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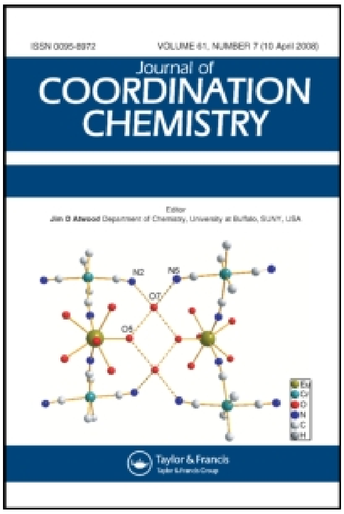

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Structural investigations of copper(II) complexes containing unsymmetrical β-diketonate and monothio-β-diketonate ligands

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STRUCTURAL INVESTIGATIONS OF COPPER(II) COMPLEXES CONTAINING UNSYMMETRICAL β-DIKETONATE AND MONOTHIO-β-DIKETONATE LIGANDS

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The crystal structures of the complexes $Cu(txhd)_2$ and $Cu(S\text{-tmhd})_2$ (where txhd is the anion of 2,2,6-trimethylheptane-3,5-dione and *S*-tmhd is the anion of 5-mercapto-2,2,6,6-tetramethyl-4-hepten-3-one) were determined. In the solid state, both complexes are square planar. In each case, only one geometrical isomer (*trans* or *cis*) was observed in the crystals; arguments are presented that both isomers are present in bulk samples of $Cu(txhd)_2$, while from electronic considerations, the monothio-β-diketonate ligands probably have *cis* geometry in $Cu(S\text{-tmhd})_2$. Calculations of molecular volumes for structurally similar $Cu[t\text{-BuC(O)CHC(O)R}]_2$ complexes showed that there is a slight decrease in packing efficiency as the steric bulk of R increases. More importantly, strong ring-stacking interactions, such as those found for $Cu(acac)_2$ are not observed, or are greatly attenuated, in complexes with bulkier peripheral substituents. $[Cu(txhd)(\mu_3\text{-OEt})]_4$, an impurity that co-sublimed with $Cu(txhd)_2$, was isolated in low yield. The tetrameric structure, which is isomorphous with known $[Cu(tmhd)(\mu_3\text{-OEt})]_4$ (where tmhd is the anion of 2,2,6,6-tetramethylheptane-3,5-dione), has a cubane-like core.

Keywords: β-Diketonate ligands; Copper complexes; Volatile complexes; Crystal structure; Chemical vapor deposition

INTRODUCTION

The application of metal–organic chemical vapor deposition (MOCVD) to the production of copper thin films [1–7], as well as copper-containing sulfided phases [8–14] and superconducting films [15–20], has been an area of ongoing research. Many of these processes utilize homoleptic or solvated ternary Cu(II) complexes, supported by β-diketonate ligands [1,3,5,6].

As part of a program aimed at identifying new, volatile Cu(II) complexes for CVD applications and at systematizing trends in volatility as a function of the substitution pattern in the ancillary ligands, we have structurally characterized a large number of

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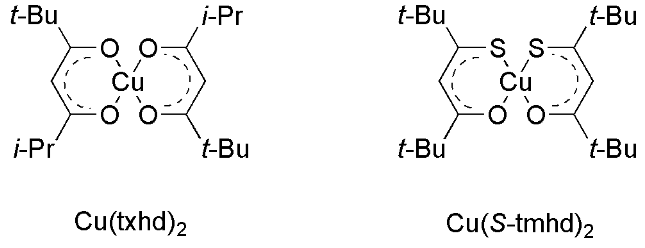

SCHEME 1.

Cu(II) β-diketonate complexes that contain silylated and fluorinated peripheral substituents [21–27]. Since Cu(txhd)$_2$ (txhd is the anion of 2,2,6-trimethylheptane-3,5-dione; see Scheme 1) has been employed in the preparation of thin films of YBCO and related superconducting materials [17–20], and since we had recently reported on the structure of Ce(txhd)$_4$ [28], we felt it would be of interest also to characterize the Cu(II) complex by diffraction methods. In addition, we report here on the solid-state structure of [Cu(txhd)(μ_3-OEt)]$_4$, a volatile impurity formed in the standard preparation of Cu(txhd)$_2$, as well as the first structure of a Cu(II) complex containing a monothio-β-diketonate, Cu(*S*-tmhd)$_2$ (*S*-tmhd is the anion of 5-mercapto-2,2,6,6-tetramethyl-4-hepten-3-one; see Scheme 1).

