, which is the product of the hydration reaction of the liberated ligand (eq 1) with an excess of water (eq 4). The integral intensities of ^{19}F NMR signals of **10**, CF_3COOH, and **9** were in the ratio of 20:1:0.5, which differs from an expected value of 14:1:1 according to the mass balance in eq 5. This



variation can be caused by the presence of the nonredox minor pathway leading to Hhfacac and CuO as discussed above, and by lability of **9** toward further reactions such as oxidation to CF_3COOH, CO_2, and H_2O. The ^{19}F NMR spectrum of this solution remained unchanged for several months, thus attesting to the hydrolytical stability of **10** and **9** in the acidic solution. When the pH of the sample was changed to 11 by an addition of NaOH, **10** instantly and completely hydrolyzed to $CF_3C(OH)_2CD_3$ and CF_3COO^- (Table 2) and the peak for **9** shifted downfield to −79.8 ppm.

The influence of substrate temperature on the nature of products was examined in the deposition reaction performed at 400 °C. The films formed on the glass substrates range in color from blue-gray to pink to red, depending on their position in the hot zone. Results of the XRD study are summarized in Table 3. They show that the hfacac ligand is not only capable of reducing CuO to Cu_2O at lower temperatures but also of reducing Cu_2O to metallic Cu at elevated temperatures. The XPS

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Table 3. XRD Results for the Reaction of $1{\cdot}H_2O$ with Water at 400 °C

substrate no[a]	appearance	composition by XRD
1	very thin, light brown	nd[b]
2	blue-gray	Cu_2O + CuO (traces)
3	pink	Cu_2O
4	pink	Cu_2O + Cu (traces)
5	blue-gray and red patches	Cu_2O + Cu (10:1)
6	red	Cu_2O + Cu (1:1)
7	red	nd
8	red	Cu + Cu_2O (traces)
9	red	Cu
10−11	red patches	nd
12	red, shiny	Cu

[a] Starting from the upstream end of the reactor. [b] nd = not determined.

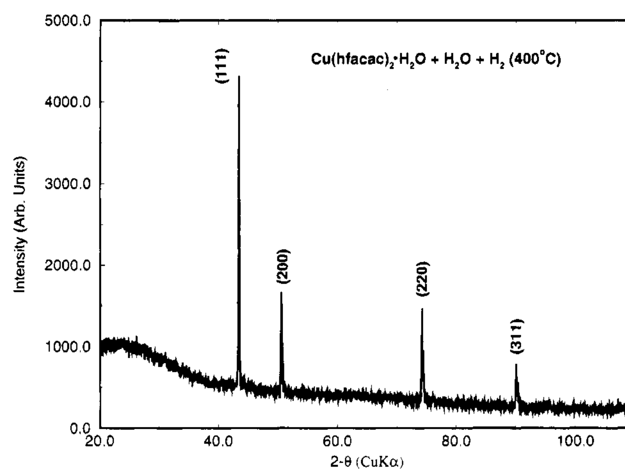

Figure 3. XRD pattern of the Cu film from the reaction of $1{\cdot}H_2O$ with H_2O and H_2 at 400 °C.

elemental analysis of the Cu_2O film showed 74 at. % of copper, 22 at. % of oxygen, and 4 at. % of carbon. For metallic copper films, the Cu content was 94 at. %, while oxygen and carbon were present at 4 and 2 at. % levels, respectively. We thus have shown that deposition of metallic Cu films does not require H_2. If we conduct similar depositions in the presence of H_2 ($Cu:H_2:H_2O$ = 1:200:900), we obtain essentially identical results at 280 °C but complete reduction to metallic Cu at 400 °C (Figure 3).

Our observations are in concert with a recent report on the preparation of copper films from $Cu(acac)_2$ at 370−400 °C in the presence of water vapor at atmospheric pressure.[51] The acac ligand was shown to reduce copper at temperatures below 350 °C to Cu_2O,

