

Unsolvated homo- and heterometallic highly fluorinated β -diketonate complexes of copper(II)

Janell M. Crowder, Haixiang Han, Zheng Wei, Evgeny V. Dikarev*, Marina A. Petrukhina*

Department of Chemistry, University at Albany, State University of New York, Albany, NY 12222, USA

ARTICLE INFO

Article history:

Received 1 August 2018

Accepted 18 September 2018

Available online 26 September 2018

Keywords:

Copper

Sodium

X-ray diffraction

Fluorinated ligands

Heterometallic complexes

ABSTRACT

The unsolvated Cu(II) complex with bis(pentafluorobenzoyl)methanide ligand (L , $C_6F_5COCHCO_2C_6F_5$) is prepared and crystallized as $[CuL_2]$ (**1**) using gas phase sublimation-deposition at 150 °C. The X-ray crystallographic characterization confirmed the centrosymmetric mononuclear structure of **1** with a square planar geometry around Cu(II) ($Cu-O_{av}$ 1.9149(8) Å). The reaction of **1** with sodium hexafluoroacetylacetonate $[Na(hfac)]$ in a solvent-free environment afforded $[Na_2Cu_2L_4(hfac)_2]$ (**2**), the first heterometallic Na–Cu β -diketonate characterized by single-crystal X-ray diffraction. In the centrosymmetric tetranuclear structure of **2**, a dimeric $[Na(hfac)]_2$ unit is sandwiched between two CuL_2 units. The L -ligands function as chelating-bridging between Cu and Na through one of their O-atoms. The $hfac$ ligands are chelating-bridging between Cu and Na and between Na(1) and Na(1A) through both O-atoms. In addition to the five primary Na–O interactions (av. 2.4109(17) Å), three secondary Na–F contacts (av. 2.6006(15) Å) contribute to the overall distorted square antiprismatic coordination environment for Na. The geometry of Cu is square pyramidal with $Cu-O(L)$ distances averaging at 1.922(14) Å and $Cu-O(hfac)$ of 2.3021(15) Å. Thermal decomposition of **2** yields a mixture of $NaCuF_3$, Na_2CuF_4 and NaF , when conducted at 230 °C in argon at ambient pressure.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Fluorinated β -diketonates are valued for their high volatility and solubility, superior mass-transport properties, and improved thermal stability relative to the non-fluorinated analogues [1]. Consequently, they are utilized extensively in various chemical vapor deposition (CVD) processes for the deposition of metal, metal oxide, and fluorine-doped metal oxide thin films and as precursors to metal fluorides and oxyfluorides [1b,1c,2]. A great number of transition metal fluorinated β -diketonates has been synthesized and interrogated as CVD precursors, as summarized in a recent comprehensive review [1b].

Fluorinated Cu(II) β -diketonates are some of the more thoroughly studied transition metal compounds of this type due to the critical application of copper metal in the manufacture of integrated circuits [2b,3] and the need for volatile sources of Cu(II) for the metal–organic CVD (MOCVD) production of superconducting cuprate YBCO films [2a,4]. Copper β -diketonate complexes without exogenous ligands are of particular interest for the above applications as well as due to the presence of coordinatively unsaturated

metal centers that are apt to additional coordination [5]. The electron-withdrawing nature of fluorinated ligands further enhances the Lewis acidity of the metal center and increases the tendency of the metal to bind to ancillary ligands [6]. Several partially fluorinated Cu(II) β -diketonates without exogenous ligands have been structurally characterized by X-ray crystallography [7], but it is of note that only two fully fluorinated Cu(II) β -diketonates have been reported, namely $[Cu(hfac)_2]$ [8] and $[Cu(pfh)_2]$ ($pfh = 1,1,1,5,5,6,6,6$ -octafluoro-2,4-hexanedionate) [9].

Understanding the influence of electron-withdrawing fluorinated ligands on metal complexation has led to advances in many fields. An area of growing interest is the use of fluorinated β -diketonates in the synthesis of unsolvated heterometallic compounds of Na or Li with transition or rare earth metals which, when prepared with the proper metal stoichiometry, are used as single-source MOCVD precursors for heterometallic fluorides [10]. When studying the catalytic performance of copper(II) β -diketonate complexes in ring expansion and rearrangement reactions of vinyl derivatives, it was found that the most fluorinated, and thus the most electrophilic, complexes outperformed the lesser- or non-fluorinated counterparts [7i,11]. Fluorinated Cu(I) carboxylates have likewise shown impressive photoluminescent properties and structural diversity driven by changes in the degree of ligand fluorination and bulkiness [12]. Furthermore, the structural study of

* Corresponding authors.

E-mail addresses: edikarev@albany.edu (E.V. Dikarev), mpetrukhina@albany.edu (M.A. Petrukhina).

fluorinated coordination complexes and organofluorine compounds has advanced the understanding of the role of fluorine in supramolecular packing as it relates to the design of advanced functional materials, enhanced doping, crystal engineering, and molecular recognition processes in medicinal chemistry [13]. These remarkable properties and applications stimulate continued interest in synthesis and study of highly electrophilic homo- and heterometallic β -diketonates.

Herein, we target the isolation of the unsolvated Cu(II) complex $[\text{CuL}_2]$ (**1**) with highly-fluorinated bis(pentafluorobenzoyl)methanide ligands followed by testing its ability to serve as a metallo-ligand or ligand-transfer reagent. We used high volatility and coordinatively unsaturated ability of the above copper complex to synthesize $[\text{Na}_2\text{Cu}_2\text{L}_4(\text{hfac})_2]$ (**2**), the first heterometallic Na–Cu β -diketonate characterized by X-ray crystallography.