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EXPERIMENTAL

Synthesis Procedures

The dione, 2,2,6-trimethylheptane-3,5-dione (txhdH), was prepared according to our method [28]. The monothio-β-diketone, 5-mercapto-2,2,6,6-tetramethyl-4-hepten-3-one (*S*-tmhdH), was prepared and purified according to literature procedures [29].

The known complex Cu(txhd)$_2$ [17–20,30,31] was prepared by the dropwise addition of a solution of copper(II) chloride dihydrate (0.82 g, 4.8 mmol) to a solution of txhdH (1.70 g, 10.0 mmol) and NaOH (0.40 g, 10 mmol) in aqueous ethanol prepared according to our method [28]. The crude material was filtered, washed well with water, then sublimed at ~120°C, 0.1 mmHg. The dark blue-purple crystals of Cu(txhd)$_2$ on the cold finger were separated from a small amount of blue-green crystals of [Cu(txhd)(μ_3-OEt)]$_4$. Crystals of Cu(txhd)$_2$ suitable for X-ray diffraction analysis were obtained by recrystallization from saturated 95% ethanol solution, while the sublimed crystals of [Cu(txhd)(μ_3-OEt)]$_4$ were directly utilized for the X-ray experiments.

The complex Cu(*S*-tmhd)$_2$ was prepared according to the method of Musso and coworkers [32,33]. Crystals for X-ray diffraction studies were obtained by recrystallization from saturated 95% ethanol solution.

Calculation of Connolly Solvent-excluded Molecular Volumes

All Connolly solvent-excluded molecular volumes were calculated via the program CambridgeSoft Chem3D Ultra Version 7.0.0, using a Dell Dimension 4500 PC running Windows XP Professional. The Connolly solvent-excluded molecular volume is defined as the volume enclosed within the contact surface created by rolling a spherical probe over the molecular model [34]. The Connolly molecular surface (contact surface) represents the solvent-accessible surface.

Coordinates for the molecular models were taken from the corresponding coordinates determined by single-crystal X-ray diffraction studies. Several spherical probe sizes were tried in the calculations, ranging in diameter from 0.010 to 2.0 Å; while variation of the probe size naturally changed the calculated solvent-excluded volume, the relative sizes of the molecular volumes did not change appreciably with respect to one another. Thus, we chose to use the default diameter of 1.4 Å for the spherical probe (approximately the size of a water molecule).

X-ray Structure Determinations

X-ray data were collected at ambient temperature using a Bruker R3m diffractometer in the $\theta/2\theta$ mode for Cu(txhd)$_2$ and Cu(*S*-tmhd)$_2$ or $\omega/2\theta$ mode for [Cu(txhd)(μ_3-OEt)]$_4$ with variable scan speed (3–20 deg min^{-1}) and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Check reflections were measured every 200 reflections during data collection and gave no indication of crystal decay. Data were corrected for background, attenuators, Lorentz and polarization effects, but not for absorption, in the usual fashion [35].

Structures were solved by direct methods and refined by full-matrix least-squares procedures on $|F^2|$ with SHELXTL 97, version 6.12 [36]. All non-hydrogen atoms were refined anisotropically except for the atoms in the disordered substituents of [Cu(txhd)(μ_3-OEt)]$_4$ and Cu(*S*-tmhd)$_2$. Rotational disorder was found for the methyl groups of the *t*-Bu substituents in [Cu(txhd)(μ_3-OEt)]$_4$. A two-site disorder model for the C(5), C(6), and C(7) atoms was utilized with site occupancies of 0.60/0.40. The C(10) methyl group of the *i*-Pr substituent was distributed over two sites, which were modelled with equal site occupancies. A two-site disorder model with site occupancies of 0.60/0.40 was employed for the C(8), C(9), and C(10) atoms in a rotationally disordered *t*-Bu group of Cu(*S*-tmhd)$_2$. Hydrogen atom positions were calculated geometrically and fixed at a C–H distance of 0.96 Å and were not refined, with the exception of the hydrogen atoms of the disordered *t*-Bu and *i*-Pr substituents in [Cu(txhd)(μ_3-OEt)]$_4$ and the disordered *t*-Bu group in Cu(*S*-tmhd)$_2$, the positions of which were neither located nor set. Crystal data and further data collection parameters are summarized in Table I.

