

Syntheses and Characterization of the Thermally Stable Cu(hexafluoroacetylacetonato)₂(μ-diethyl 2-allylmalonate)

Seong-Joo Kang

Department of Chemistry Education, Korea National University of Education, Cheongwon, Chungbuk 363-791, Korea

*E-mail: sjkang@knue.ac.kr

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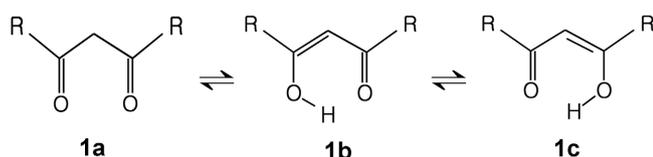
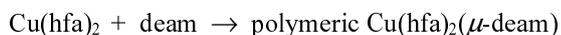
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Much attention has been paid to the structural chemistry of β-diketones and β-diketonates involving keto-enol tautomerism and the intramolecular hydrogen bond.¹ For the majority of cases in keto-enol tautomerism, the keto form (**1a**) is far more stable. Such factors as intramolecular hydrogen bond and conjugation, however, increase the stability of the enol form (**1b** and **1c**).

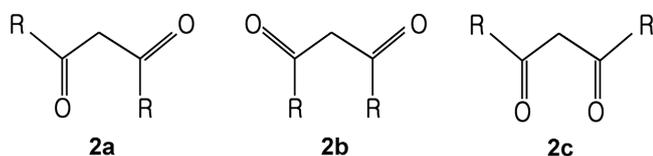
The geometry of the gas phase acetylacetonate anion is predicted using ab initio molecular orbital theory. There are three stable conformers in the diketo geometry of the acetylacetonate anion; (1) a C_s structure with the carbonyls in an anti conformation (**2a**), (2) a C₂ structure with the carbonyls pointed exo (**2b**), and (3) a C_{2v} structure with the carbonyls endo (**2c**).² A C_s structure (**2a**) is most stable and a C_{2v} structure (**2c**) is least stable conformation of the gas phase acetylacetonate anion.

Most β-diketonate ligands in metal complexes exhibit a C_{2v} bonding modes (**2c**).³ Any β-diketones, however, is not known to bind to two different metal atoms yielding one-dimensional chain structure. In this paper we report the reaction of β-diketone with Cu(hfa)₂ (hfa = hexafluoroacetylacetonate) and discuss the structural characterization and thermal stability of Cu(hfa)₂(μ-deam) (deam = diethyl allylmalonate).

Cu(hfa)₂(μ-deam) was obtained by the reaction of Cu(hfa)₂ and diethyl allylmalonate(deam) in benzene. Suitable crystals were harvested from slow cooling of a saturated hexane solution.

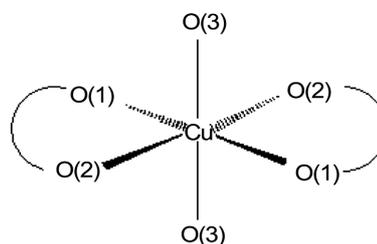


Scheme 1



Scheme 2

The copper ion is hexa-coordinated with an elongated distorted octahedral geometry.



Copper atom binds to four oxygen atoms, contributed by two bidentate hfa anionic ligands, resulting in a square planar structure. The square planar Cu(hfa)₂ unit is bridged by diethyl allylmalonate to give one-dimensional structure.

The extended one-dimensional polymeric structure of this compound is depicted in Figure 1.

The questions of whether the diketo or enol form predominates for β-diketones and whether or not the enol intramolecular hydrogen bond is symmetrical have been examined in the crystal structure determinations of bis(*m*-bromobenzoyl)methane, bis(*m*-chlorobenzoyl)methane, dibenzoylmethane, and tetraacetylene. All of these compounds were found to be in the enol configuration in the crystalline state and were characterized by equidimensional