2. Results and discussion

2.1. Synthesis and crystal growth

The preparation of unsolvated $[\text{CuL}_2]$ (**1**) in the single-crystalline form suitable for X-ray crystallographic characterization began with the synthesis of benzene-solvated $[\text{CuL}_2] \cdot 3(\text{C}_6\text{H}_6)$ adduct as previously reported [14], except that anhydrous starting reagents and dry solvents were employed in an oxygen-free and moisture-free environment (see Supporting Information (SI) for more details). Superstitial benzene was removed by heating *in vacuo*, and single crystals of **1** were grown using a small-scale sublimation-deposition method at 150 °C in 3 days. This procedure was optimized to produce bulk crystals of **1** in ca. 80% yield, allowing the effective use of **1** in subsequent reactions. The purity of bulk crystalline product was confirmed by comparing the X-ray powder diffraction pattern to the one calculated from the single crystal data (see Fig. S11 and Table S9). The preparation of **1** in the unsolvated form was a critical step which allowed the exploration of its synthetic potential in further reactions. The avidity of **1** for additional coordination has been illustrated by the formation of $[\text{CuL}_2(\text{H}_2\text{O})]$ (**3**) crystallized from regular hexanes via slow evaporation of the solvent at room temperature (see SI for the details). This experimental evidence further reinforced the need to use the high-quality anhydrous solvents or solvent-free conditions when **1** is utilized as a new metallo-ligand.

For the next step, bulk crystals of **1** were combined with sodium hexafluoroacetylacetonate $[\text{Na}(\text{hfac})]$ in a 1:1 molar ratio and the mixture was sealed under vacuum in a small glass ampule. The ampule was heated at 120 °C for 7 days resulting in the formation of bright teal green product, $[\text{Na}_2\text{Cu}_2\text{L}_4(\text{hfac})_2]$ (**2**), in nearly quantitative yield. The purity of the bulk crystalline product was confirmed by X-ray powder diffraction analysis (see Fig. S12 and Table S10). The X-ray quality single crystals of **2** were grown at slightly lower temperature in a 110 °C oven with ca. 5 °C temperature gradient in 10 days (yield 60–80%). To the best of our knowledge, the only other known Na–Cu heterometallic β -diketonate derivative is β -diketonatofluoroalkoxide $[\text{NaCu}\{\text{OCH}(\text{CF}_3)_2\}_2(\text{thd})]_m$ (thdH = 2,2,6,6-tetramethylheptane-3,5-dione) [15]. This mixed-ligand complex, comprised of fluoroisopropoxide and non-fluorinated β -diketonate ligands, was characterized by elemental analysis, IR, and mass spectrometry; however, an X-ray crystallographic investigation was not reported.

2.2. X-ray crystallographic study

The unsolvated mononuclear complex $[\text{CuL}_2]$ (**1**) (Fig. 1) crystallizes in the centrosymmetric space group $P\bar{1}$ with the copper atom residing on the inversion center. The asymmetric unit therefore

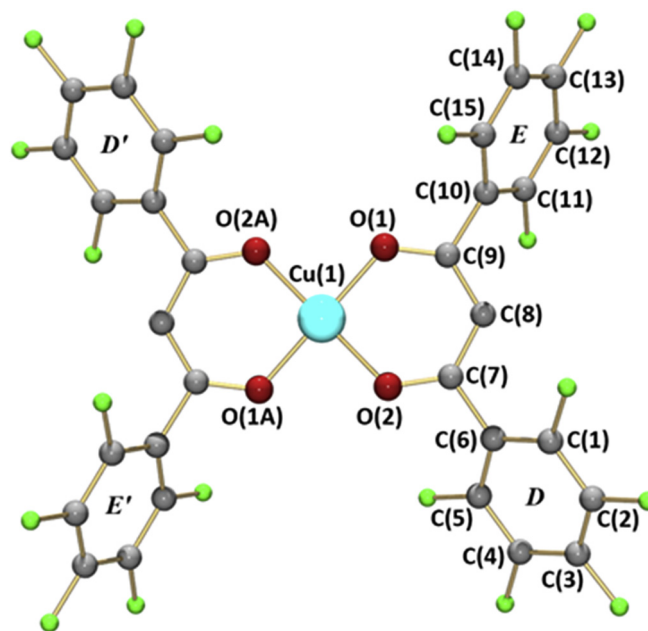


Fig. 1. Molecular structure of **1**. Color scheme: copper – blue; oxygen – red; carbon – grey; fluorine – green. Hydrogen atoms are omitted. Carbon atoms C(7), C(8) and C(9) deviate slightly from the Cu–O(L) plane by 0.127, 0.300 and 0.259 Å, respectively. (Color online.)

contains only one bis(pentafluorobenzoyl)methanide ligand (L). The copper coordination environment is square planar with Cu–O(1) and Cu–O(2) bond distances of 1.9063(8) and 1.9236(7) Å, respectively. These distances are within the range of those reported for related Cu(II) diketonate structures (Table 1) [7c,8,14,16]. The pentafluorophenyl groups of L are twisted relative to the metal–oxygen coordination plane with dihedral angles of 36.4 and 68.9° between the [O(1)–O(2)–O(1A)–O(2A)] plane and the planes created by the aromatic rings D and E (Fig. 1). Furthermore, the planes formed by rings D and E are nearly orthogonal with an angle of 87.1°. For comparison, the pentafluorophenyl groups in $[\text{CuL}_2] \cdot 3(\text{C}_6\text{H}_6)$ [14] are similarly twisted, whereas the dibenzoylmethanato (dbm) ligands in $[\text{Cu}(\text{dbm})_2]$ [16] (the non-fluorinated analogue of **1**) are nearly coplanar with the metal–oxygen plane. The X-ray single-crystal data and structure refinement parameters of **1** are given in Table S5, and the thermal ellipsoid plot is shown in Fig. S5. Bond angles for **1** are listed in Table S6, and an alternative view of **1**, illustrating the planarity of the Cu–O core and the twisted nature of L, is shown in Fig. S6.

In the solid state, the molecules of **1** form the columns down the crystallographic *a*-axis with intermolecular C–F... π_F interactions between C(15)–F(10) of one molecule and pentafluorophenyl ring D of the adjacent molecule (Fig. S7), and the distances and angles are similar to those previously reported [7c,17]. The distance

Table 1

Comparison of interatomic distances between **1** and related structurally characterized copper diketonates.