RESULTS AND DISCUSSION

Single-crystal X-ray Diffraction Studies

Cu(txhd)$_2$ has the familiar square planar geometry (Fig. 1) typically found for Cu(II) β-diketonate complexes supported by non-fluorinated ligands. Bond lengths and angles in the coordination sphere (Table II) are comparable to those found in Cu(tmhd)$_2$ (tmhd is the anion of 2,2,6,6-tetramethylheptane-3,4-dione) [37–39] and in other similar Cu(II) complexes [40–42].

The unsymmetrical substitution of the β-diketonate ligand in Cu(txhd)$_2$ allows for the possibility of geometrical isomerism. The molecules in the crystal of Cu(txhd)$_2$

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TABLE I Crystallographic data and parameters for Cu(txhd)$_2$, [Cu(txhd)(μ_3-OEt)]$_4$ and Cu(*S*-tmhd)$_2$

	Cu(txhd)$_2$	*[Cu(txhd)(μ_3-OEt)]$_4$*	*Cu(S-tmhd)$_2$*
Formula	$C_{20}H_{34}CuO_4$	$C_{48}H_{88}CuO_4$	$C_{22}H_{38}CuO_2S_2$
Formula weight	402.0	1111.3	462.2
Crystal color; habit	Dark blue; block	Blue-green; prism	Red-brown; parallelepiped
Crystal dimensions (mm)	0.30 × 0.40 × 0.40	0.35 × 0.35 × 0.50	0.40 × 0.40 × 0.50
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (No. 14)	*Fddd* (No. 70)	$P2_1/c$ (No. 14)
a (Å)	10.031(3)	14.926(4)	19.877(5)
b (Å)	9.489(3)	18.813(4)	10.326(2)
c (Å)	11.923(4)	40.938(12)	12.507(3)
β (°)	98.46(3)	90	102.43(2)
V (Å^3)	1122.5(6)	11496(5)	2506.9(10)
Z	2	8	4
$D_{\text{calc.}}$ (g cm^{-3})	1.189	1.284	1.225
μ (Mo $K\alpha$) (mm^{-1})	0.991	1.511	1.051
$F(000)$	430	4704	988
2θ max (°)	45.0	43.0	53.0
Reflections collected	1547	1622	5337
Independent reflections	1463 ($R_{\text{int}} = 6.08\%$)	1622 ($R_{\text{int}} = 0.00\%$)	5189 ($R_{\text{int}} = 2.41\%$)
Observed reflections	1115 ($F > 4.0\sigma(F)$)	849 ($F > 4.0\sigma(F)$)	3903 ($F > 4.0\sigma(F)$)
No. of parameters	115	141	271
R_1[a], wR_1[b] ($I > 2.0\sigma(I)$)	0.0475, 0.1135	0.0834, 0.2156	0.0457, 0.1213
R_1[a], wR_1[b] (all data)	0.0694, 0.1264	0.1808, 0.2954	0.0690, 0.1339
GOF[c]	1.035	1.094	1.058

[a] $R_1 = \Sigma F_o| - |F_c/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (a * P)^2 + b * P]$.

[c] $\text{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{\text{obs}} - N_{\text{params}})]^{1/2}$, based on F^2 for all data.

