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Note

Observation of specific intermolecular interactions in the X-ray crystal structure of Cu(I) (1,1,1,3,5,5,5-hepta-fluoropentane-2,4-dionato) (vinyltrimethylsilane)

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Abstract

The determination of the X-ray crystal structure of $Cu^{(I)}$ (1,1,1,3,5,5,5-heptafluoro-pentane-2,4-dionato) (vinyltrimethylsilane) or Cu(pfac)(VTMS), a close analogue to Cu(hfac)(VTMS), which is the most widely used precursor for copper CVD, gives us an unique insight about the molecular structure of such compounds. In particular, two short F...H distances between CF_3 groups of a molecule and the alkenyl hydrogen atoms of the neighboring molecule reveal intermolecular interactions specifically related to the structure of the VTMS ligand.

Keywords: Cu CVD; Precursor; Intermolecular interaction

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1. Introduction

As a result of the miniaturization race, the semiconductor industry seeks for conductors of low resistivity to carry the high current density. Copper is an ideal candidate for this role as it has a resistivity well below that of aluminum. Chemical vapor deposition (CVD) is an adequate process for deposition of copper because it provides highly conformal films. Therefore, the design of appropriate precursors is a new field of research for synthetic chemists. In that context, recent materials proved to be especially efficient for the deposition of copper films. In particular, copper (I) complexes in which copper is coordinated to a fluorinated β-diketone and the ligand is either an alkyne or an alkene, have shown great potential [1,2]. Indeed, these species fulfill most of the requirements of MOCVD processes such as sufficient volatility and deposition of high purity films via a thermally induced disproportionation reaction [3]:

$$2(\beta\text{-diketonate})Cu^{I}(L) \rightarrow Cu^{0} + Cu^{II}(\beta\text{-diketonate})_2 + 2L$$

Although several examples of such compounds are reported in the literature [1,2], little is known about the relationship between the molecular structure of the precursors and the CVD deposition process. Here, we report on the synthesis and the characterization of a new Cu(I) complex, Cu(pfac)(VTMS) (where pfac = 1,1,1,3,5,5,5-heptafluoropentane-2,4-dione and VTMS = vinyltrimethylsilane), with a particular emphasis of the intermolecular interactions revealed by its X-ray crystal structure.

Among the numerous precursors for copper CVD, Cu(hfac)(VTMS) (hfac = hexafluoroacetylacetonate), trade name Cupraselect® [4], is by far the most widely used. Recently, a new precursor Cu(hfac)(MHY)® (MHY = 2-methyl-1-hexen-3-yne), trade name Giga Copper® (Merck KGaA product), was synthesized and gave promising results in terms of deposition temperature, stability in time, film resistivity and uniformity [2,5].

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Although noticeable differences have recently been reported [6] concerning the properties of Cu(hfac)(VTMS) and Cu(hfac)(MHY), such as their volatility and the deposition rates observed during CVD experiments, no comparison have yet been undertaken between these two precursors in terms of molecular structure and/or intermolecular interactions. This lack of information is mainly due to the difficulty of obtaining a precise X-ray crystal structure of Cu(hfac)(VTMS). Indeed, the only structure so far reported [4] simply mentioned a planar conformation of the Cu(hfac) moiety and the Cu–C (1.99 Å) and C=C (1.38 Å) bond lengths. On the other hand, Cu(hfac)(MHY) was fully described [5] as well as similar compounds such as Cu(tfac)(MHY) and Cu(pfac)(MHY). Such difference mainly originates from the low melting point of Cu(hfac)(VTMS) (mp = 5 °C), which precludes a good crystallization of the product. Since Cu(pfac)(MHY) exhibits a higher melting point than Cu(hfac)(MHY) (mp = 31 and 13 °C, respectively), it seemed reasonable to envisage a similar effect for Cu(pfac)(VTMS) versus Cu(hfac)(VTMS). Hence, we have synthesized Cu(pfac)(VTMS) following the procedure previously reported for similar compounds (see Section 2). This Cu(I) complex was obtained as a yellow liquid in a 77% yield which showed a higher melting point than Cu(hfac)(VTMS), namely 29 °C. In addition, crystals suitable for X-ray analysis were grown at 5 °C by sublimation (5×10^{-2} mBar). The X-ray crystallographic molecular structure (Fig. 1) is comparable to that reported for Cu(hfac)(VTMS) as the two structures are both almost perfectly planar like structures of Cu (β-diketone)(L) compounds [5]. The copper–carbon bond distances (selected bond lengths and angles can be found in Table 1), 2.025(6) and 2.011(5) Å are very similar to the corresponding distances found in the Cu(hfac)(alkene) family (between 2.013(5) and 2.277(7) Å) in Cu(hfac)(COD) [7–9] (where COD = 1,5-cyclooctadiene) or 2.011(3) and 2.029(3) Å in Cu(hfac)(7-t-BuO-NBD) (7-t-BuO-NBD = 7-tert-butoxy-2,5-norbornadiene) [10]. The C=C bond length of 1.370(8) Å is remarkably close to the equivalent distance reported for Cu(hfac)(VTMS). The C(1)=C(2)–Si angle value was found to be 124.4(4)°, which is somewhat higher than the expected 120°.

