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Structures of Anhydrous and Hydrated Copper(II) Hexafluoroacetylacetonate

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Crystal structure analyses are reported for anhydrous copper(II) hexafluoroacetylacetonate (Cu(hfac)$_2$) and for two of its hydrates. The anhydrous compound (Cu(hfac)$_2$, **1**: $P\bar{1}$; at 100 K, $a = 5.428(1)$, $b = 5.849(1)$, $c = 11.516(3)$ Å; $\alpha = 81.47(2)$, $\beta = 74.57(2)$, $\gamma = 86.96(2)°$; $Z = 1$) contains centrosymmetric square-planar complexes with close intermolecular Cu···F contacts. The geometry of the complex is similar to that previously reported for Cu(hfac)$_2$·toluene. The monoaquo compound (Cu(hfac)$_2$(H$_2$O), **2**: $P2_1/c$; at 100 K, $a = 10.8300(8)$, $b = 6.5400(6)$, $c = 21.551(3)$ Å; $\beta = 90.282(8)°$; $Z = 4$) consists of square-pyramidal molecules with apical H$_2$O ligands, and close-lying F atoms in the sixth coordination sites. The major difference between this structure and the two other polymorphs previously reported is the nature and direction of hydrogen bonds. The yellow-green solid formed from Cu(hfac)$_2$ with excess H$_2$O is identified as the trihydrate. In crystalline form it is the previously unreported [*trans*-Cu(hfac)$_2$(H$_2$O)$_2$]·H$_2$O (**3**: $P\bar{1}$; at 150 K, $a = 8.3899(3)$, $b = 9.6011(3)$, $c = 11.4852(4)$ Å; $\alpha = 72.397(2)$, $\beta = 79.161(2)$, $\gamma = 87.843(2)°$; $Z = 2$). There is no conclusive evidence in favor of any solid with the composition Cu(hfac)$_2$·2H$_2$O.

Introduction

Fluorinated β-diketonate complexes of metals have been studied extensively in recent years: their relatively high volatility makes them attractive as precursors for chemical vapor deposition of metals[1] and oxides.[2] The high affinity of copper(II) hexafluoroacetylacetonate (Cu(hfac)$_2$) and related compounds for donor ligands has been utilized in thermodynamic studies of adduct formation,[3] and in the construction of discrete[4] and polymeric[4b,4c,5] supramolecular systems.

Cu(hfac)$_2$ is normally obtained commercially or synthesized in hydrated form. However, the state of hydration of commercial material is uncertain: of six companies offering the compound for sale, five list it as Cu(hfac)$_2$·xH$_2$O and one as Cu(hfac)$_2$·2H$_2$O. This uncertainty is probably attributable to confusion in the early literature over the identity of the solid phases in the Cu(hfac)$_2$−H$_2$O system. Reaction of hfac$^-$ with Cu^{2+} in water produces a yellow-green precipitate,[6] which has never been clearly characterized but was believed to be the dihydrate.[7] This material loses water readily in air to form the blue-green monohydrate, whose composition was first demonstrated conclusively by Funck and Ortolano.[7] Both hydrates can be dehydrated completely to dark blue-violet anhydrous Cu(hfac)$_2$. X-ray analyses of two polymorphs of Cu(hfac)$_2$(H$_2$O),[8,9] and the toluene solvate

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of the anhydrous compound (Cu(hfac)$_2$•toluene),[10] have been published. However, the ansolvous compound has not been crystallographically characterized, and the yellow-green "dihydrate" has never been identified conclusively. We now report the crystal structures of ansolvous Cu(hfac)$_2$ (**1**) and a new polymorph of the monohydrate Cu(hfac)$_2$(H$_2$O) (**2**). We have also found that the yellow-green material isolated from aqueous solution[6] is actually the *tri*hydrate, and it can be crystallized as [*trans*-Cu(hfac)$_2$(H$_2$O)$_2$]•H$_2$O (**3**).

Experimental Section

Cu(hfac)$_2$(H$_2$O) (hfacH = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) was either obtained commercially (Gelest or Strem) or synthesized by the method of Bertrand and Kaplan[6] (reaction of hfacH, sodium acetate, and copper(II) nitrate in water, followed by drying of the precipitate in air). This material was converted to the anhydrous compound on storage in a vacuum desiccator over P_2O_5 or concentrated H_2SO_4. X-ray quality crystals were obtained by the following methods:

Cu(hfac)$_2$ (1). The powdery anhydrous material, prepared as above, was sublimed under vacuum to give dark blue-violet crystals.

