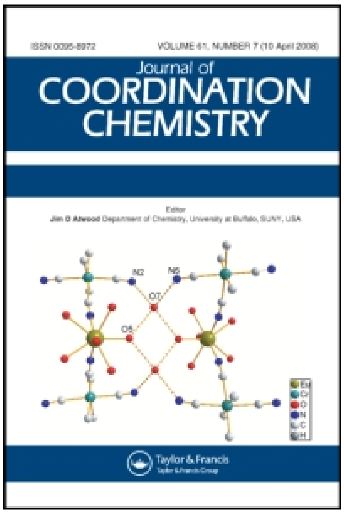

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STRUCTURAL STUDIES OF THE COPPER(II) ACETATE COMPLEXES $Cu(O_2CCH_3)_2(pyridine)_3$ AND $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$

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$[Cu(O_2CCH_3)_2]_2$, **1**, reacts with pyridine to form violet-blue $Cu(O_2CCH_3)_2(pyridine)_3$, **2**, in $> 90\%$ yield. **2** crystallizes from pyridine with a distorted square-pyramidal geometry around copper with the monodentate acetate ligands located diagonally in the basal positions. **1** reacts with $Bi(OCMe_3)_3$ in THF to form blue $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, **3**. **3** crystallizes from THF/hexanes with a hexagon of copper atoms linked by six doubly-bridging tert-butoxide ligands, four doubly-bridging bidentate acetates, and two quadruply-bridging bidentate acetate ligands.

Keywords: Copper(II); square-pyramidal; acetate; hexacopper; alkoxide

INTRODUCTION

A synthetic challenge in inorganic chemistry is to synthesize molecular complexes containing specific combinations of different metals.[1–4] These complexes have the potential to be precursors to a wide variety of mixed-metal materials of great practical importance. The discovery that copper-containing mixed-metal oxides such as $YBa_2Cu_3O_{7-x}$ are superconducting at temperatures above 90 K[5–7] has stimulated considerable

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interest in developing new methods to introduce copper into heteropolymetallic systems. We report here the synthesis and structure of two copper acetate complexes that may be of interest in this regard. Both arise directly from a readily available copper(II) precursor $[Cu(O_2CCH_3)_2]_2$, **1**, and both have ligands suitable for bridging to other metals. The chemistry of one of these systems was reported earlier but no structural data were included.[8]

EXPERIMENTAL

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line and glove box techniques. Anhydrous $[Cu(O_2CCH_3)_2]_2$, was obtained from Alfa and used without purification. $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, **3**, was prepared as previously described.[8] Pyridine (Aldrich) was dried and distilled from CaH_2. THF was dried and degassed as previously described.[9] Infrared spectra were obtained on a Perkin Elmer 1600 FT-IR spectrometer. Elemental analyses were done by Analytische Laboratorien, D-51779 Lindlar, Germany.

$Cu(O_2CCH_3)_2(pyridine)_3$, 2

On a Schlenk line, pyridine (50 mL) was added *via* cannula to dark blue-green $[Cu(O_2CCH_3)_2]_2$, **1** (1.00 g, 2.8 mmol). The suspension was stirred for 20 min producing a violet-blue colored solution and small violet-blue crystals. The solvent was removed *in vacuo* yielding violet-blue $Cu(O_2CCH_3)_2$ $(pyridine)_3$, **2** (1.09 g, 93%), which was identified by X-ray crystallography. *Anal.* Calcd. for $C_{19}H_{21}N_3O_4Cu$: C, 41.45; H, 4.26; N, 5.37; Cu, 24.37. Found: C, 41.62; H, 4.17; N, 5.32; Cu, 24.20. IR (KBr): 3068(w), 2964(w), 2923(w), 1740(w), 1623(s), 1442(s), 1323(w), 1256(w), 1215(m), 1149(w), 1072(w), 1036(m), 1010(m), 763(w), 704(m), 682(m), 626(w) cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $Cu(O_2CCH_3)_2(pyridine)_3$, 2

A violet-blue crystal of approximate dimensions 0.20 × 0.20 × 0.32 mm was mounted on a glass fiber and transferred to the Siemens R3m/V diffractometer which is equipped with a modified LT-1 apparatus. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard procedures similar to Churchill.[10] Intensity data were collected at 183 K using a θ–2θ scan technique with MoKα radiation under the conditions described in Table I. All 1345 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/m with systematic absences *hkl* for $h+k=2n+1$. The centrosymmetric monoclinic space group C2/c was later determined to be correct.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[11] or the SHELXTL PLUS program set.[12] The analytical scattering factors for

TABLE I Experimental data for the X-ray diffraction study for $Cu(O_2CCH_3)_2(pyridine)_3$, **2**, and $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, **3**