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while above this temperature, metallic films were formed on silicon substrates. Interestingly, three reports on CVD studies on $Cu(hfacac)_2$[52] and $Cu(acac)_2$[53,54] in oxidizing atmospheres of air, O_2, and N_2O concluded that the copper oxidation state decreases when the deposition temperature increases, regardless of the presence of an oxidizer. CuO, Cu_2O, and Cu were observed by XRD as the substrate temperatures were raised. Explaining these observations requires a temperature-dependent reducing action of the ligand such as observed in our system. Obviously, the oxidizing agent does not take part in these reactions at reduced pressure within the studied temperature window, as one would expect a higher degree of copper oxidation with increasing reaction temperature if it did. Conversely, when the ligand is the reducing species, more extensive reduction is anticipated at higher temperature as is the present case. However, recent results on the low pressure CVD of $Cu(acac)_2/O_2$ show that formation of CuO is feasible at high temperatures (above 450 °C) and with a large molar excess (1000:1) of O_2 over the precursor. At low temperatures and molar ratios, Cu_2O and Cu were observed in the films.[55] The influence of an oxidizing agent on the nature of the products was studied and will be described below.

Reaction of 1·H_2O in Ar. The necessity of having an excess of H_2O vapor in the CVD system was demonstrated by using 1·H_2O without an external source of H_2O at a deposition temperature of 280 °C. Argon (flow rate 100.0 mL/min, total pressure 1.1–2.0 Torr) was used as a carrier gas. No deposition was observed and the dehydrated precursor **1** condensed as dark blue crystals downstream of the hot zone. 1·H_2O under vacuum readily loses the weakly coordinated water molecule as was substantiated by our preparative dehydration of the monohydrate to the anhydrous precursor under vacuum and by the absence of the parent ion peak in the mass spectrum of 1·H_2O even under mild conditions of CH_4 chemical ionization. A relatively long Cu–OH_2 bond distance found in the solid-state structure of 1·H_2O (see Structural Considerations below) attests to the weak Cu–O bond and explains the lability of the monohydrate at a reduced pressure. Thus in the absence of excess water, the loss of coordinated H_2O from the precursor frustrates the facile decomposition at low temperatures by preventing the proton-transfer reaction, as was discussed above.

Reaction of 1 with $H_2{}^{18}O$. Strong support for our proposed mechanism was gained from a labeling experiment using ^{18}O-enriched water (^{18}O, 53.97%; ^{17}O, 2.57%; ^{16}O, 43.46%) as a reactant. The deposition at 280 °C under conditions identical to previous experiments provided blue-gray films identified by XRD again as a mixture of Cu_2O and a small amount of CuO. The content of the three oxygen isotopes in the film was established by a SIMS experiment to be ^{18}O, 45.7%; ^{17}O, 2.5%; ^{16}O, 51.8%. This result clearly shows that oxygen in the copper oxide films is derived from water and not from the hfacac[56] ligand. Deriving oxygen from the hfacac ligand would involve C–O bond breaking, a process that would require more energy and facilitate incorporation of impurities (C and F) into the film. Similar results were reported recently for the (hfacac)-CuL (L = $Me_3SiCH{=}CH_2$, 2-butyne) systems.[57]

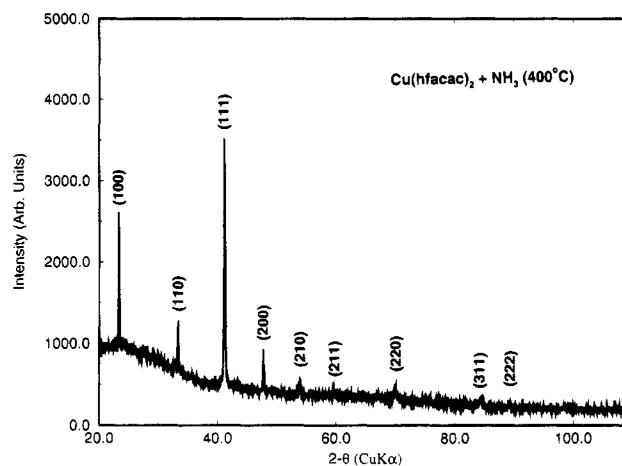

Figure 4. XRD pattern of the Cu_3N film from the reaction of **1** with NH_3 at 400 °C.

Reaction of 1 with NH_3. As an additional mechanistic test of our hypothesis about the proton transfer from a coordinated water molecule to the hfacac ligand, we used ammonia as a protonating agent even though the acidity of its protons is much lower than that of H_2O. The reaction was performed at a substrate temperature of 400 °C. Ammonia was delivered in the CVD reactor at the rate of 50 mL/min, and the total pressure in the system was 1 Torr. A gray compact deposit was identified by XRD as Cu_3N (Figure 4). A green solid condensed beyond the hot zone was identified as the 1·NH_3 adduct[58] by IR and MS spectra. Rather complex ^{19}F NMR spectra of the cold trap content revealed the presence of CF_3COOH and several other unidentified species, presumably products of Hhfacac reactions with NH_3. The proton transfer from NH_3 to the hfacac ligands apparently promotes their removal in a manner similar to the above model for H_2O. Cu^{2+} is reduced to Cu^+, and nitrogen is retained in the film. In reactions performed at 450 °C, a mixture of Cu_3N and metallic copper was formed.