Table 1
Selected bond lengths (Å) and angles (°) related to the X-ray crystallographic molecular structure of Cu(pfac)(VTMS)

Cu–O(1)	1.967(3)	Cu–O(2)	1.964(3)
Cu–C(1)	2.025(6)	Cu–C(2)	2.011(5)
C(1)–C(2)	1.370(8)		
Cu–C1	2.025(6)	Cu–C2	2.011(6)
O1–C11	1.244(6)	O2–C13	1.240(6)
C11–C12	1.392(7)	C11–C14	1.549(7)
C12–C13	1.385(7)	Si1–C2	1.880(6)
C(12)–F(7)	1.369(6)	C(14)–F(1)	1.311(6)
C(14)–F(2)	1.327(7)	C(14)–F(3)	1.292(7)
O(1)–Cu–O(2)	92.5(1)	O(2)–Cu–C(2)	154.5(2)
C(1)–C(2)–Si	124.4(4)	C(1)–Cu–C(2)	39.7(2)

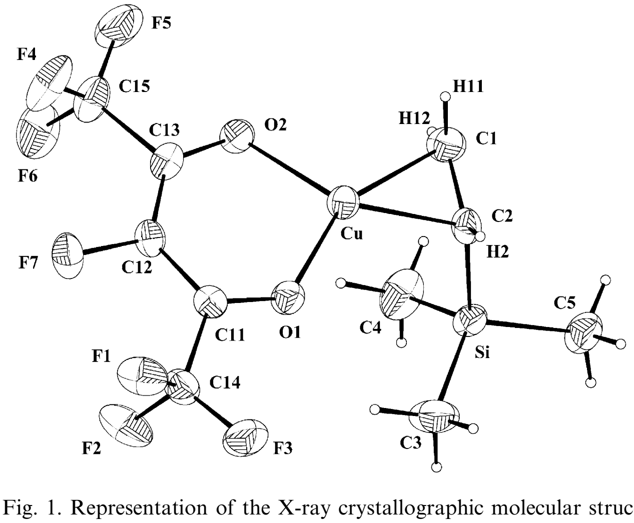

Fig. 1. Representation of the X-ray crystallographic molecular structure of Cu(pfac)(VTMS), showing a 30% probability thermal ellipsoids.

This distortion can be attributed to the bulky nature of the Si(Me)$_3$ group which can also be at the origin of the high dihedral angle between the Cu(C=C) and C=C–Si plans (99° instead of the expected value of 90°). Remarkably, the F–Csp^3 bonds (–CF$_3$, averaged at 1.31 Å) are slightly shorter than the F(7)–Csp^2 bond (1.369(6) Å) although F–Csp^3 bonds and F–Csp^2 bonds are commonly reported to be equal to 1.38 and 1.35 Å. However, this inversion was already observed in the case of Cu(pfac)(MHY) [5] and short F–Csp^3 bonds are frequently observed in CF$_3$-containing organic compounds [11]. In the three dimension cell, the molecules adopt a stacked structure with one molecule oriented in the opposite direction to its neighbor giving a structure in which short intermolecular distances (dimers) of 3.304(27) Å alternate with long intermolecular distances of 4.224(27) Å. The longest intermolecular distance corresponds to the situation where the –Si(Me)$_3$ groups of neighboring molecules point towards each other, giving rise to repulsive forces between bulky groups.

On the other hand the short intermolecular interactions found their origin in the presence of weak hydrogen bond between two fluorine of two different CF$_3$ groups and two hydrogen of the C=C bond as represented in Fig. 2. The F...H distances, F4...H2′ and F1...H11′ are respectively 2.35(6) and 2.49(3) Å showing that these intermolecular interactions are weak in comparison with those existing in liquid HF (F...H = 1.20 Å) but rather close to the shortest C–F...H–C interactions of 2.30 Å reported in the literature [12]. Although the same type of arrangement of the molecules was observed for Cu(pfac)(MHY), there was no report of such F...H interactions involving the CF$_3$ groups. As a contrary, the shortest F...H distance observed (2.421(4) Å) result from the interaction between