	Cu–O distances (Å)	O–C distances (Å)
$[\text{CuL}_2]$ (1) [a]	1.9063(8), 1.9236(7)	1.2714(12), 0.2681(12)
$[\text{CuL}_2(\text{H}_2\text{O})]$ (3) [a]	1.932(2), 1.923(2) [b]	1.265(3), 1.270(3)
$[\text{CuL}_2] \cdot 3(\text{C}_6\text{H}_6)$ [14]	1.9104(13), 1.9295(14)	1.265(3), 1.268(3)
$[\text{CuL}_2]$ [7c]	1.9100(19), 1.9216(18)	1.271(3), 1.271(3)
$[\text{Cu}(\text{dbm})_2]$ [16]	1.892(3), 1.914(3)	1.274(5), 1.266(5)
$[\text{Cu}(\text{hfac})_2]$ [8]	1.914(2), 1.924(2)	1.259(2), 1.264(3)

[a] This work.

[b] Cu–O(L) distances. L' = $\text{C}_6\text{H}_5\text{COCHCOC}_6\text{F}_5$. dhbm = $\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5$.

between F(10) and the plane of ring D is 3.089 Å and between F(10) and ring D centroid (CgD) is 3.201 Å. The C(15)–F(10)–CgD angle is 151.3°. The highly twisted orientation of the pentafluorophenyl rings permits intermolecular $\pi_F\cdots\pi_F$ interactions between pentafluorophenyl groups of neighboring molecules in adjacent columns in both the *b*- and *c*-axis directions (Fig. 2). Ring D of one molecule interacts with ring D' of a second molecule located in the neighboring column (moving across to the next column in the *b*-direction and down one molecule in the *a*-direction). Ring E of one molecule interacts with ring E' of a second molecule directly across to the adjacent column in the *c*-direction. Each pair of interacting rings have an offset face-to-face (*off*) alignment with separations of 3.467 and 3.293 Å between the D $\cdots$ D' and E $\cdots$ E' planes, respectively. These separations are on par with those reported for other perfluoroaryl $\pi_F\cdots\pi_F$ interactions (3.23–3.62 Å) [14,18].

The Na–Cu heterometallic β -diketonate compound (**2**) crystallizes in the space group $P\bar{1}$. It possesses a centrosymmetric tetranuclear molecular structure with two neutral electrophilic Na(hfac) units at the center terminated by a neutral Cu₂ unit on each end (Fig. 3). Both L ligands of the Cu₂ unit act as bridging to sodium atoms through one oxygen each (O(2) and O(4)). The second oxygen atom of each L ligand (O(1) and O(3)) is purely chelating to Cu. Each hfac ligand is chelating-bridging through both of its oxygen atoms – between Na(1) and Cu(1) through O(5) on one side and between Na(1) and Na(1A) through O(6) on the other. The X-ray single-crystal data and structure refinement parameters of **2** are given in Table S5, and the thermal ellipsoid view of the asymmetric unit is presented in Fig. S8. The full list of bond distances and bond angles for **2** can be found in Table S7.

Considering the coordination environment of copper (Fig. 4), it can be seen that the Cu(II) center exhibits square pyramidal coordination formed by oxygen atoms. The purely chelating Cu–O(L) bonds (av. 1.9109(14) Å) are slightly shorter than the chelating-bridging Cu–O(L) bonds (av. 1.9416(14) Å). The Cu–O chelating-bridging bond with O(5) (2.3021(15) Å) of the hfac ligand, located in the axial coordination position, is significantly longer due to the Jahn–Teller effect [19]. This distance is comparable to the Cu–O (H₂O) distance (2.289(4) Å) observed in **3** for water coordinated

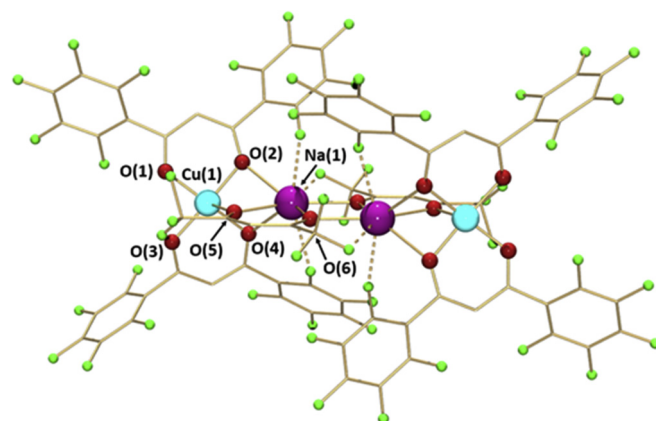


Fig. 3. Molecular structure of **2**. Only the Na, Cu and O atoms of the asymmetric unit are labeled. Interactions between sodium and fluorine atoms are indicated by dashed lines. Color scheme: copper – blue; sodium – purple; oxygen – red; fluorine – green. Hydrogen atoms are omitted. (Color online.)

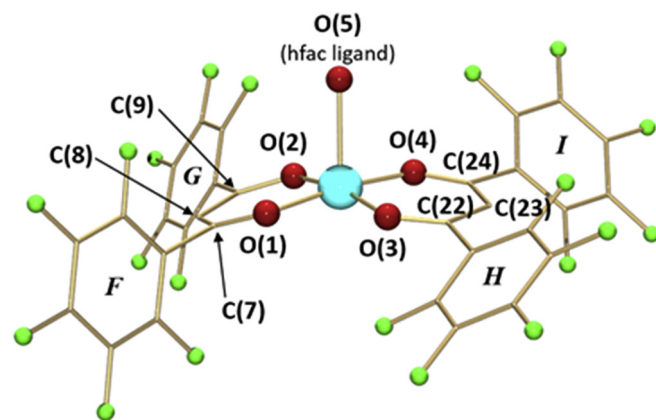


Fig. 4. Fragment of the solid-state structure of **2** showing the square pyramidal coordination environment of the copper atom. Ring F = C(1)–C(2)–C(3)–C(4)–C(5)–C(6); ring G = C(10)–C(11)–C(12)–C(13)–C(14)–C(15); ring H = C(16)–C(17)–C(18)–C(19)–C(20)–C(21); ring I = C(25)–C(26)–C(27)–C(28)–C(29)–C(30).