Cu(hfac)$_2$(H$_2$O) (2). Blue-green crystals were obtained over a period of several months by sublimation in a closed container at room temperature and atmospheric pressure.

[*trans*-Cu(hfac)$_2$(H$_2$O)$_2$]•H$_2$O (3). The method of Bertrand and Kaplan[6] was modified as follows: A solution of $CuSO_4 \cdot 5H_2O$ (0.315 g, 1.26 mmol) in 3 mL of H_2O was layered on a solution prepared from hfacH (0.525 g, 2.52 mmol) and NaOAc (0.23 g, 2.8 mmol) in ca. 0.5 mL of H_2O. Yellow-green platelike crystals were obtained over a period of 2−3 days. Crystals can also be obtained by substituting $Cu(NO_3)_2$(aq) for $CuSO_4$(aq) in the above method, or by layering $Cu(OAc)_2$(aq) on hfacH(aq). Diffraction patterns were examined for several crystals from each type of experiment; these all showed the unit-cell parameters of **3**.

Material with the same composition was prepared in powder form starting from solid Cu(hfac)$_2$(H$_2$O) by placing it in an atmosphere saturated with water vapor. The blue-green monohydrate turned yellow-green, reaching constant weight after 2 days. The observed weight gains in two such experiments were 7.36% and 7.49%; the calculated weight gain is 7.27% for the formation of Cu(hfac)$_2$•3H$_2$O.

Both powdered and crystalline **3** begin to lose water (with a color change from yellow-green to blue-green) within a few minutes in normal laboratory air.

Crystal-Structure Analyses. Crystals were mounted on glass fibers with the use of mineral oil, and immediately cooled in the N_2 gas stream of the diffractometer for data collection. For **1** and **2**, the diffractometer was an Enraf-Nonius CAD4 instrument fitted with a graphite monochromator, and the $\theta-2\theta$ scan method was used. The intensities were corrected for absorption using ψ scan data. A Nonius KappaCCD instrument was used for **3**. Data collection and refinement parameters for **1**, **2**, and **3** are presented in Table 1. Details of structure solution and refinement, modeling of disordered groups, and thermal-motion analysis are in the Supporting Information.

Table 1. Data Collection and Refinement Parameters[a]

	Cu(hfac)$_2$ (**1**)	Cu(hfac)$_2$(H$_2$O) (**2**)	[*trans*-Cu(hfac)$_2$-(H$_2$O)$_2$]•H$_2$O (**3**)
formula	$C_{10}H_2CuF_{12}O_4$	$C_{10}H_4CuF_{12}O_5$	$C_{10}H_8CuF_{12}O_7$
color	dark blue-violet	blue-green	yellow-green
fw	477.65	495.67	531.70
space group	$P\bar{1}$, No. 2	$P2_1/c$, No. 14	$P\bar{1}$, No. 2
a/Å	5.428(1)	10.8300(8)	8.3899(3)
b/Å	5.849(1)	6.5400(6)	9.6011(3)
c/Å	11.516(3)	21.551(3)	11.4852(4)
α/deg	81.47(2)	90	72.397(2)
β/deg	74.57(2)	90.282(8)	79.161(2)
γ/deg	86.96(2)	90	87.843(2)
V/Å^3	348.5(2)	1526.4(4)	865.91(5)
ρ_x/g cm^{-3}	2.258	2.157	2.039
Z	1	4	2
μ_x/mm^{-1}	1.72	1.59	1.42
temp/K	100 ± 1	100 ± 1	150 ± 1
λ/Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
θ_{max}/deg	32.6	35.0	35.0
unique/obsd/nvar[b]	2535/2255/128	5727/5298/253	7434/3878/293
transm coeff	0.65−0.68	0.67−0.73	0.55−0.87
$R(F)$ (all data)[c]	0.046	0.072	0.087
$R_w(F^2)$ (all data)[c]	0.105	0.124	0.116
w_1, w_2[c]	0.2007, 0.0585	4.0042, 0.0195	0, 0.0545

[a] In Tables 1−3, estimated standard deviations in the least significant digits of the values are given in parentheses. [b] Observed data have $I > 2\sigma(I)$. [c] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{1/2}$; $w = 1/(\sigma^2(F_o^2) + w_1P + (w_2P)^2)$; $P = (F_o^2 + 2F_c^2)/3$.