Reaction of CuO with Hhfacac. To evaluate the reducing capability of Hhfacac and to test independently the reduction step in our proposed mechanism (eq 2), the reaction of powdery bulk CuO with gaseous Hhfacac was carried out in the CVD reactor at 280 °C. During the reaction, a green solid was deposited beyond the hot zone, and this was identified by its melting point and IR spectrum as 1·H_2O. XRD of a black powder left in the reactor revealed no detectable amount of crystalline Cu_2O, and ^1H and ^{13}C NMR spectra showed the presence of unreacted Hhfacac in the downstream cold trap. Under the conditions used in this experiment, the formation of 1·H_2O by the dry etching process[59] is

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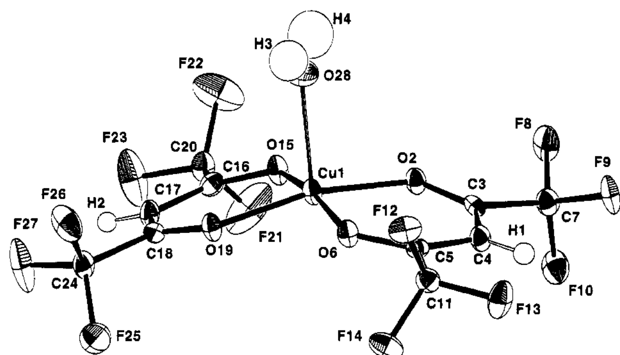

Figure 5. ORTEP drawing of $Cu(hfacac)_2(H_2O)$. Ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $Cu(hfacac)_2(H_2O)$

Cu1–O2	1.9471(23)	Cu1–O6	1.9381(23)
Cu1–O15	1.9295(24)	Cu1–O19	1.9455(23)
Cu1–O28	2.204(3)		
O2–Cu1–O6	92.99(10)	O15–Cu1–O19	93.01(10)
O2–Cu1–O15	86.40(10)	O6–Cu1–O19	85.23(10)

preferred to the redox reaction. Apparently, CuO in the form of a powder is not an adequate model for species present during the CVD process. This leads us to speculate that the reduction step starts before the stepwise formation of bulk solid CuO is completed. While in the form of oligomers, the copper atoms are in much more intimate contact with the hfacac ligands than our heterogeneous bulk solid model can provide, thus facilitating the reduction.

Reaction of $1{\cdot}H_2O$ with Water and O_2. As noted above, an oxidizing agent does not seem to influence the nature of the products in the CVD of $Cu(hfacac)_2$ at this low temperature while the ligand governs the degree of metal reduction. The reaction was carried out at 350 °C, the oxygen flow rate was 20 mL/min, and the pressure was 1 Torr. The composition of the deposited films was determined by XRD and showed Cu_2O with a small amount of CuO for the films in the front part of the hot zone and pure Cu_2O in the center and the end part. The absence of CuO in the center of the deposition zone is consistent with the higher temperature causing a higher degree of the copper reduction by the hfacac ligand. As discussed above, oxygen, though an oxidizing agent and oxygen atom donor, is apparently unable at these conditions to counterbalance the reducing action of the ligand and to maintain the copper oxide in the highest oxidation state. It seems necessary to look for more active oxidizing agents for the low-temperature preparation of copper(II) oxide films from $Cu(hfacac)_2$.