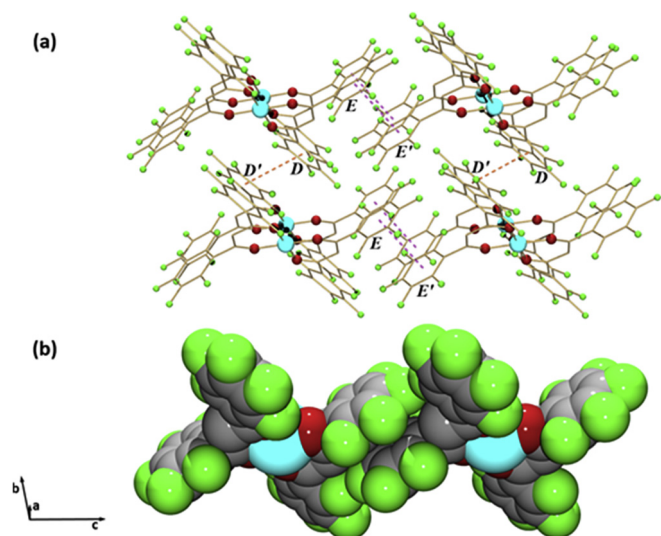


Fig. 2. (a) Crystal packing in the structure of **1** showing the columnar arrangement of molecules down the *a*-axis and the intermolecular *off* $\pi_F\cdots\pi_F$ interactions between pentafluorophenyl groups indicated by dashed orange (CgD $\cdots$ CgD') and purple (CgE $\cdots$ CgE') lines; CgX represents the centroid of ring X. (b) Space-filling model showing a single instance of the E $\cdots$ E' *off* $\pi_F\cdots\pi_F$ paired interaction. Color scheme: copper – blue; oxygen – red; fluorine – green. Hydrogen atoms are omitted. (Color online.)

in the apical position and to other reported Cu–O distances for oxygen atoms located in the apical position of square pyramidal copper [5c,7b,8,20]. The Cu–O(L) coordination environment in **2** is less planar compared to **1** because the pentafluorophenyl groups are pushed outward to make room for the hfac ligand. The copper atom moves above the O(L) plane by 0.162 Å, while C(7), C(8), C(9), C(22), C(23) and C(24) atoms deviate by 0.136–0.506 Å below the plane resulting in a slightly curved (*boat*) arrangement of the L ligands away from the hfac ligand coordinated to Cu. As in **1**, the pentafluorophenyl groups are twisted relative to the basal oxygen coordination plane with dihedral angles of 80.5, 61.4, 32.6 and 54.1° between the [O(1)–O(2)–O(4)–O(3)] plane and each of the planes created by pentafluorophenyl rings F, G, H and I (Fig. 4).

Considering the sodium center, a fragment of the solid-state structure of **2** depicting its coordination environment is shown in Fig. 5. As previously mentioned, one oxygen atom from each of the L ligands is bridging between sodium and copper with Na–O distances of 2.4986(17) Å and 2.5112(16) Å for Na(1)–O(2) and Na(1)–O(4), respectively. Both oxygen atoms of the hfac ligand, O(5) and O(6), serve as chelating-bridging. Na and Cu are bridged by O(5) with the Na(1)–O(5) distance of 2.3390(16) Å, and Na(1) and Na(1A) are bridged by O(6) with the Na(1)–O(6) distance of 2.3355(17) Å. Due to the inversion symmetry operation, Na(1) and Na(1A) are also bridged by O(6A) at 2.3702(16) Å. In addition

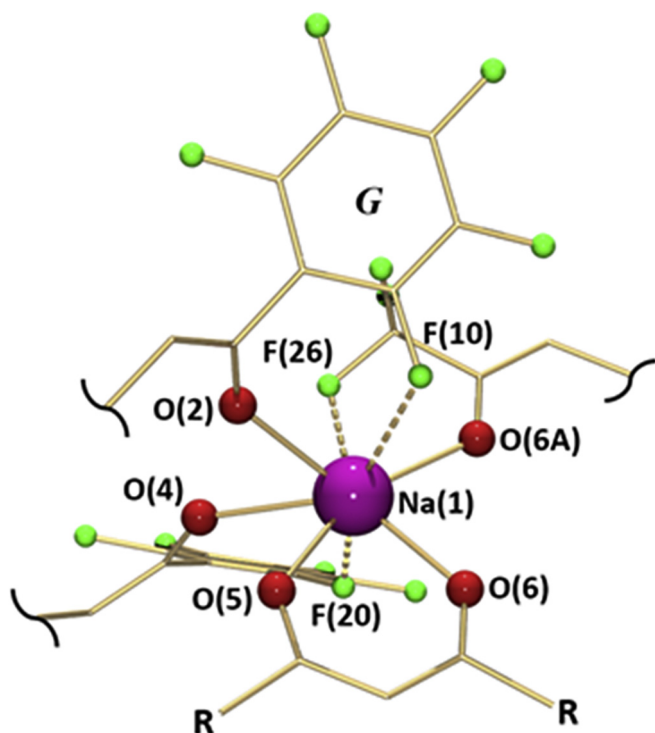


Fig. 5. Fragment of the solid-state structure of **2** showing the coordination environment of the sodium atom. For clarity, only half of each ligand is shown when the other half is chelating-bridging to copper or to the other sodium atom. R = CF₃.

to the five primary interactions with oxygen atoms, three fluorine atoms, F(10), F(20), and F(26), interact with sodium at distances of 2.6307(16), 2.5062(15) and 2.6648(16) Å. These values are smaller than the sum of the van der Waals radii [21] and are on par with Na...F interactions reported in literature (ranging from 2.3 to 3.0 Å) [10b,22]. Therefore, the sodium atom coordination can be described as distorted square-antiprismatic composed of five oxygens and three fluorine atoms.