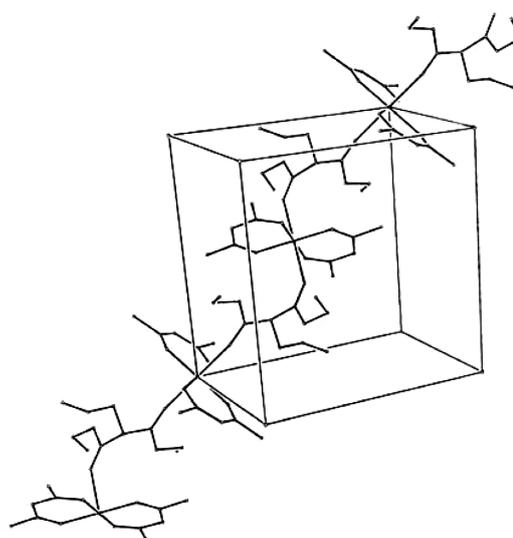
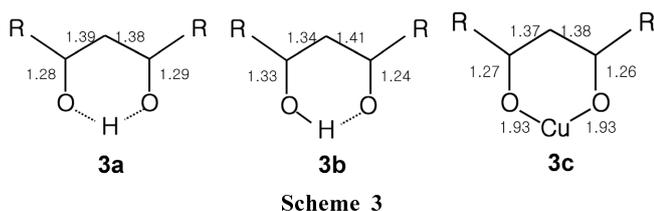


Figure 1. Unit cell packing diagram of Cu(hfa)₂(μ-deam) showing one-dimensional chains.



C-O distances and a symmetric intramolecular hydrogen bond. The X-ray crystal structures of the prototype of β -diketones, acetylacetone, were also found to be in the enol configuration, yet showed two types of structures with symmetric and asymmetric intramolecular hydrogen bond (Scheme 3).

The inclusion compound of 1,1'-binaphthyl-2,2'-dicarboxylic acid (BNDA) with acetylacetone has been investigated by single crystal X-ray diffraction at room temperature. There is no significant difference between two C-O bonds, nor between two C-C bonds or two O-H contacts (**3a**).^{4,5} An inclusion complex of (R,R)-(-)-trans-4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane and acetylacetone was analyzed at 100 K. Only one resonance form with an asymmetric intramolecular hydrogen bond is observed (**3b**).⁶ The anionic β -diketonates in a wide variety of copper- β -diketonato complexes show a C_{2v} symmetry (**2c**).⁷ The hfa ligand in the $Cu(hfa)_2(\mu\text{-deam})$ also shows a C_{2v} symmetry and the Cu-O, C-O and C-C bond distances in the $Cu(hfa)_2(\mu\text{-deam})$ are symmetric shown in Figure 3c.

The molecular structure of $Cu(hfa)_2(\mu\text{-deam})$ is shown in Figure 2, and F atoms of hfa anionic ligands are omitted for clarity.

The Cu-O bond lengths in $Cu(hfa)_2(\mu\text{-deam})$ fall into two distinct classes of shorter Cu-O bonds [Cu-O(1) and Cu-O(2); av. 1.933(3) Å] and longer Cu-O bond [Cu-O(5); 2.399(4) Å]. The reason for the longer Cu-O bond can be explained in terms of the neutral oxygen atom of diethyl allylmalonate ligand as well as a Jahn-Teller distortion. The Cu(1)-O(5) bond (2.399(4) Å) is longer than the Cu-OH₂ distance (2.204(3) Å) in $Cu(hfa)_2(H_2O)_2$ or the Cu-O (EtOH)

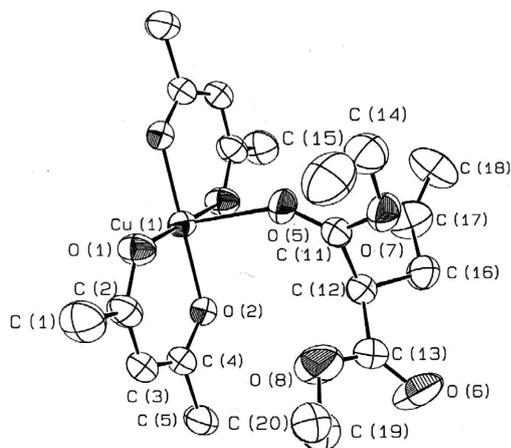


Figure 2. ORTEP diagram of the crystal structure of $Cu(hfa)_2(\mu\text{-deam})$ showing the atomic labelling scheme and thermal ellipsoidal at 50% level.

