

The Self-Assembly of $Y(\text{hfa})_3(\text{H}_2\text{O})_2$ with $\text{Cu}(\text{acac})_2$

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The formulation of high-temperature superconductors requires three different metallic precursors for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, but even more source precursors are needed for system such as the Ti-Ba-Ca-Cu-O or Bi(Pb)-Sr-Ca-Cu-O .¹ It is well established that, for obtaining conductors by metalloorganic chemical vapor deposition (MOCVD) techniques, use of a "single-source" precursor increases the quality of the final material.² To prepare these single-source precursors, several research groups have reported the syntheses of heterometallic complexes containing the cross-linking reagents.³ Heterometallic complexes having β -diketonate ligands have been targeted as potential precursors for the high-temperature superconducting materials.⁴ These single-source precursors, however, show considerably higher boiling points and lower sublimation properties than monomeric precursors. This observation stimulates us to try for the preparation of the single-source precursors having intermolecular interactions such as hydrogen bonding interaction, π - π interaction, etc. Herein, we describe our attempts to obtain the complex having the 1:1 ratio of Cu to Y metal ion through intermolecular hydrogen bondings.

Experimental Section

General procedures. All manipulations were performed under an inert atmosphere using Schlenk techniques. All solvents were distilled by standard techniques. Yttrium oxide, CuCl_2 , Hhfa, and Hacac were purchased from Aldrich and used as received.⁵ Infrared spectra were recorded as KBr pellets on a Shimadzu FTIR-8501 model. TGA/DTA analysis was carried out on a SETARAM TGA-92 instrument, which simultaneously performs thermogravimetry (TGA) and differential thermal analysis (DTA). The weight of the sample was between 10 and 25 mg. The measurement was performed in alumina crucibles under an atmosphere of flowing argon, using heating rates of 5 °C/min from 40 °C up to 530 °C.

Preparation of $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$. To a benzene solution of $\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2$ (0.10 g, 0.134 mmol) was added $\text{Cu}(\text{acac})_2$ (0.035 g, 0.134 mmol). The resulting solution was refluxed for 2h. On cooling to ambient temperature blue crystals suitable for X-ray crystallography were obtained. Yield: 0.13 g, 96%. mp 104-107 °C. IR (KBr, cm^{-1}): 3000-3500 (s), 1650 (s), 1640 (s), 1550 (s), 1520 (s), 1485 (s), 1395 (m), 1360 (m), 1250 (s), 1200 (s), 1195 (s), 1150 (s), 1140 (s), 1100 (m), 1025 (m), 940 (w), 800 (m), 740 (w), 665 (m)

X-ray Crystal Analysis. Crystallographic parameters and information related to data collection and structural re-

finements for the complex are given in Table 1. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ϕ -scan method.⁶ The structure was solved by the Patterson method (SHELXS-86) and was refined by full-matrix least squares techniques (SHELXL-93). All non-hydrogen atoms were refined anisotropically and the positions of hydrogen atoms were idealized, assigned isotropic thermal parameters [U_{iso}

Table 1. Crystal Data and Structure Refinement for $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$

formula	$\text{C}_{25} \text{H}_{21} \text{F}_{18} \text{O}_{12} \text{Cu Y}$
fw	1007.88
T (°C)	20
wavelength, Å	0.71070
space group	$P2_1/c$ (# 14)
a, Å	12.463(1)
b, Å	19.984(5)
c, Å	16.509(3)
β , deg	111.78(1)
V, Å ³	3818(1)
Z	4
ρ_{calcd} , g cm^{-3}	1.774
$\mu(\text{Mo K}\alpha)$, cm^{-1}	22.11
no. of rflns collectd	7773
no. of indep rflns	7406 [R(int)=0.0653]
no. of params	527
GOF on F^2	1.023
final R indices [$I > 2\sigma(I)$]	$R1^a=0.0629$, $wR2=0.1406$
R indices (all data)	$R1=0.0817$, $wR2=0.1658$
largest diff. peak and	+0.664 and -0.713

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \}^{1/2}$, where $w = 1 / \{ \sigma^2 F_o^2 + (0.0786P)^2 + 5.28P \}$ and where $P = \{ a x(F_o^2 + 2F_c^2) \} / 3$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$

	x	y	z	U(eq) ^a
Y	2928(1)	7270(1)	1529(1)	51(1)
Cu	4429(1)	4794(1)	3547(1)	58(1)
O(1)	4709(5)	6754(3)	1874(5)	65(2)
O(2)	2608(6)	6258(4)	791(5)	68(2)
O(3)	3871(6)	7818(4)	2841(4)	64(2)
O(4)	1916(6)	8269(4)	1512(5)	73(2)
O(5)	1031(6)	7000(4)	1274(4)	62(2)