Structural Considerations. The molecular structure of $1{\cdot}H_2O$ is shown in Figure 5 and selected bond distances and angles are summarized in Table 4. The coordination environment around the copper center is square pyramidal with the water ligand in the apical position and the oxygens of the chelating hfacac ligands occupying the basal sites. The copper atom is displaced 0.2 Å above the basal oxygen array toward the apical site. The planes of the two hfacac ligands are canted to 155° with respect to each other. The coordination bond distance Cu1–O28 of 2.204(3) Å is very similar to the values of 2.191(4) and 2.212(6) Å which were found for the apical ethanol in the square-pyramidal complexes $Cu(hfacac)_2(EtOH)$[31a] and $Cu[C_3F_7C(O)CHC(O)C_3F_7]_2(EtOH)$,[60] respectively, and falls between the values of 1.95 Å reported for four-coordinate copper complex **3**[44] and 2.59 Å in six-coordinate dihydrate complex $Cu[CF_3C(O)CHC(O)C_6H_4NO_2]_2(H_2O)_2$.[61] The Cu–O distances in the basal plane are slightly longer than the ones in anhydrous $Cu(hfacac)_2$[62] and similar to the ones in Cu(hfacac)(acac).[63]

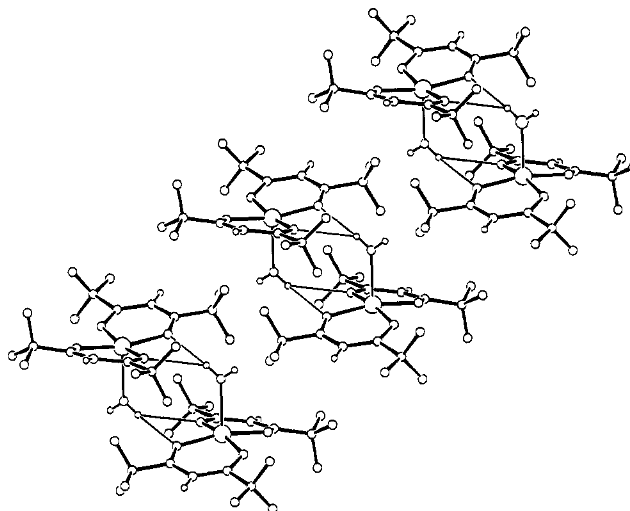

Figure 6. Packing diagram of the content of several unit cells of $Cu(hfacac)_2(H_2O)$, showing its dimeric nature, the hydrogen bonding, and the linear chains of dimers along the *y* axis.

The crystal structure of $1{\cdot}H_2O$, as shown in Figure 6, consists of chains of hydrogen-bonded dimeric units. Two $Cu(hfacac)_2(H_2O)$ molecules are connected via unsymmetrical bifurcated hydrogen bonds[64,65] between one hydrogen of the water molecules and oxygens of the hfacac ligands with the O···H distances of 2.46 and 2.60 Å. The corresponding O···O distances and O–H···O angles are 3.17 and 3.20 Å and 151.2 and 135.1°, respectively. These values are in good agreement with the reported geometries for bifurcated hydrogen bond systems.[66] The second hydrogen of H_2O is stabilized by a close H···F intermolecular contact of 2.72 Å (the F···O distance is 3.13 Å) with a fluorine in a neighboring parallel chain. However, this distance is close to the sum of the van der Waals radii of hydrogen and fluorine (2.67 Å).[67] Dimeric units form linear chains held together by interactions of methine hydrogens with fluorines of the CF_3 groups at distances of 2.60 and 2.77 Å. The solid-state structure, displaying the close approach of water hydrogens to oxygens of the hfacac ligands, supports the idea of a facile proton transfer. This may be accomplished intramolecularly, as was suggested above, or intermolecularly as may be inferred from the dimeric structure of $1{\cdot}H_2O$.

Concluding Remarks. This work has presented a systematic study of the role of the ancillary ligand, H_2O,

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in the CVD of $Cu(hfacac)_2$. Water is shown to provide the key step of proton transfer in facilitating elimination of the fluorinated ligand and the water oxygen atom is retained in the solid oxide product. These mechanistic conclusions are underscored by isotope labeling studies using $H_2{}^{18}O$ and by reactions involving added NH_3 that yield Cu_3N films. Ligand-mediated reduction of the metal from Cu^{2+} to Cu^{+} to Cu^{0} oxidation state occurs, and the fluorinated compounds CF_3COOH and $CF_3C(OH)_2CH(OH)_2$ have been identified as the decomposition products of the hfacac ligand in the presence of water. We have also suggested that the formation of oligomers may play an important role in this ligand-induced reduction of the metal.

Acknowledgment. The authors thank to Mr. D. Perry and Mr. M. Falatic for their assistance with the XPS measurements and Dr. R. Caretta for acquiring SIMS spectra. This work was supported by DOE Grant No. DE-FG02-90ER45427 through the Midwest Superconductivity Consortium.

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