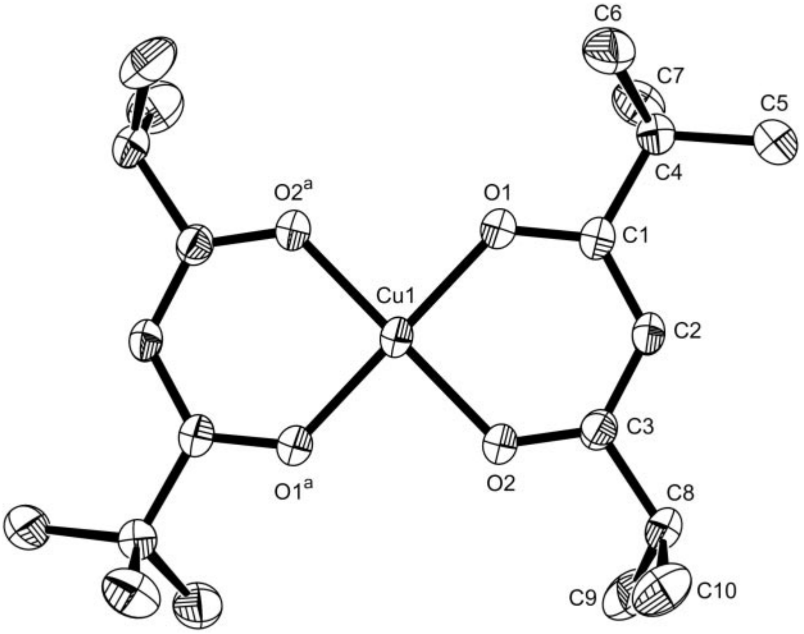

FIGURE 1 Molecular structure and atom numbering scheme for Cu(txhd)$_2$. Atoms related by the symmetry transformation ($-x$, $-y$, $-z$) are designated by '*a*'. Hydrogen atoms have been omitted for clarity.

TABLE II Selected bond lengths (Å) and angles (°) for $Cu(txhd)_2$

Cu(1)–O(1)	1.902(3)
Cu(1)–O(2)	1.902(3)
O(1)–Cu(1)–O(2)	92.9(1)
O(1)–Cu(1)–O(2a)[a]	87.1(1)
O(1)–Cu(1)–O(1a)[a]	180[b]
O(2)–Cu(1)–O(2a)[a]	180[b]

[a] Symmetry transformation ($-x$, $-y$, $-z$).
[b] Symmetry enforced.

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studied here have the *trans* geometry. Several structures of $Cu[t\text{-BuC(O)CHC(O)R}]_2$ complexes with non-fluorinated ancillary ligands are now known [37–43]. For the unsymmetrically substituted cases, both *cis* (R = *i*-Bu [40] or 1-Me-vinyl [42]) and *trans* geometries (R = *i*-Pr, Me [41], or Ph [43]) have been observed. Clearly, there does not appear to be any pattern to the geometry that one obtains in the solid state. We have argued previously that both geometrical isomers are probably present in bulk samples and that either spontaneous separation or interconversion of isomers occurs during crystallization, based upon our ability to isolate both isomers of $Cu[Me_3SiC(O)CHC(O)(n\text{-Pr})]_2$ among other circumstantial evidence [25–27].

While purifying freshly prepared $Cu(txhd)_2$ by sublimation, without any prior recrystallization, we noticed that a very small amount of blue-green crystals co-sublimed with the dark-blue crystals of the main product. X-ray diffraction revealed that the blue-green crystals contained the mixed ligand complex, $[Cu(txhd)(\mu_3\text{-OEt})]_4$.

Three structural types for $[Cu(\beta\text{-diketonate})(OR)]_n$ complexes have been identified, namely, tetramers ($n = 4$) having a cubane-like structure [44–46], tetramers ($n = 4$) with a side-slipped ladder-like structure [39,45–47], and discrete dimers ($n = 2$) [45,48]. The D_2-symmetric tetramers of $[Cu(txhd)(\mu_3\text{-OEt})]_4$ consist of two ethoxide-bridged dimers, which loosely interact via further longer range bridging of the ethoxide ligands to form the cubane-like core (Fig. 2). The structure is isomorphous with that of $[Cu(tmhd)(\mu_3\text{-OEt})]_4$ [44], with a likewise disordered *t*-Bu substituent in the β-diketonate ligand; one of the Me groups of the *i*-Pr substituent in $[Cu(txhd)(\mu_3\text{-OEt})]_4$ is disordered amongst two of the sites occupied by Me groups of the other *t*-Bu substituent of $[Cu(tmhd)(\mu_3\text{-OEt})]_4$ [44]. Consequently, bond lengths and angles for $[Cu(txhd)(\mu_3\text{-OEt})]_4$ (Table III) are entirely analogous to those of $[Cu(tmhd)(\mu_3\text{-OEt})]_4$ and will not be discussed further.