Table 2. (continued)

	x	y	z	U(eq) ^a
O(6)	1965(6)	7508(4)	66(5)	68(2)
O(7)	3048(6)	6527(3)	2677(4)	65(2)
O(8)	4030(6)	8053(4)	1119(5)	68(2)
O(11)	2950(6)	5125(3)	2825(4)	62(2)
O(12)	4069(6)	3903(4)	3135(5)	69(2)
O(13)	5905(6)	4455(3)	4291(5)	63(2)
O(14)	4829(6)	5701(3)	3894(5)	71(2)
C(1)	6307(12)	6051(9)	2243(13)	104(5)
C(2)	5049(9)	6196(5)	1764(7)	63(3)
C(3)	4389(10)	5666(6)	1274(8)	81(4)
C(4)	3209(11)	5762(6)	809(7)	68(3)
C(5)	2566(15)	5221(9)	167(14)	112(6)
C(6)	4685(13)	8484(7)	4065(10)	86(4)
C(7)	3770(10)	8355(6)	3153(7)	62(3)
C(8)	2916(11)	8826(6)	2811(8)	81(4)
C(9)	2028(9)	8737(6)	2009(8)	66(3)
C(10)	1079(15)	9253(11)	1680(13)	122(7)
C(11)	-959(10)	6896(9)	787(9)	82(4)
C(12)	125(9)	7068(5)	628(7)	64(3)
C(13)	18(9)	7263(7)	-214(7)	79(4)
C(14)	935(10)	7458(6)	-425(6)	66(3)
C(15)	722(13)	7592(10)	-1363(8)	102(5)
C(21)	989(10)	5163(6)	1959(9)	93(4)
C(22)	2086(9)	4763(7)	2393(7)	68(3)
C(23)	2099(9)	4092(6)	2340(7)	70(3)
C(24)	3057(10)	3691(6)	2678(7)	71(3)
C(25)	2988(11)	2944(6)	2505(10)	107(5)
C(26)	7717(9)	4412(6)	5410(7)	77(3)
C(27)	6693(9)	4792(6)	4863(7)	60(3)
C(28)	6633(9)	5473(6)	4997(7)	64(3)
C(29)	5751(10)	5894(5)	4499(8)	67(3)
C(30)	5790(13)	6631(6)	4654(9)	109(5)
F(1)	6882(8)	6240(10)	1784(8)	225(8)
F(2)	6557(9)	5435(5)	2435(13)	256(10)
F(3)	6795(7)	6379(5)	2957(6)	121(3)
F(4)	1538(12)	5117(10)	165(13)	211(8)
F(5)	3141(12)	4923(7)	-244(8)	181(5)
F(6)	2652(21)	4644(8)	602(12)	258(10)
F(7)	4453(10)	8095(5)	4656(6)	155(4)
F(8)	4694(7)	9107(4)	4341(5)	115(3)
F(9)	5672(8)	8315(5)	4142(7)	156(4)
F(10)	1110(9)	9731(6)	2236(8)	169(5)
F(11)	120(10)	9015(6)	1578(13)	226(9)
F(12)	1045(18)	9559(9)	1054(11)	295(13)
F(13)	-1274(9)	7379(7)	1147(9)	179(5)
F(14)	-1854(7)	6829(7)	101(6)	184(6)
F(15)	-878(8)	6418(7)	1278(9)	204(7)
F(16)	124(12)	7211(7)	-1889(6)	207(7)
F(17)	1565(11)	7741(11)	-1539(6)	243(10)
F(18)	134(21)	8131(9)	-1599(8)	288(12)

^aU(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

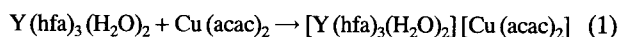
Table 3. Selected Bond Lengths [Å] and Angles [deg] for [Y(hfa)₃(H₂O)₂][Cu(acac)₂]