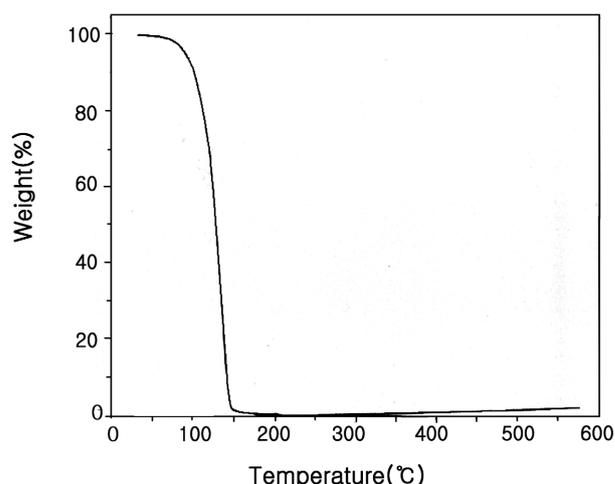


Figure 3. TGA diagram of $Cu(hfa)_2(\mu\text{-deam})$.

distance (2.191(4) Å) in $Cu(hfa)_2(C_2H_5OH)$.^{8,9} There is a weak hydrogen bonding between the ethyl group of diethyl 2-allylmalonate and the oxygen atom of hfa.

As mentioned earlier, there are three stable conformers in the diketo geometry of the β -diketonate; (1) a C_s structure, (2) a C_2 structure, and (3) a C_{2v} structure.² The $Cu(hfa)$ unit of the $Cu(hfa)_2(\mu\text{-deam})$ is a C_{2v} structure.¹⁰ The acac ligand in $[Mo_2(acac)(CO)_6(dppe)_2]^+$ shows a C_2 structure.¹¹ It is quite rare to find a C_s structure in metal(diketo ligand) complexes. The deam ligand in $Cu(hfa)_2(\mu\text{-deam})$, however, shows a C_s diketo structure with distinct single C-C [1.51(1) Å] and double C=O [1.20(1) Å] bond distances. In addition, the deam ligand in $Cu(hfa)_2(\mu\text{-deam})$ is bridging to two copper atoms resulting in an one-dimensional polymeric structure.

To evaluate the utility of $Cu(hfa)_2(\mu\text{-deam})$ as precursor for CVD, the thermogravimetric behavior of the complexes has been investigated by TGA over the temperature range 30-570 °C and shown in Figure 3. The TGA plot shows a singular sublimation step in the 60-140 °C temperature range and no weight loss after 150 °C. Over 99% of the material vaporized leaving about 1% residue.

In summary, we have synthesized the extended one-dimensional polymeric $Cu(hfa)_2(\mu\text{-deam})$ from the reaction of $Cu(hfa)_2$ and deam. The hfa ligand shows a symmetric C_{2v} enol structure and the deam ligand exhibits a unique C_s diketo structure with the carbonyl groups in an anti conformation. In addition, $Cu(hfa)_2(\mu\text{-deam})$ is a stable potential precursor with low melting point and high volatility.

Experimental Section

General procedures. All manipulations were performed under an inert atmosphere using Schlenk techniques. All solvents were distilled by standard techniques. Hhfa, diethyl allylmalonate(deam) were purchased from Aldrich and used as received.¹² $Cu(hfa)_2(H_2O)_2$ was prepared as previously described.⁷ TGA analysis was carried out on a SETARAM TGA-92 instrument. The weight of sample was 25 mg. The