It is tempting to speculate on the origin of the small $[Cu(txhd)(\mu_3\text{-OEt})]_4$ impurity in the bulk $Cu(txhd)_2$ sample. Ternary Cu(II) β-diketonate/alkoxide complexes such as $[Cu(tmhd)(\mu_3\text{-OEt})]_4$ are readily prepared by the action of NaOEt on the homoleptic Cu(II) β-diketonate complex in ethanol solution [44]. On the other hand, the action of NaOH on $Cu(acac)_2$ in methanolic solution produced $[Cu(acac)(OMe)]_2$ [49]. Thus, the appearance of very small amounts of $[Cu(txhd)(\mu_3\text{-OEt})]_4$ in our $Cu(txhd)_2$ samples may be due to a slight excess of base being present during the preparation. The amount of impurity is quite small and can be removed by recrystallization; we only noticed its presence because we directly sublimed the isolated material and because the impurity has comparable volatility to the desired $Cu(txhd)_2$.

$Cu(S\text{-tmhd})_2$ represents the first structural determination, to our knowledge, of a Cu(II) monothio-β-diketonate complex. The structure is isomorphous to that of $Ni(S\text{-tmhd})_2$ [50], but is of considerably higher precision. The general geometry is slightly distorted square planar (Fig. 3), with the two sulfur atoms situated at *cis*