In the solid state, the molecules of **2** pack in rows keeping the same orientation within each row (Fig. 6). In contrast to **1**, no $\pi_F-\pi_F$ interactions are formed. However, similar to **1**, an intermolecular C-F... π_F interactions occur between C(12)–F(7) of ring G and pentafluorophenyl ring I [C(25)–C(26)–C(27)–C(28)–C(29)–C(30)] of the neighboring molecule where the F(7)... π_F (centroid) distance

is 3.029 Å and the C(12)–F(7)... π_F (centroid) angle is 144.5° [7c,17]. The distance between F(7) and the plane of the C₆F₅ ring is 2.970 Å. Two instances of intermolecular C–H...F–C short contacts are observed in **2**, although none are present in **1**. The H(8) and H(23) atoms of the L ligands interact with F(4) and F(1) of neighboring molecules at the distances of 2.641 and 2.639 Å, respectively. The angles of interaction are 150.0 and 141.5° for C(8)–H(8)...F(4) and C(23)–H(23)...F(1). These distances and angles are consistent with the previously reported C–H...F interactions [17a,18c,18d,23]. Although C–H...F–C and C–F... π_F interactions are weak, it has been shown that they can influence crystal packing when stronger interactions are not present [13].

2.3. Thermal decomposition study

Thermal decomposition of **2** has been investigated in the range of temperatures from 150 to 280 °C with the time varying from 0.5 to 24 h. No decomposition was observed below 180 °C when the sample was heated for up to 24 h. Weak signals from the target decomposition products, NaCuF₃ and Na₂CuF₄, were detected by X-ray powder diffraction analysis following experiments conducted at 200 and 215 °C for short periods of time (30 min), but all NaCuF₃ was lost when compound **2** was heated at 210 °C for 4 h. The strongest X-ray powder diffraction signals corresponding to decomposition products NaCuF₃ and Na₂CuF₄ were observed when utilizing 230 °C for a short time. Specifically, it was found that heating **2** for 30 min at 230 °C under argon at ambient pressure results in the formation of a mixture of NaCuF₃, Na₂CuF₄ and NaF (see Fig. S13 and Table S11 for X-ray powder diffraction pattern and Le Bail fit of unit cell parameters compared to the literature values). Decomposition at 230 °C for 2 h resulted in the loss of NaCuF₃; and decomposition at 230 °C for 24 h resulted in the loss of both NaCuF₃ and Na₂CuF₄. Decomposition at temperatures over 230 °C caused loss of all mixed-metal products.

The formation of a mixture of decomposition products is congruous with the gas-phase composition of **2** observed by DART-MS (direct analysis in real time mass spectrometry) (Fig. S2, Tables S3 and S4) in which various heterometallic ion fragments with Na-Cu ratios of 1:1, 2:1 and 1:2, such as [NaCuL(hfac)]⁺, [Na₂CuL₂(-hfac)]⁺ and [NaCu₂L₃(hfac)]⁺, are present along with several homometallic fragments containing Cu and L.

3. Conclusions

In this work, we prepared the unsolvated complex [CuL₂] (**1**) in bulk crystalline form using gas-phase sublimation-deposition

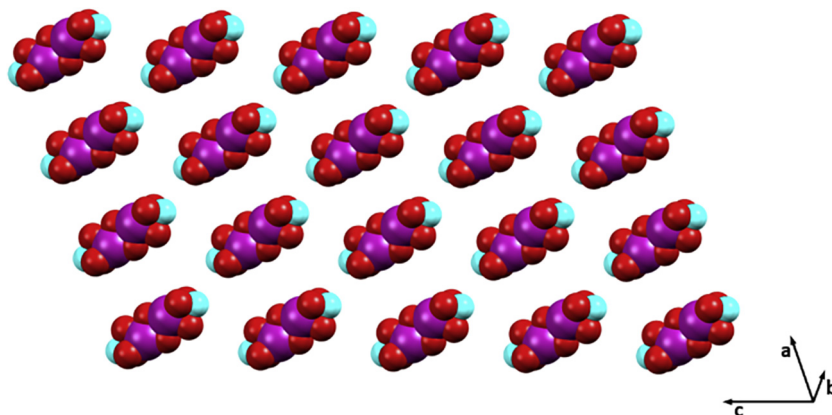


Fig. 6. Packing diagram of **2** rendered as space-filling models. Only [Na₂Cu₂O₈] cores are shown for clarity. Color scheme: copper – blue; sodium – purple; oxygen – red. (Color online.)

procedures. The X-ray crystallographic characterization of **1** confirmed that the complex possesses a coordinatively unsaturated metal center with a square planar coordination environment. The electrophilic nature of the Cu(II) center in **1** allowed for facile reaction with [Na(hfac)] to form [Na₂Cu₂L₄(hfac)₂] (**2**) – the first heterometallic Na–Cu β-diketonate product crystallographically characterized. This study provides ready access to a new copper (II) metallo-ligand and demonstrates how the electrophilicity of a coordinatively unsaturated metal complexed by highly-fluorinated β-diketonate ligands can be utilized for the formation of new and interesting heterometallic complexes.

4. Experimental

4.1. Materials

[AlI₃] was synthesized according to the previously published procedure [14]. Anhydrous copper(II) acetate from Strem Chemicals and sodium hexafluoroacetylacetonate [Na(hfac)] from Sigma-Aldrich were used as received. All solvents were reagent grade from Sigma-Aldrich. Anhydrous dichloromethane was used as received. Ethanol and benzene were dried and degassed over molecular sieves prior to use. Except where noted, hexanes were dried over sodium with benzophenone in an argon atmosphere and freshly distilled before use. All manipulations were performed under a dry dinitrogen atmosphere by employing standard Schlenk line and glove box techniques except in the crystallization of [CuL₂(H₂O)]·(C₆H₁₄)_{0.5} (**3**·(C₆H₁₄)_{0.5}).

4.2. Characterization methods

A Thermo Scientific Evolution 300 was used to collect the UV–Vis spectra (300–1000 nm), and a Perkin Elmer Spectrum One FT-IR spectrometer was used to obtain the attenuated total reflection (ATR) spectra (4000–500 cm^{−1}). DART mass spectra were recorded with a DART-SVP ion source (IonSense, Saugus, MA, USA) coupled to a JEOL AccuTOF time-of-flight mass spectrometer (JEOL USA, Peabody, MA, USA) in positive ion mode. Mass spectra were recorded over the mass range of *m/z* 200–2500 at a rate of one spectrum per second with the gas heater at 300 °C. The mass spectra were examined with Mass Mountaineer version 2.3.0.0 software (R. B. Cody 2012). X-ray powder diffraction data were collected on a Bruker D8 Advance diffractometer (Cu Kα radiation, focusing Göbel Mirror, LynxEye one-dimensional detector, step of 0.02° 2θ, 20 °C). Le Bail fit for powder diffraction patterns was performed using TOPAS, version 4 software package (Bruker AXS, 2006).