Table 1. Crystal Data and Structure Refinement for Cu(hfa)₂(μ-deam)

formula	C ₂₀ H ₁₈ CuF ₁₂ O ₈
fw	677.88
T (°C)	20(2)
Wavelength Å	0.71073
Space group	P1-bar
a Å	9.2267(4)
b Å	12.9007(6)
c Å	12.9442(6)
α°	75.519(1)
β°	71.979(1)
γ°	72.855(1)
V Å ³	1378.50(11)
Z	2
ρ _{calcd} g cm ⁻³	16.33
μ (Mo K α) cm ⁻¹	0.914
F(000)	678
θ range deg	1.68 to 24.71
h k l ranges	-10 to 9 -15 to 10 -15 to 15
no. of rflns collectd	6553
no. of indep rflns	4582 [R(int) = 0.0550]
no. of params	4582 / 0 / 375
GOF on F ²	1.114
final R indices [I > 2σ(I)]	R1 ^a = 0.0741 wR2 = 0.2168
R indices (all data)	R1 = 0.0866 wR2 = 0.2301
largest diff. peak and hole e Å ⁻³	0.889 and -1.202

^aR1 = $\sum ||F_0| - |F_c|| / \sum |F_0|$. wR2 = $\{\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4\}^{1/2}$, where $w = 1 / \{\sigma^2 F_0^2 + (0.0786P)^2 + 5.28P\}$ and where $P = \{\text{Max}(F_0^2, 0) + 2F_c^2\} / 3$

measurement was performed in alumina crucibles under an atmosphere of flowing argon, using heating rate of 5 °C/min.

Preparation of Cu(hfa)₂(μ-deam). To a benzene solution of Cu(hfa)₂ (0.47 g, 0.98 mmol) was added diethyl allylmalonate (0.20 g, 0.98 mmol). The resulting solution was refluxed for 24hr. After cooling to ambient temperature, the solution was filtered. The solvent was removed in vacuo to yield green precipitates. Slow cooling of the saturated hexane solution gave rectangular crystals suitable for x-ray crystallography. Yield: 0.78 g, 92%. mp: 60-63 °C. IR (KBr, cm⁻¹): 2970 (w), 1695 (s), 1625 (s), 1550 (m), 1515 (m), 1470 (s), 1240 (s), 1200 (s), 1135 (s), 1100 (m), 790 (s), 670 (s).

Crystal data for Cu(hfa)₂(μ-deam). Crystallographic parameters and information related to data collection and structural refinements for the complex is shown in Table 1. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ϕ-scan method. The structure were solved by the Patterson method (SHELXS-86) and were refined by full-matrix least squares techniques (SHELXL-93). All non-hydrogen atoms were refined anisotropically. All calculations were carried out on the personal computer with use of the SHELXS-86 and SHELXL-93 programs.^{13,14} Selected bond lengths and angles are given in Table 2. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data centre (Deposition No. CCDC-278641). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

Table 2. Selected Bond Lengths [Å] and Angles [°] for Cu(hfa)₂(μ-deam)

Cu(1)-O(1)	1.932(3)	Cu(1)-O(2)	1.934(3)
Cu(1)-O(5)	2.399(4)	O(1)-C(2)	1.268(6)
O(2)-C(4)	1.257(6)	O(5)-C(11)	1.185(6)
O(7)-C(11)	1.324(6)	O(8)-C(13)	1.308(7)
O(7)-C(14)	1.457(7)	O(8)-C(19)	1.465(8)
C(1)-C(2)	1.535(8)	C(2)-C(3)	1.371(8)
C(3)-C(4)	1.378(8)	C(4)-C(5)	1.550(8)
C(11)-C(12)	1.510(7)	C(12)-C(13)	1.515(7)
C(12)-C(16)	1.536(7)	C(14)-C(15)	1.470(11)
C(16)-C(17)	1.487(9)	C(17)-C(18)	1.233(13)
C(19)-C(20)	1.302(13)		
C(1)-C(2)-C(3)	118.7(4)	C(6)-C(7)-C(8)	119.4(5)
C(2)-C(3)-C(4)	121.8(4)	C(7)-C(8)-C(9)	122.1(5)
C(3)-C(4)-C(5)	118.5(4)	C(8)-C(9)-C(10)	120.1(5)
C(11)-C(12)-C(13)	110.4(4)	C(11)-C(12)-C(16)	112.5(4)
C(13)-C(12)-C(16)	111.0(4)	C(12)-C(16)-C(17)	110.8(5)

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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- Abbreviations used in this paper include: hfa, anion of hexafluoropentanedione; deam, diethyl 2-allylmalonate; BNDA, 1,1'-binaphthyl-2,2'-dicarboxylic acid.
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