Compound	**2**	**3**
Formula	$C_{19}H_{21}N_3O_4Cu$	$C_{36}H_{72}O_{18}Cu_6$
Fw	418.9	1174.2
Temperature (K)	183	183
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$
a (Å)	12.658(2)	13.149(2)
b (Å)	9.8146(16)	9.7566(15)
c (Å)	16.055(3)	19.535(3)
β (deg)	105.234(12)	90.580(11)
V (Å^3)	1924.5(5)	2506.0(6)
Z	4	2
D_{calcd} (Mg/m^3)	1.446	1.556
Diffractometer	Siemens R3m/V	Syntex $P2_1$
Data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
Index ranges	$0\leq h\leq 13$, $0\leq k\leq 10$, $-17\leq l\leq 16$	$0\leq h\leq 14$, $0\leq k\leq 10$, $-21\leq l\leq 21$
Scan type	θ–2θ	θ–2θ
Scan width, in ω	1.2°	1.2°
Scan speed, in ω (deg min^{-1})	2.0	3.0
2θ range (deg)	4.0–45.0	4.0–45.0
μ(Mo Kα) (mm^{-1})	1.164	2.57
Reflections collected	1345	3468
Independent reflections ($\lvert F_0\rvert > 0$)	1220	3027
No. of variables	124	272
Refinement	$R_F=3.4\%$; $R_{wF}=3.8\%$ for data $\lvert F_0\rvert > 3.0\sigma\lvert F_0\rvert$	$R_F=3.4\%$; $R_{wF}=5.1\%$ for data $\lvert F_0\rvert > 6.0\sigma\lvert F_0\rvert$
Refinement (all data)	$R_F=4.0\%$; $R_{wF}=4.5\%$	$R_F=5.2\%$; $R_{wF}=6.1\%$
Goodness of fit	1.64	1.01

Radiation: Mo Kα ($\lambda=0.710730$ Å); Monochromator: highly oriented graphite; Absorption correction: semi-empirical (ψ-scan method); $R_F=[\sum\lVert F_0\rvert-\lvert F_c\rVert/\sum\lvert F_0\rvert]$; $R_{wF}=[\sum w(\lVert F_0\rvert-\lvert F_c\rVert)/\sum w\lvert F_0\rvert]$.

neutral atoms were used throughout the analysis,[13] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(F_0 - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0020F^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(\text{C–H}) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2. The molecule is located on a two-fold rotation axis. Refinement of positional and thermal parameters led to convergence with $R_F = 3.4\%$; $R_{wF} = 3.8\%$ and GOF = 1.64 for 124 variables refined against those 1123 data with $F > 3.0\sigma(F)$. A final difference-Fourier synthesis yielded $\rho(\max) = 0.25$ eÅ^{-3}.

X-ray Data Collection, Structure Determination, and Refinement for $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, 3

A bright blue crystal of approximate dimensions 0.18 × 0.20 × 0.22 mm was handled at 183 K on a Syntex P2 diffractometer as described for **2**. Details appear in Table I. All 3468 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_0| = 0$. A careful examination of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n+1$ and $h0l$ for $h+1 = 2n+1$; the diffraction symmetry was 2/m. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ [C_{2h}^5; No. 14], is thus uniquely defined.

All crystallographic calculations were carried out as for **2**. The quantity minimized during least-squares analysis was $\sum w(|F_0| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_0|) + 0.0020(|F_0|)^2$. The structure was solved by direct methods (SHELXTL PLUS); and refined by full-matrix least-squares techniques. The molecule lies on an inversion center. Hydrogen atom contributions were included using a riding model with $d(\text{C–H}) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2. Refinement of positional and anisotropic thermal parameters led to convergence with $R_F = 5.2\%$, $R_{wF} = 6.1\%$ and GOF = 1.01 for 272 variables refined against all 3027 unique data, ($R_F = 3.4\%$; $R_{wF} = 5.1\%$ for those 2370 data with $|F_0| > 6.0\sigma(|F_0|)$). A final difference-Fourier map was devoid of significant features, $\rho(\max) = 0.49$ eA^{-3}. The details of the structures of **2** and **3** are given in Tables II–V.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^4$) for $Cu(O_2CCH_3)_2(pyridine)_3$, **2**

	x	*y*	*z*	*U* (eq)*
Cu(1)	5000	2404(1)	2500	254(2)
O(1)	6483(2)	2475(2)	3260(1)	309(8)
O(2)	6487(2)	207(3)	3312(2)	446(11)
N(1)	4420(2)	2050(3)	3558(2)	272(10)
N(2)	5000	4745(4)	2500	283(14)
C(1)	4523(3)	2980(4)	4180(2)	393(14)
C(2)	4189(3)	2760(4)	4918(2)	432(14)
C(3)	3738(3)	1536(4)	5038(2)	405(15)
C(4)	3638(3)	577(4)	4404(3)	501(17)
C(5)	3977(3)	863(4)	3676(2)	428(15)
C(6)	5939(3)	5455(3)	2738(2)	369(14)
C(7)	5968(3)	6864(4)	2741(2)	429(15)
C(8)	5000	7575(5)	2500	432(21)
C(9)	6912(3)	1320(4)	3531(2)	328(14)
C(10)	8024(3)	1399(4)	4177(2)	479(16)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^4$) for $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, **3**