4.3. Synthesis and crystallization of [CuL₂·3(C₆H₆)]

The procedure for synthesis of [CuL₂·3(C₆H₆)] was adapted from the literature method [14]. Copper(II) acetate (44 mg, 0.24 mmol) and [AlI₃] (200 mg, 0.16 mmol) were dissolved in a mixture of ethanol (20 mL) and dichloromethane (10 mL). The reaction was stirred for 6 h at room temperature before the solvent was evaporated to yield a green-gray powder. The powder was extracted with dichloromethane (30 mL) and filtered by cannula. The filtrate was concentrated to ca. 10 mL by evaporation of the solvent *in vacuo*. Hexanes (10 mL) and benzene (1 mL) were added and the mixture was kept at −20 °C until blue-green crystals of [CuL₂·3(C₆H₆)] were obtained. The solvent was removed, and the crystals were quickly washed 3 times with hexane (yield 90%). The single-crystal unit cell parameters and the UV–Vis and IR spectra are consistent with those previously reported [14]. UV–Vis (CH₂Cl₂, λ nm): 329. IR

(cm^{−1}): 1649, 1566, 1501, 1488, 1425, 1404, 1342, 1318, 1229, 1198, 1116, 997, 933, 816, 647.

4.4. Synthesis and crystallization of unsolvated [CuL₂] (**1**)

[CuL₂·3(C₆H₆)] was dried by heating at 70 °C *in vacuo* for 6 hr. The color of the material changed from dark blue-green to greenish-gray during the drying process. An aliquot of 5 mg was sealed in a glass ampule (ca. 7 cm long with an I.D. of 0.9 cm) under vacuum (ca. 40 mTorr) and placed in an electric furnace at 150 °C with a temperature gradient (ca. 5 °C) along the length of the tube. Green blocks of unsolvated [CuL₂] (**1**) suitable for single-crystal X-ray crystallographic analysis formed in the cold zone of the ampule within 3 days (yield 30–50%). Bulk crystals of **1** were produced by larger-scale sublimation-deposition of ca. 40 mg sealed in a glass ampule (ca. 8 cm long with an I.D. of 0.9 cm) under vacuum (ca. 40 mTorr). The ampule was placed in an electric furnace at 140 °C with a temperature gradient (ca. 5 °C) along the length of the tube (yield 50–80%). The purity of the bulk crystalline product was confirmed by X-ray powder diffraction analysis (Fig. S11 and Table S9). IR (cm^{−1}): 1651, 1580, 1497, 1406, 1336, 1229, 1190, 1117, 996, 938, 822, 663, 628.

4.5. Synthesis and crystallization of [Na₂Cu₂L₄(hfac)₂] (**2**)

Unsolvated [CuL₂] (19 mg, 22 mmol) and [Na(hfac)] (5 mg, 22 mmol) were combined and sealed in a glass ampule (ca. 5 cm long with an I.D. of 0.9 cm) under vacuum (ca. 40 mTorr) and placed in an electric furnace at 120 °C without a temperature gradient. Bulk crystals of the teal green product, [Na₂Cu₂L₄(hfac)₂] (**2**), formed within 7 days (yield 95%). The purity of the bulk crystalline product was confirmed by X-ray powder diffraction analysis (see Fig. S12 and Table S10). An aliquot of 5 mg was sealed in a glass ampule (ca. 5 cm long with an I.D. of 0.9 cm) under vacuum (ca. 40 mTorr) and placed in an electric furnace at 110 °C with a temperature gradient (ca. 5 °C) along the length of the tube. Green plate crystals of [Na₂Cu₂L₄(hfac)₂] (**2**) suitable for single-crystal X-ray crystallographic analysis formed in the cold zone of the ampule within 10 days (yield 60–80%). IR (cm^{−1}): 1655, 1582, 1496, 1420, 1335, 1256, 1201, 1155, 1109, 992, 938, 822, 665.

4.6. Thermal decomposition of **2**

[Na₂Cu₂L₄(hfac)₂] (**2**) (15 mg bulk crystals) was heated in a 15-mL porcelain crucible with cover (Fisher Scientific) under continuous flow (ca. 10 L/min) of 99.999% pure argon (Airgas) at ambient pressure within a muffle furnace (Lindberg Blue M). The oven temperature was increased at ca. 35 °C/min to the target temperature of 230 °C and held at 230 °C for 30 min. The crucible was allowed to cool down to room temperature prior to removal from the argon atmosphere. The residue (brown powder) was analyzed by X-ray powder diffraction. The experimental powder diffraction pattern and Le Bail fit are presented in Fig. S13. The unit cell parameters calculated by Le Bail fit are compared with the literature values in Table S11. Additional experiments were performed at various temperatures and times ranging from 150 °C to 280 °C and from 0.5 to 24 h.

4.7. Single crystal X-Ray crystallographic procedures for **1** and **2**

Data collection was performed on a Bruker D8 VENTURE X-ray diffractometer with a PHOTON 100 CMOS shutterless mode detector equipped with a Mo-target X-ray tube (λ = 0.71073 Å) at *T* = 100 (2) K. Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A) [24]. Data were corrected for absorption effects using the empirical methods as

implemented in *SADABS* (version 2016/2) [25]. The structures were solved by *SHELXT* [26] and refined by full-matrix least-squares procedures using the Bruker *SHELXTL* (version 2016/6) [27] software package. All non-hydrogen atoms, including those in disordered parts, were refined anisotropically. The rotationally disordered CF_3 group was modeled in two orientations with relative occupancies of 0.61:0.39, and the geometries of the disordered parts were restrained to be similar. All H atoms were included at calculated positions and refined as riders with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Acknowledgements

The authors gratefully acknowledge financial support of this work from the National Science Foundation (CHE-1152441, E. V. D.; CHE-1608628, M. A. P.). E. V. D. also thanks CRDF:FSCX-17-63339-0.