Results and Discussion

Chemistry of the Cu(hfac)$_2$−H$_2$O System. Hexafluoroacetylacetone and its copper(II) complex were first reported by Henne et al. in 1947.[11] The blue-green (or "grass-green") solid that is stable under normal laboratory conditions was recognized by early investigators to contain water,[12] but its state of hydration was not well established until the late 1960s. Walker and Li,[13] and Bertrand and Kaplan,[6] first reported the anhydrous material, prepared by dehydration over P_2O_5 or H_2SO_4. Attempts in these studies to establish the composition of the hydrated material by microanalysis and by weight gain in the presence of H_2O were conflicting or ambiguous. However, Funck and Ortolano's electronic spectral data[7] clearly identified the three important species in the system: (a) the anhydrous material, which is stable in dry organic solvents; (b) blue-green Cu(hfac)$_2$(H$_2$O); and (c) the yellow-green material, which (like dilute aqueous solutions of Cu(hfac)$_2$) was inferred to contain Cu(hfac)$_2$(H$_2$O)$_2$ molecules.

Since that time, X-ray analyses of two polymorphs of blue-green Cu(hfac)$_2$(H$_2$O) have been published.[8,9] Pinkas et al. reported the structure of the anhydrous compound in the form of its toluene solvate;[10] however, they were unable to mount crystals of the ansolvous compound without damage. No studies of the composition of the yellow-green solid have appeared between Funck and Ortolano's 1968 report and the present work.

Structure of Anhydrous Cu(hfac)$_2$ (1). This compound consists of centrosymmetric Cu(hfac)$_2$ molecules; see the

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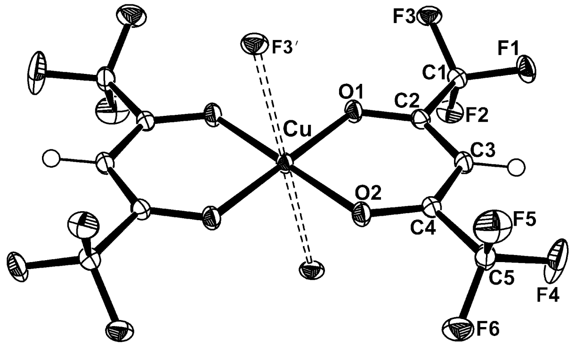

Figure 1. ORTEP drawing of Cu(hfac)$_2$ molecule in **1**, with displacement ellipsoids at the 50% probability level. Dashed lines indicate close intermolecular contacts between Cu and F3 in adjacent molecules (2.709(2) Å). (A packing diagram for this structure is available in the Supporting Information.)

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

Cu(hfac)$_2$ (**1**)					
Cu−O1	1.914(2)	Cu−O2	1.924(2)	Cu···F3′	2.709(2)
O1−Cu−O2	93.24(10)				
Cu(hfac)$_2$(H$_2$O) (**2**)					
Cu−O1	1.9545(17)	Cu−O3	1.9411(18)	Cu−O5	2.260(2)
Cu−O2	1.9370(18)	Cu−O4	1.9410(18)	Cu···F6′	2.895(2)
O1−Cu−O2	91.88(7)	O2−Cu−O3	86.51(8)	O3−Cu−O4	92.16(8)
O1−Cu−O3	165.87(8)	O2−Cu−O4	170.11(8)	O3−Cu−O5	103.22(9)
O1−Cu−O4	87.02(7)	O2−Cu−O5	100.47(8)	O4−Cu−O5	89.38(8)
O1−Cu−O5	90.88(8)				
[*trans*-Cu(hfac)$_2$(H$_2$O)$_2$]·H$_2$O (**3**)					
Cu−O1	1.9492(13)	Cu−O3	1.9517(13)	Cu−O5	2.2916(17)
Cu−O2	1.9632(13)	Cu−O4	1.9770(14)	Cu−O6	2.3109(17)
O1−Cu−O2	93.28(6)	O2−Cu−O3	85.93(6)	O3−Cu−O5	89.41(6)
O1−Cu−O3	178.25(6)	O2−Cu−O4	177.12(6)	O3−Cu−O6	94.99(6)
O1−Cu−O4	88.22(6)	O2−Cu−O5	94.81(7)	O4−Cu−O5	87.67(7)
O1−Cu−O5	89.10(6)	O2−Cu−O6	90.24(6)	O4−Cu−O6	87.39(7)
O1−Cu−O6	86.56(6)	O3−Cu−O4	92.64(6)	O5−Cu−O6	173.52(6)

ORTEP drawing in Figure 1. Bond distances and angles (see data for **1** in Table 2 and comparison with other structures in Table 3) are similar to those determined via gas-phase electron diffraction by Thomas et al.,[14] and to those obtained by Pinkas et al.[10] for crystalline Cu(hfac)$_2$·toluene. The most significant new interaction in **1** is between the Cu atom and F3 in two neighboring molecules; the intermolecular Cu···F3 distance is 2.709(2) Å (see Figure 1 and a packing drawing in the Supporting Information). In all three of these anhydrous Cu(hfac)$_2$ structures, the Cu, O, and C atoms are coplanar (maximum deviation in **1**, 0.066(2) Å).