Y-O(1)	2.320(6)	Y-O(2)	2.319(7)
Y-O(3)	2.320(7)	Y-O(4)	2.355(8)
Y-O(5)	2.306(6)	Y-O(6)	2.312(7)
Y-O(7)	2.369(7)	Y-O(8)	2.342(7)
Cu-O(11)	1.904(7)	Cu-O(12)	1.900(7)
Cu-O(13)	1.917(7)	Cu-O(14)	1.910(7)
O(1)-C(2)	1.230(11)	O(2)-C(4)	1.236(13)
O(3)-C(7)	1.217(11)	O(4)-C(9)	1.217(13)
O(5)-C(12)	1.241(11)	O(6)-C(14)	1.242(11)
O(11)-C(22)	1.273(13)	O(12)-C(24)	1.278(12)
O(13)-C(27)	1.274(12)	O(14)-C(29)	1.270(12)
O(1)-Y-O(2)	72.7(2)	O(1)-Y-O(3)	82.7(2)
O(1)-Y-O(4)	147.1(3)	O(1)-Y-O(5)	139.8(3)
O(1)-Y-O(6)	115.2(3)	O(1)-Y-O(7)	75.8(2)
O(1)-Y-O(8)	75.9(2)	O(2)-Y-O(3)	146.2(3)
O(2)-Y-O(4)	138.3(3)	O(2)-Y-O(5)	74.6(3)
O(2)-Y-O(6)	73.1(3)	O(2)-Y-O(7)	79.7(3)
O(2)-Y-O(8)	115.8(3)	O(3)-Y-O(4)	72.2(3)
O(3)-Y-O(5)	114.3(3)	O(3)-Y-O(6)	139.9(3)
O(3)-Y-O(7)	71.9(2)	O(3)-Y-O(8)	78.8(3)
O(4)-Y-O(5)	71.8(3)	O(4)-Y-O(6)	75.3(3)
O(4)-Y-O(7)	114.6(3)	O(4)-Y-O(8)	78.4(3)
O(5)-Y-O(6)	76.0(2)	O(5)-Y-O(7)	75.9(2)
O(5)-Y-O(8)	140.8(2)	O(6)-Y-O(7)	144.9(2)
O(6)-Y-O(8)	72.2(3)	O(7)-Y-O(8)	141.3(2)
O(11)-Cu-O(12)	93.2(3)	O(11)-Cu-O(13)	178.8(3)
O(11)-Cu-O(14)	86.7(3)	O(12)-Cu-O(13)	86.6(3)
O(12)-Cu-O(14)	175.8(3)	O(13)-Cu-O(14)	93.6(3)
C(2)-O(1)-Y	135.9(7)	C(4)-O(2)-Y	134.6(7)
C(7)-O(3)-Y	135.6(7)	C(9)-O(4)-Y	135.7(7)
C(12)-O(5)-Y	132.6(7)	C(14)-O(6)-Y	132.6(7)
C(22)-O(11)-Cu	125.0(7)	C(24)-O(12)-Cu	124.9(7)
C(27)-O(13)-Cu	125.5(7)	C(29)-O(14)-Cu	125.6(7)

(H)=1.2 U_{eq} (C)] and allowed to ride on the parent carbon atoms. All calculations were carried out on the personal computer with use of the SHELXS-86 and SHELXL-93 programs.⁷ Selected bond lengths and angles are given in Table 3.

Results and Discussion

Synthesis. We are interested in the synthesis of single-source precursors in which the different elements are incorporated in a single precursor molecule through intermolecular hydrogen bondings. The major application of such precursors is in the field of the electroceramics, e.g. LaCuO₂, YBa₂Cu₃O_{7-x}, Pb₂Sr₂LaCu₃O_{8-x}, etc. Addition of 1 equiv of Cu(acac)₂ to a benzene solution of Y(hfa)₃(H₂O)₂ yields a dark green solution, (1). Cooling of the resulting solution affords crystalline products. The IR spectrum of this product displayed two carbonyl stretching bands at 1640 and 1550 cm⁻¹ for the hfa and acac ligands, respectively.