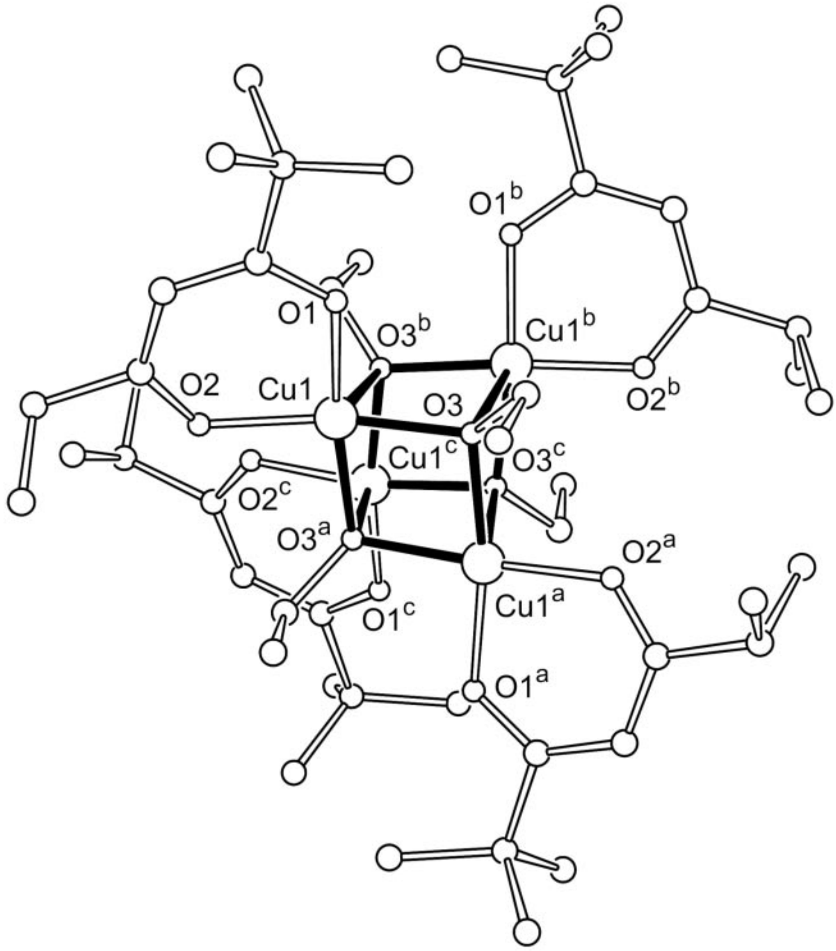

FIGURE 2 Pluto molecular structure and atom numbering scheme for the inner coordination core of [Cu(txhd)(μ_3-OEt)]$_4$. Atoms related by the symmetry transformations $(1.25-x,\ y,\ 0.25-z)$, $(x,\ 1.25-y,\ 0.25-z)$, and $(1.25-x,\ 1.25-y,\ z)$ are designated by '*a*', '*b*', and '*c*', respectively. For the disordered side groups, only the positions of higher site occupancy are shown. Hydrogen atoms have been omitted for clarity.

positions. This is the stereochemistry that is assumed in all the known structures of square-planar bis(monothio-β-diketonate) complexes of Ni(II) [50–53] and Pd(II) [54,55], and presumbly arises from an electronic *trans* influence of the sulfur atoms.

The Cu–S and Cu–O bonds in Cu(*S*-tmhd)$_2$ (Table IV) are *ca.* 0.08 Å longer than those in the Ni analog, in accord with the larger ionic radius of Cu(II) *vs.* Ni(II) [56]. The Cu–O bonds are *ca.* 0.03–0.04 Å *longer* than those found in Cu(txhd)$_2$ and similar Cu(II) β-diketonate complexes [37–42], while the Cu–S bonds are *ca.* 0.03 to 0.06 Å *shorter* than those found on average in homoleptic Cu(II) dialkyldithiocarbamate complexes [57,58]. These observations probably reflect the relative *trans* influences of the opposing atoms.

While the bite angles of the ligands in Cu(*S*-tmhd)$_2$ are comparable to those reported for Cu(tmhd)$_2$ [37–39], the interligand S–Cu–S angle is somewhat larger

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TABLE III Selected bond lengths (Å) and angles (°) for $[Cu(txhd)(\mu_3\text{-OEt})]_4$

Cu(1)–O(1)	1.917(11)
Cu(1)–O(2)	1.944(10)
Cu(1)–O(3)	1.936(9)
Cu(1)–O(3a)[a]	1.941(9)
Cu(1)–O(3b)[b]	2.370(10)
O(1)–Cu(1)–O(2)	92.7(5)
O(1)–Cu(1)–O(3)	93.1(4)
O(1)–Cu(1)–O(3a)[a]	170.3(5)
O(1)–Cu(1)–O(3b)[b]	103.2(4)
O(2)–Cu(1)–O(3)	169.8(5)
O(2)–Cu(1)–O(3a)[a]	94.1(4)
O(2)–Cu(1)–O(3b)[b]	106.0(4)
O(3)–Cu(1)–O(3a)[a]	79.2(4)
O(3)–Cu(1)–O(3b)[b]	80.8(4)
O(3a)–Cu(1)–O(3b)[a,b]	81.6(4)
Cu(1)–O(3)–Cu(1a)[a]	100.2(4)
Cu(1)–O(3)–Cu(1b)[b]	98.5(4)
Cu(1a)–O(3)–Cu(1b)[a,b]	97.5(4)

[a] Symmetry transformation ($1.25 - x$, y, $0.25 - z$).
[b] Symmetry transformation (x, $1.25 - y$, $0.25 - z$).