Appendix A. Supplementary data

CCDC 1850163, 1850164 and 1850165 contains the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2018.09.048>.

References

- [1] (a) R.C. Mehrotra, R. Bohra, D.P. Gaur, *Metal β -diketonates and allied derivatives*, Academic Press, New York, 1978; (b) R.E. Sievers, J.E. Sadowski, *Science* **F201** (1978) 217; (c) G.G. Condorelli, G. Malandrino, I.L. Fragala, *Coord. Chem. Rev.* **251** (2007) 1931; (d) S. Mishra, S. Daniele, *Chem. Rev.* **15** (2015) 8379.
- [2] (a) P. Doppelt, T.H. Baum, *MRS Bull.* **19** (1994) 41; (b) T.J. Marks, *Pure Appl. Chem.* **67** (1995) 313.
- [3] (a) A.E. Kaloyeros, M.A. Fury, *MRS Bull.* **18** (1993) 22; (b) J. Pinkas, J.C. Huffman, D.V. Baxter, M.H. Chisholm, K.G. Caulton, *Chem. Mater.* **7** (1995) 1589.
- [4] D.J. Otway, W.S. Rees, *Coord. Chem. Rev.* **210** (2000) 279.
- [5] (a) D.P. Graddon, E.C. Watton, *J. Inorg. Nucl. Chem.* **21** (1961) 49; (b) W.R. May, M.M. Jones, *J. Inorg. Nucl. Chem.* **25** (1963) 507; (c) D.P. Graddon, *Coord. Chem. Rev.* **4** (1969) 1; (d) B.P. Baranwal, G.K. Parashar, R.C. Mehrotra, *Z. Naturforsch.* **36b** (1981) 42; (e) J.K. Clegg, L.F. Lindoy, J.C. McMurtie, D. Schilter, *Dalton Trans.* (2005) 857; (f) D.J. Bray, J.K. Clegg, L.F. Lindoy, D. Schilter, *Adv. Inorg. Chem.* **59** (2006) 1.
- [6] (a) R.D. Gillard, G. Wilkinson, *J. Chem. Soc.* (1963) 5885; (b) W.R. Walker, N.C. Li, *J. Inorg. Nucl. Chem.* **27** (1965) 2255; (c) L.L. Funck, T.R. Ortolano, *Inorg. Chem.* **7** (1968) 567; (d) W. Partenheimer, R.S. Drago, *Inorg. Chem.* **9** (1970) 47; (e) D.R. McMillin, R.S. Drago, J.A. Nusz, *J. Am. Chem. Soc.* **98** (1976) 3120.
- [7] (a) P.C. Le Brun, W.D. Lyon, H.A. Kuska, *Inorg. Chem.* **25** (1986) 3106; (b) I.A. Baidina, P.A. Stabnikov, I.K. Igumenov, S.V. Borisov, *Koord. Khim.* **12** (1986) 543; (c) I.A. Baidina, P.A. Stabnikov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* (1990) 29; (d) I.A. Baidina, S.A. Gromilov, *Zh. Strukt. Khim.* **32** (1991) 96; (e) S.A. Gromilov, I.A. Baidina, *J. Struct. Chem.* **38** (1997) 685; (f) D.V. Soldatov, J.A. Ripmeester, S.I. Shergina, I.E. Sokolov, A.S. Zanina, S.A. Gromilov, Yu. A. Dyadin, *J. Am. Chem. Soc.* **121** (1999) 4179; (g) M.J. DelaRosa, K.K. Banger, S. Higashiya, S.C. Ngo, D.H. Hunt, K.S. Bousman, P.J. Toscano, J.T. Welch, *J. Fluorine Chem.* **123** (2003) 109; (h) I.A. Baidina, S.A. Gromilov, A.D. Vasilyev, *J. Struct. Chem.* **46** (2005) 177; (i) L.A. Batory, C.E. McInnis, J.T. Njardarson, *J. Am. Chem. Soc.* **128** (2006) 16054; (j) I.A. Baidina, P.A. Stabnikov, S.A. Gromilov, A.I. Smolentsev, *J. Struct. Chem.* **49** (2008) 957; (k) V.K. Khamylov, T.S. Pochekutova, B.I. Petrov, M.V. Sizov, G.K. Fukin, Yu.A. Kurskii, A.V. Arapova, *Russ. J. Gen. Chem.* **79** (2009) 31; (l) D.F. Xu, Z.H. Shen, Y. Shi, Q. He, Q.C. Xia, *Russ. J. Coord. Chem.* **36** (2010) 458; (m) A. Hori, M. Mizutani, *Int. J. Inorg. Chem.* (2011), No. 291567.
- [8] A.W. Maverick, F.R. Fronczek, E.F. Maverick, D.R. Billodeaux, Z.T. Cygan, R.A. Isovitsch, *Inorg. Chem.* **41** (2002) 6488.
- [9] V.I. Ovcharenko, E.V. Tretyakov, S.V. Fokin, E.Yu. Fursova, O.V. Kuznetsova, S.E. Tolstikov, G.V. Romanenko, A.S. Bogomyakov, R.Z. Sagdeev, *Russ. Chem. Bull.* **60** (2011) 2457.
- [10] (a) Z. Wei, A.S. Filatov, E.V. Dikarev, *J. Am. Chem. Soc.* **135** (2013) 12216; (b) M.C. Barry, Z. Wei, T. He, A.S. Filatov, E.V. Dikarev, *J. Am. Chem. Soc.* **138** (2016) 8883; (c) H. Han, Z. Wei, M.C. Barry, A.S. Filatov, E.V. Dikarev, *Dalton Trans.* **46** (2017) 5644.
- [11] J.T. Njardarson, *Synlett* **24** (2013) 787.
- [12] (a) Y. Sevryugina, O. Hietsoi, M.A. Petrukhina, *Chem. Commun.* (2007) 3853; (b) Y. Sevryugina, A.Yu. Rogachev, M.A. Petrukhina, *Inorg. Chem.* **46** (2007) 7870; (c) Y. Sevryugina, M.A. Petrukhina, *Eur. J. Inorg. Chem.* (2008) 219; (d) A.S. Filatov, O. Hietsoi, Yu. Sevryugina, N.N. Gerasimchuk, M.A. Petrukhina, *Inorg. Chem.* **49** (2010) 1626; (e) O. Hietsoi, C. Dubceac, A.S. Filatov, M.A. Petrukhina, *Chem. Commun.* **47** (2011) 6939; (f) O. Hietsoi, A.S. Filatov, C. Dubceac, M.A. Petrukhina, *Dalton Trans.* **40** (2011) 8598; (g) O. Hietsoi, A.S. Filatov, C. Dubceac, M.A. Petrukhina, *Coord. Chem. Rev.* **295** (2015) 125.