Structure of the New Polymorph of Cu(hfac)$_2$(H$_2$O) (2). The structure of the copper complex in **2** (see Figure 2) is similar to those obtained by Pinkas et al.[8] and Jain et al.[9] (Our unit-cell parameters are very close to those of Jain et al.,[9] but the structures are significantly different; see detailed discussion in the Supporting Information.) The Cu atom in **2** is displaced 0.2034(3) Å out of the plane of the four hfac O atoms toward the coordinated water molecule. The hydrogen bonding of the water molecule differs in the three polymorphs, as does the Cu−OH$_2$ distance; in addition, all three Cu(hfac)$_2$(H$_2$O) structures show larger Cu−O(hfac) distances (weighted average 1.942 Å) than the anhydrous compound (1.917 Å); see Table 3.

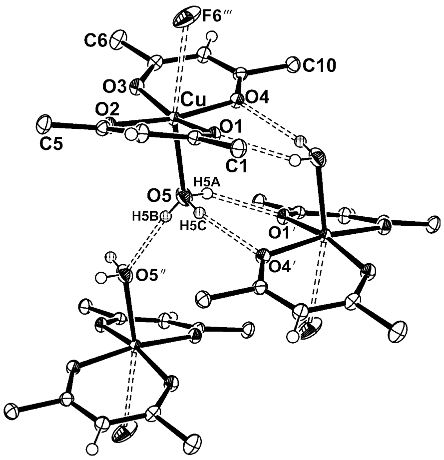

Figure 2. ORTEP drawing of three Cu(hfac)$_2$(H$_2$O) molecules in **2**. Close-lying atoms F6 in neighboring molecules are shown; all other F atoms are omitted for clarity. Dashed lines indicate hydrogen bonds and close Cu···F6‴ contacts (2.895(2) Å). H5B and H5C (occupancy 0.5) are shaded; H5B is disordered across the center of symmetry and is shown in one of its two equivalent positions.

The water H atoms in **2** are disordered over three positions. The water molecule is hydrogen-bonded to hfac and water O atoms in two neighboring complexes (H5A···O1′, 2.24; H5B···O5″, 2.05; H5C···O4′, 2.19 Å). The O atoms are in a square-pyramidal arrangement, but the environment about Cu is nearly octahedral due to a close intermolecular Cu···F contact; see Figure 2. Similar close Cu···F contacts are present in the other two Cu(hfac)$_2$(H$_2$O) structures (see Table 3), and also in two other "five-coordinate" Cu(hfac)$_2$ adducts: [Cu(hfac)$_2$]$_2$(μ-pyrazine), 3.069 Å;[15] [Cu(hfac)$_2$]$_3$(μ-5-methylpyrimidine)$_2$, 2.962 Å.[16]

To summarize, Cu(hfac)$_2$(H$_2$O) is now known to crystallize in three different polymorphs, all of which have similar molecular geometry and close intermolecular contacts. Other packings of the molecules might well produce similarly stable structures.

Structure of [*trans*-Cu(hfac)$_2$(H$_2$O)$_2$]·H$_2$O (3). These crystals consist of approximately centrosymmetric *trans*-Cu(hfac)$_2$(H$_2$O)$_2$ molecules (Figure 3), each with a water molecule of solvation. All atoms are in general positions. In **3**, the Cu−O(hfac) distances are approximately 0.02 Å longer (weighted average 1.960 Å), and the Cu−OH$_2$ distances approximately 0.07 Å longer, than in the Cu(hfac)$_2$(H$_2$O) polymorphs; see Table 3.

Hydrogen bonds are also present in the structure of **3**. The water of hydration (O7) lies approximately in the Cu(hfac)$_2$ plane, so that its hydrogen atoms make close approaches to O3, F6, and F8 (2.04, 2.27, and 2.63 Å, respectively). The coordinated water molecules (O5 and O6) are also hydrogen-bonded to O atoms in two adjacent asymmetric units; see the Supporting Information for details.