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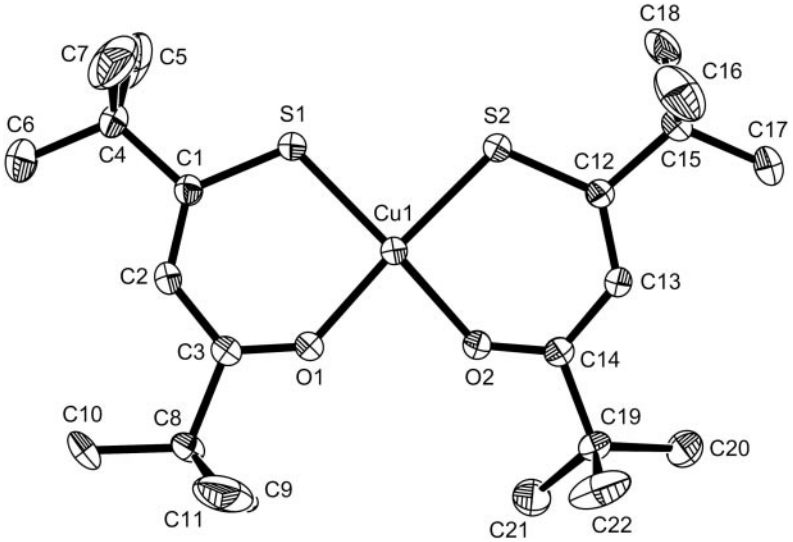

FIGURE 3 Molecular structure and atom numbering scheme for Cu(*S*-tmhd)$_2$. For the disordered *t*-Bu substituent, only the positions of higher site occupancy are shown. Hydrogen atoms have been omitted for clarity.

(*ca.* 2.5°) than, and the interligand O–Cu–O angle is somewhat smaller (*ca.* 3.0°) than, the corresponding interligand O–Cu–O angles in the Cu(II) β-diketonate analog. This effect appears to be a direct result of the large difference in Cu–S and Cu–O bond lengths in Cu(*S*-tmhd)$_2$. The dihedral angle between the planes of the nearly planar chelate rings is 11.6(1)°, while Cu(tmhd)$_2$ has crystallographically imposed planarity [37–39]. Thus, the chelate rings of Cu(*S*-tmhd)$_2$ are slightly twisted with respect to one another, probably in response to solid-state packing requirements [25].

TABLE IV Selected bond lengths (Å) and angles (°) for Cu(*S*-tmhd)$_2$

Cu(1)–S(1)	2.2163(9)
Cu(1)–S(2)	2.2166(10)
Cu(1)–O(1)	1.934(2)
Cu(1)–O(2)	1.927(2)
S(1)–Cu(1)–S(2)	89.24(4)
S(1)–Cu(1)–O(1)	94.07(7)
S(1)–Cu(1)–O(2)	174.00(8)
S(2)–Cu(1)–O(1)	173.81(9)
S(2)–Cu(1)–O(2)	93.70(7)
O(1)–Cu(1)–O(2)	83.49(9)

TABLE V Calculated molecular volumes and packing densities (α) for selected Cu(II) β-diketonate complexes, CuL$_2$

Ligand (*L*)	$V_{molecule}$[a] (Å)^3	Z[b]	$V_{unit\ cell}$[c] (Å)^3	α[d]	*Ref.*
MeC(O)CHC(O)Me	167	2	547	0.611	[59]
MeC(O)CHC(O)(*t*-Bu)	261	4	1732	0.603	[41]
(*i*-Pr)C(O)CHC(O)(*t*-Bu)	329	2	1123	0.586	This work
(*i*-Bu)C(O)CHC(O)(*t*-Bu)	362	4	2435	0.595	[40]
(1-MeVi)C(O)CHC(O)(*t*-Bu)[e]	305	2	1087	0.561	[42]
(*t*-Bu)C(O)CHC(O)(*t*-Bu)	366	2	1190	0.615	[37]
(*t*-Bu)C(S)CHC(O)(*t*-Bu)	386	4	2507	0.616	This work

[a] Calculated Connolly solvent-excluded molecular volume.
[b] Number of molecules in the unit cell.
[c] Volume of the unit cell.
[d] Packing density or efficiency, calculated as described in the text.
[e] 1-MeVi = 1-methylvinyl (1-propenyl).

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Comparisons of Solid-state Packing Efficiencies

Troyanov *et al.* [41] have examined the packing efficiencies of Me and *t*-Bu substituted Cu(II) β-diketonate complexes using approximate molecular volumes based upon van der Waals radii in order to assess differences in volatility. We have extended this approach to the study of Cu(II) complexes containing trialkylsilyl- [25] and fluorine-substituted [26] β-diketonate ligands by utilizing calculations based on solvent-excluded molecular volumes derived from the Connolly surfaces of the molecules [34].