- [13] (a) L. Shimoni, J.P. Glusker, *Struct. Chem.* **5** (1994) 383; (b) K. Reichenbacher, H.I. Süss, J. Hulliger, *Chem. Soc. Rev.* **34** (2005) 22; (c) D. Chopra, T.N. Guru Row, *CrystEngComm* **13** (2011) 2175; (d) G. Schmid, J.H. Wemken, A. Maltenberger, C. Diez, A. Jaeger, T. Dobbertin, O. Hietsoi, C. Dubceac, M.A. Petrukhina, *Adv. Mater.* **26** (2014) 878; (e) S. Pecqueur, A. Maltenberger, M.A. Petrukhina, M. Halik, A. Jaeger, D. Pentlehn, G. Schmid, *Angew. Chem., Int. Ed.* **55** (2016) 10493.
- [14] A. Hori, A. Shinohe, S. Takatani, T.K. Miyamoto, *Bull. Chem. Soc. Jpn.* **82** (2009) 96.
- [15] F. Labrize, L.G. Hubert-Pfalzgraf, *Polyhedron* **14** (1995) 881.
- [16] B.-Q. Ma, S. Gao, Z.-M. Wang, C.-S. Liao, C.-H. Yan, G.-X. Xu, *J. Chem. Crystallogr.* **29** (1999) 793.
- [17] (a) S. Lorenzo, G.R. Lewis, I. Dance, *New J. Chem.* **24** (2000) 295; (b) V.R. Vangala, A. Nangia, V.M. Lynch, *Chem. Commun.* (2002) 1304; (c) A. Hori, K. Nakajima, H. Yuge, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **70** (2014) 960.
- [18] (a) M.D. Blanchard, R.P. Hughes, T.E. Concolino, A.L. Rheingold, *Chem. Mater.* **12** (2000) 1604; (b) P.A. Deck, M.J. Lane, J.L. Montgomery, C. Slebodnick, F.R. Fronczek, *Organometallics* **19** (2000) 1013; (c) M.P. Thornberry, C. Slebodnick, P.A. Deck, F.R. Fronczek, *Organometallics* **19** (2000) 5352; (d) N. Adams, A.R. Cowley, S.R. Dubberley, A.J. Sealey, M.E.G. Skinner, P. Mountford, *Chem. Commun.* (2001) 2738; (e) E. Martin, C. Spendley, A.J. Mountford, S.J. Coles, P.N. Horton, D.L. Hughes, M.B. Hursthouse, S.J. Lancaster, *Organometallics* **27** (2008) 1436.
- [19] J.E. Huheey, E.A. Keiter, R.L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., HarperCollins College Publishers, New York, 1993, pp. 449–455.
- [20] (a) S.C. Thompson, D.J. Cole-Hamilton, D.D. Gilliland, M.L. Hitchman, J.C. Barnes, *Adv. Mater. Opt. Electron.* **1** (1992) 81; (b) C.T. Vogelson, C.L. Edwards, A.N. Kobylivker, S.B. Chacko, C.E. Moran, K. Dalton, S.M. Stewart, B.C. Werner, S.G. Bott, A.R. Barron, *J. Chem. Crystallogr.* **28** (1998) 815.
- [21] (a) A. Bondi, *J. Phys. Chem.* **68** (1964) 441; (b) S.S. Batsanov, *J. Mol. Struct.* **990** (2011) 63; (c) S. Alvarez, *Dalton Trans.* **42** (2013) 8617.
- [22] (a) H. Plenio, *Chem. Rev.* **97** (1997) 3363, and references therein; (b) H.V.R. Dias, T.K.H.H. Goh, *Polyhedron* **23** (2004) 273; (c) A. Monguzzi, A. Milani, A. Mech, L. Brambilla, R. Tubino, C. Castellano, F. Demartin, F. Meinardi, C. Castiglione, *Synth. Met.* **161** (2012) 2693; (d) W.D. Buchanan, K. Ruhlandt-Senge, *Chem. Eur. J.* **19** (2013) 10708.
- [23] (a) J.H. Williams, J.K. Cockcroft, A.N. Fitch, *Angew. Chem., Int. Ed. Engl.* **31** (1992) 1655; (b) V.R. Thalladi, H.-C. Weiss, D. Bläser, R. Boese, A. Nangia, G.R. Desiraju, *J. Am. Chem. Soc.* **120** (1998) 8702; (c) C. Dai, P. Nguyen, T.B. Marder, A.J. Scott, W. Clegg, C. Viney, *Chem. Commun.* (1999) 2493; (d) E. D'Oria, J.J. Nova, *CrystEngComm* **10** (2008) 423; (e) T.S. Thakur, M.T. Kirchner, D. Bläser, R. Boese, G.R. Desiraju, *CrystEngComm* **12** (2010) 2079.
- [24] SAINT; part of Bruker APEX3 software package (version 2016.9-0): Bruker AXS, 2016.
- [25] (a) SADABS; part of Bruker APEX3 software package (version 2016.9-0): Bruker AXS, 2016; (b) L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **48** (2015) 3.
- [26] (a) SHELXT; Version 2014/5; (b) G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* **71** (2015) 3.
- [27] (a) XL refinement program version 2016/6; (b) G.M. Sheldrick, *Acta Crystallogr., Sect. C Struct. Chem.* **71** (2015) 3.