Other M(hfac)$_2$(H$_2$O)$_2$ Structures. A search of the Cambridge Structural Database[17] for structures similar to **3**

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Table 3. Comparison of Interatomic Distances (Å) in the Cu(hfac)$_2$−H_2O System

compd	Cu−O(hfac)	Cu−OH_2	Cu···F
Cu(hfac)$_2$ (**1**)[a]	1.914(2), 1.924(2)	n/a[b]	2.709(2)
Cu(hfac)$_2$(g)[c]	1.919(8)	n/a	n/a
Cu(hfac)$_2$·toluene[d]	1.908(7), 1.914(6)	n/a	n/a
Cu(hfac)$_2$(H_2O) (**2**)[a]	1.937(2)−1.954(2)	2.260(2)	2.895(2)
Cu(hfac)$_2$(H_2O)[e]	1.929(2)−1.947(2)	2.204(3)	2.817
Cu(hfac)$_2$(H_2O)[f]	1.932(4)−1.947(4)	2.221(6)	3.106
[*trans*-Cu(hfac)$_2$(H_2O)$_2$]·H_2O (**3**)[a]	1.9492(13)−1.9770(14)	2.2916(17), 2.3109(17)	n/a

[a] This work. [b] Not applicable (no such contact is found in this structure). [c] Gas-phase electron diffraction; ref 14. [d] Reference 10. [e] Reference 8. [f] Reference 9.

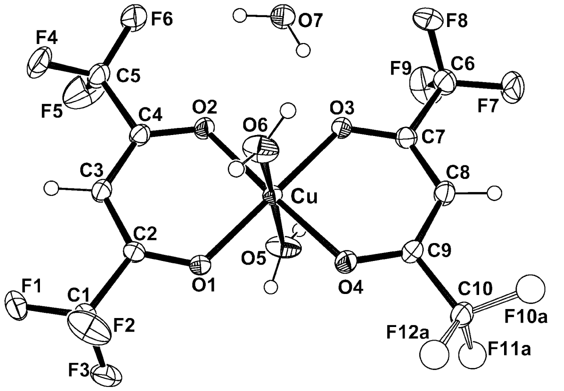

Figure 3. ORTEP drawing of *trans*-Cu(hfac)$_2$(H_2O)$_2$ molecule and water of hydration (O7) in **3**, with displacement ellipsoids at the 40% probability level. One orientation of the disordered CF_3 group at C10 is shown.

identified two others with the same [*trans*-M(hfac)$_2$(H_2O)$_2$]·H_2O formula (M = Zn,[18] Mn[19]). The Zn and Mn compounds are isomorphous with each other, but they are clearly different from **3**. In the Zn[18] and Mn[19] structures, the hfac ligands are bent substantially out of the equatorial plane; in contrast, in **3**, the Cu(hfac)$_2$ moiety is nearly planar (maximum deviation 0.158(2) Å, excluding F atoms).

Two isomorphous *cis*-M(hfac)$_2$(H_2O)$_2$ structures (M = Zn,[18] Ni[20]) have also been reported. The unit-cell parameters for these compounds are similar to those reported by Kidd et al. for "Cu(hfac)$_2$·2H_2O".[21] Thus, at first, we thought the "yellow-green" material of Funck and Ortolano[7] and the "blue-green" material of Kidd et al.[21] might both be *cis*-Cu(hfac)$_2$(H_2O)$_2$. However, the yellow-green **3** as prepared in our laboratory includes a third water molecule, contains trans complexes, and forms crystals with unit-cell volume about 53% of that of the material of Kidd et al. We did not observe any materials with unit-cell parameters similar to those of Kidd et al. Also, the melting point of their Cu compound was 207 °C. In contrast, **3** loses water rapidly on heating, turning blue-green, and then melts at ca. 130 °C, close to the published melting point for Cu(hfac)$_2$(H_2O) (133−136 °C[7]). Thus, **3** is clearly different from any of the previously described M(hfac)$_2$(H_2O)$_2$-containing phases.