Only modest gains in volatility are realized as the steric bulk of R is increased in the complexes, Cu[*t*-BuC(O)CHC(O)R]$_2$ [25,42]; however, these complexes are considerably more volatile than Cu(acac)$_2$. In Table V we present the results of our analysis of molecular packing densities (α) for Cu(acac)$_2$ and several *t*-Bu substituted Cu(II) β-diketonate complexes, where α is defined as the product of the Connolly solvent-excluded molecular volume times the number of molecules in the unit cell, divided by the volume of the unit cell. As we have found previously, the α values decrease slightly within the series of complexes Cu[*t*-BuC(O)CHC(O)R]$_2$ as the bulk of R increases (though $R = t$-Bu seems not to follow this trend) [25]. We note that the complex with $R =$ 1-methylvinyl (1-propenyl) has a significantly lower α value, probably due to the flat, rigid vinylic substituent, the plane of which coincides with the plane of the chelate ligand [42]. There are correspondingly small differences in volatility in this series, since the volatilities of these compounds probably depend in a complex manner on various factors such as molecular weight, packing pattern, intermolecular and intramolecular contacts and repulsions (including ring stacking and interactions between alkyl side chains), among other properties.

We decided to look more closely at the solid-state packing patterns for the complexes listed in Table V. For Cu(acac)$_2$, the molecules pack in infinite staggered chains parallel to the *b* axis [59]. Within the chains, alternating chelate rings of neighboring molecules stack with a separation of only 3.14 Å. The only other complex in Table V that has a ring stacking interaction is Cu[*t*-BuC(O)CHC(O)Me]$_2$, where the distance between ring centroids along the *a* axis is 3.47 Å [41]. The main intermolecular interactions for the remainder of the listed molecules, with larger peripheral substituents than Me, are of the van der Waals type, including relatively long-range contacts between alkyl substituents and between the Cu centers and peripheral C–H groups. The ring-stacking distance for Cu(acac)$_2$ is considerably shorter than those observed for any Cu(II) β-diketonate complex [25] and probably contributes to the lower volatility observed for this complex.

SUMMARY

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The solid-state structure of Cu(txhd)$_2$ has been determined. Cu(txhd)$_2$ is a typical square-planar Cu(II) β-diketonate complex, that has *trans* geometry in the crystals studied. Analysis of α values suggests that there is a slight decrease in packing efficiency as the steric bulk of R increases for Cu[*t*-BuC(O)CHC(O)R]$_2$ complexes; however, the effect is small. The low volatility for Cu(acac)$_2$ appears to originate from very close ring-stacking interactions in the solid state, which are either not present or greatly attenuated as the size of the peripheral substituents in the ancillary ligands increases.

The complex [Cu(txhd)(μ_3-OEt)]$_4$ was isolated by sublimation of freshly prepared Cu(txhd)$_2$. The tetrameric complex apparently co-sublimed, either as the tetramer or dimer, with the desired homoleptic Cu(II) complex. The tetrameric core is cubane-like and the structure was isomorphous to the known [Cu(tmhd)(μ_3-OEt)]$_4$ [44]. While Cu(II) and Cu(I) alkoxide complexes have been utilized in CVD processes [1,3,5], this type of mixed alkoxide/β-diketonate complex has not. The present studies indicate that the volatilities of this class of complex are adequate for CVD work; further increases in volatility might be possible by incorporation of fluorinated substituents [45] or by variation of the core structure by judicious choice of peripheral substituents on the ligands [44].

Finally, the first structure of a homoleptic, monothio-β-diketonate Cu(II) complex was determined, namely Cu(*S*-tmhd)$_2$. The complex is essentially square planar, with the sulfur atoms situated in *cis* positions. The angles around the Cu center are slightly distorted, owing to the significant difference in bond lengths of Cu–S *vs.* Cu–O bonds. Significant *trans* influences on bond lengths in the coordination sphere were apparent.

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Supplementary Data

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 204903 for Cu(txhd)$_2$, No. 204904 for [Cu(txhd)(μ_3-OEt)]$_4$ and No. 204905 for Cu(S-tmhd)$_2$. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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