Since the hydrogen bonds are the key elements responsible for association, it is reasonable to expect that any solvent that disrupts these interactions should likewise disrupt the ability of the aggregation. Indeed, the addition of acetone to the $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$ produces the blue $\text{Cu}(\text{acac})_2$ precipitates and the colorless solution containing $\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2$. The ^1H NMR spectrum (C_6D_6) shows the line broadening and this is due to the paramagnetic $\text{Cu}(\text{II})$. The thermal behavior of this compound has been examined by thermogravimetric analysis. The weight loss occurred in three steps. The first step took place between 70 and 130 $^\circ\text{C}$, and it corresponds to the loss of two water molecules. The second weight loss occurred between 130 and 210 $^\circ\text{C}$, and it is attributed to the loss of $\text{Y}(\text{hfa})_3$. The third weight loss occurred between 210 and 330 $^\circ\text{C}$, and it is attributed to the decomposition of the $\text{Cu}(\text{acac})_2$.

Structural Description of $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$. $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$ complex is composed by two metal components; $\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2$ and $\text{Cu}(\text{acac})_2$. Two components are connected through intermolecular hydrogen bond interactions. The molecular structure of $\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2$ is shown in Figure 1, where the CF_3 groups were omitted for clarity. The yttrium environment is a distorted square antiprism of oxygen atoms, six belonging to the hfa ligands and two belonging to water molecules. The dihedral angle between upper $[\text{O}(1)-\text{O}(2)-\text{O}(6)-\text{O}(8)]$ and lower $[\text{O}(3)-\text{O}(4)-\text{O}(5)-\text{O}(7)]$ planes is 3.2° and the mean plane separation between two squares is about 2.50 \AA . The Y-O bond distances range from 2.31 to 2.37 \AA and the average C-O distance of hfa ligands is 1.23[1] \AA . The average Y-O bond distance of hfa is about 2.322[7] \AA while that of water is about 2.356[7] \AA . This tendency is consistent with Ho

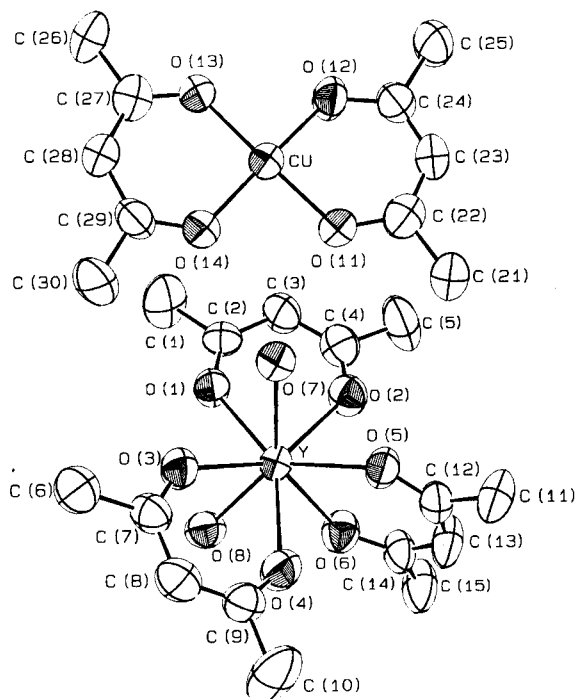


Figure 1. ORTEP drawing of the crystal structure of $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$ showing the atomic labelling scheme and thermal ellipsoidal at 50% level.

$(\text{hfa})_3(\text{H}_2\text{O})_2$; 2.338[5] and 2.359[5] \AA .⁸ The C-C bond distances of the hfa ligands fall into two distinctly different groups; C(1)-C(2) and C(4)-C(5), 1.51[2] \AA and C(2)-C(3) and C(3)-C(4), 1.39[2] \AA . The O...O distances range from 2.87 to 3.02 \AA . The average O-Y-O angle of the hfa ligands is $73.6[2]^\circ$ and the corresponding angle of the water ligands is $141.3[2]^\circ$. The molecular structure of $\text{Cu}(\text{acac})_2$ is shown in Figure 1. The copper(II) ion is four-coordinated to the oxygen atoms of the acac ligands in an approximately square-planar environment. The Cu-O average bond distance is 1.91[1] \AA and the O-Cu-O angles are close to 90° . These bond distances and angles are similar with those of $\text{Cu}(\text{hfa})_2$; 1.91[1] \AA and $87.0, 93.0^\circ$.⁹ The copper(II) ion is displaced 0.03 \AA out of the square plane. As mentioned, the crystal structure of $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$ contains infinite ribbons held together by O-H...O hydrogen bondings. Figure 2 shows a unit cell packing diagram consisting of three parallel rods for $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$. Only CuO_4 and YO_2 (water molecules) atoms are depicted for clarity. Two water molecules in $\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2$ are hydrogen bonded to the acetylacetonate oxygen atoms: O(7) is hydrogen bonded to O(11)/O(14) and O(8) to O(12)/O(13) with distances of 2.820, 2.894, 2.801, and 2.892 \AA , respectively. These ribbons are oriented in a zig-zag fashion, parallel with b. The Cu-Y-Cu angle in polymeric chain is about 118° . The Y...Y or Cu...Cu separation is longer than 8.0 \AA