Another Cu(hfac)$_2$ adduct has been reported with a high melting point (205 °C): Cu(hfac)$_2$(NH_3).[22] The unit-cell parameters for the NH_3 complex reported by Pinkas et al.[22] are considerably closer to those for the "dihydrate" of Kidd et al.[21] than are those for the other M(hfac)$_2$(H_2O)$_2$ crystals. Furthermore, in contrast to the usual preparative methods for hydrated Cu(hfac)$_2$, Kidd et al. used aqueous ammonia. Pinkas et al.[22] prepared the NH_3 complex by using NH_3(g) in toluene solution, but Anker et al.[23] showed that it can also be made with aqueous NH_3. For these reasons, we believe it is likely that the high-melting compound studied by Kidd et al. was actually Cu(hfac)$_2$(NH_3). Thus, there is no conclusive evidence for any solid with the composition Cu(hfac)$_2$(H_2O)$_2$; the previously described yellow-green phase actually contains three water molecules per Cu(hfac)$_2$ unit.

Relationship to Chemical Vapor Deposition (CVD). The structures of these compounds provide insights into intermolecular forces and bond distances that may affect their volatility and reactivity.

Cu(hfac)$_2$ is more volatile than Cu(hfac)$_2$(H_2O).[24] This behavior might be expected if the anhydrous compound is relatively nonpolar and Cu(hfac)$_2$(H_2O) is capable of forming intermolecular hydrogen bonds. However, the difference in volatility is small enough that both compounds are sufficiently volatile for use as CVD precursors.[25] The X-ray analyses of Cu(hfac)$_2$ (**1**) and Cu(hfac)$_2$(H_2O) suggest two reasons for this small difference in volatility. First, although anhydrous Cu(hfac)$_2$ is nonpolar, it also possesses significant intermolecular attractions, primarily in the form of the short Cu···F contacts. Second, in Cu(hfac)$_2$(H_2O), the hydrogen-bond-accepting ability of the O atoms is weakened by the electronegative F atoms; thus, water may not provide as great a stabilizing effect in the solid as expected.

Structural changes in Cu(hfac)$_2$ on binding of H_2O may also be related to the effects of water on the reactivity of Cu(hfac)$_2$ as a precursor for CVD of Cu metal. Normally, H_2 is used as a reducing carrier gas in these systems. Awaya

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and Arita[26] showed early on that the Cu deposition rate (under H_2, with metallic substrates) increases substantially as the amount of added water increases. Pinkas et al.[8] attributed this increase to the ability of H_2O to assist in dissociation of hfacH. Kinetic studies in the absence of water by Borgharkar and Griffin[27] suggested that the rate-limiting step is the reaction of adsorbed H atoms and hfac groups to produce hfacH:

$$\mathrm{H(ads)} + \mathrm{hfac(ads)} \rightarrow \mathrm{hfacH(g)} \qquad (1)$$

Two mechanisms could account for the enhanced deposition rates in the presence of water:[8,26]
(a) Water can dissociate to H(ads) and OH(ads) on the surface, increasing [H(ads)] and thereby raising the rate of reaction 1; or (b) water can coordinate to an adsorbed Cu complex (e.g., making $Cu(hfac)_2(H_2O)(ads)$), which can be followed by intramolecular proton transfer to produce hfacH, effectively bypassing reaction 1.

If the reaction occurs by mechanism b, then differences in Cu−O(hfac) bond distances between $Cu(hfac)_2$ and its water adducts may be important. These bonds are longer in $Cu(hfac)_2(H_2O)$ than in $Cu(hfac)_2$ (and they are longer still in $Cu(hfac)_2(H_2O)_2$), meaning that dissociation of hfac could be more favorable when water is present. *trans*-$Cu(hfac)_2(H_2O)_2$ (as found in **3**) is less directly relevant to CVD, because even at room temperature it is stable only under very high partial pressures of water vapor. However, if a species such as $Cu(hfac)_2(H_2O)$ adsorbs (see above) by coordination of a surface O atom to Cu, the Cu atom will be effectively six-coordinate, and the Cu−O(hfac) bonds may be lengthened and weakened further, leading to still greater reactivity in Cu CVD.

Conclusions. The high affinity of $Cu(hfac)_2$ for axial donors is evident in all three of the present structures: hfac F atoms occupy coordination sites if water molecules are not available. Also, the structures of the three polymorphs of $Cu(hfac)_2(H_2O)$ suggest that hydrogen bonding and close Cu···F interactions can be achieved in a variety of packing arrangements. Finally, the yellow-green compound **3** that forms in the presence of excess water is [*trans*-$Cu(hfac)_2(H_2O)_2$]·H_2O, not the dihydrate as previously believed.

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Supporting Information Available: Details of X-ray analyses (5 pages, and CIF files). This information is available free of charge via the Internet at http://pubs.acs.org.

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