	x	*y*	*z*	*U* (eq)*
Cu(1)	7017.6(.5)	377.1(.7)	5420.0(.3)	233(3)
Cu(2)	5552.6(.5)	−737.0(.8)	6439.1(.3)	230(3)
Cu(3)	3341.8(.5)	1245.3(.8)	6074.9(.3)	239(3)
O(1)	5615(3)	1002(4)	5899(2)	227(13)
O(2)	6965(3)	−697(4)	6236(2)	242(13)
O(3)	8079(3)	−655(4)	4948(2)	290(14)
O(4)	7073(3)	1914(4)	4822(2)	252(13)
O(5)	4218(3)	−435(4)	6763(2)	293(14)
O(6)	5844(3)	−406(5)	4598(2)	293(15)
O(7)	5465(3)	−2672(5)	6648(2)	376(16)
O(8)	3849(3)	−3045(4)	6353(2)	355(15)
O(9)	2236(3)	92(5)	6146(2)	312(14)
C(1)	7804(5)	2975(7)	4972(3)	347(22)
C(2)	8103(6)	2857(7)	5725(3)	408(24)
C(3)	8745(6)	2771(9)	4530(4)	625(33)
C(4)	7338(7)	4381(7)	4839(4)	568(30)
C(5)	4006(5)	181(6)	7407(3)	272(20)
C(6)	4913(5)	−67(8)	7881(3)	429(25)
C(7)	3075(6)	−430(9)	7698(3)	512(29)
C(8)	3883(8)	1697(7)	7291(4)	615(32)
C(9)	4676(5)	−3400(7)	6615(3)	300(22)
C(10)	4748(6)	−4811(7)	6901(4)	438(25)
C(11)	7770(5)	−1534(7)	6552(3)	291(21)
C(12)	8762(5)	−754(8)	6483(3)	383(23)
C(13)	7525(6)	−1699(8)	7301(3)	431(25)
C(14)	7812(6)	−2915(7)	6197(3)	415(25)
C(15)	8224(5)	−723(7)	4317(3)	285(21)
C(16)	9042(6)	−1729(8)	4098(4)	465(26)
C(17)	4810(5)	1273(7)	5524(3)	274(21)
C(18)	4713(6)	2679(7)	5259(3)	388(23)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE IV Interatomic distances (Å) and angles (Deg.) for Cu(O$_2$CCH$_3$)$_2$(pyridine)$_3$, **2**

Cu(1)–O(1)	1.952(2)	Cu(1)–N(1)	2.049(3)
Cu(1)–N(2)	2.298(4)	Cu(1)· ·O(2)	2.933
O(1)–C(9)	1.283(4)	O(2)–C(9)	1.227(4)
N(1)–C(1)	1.334(4)	N(1)–C(5)	1.327(5)
N(2)–C(6)	1.344(4)	C(1)–C(2)	1.376(6)
C(2)–C(3)	1.365(5)	C(3)–C(4)	1.368(5)
C(4)–C(5)	1.376(6)	C(6)–C(7)	1.383(5)
C(7)–C(8)	1.374(5)	C(9)–C(10)	1.516(5)
O(1)–Cu(1)–N(1)	89.1(1)	O(1)–Cu(1)–N(2)	88.0(1)
N(1)–Cu(1)–N(2)	99.8(1)	O(1)–Cu(1)–O(1′)	175.9(1)
N(1)–Cu(1)–O(1′)	91.6(1)	N(1)–Cu(1)–N(1′)	160.4(2)
O(1)–Cu(1)· ·O(2)	49.4	O(1)–Cu(1)· ·O(2′)	134.7
N(1)–Cu(1)· ·O(2)	80.5	N(1)–Cu(1)· ·O(2′)	85.1
N(2)–Cu(1)· ·O(2)	137.3	O(2)· ·Cu(1)· ·O(2′)	85.4
Cu(1)–O(1)–C(9)	115.6(2)	Cu(1)–N(1)–C(1)	121.2(2)
Cu(1)–N(1)–C(5)	121.6(2)	C(1)–N(1)–C(5)	117.1(3)
Cu(1)–N(2)–C(6)	121.3(2)	C(6)–N(2)–C(6′)	117.5(4)
N(1)–C(1)–C(2)	123.1(3)	C(1)–C(2)–C(3)	119.6(3)
C(2)–C(3)–C(4)	117.4(4)	C(3)–C(4)–C(5)	120.2(4)
N(1)–C(5)–C(4)	122.6(3)	N(2)–C(6)–C(7)	122.7(3)
C(6)–C(7)–C(8)	119.1(4)	C(7)–C(8)–C(7′)	118.9(5)
O(1)–C(9)–O(2)	125.1(3)	O(1)–C(9)–C(10)	114.9(3)
O(2)–C(9)–C(10)	120.0(3)		