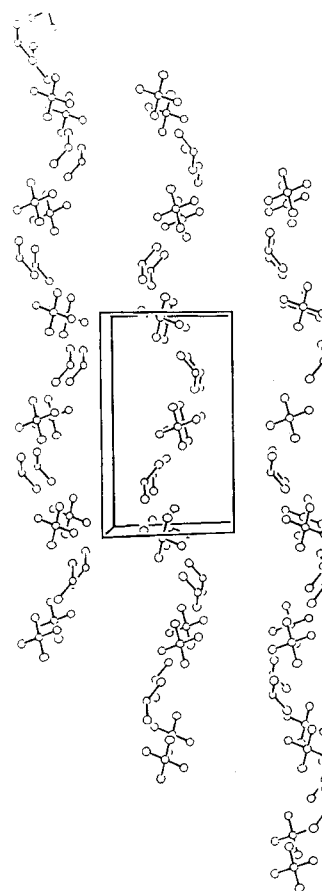


Figure 2. Unit cell packing diagram of $[\text{Y}(\text{hfa})_3(\text{H}_2\text{O})_2][\text{Cu}(\text{acac})_2]$ showing the chains running along the y axis. Only CuO_4 and YO_2 (water molecules) atoms are shown for clarity.

and the Y--Cu separation is about 6.3 Å. There are no hydrogen bonds between neighboring ribbons. Addition of Cu(acac)₂ to the benzene solution of Y(hfa)₃(H₂O)₂ yields the 1 : 1 adduct of [Y(hfa)₃(H₂O)₂][Cu(acac)₂] connected through intermolecular hydrogen bondings. This adduct dissociates to the each component by adding polar solvents. The crystal structure shows that [Y(hfa)₃(H₂O)₂][Cu(acac)₂] molecules have one-dimensional networks by intermolecular hydrogen bondings. Further studies on the control of 1 : 2 or 1 : 3 ratio of Cu to Y metal complex through intermolecular interactions are in progress in our laboratory.

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Synthesis of Barium Titanyl Oxalate by Homogeneous Precipitation from Dimethyl Oxalate Solution

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Barium titanate (BT) is considered an attractive material as its ceramics are widely used in electronic components such as multilayer capacitors and nonlinear resistors.^{1,2} In order to produce high-quality ceramics, the starting powders require to have a uniform particle size and shape.³ Similarly, the powder of barium titanyl oxalate (BTO), known as the precursor of BT, need to have a uniform particle size and shape. In order to obtain BTO powder with such a high quality, a homogeneous precipitation method has been adopted.

A common way of homogeneous precipitation methods are the controlled release of precipitants by another chemical source in the solution. Diethyl oxalate (DEO), which can slowly decompose to yield oxalate ions, had been used as the precipitant source by present authors^{4,5} and was found to produce BTO particles of spherical shape with a narrow size distribution. Unfortunately, the DEO is sparingly soluble in aqueous solution at room temperature and is not practical for BTO powder production.⁵ Later, present authors employed the thermal decomposition of dimethyl oxalate (DMO) in nitrate ion systems as an alternative to DEO.

In this case, however, the morphology of BTO was found to be multisized instead of being monosized. The final barium titanate (BT) powders were about 3 μm in diameter and consisted of different phases.⁶

In the present study, dimethyl oxalate (DMO) and chloride ions were chosen as an oxalate anion source and as supporting anions respectively. The primary purpose of present study is to investigate systematically the influence of experimental variables such as DMO concentrations, chloride concentrations, temperatures, aging times and etc. on the properties and morphology of the BTO particles produced.

Experimental

A stock solution of barium chloride was prepared by dissolving the salt of reagent grade (Katayama Chem. Co.) in deionized water to give the nominal barium concentration of 0.2 M. A stock solution of titanium tetrachloride of reagent grade (Yakuri Chem. Co.) was prepared by adding a 160 mL volume of the reagent slowly to a cold distilled water stirred rapidly and diluting to 1 L. The exact titanium