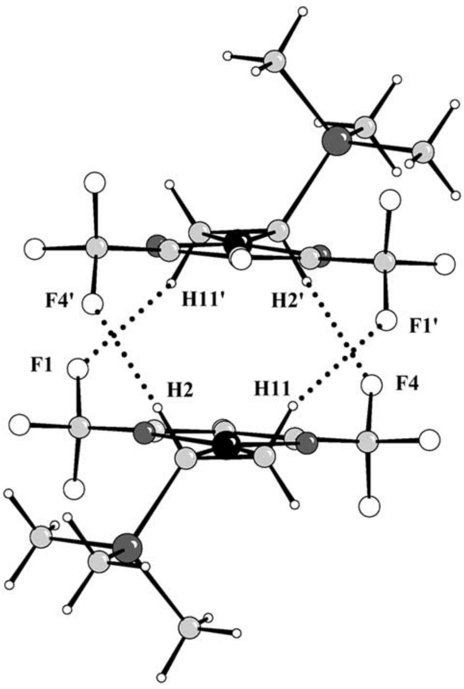

Fig. 2. Intermolecular interactions between two hydrogen atoms of the vinyl group and two fluorine atoms of the CF_3 groups in Cu(pfac)(VTMS).

the fluorine atom in position 3 on the β-diketone moiety (i.e. F7) and the hydrogens atoms of the free double bond. Since the intermolecular interactions identified in the case of Cu(pfac)(VTMS) are not specifically related to the structure of the (pfac) ligand (i.e. F7 do not get involved), one might consider that they most probably also exist in Cu(hfac)(VTMS). Thus, a change of ligand from VTMS to MHY not only changes the chemical nature of the compound but also influences the intermolecular interactions. Such differences might have repercussion on the behavior of the molecules in the gas phase and more specifically at the substrate surface during the deposition process.

Those observations highlight the influence of interactions at the molecular level on the deposition mechanism. Hence, further studies are needed to better understand the relation between the chemical nature of the precursors and the structural nature of the films, especially in terms of conformality and contamination by hetero-atoms such as fluorine atoms.

2. Experimental

2.1. Synthesis and characterisation of Cu(pfac)(VTMS)

A three neck round-bottom flask was loaded, under an atmosphere of nitrogen, with 1.6 g (11 mmol) of Cu_2O (Aldrich) and 20 ml of spectroscopic grade pentane. 1,1,1,3,5,5,5-Heptafluoroacetylacetone (2.5 g, 16 mmol, ABCR) was added dropwise to the magnetically stirred solution which contained 2.3 ml (11 mmol) of vinyltrimethylsilane (VTMS, ABCR). The mixture was stirred throughout the addition and for a further 30 min. The brick-red cuprous oxide was suspended in the solution, which had become yellow-green as the reaction proceeded. Excess Cu_2O was filtered off and the pentane solution purified by flash chromatography under nitrogen with a 1.3 in. (diameter) by 5 in. (height) alumina column (6 g). After chromatography and distillation of the solvent, Cu(pfac)(VTMS) was obtained as a yellow liquid in a 77% yield. mp = 29 °C. IR(neat): 3282 (w), 2958 (m), 2899 (w), 1647 (s), 1530 (m), 1478 (m), 1451 (s), 1352 (m), 1271 (s), 1219 (s), 1197 (s), 1155 (s), 1059 (w), 970 (w), 842 (s), 761 (m), 720 (w), 677 (m), 674 (m), 597 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 298 K), δ (ppm): 0.2 (s, CH_3), 4.65 (m, CH), 4.96 (m, CH_2). ^{13}C NMR ($CDCl_3$, 298 K), δ (ppm): −1.3 (s, CH_3), 90.8 (s, CH), 101.9 (s, CH_2), 117.9 (q, 284 Hz, CF_3), 141.8 (d, 230 Hz, CF), 178.4 (q, 34.4 Hz, C=O). ^{19}F NMR ($CFCl_3$ as standard), δ (ppm): −183.9 (d, 17 Hz, CF), −70.7 (d, 17 Hz, CF_3).

2.2. X-ray crystallographic analysis for Cu(pfac)(VTMS)

Accurate cell dimensions and orientation were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. The data were corrected for Lorentz and polarisation effects. Computations were performed using the PC version of CRYSTAL [13]. Scattering factors and corrections for anomalous absorption were found in the literature [14]. The structures were solved by direct methods (SHELXS) [15,16]. The final refinements were carried out by full-matrix least-squares using anisotropic displacements parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions and only one overall isotropic displacement parameter was refined. Crystal data for $C_{10}H_{12}CuF_7O_2Si$: $M = 388.8$, monoclinic, Space group P2/n, $a = 13.469(7)$ Å, $b = 8.418(6)$ Å, $c = 13.613(8)$ Å, $\beta = 95.86(5)^\circ$, $V = 1535(2)$ Å^3, $Z = 4$, $D_c = 1.68\ \mathrm{g\,cm^{-3}}$, $N = 3019$, $N_{ind} = 2687$ ($R = 0.05$), $N_{obs} = 1622$ ($(F_0)^2 > 3\sigma(F_0)^2$), $R = \sum \|F_0\| - |F_c| / \sum |F_0| = 0.0441$, $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2} = 0.0534$.

3. Supplementary material

Atomic coordinates, bond lengths, angles and thermal parameters are available at the Cambridge Crystallography Data Centre.

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