TABLE V Interatomic distances (Å) and Angles (Deg.) for Cu$_6$(μ-O$_2$CCH$_3$)$_4$(μ_4-O$_2$CCH$_3$)$_2$(μ-OCMe$_3$)$_6$, **3**

Cu(1)· ·Cu(2)	2.989	Cu(2)· ·Cu(3)	3.027	Cu(1)· ·Cu(3′)	3.073
Cu(1)–O(1)	2.164(4)	Cu(1)–O(2)	1.910(4)	Cu(1)–O(3)	1.959(4)
Cu(1)–O(4)	1.903(4)	Cu(1)–O(6)	2.344(4)	Cu(2)–O(1)	2.001(4)
Cu(2)–O(2)	1.904(4)	Cu(2)–O(5)	1.895(4)	Cu(2)–O(7)	1.935(5)
Cu(3)–O(5)	1.930(4)	Cu(3)–O(8)	1.954(4)	Cu(3)–O(9)	1.960(4)
Cu(3)–O(4′)	1.942(4)	Cu(3)–O(6′)	2.345(4)	O(3)–C(15)	1.252(7)
O(1)–C(17)	1.308(7)	O(2)–C(11)	1.468(7)		
O(4)–C(1)	1.441(8)	O(5)–C(5)	1.425(7)	O(6)–C(17′)	1.228(8)
O(7)–C(9)	1.259(8)	O(8)–C(9)	1.246(8)	O(9)–C(15′)	1.245(7)
C(1)–C(2)	1.523(9)	C(1)–C(3)	1.529(11)	C(1)–C(4)	1.524(10)
C(5)–C(6)	1.521(9)	C(5)–C(7)	1.481(10)	C(5)–C(8)	1.504(10)
C(9)–C(10)	1.488(9)	C(11)–C(12)	1.518(9)	C(11)–C(13)	1.510(9)
C(11)–C(14)	1.517(9)	C(15)–C(16)	1.520(10)	C(17)–C(18)	1.472(9)

O(1)–Cu(1)–O(2)	75.9(2)	O(1)–Cu(1)–O(3)	164.3(2)
O(2)–Cu(1)–O(3)	98.2(2)	O(1)–Cu(1)–O(4)	94.7(2)
O(2)–Cu(1)–O(4)	161.3(2)	O(3)–Cu(1)–O(4)	94.8(2)
O(1)–Cu(1)–O(6)	80.2(1)	O(2)–Cu(1)–O(6)	111.3(2)
O(3)–Cu(1)–O(6)	88.7(2)	O(4)–Cu(1)–O(6)	82.2(2)
O(1)–Cu(2)–O(2)	80.1(2)	O(1)–Cu(2)–O(5)	95.0(2)
O(2)–Cu(2)–O(5)	167.3(2)	O(1)–Cu(2)–O(7)	160.3(2)
O(2)–Cu(2)–O(7)	97.1(2)	O(5)–Cu(2)–O(7)	91.4(2)
O(S)–Cu(3)–O(8)	88.6(2)	O(5)–Cu(3)–O(9)	96.6(2)
O(8)–Cu(3)–O(9)	146.1(2)	O(5)–Cu(3)–O(4′)	157.8(2)
O(8)–Cu(3)–O(4′)	92.3(2)	O(9)–Cu(3)–O(4′)	94.9(2)
O(S)–Cu(3)–O(6′)	80.6(2)	O(8)–Cu(3)–O(6′)	128.1(2)
O(9)–Cu(3)–O(6)	85.7(2)	O(4′)–Cu(3)–O(6′)	81.4(2)

TABLE V (*Continued*)

Cu(1)–O(1)–Cu(2)	91.6(2)	Cu(1)–O(1)–C(17)	120.2(3)
Cu(2)–O(1)–C(17)	115.4(4)	Cu(1)–O(2)–Cu(2)	103.2(2)
Cu(1)–O(2)–C(11)	128.7(3)	Cu(2)–O(2)–C(11)	127.0(3)
Cu(1)–O(3)–C(15)	127.4(4)	Cu(1)–O(4)–C(1)	118.1(3)
Cu(1)–O(4)–Cu(3′)	106.1(2)	C(1)–O(4)–Cu(3′)	127.3(3)
Cu(2)–O(5)–Cu(3)	104.6(2)	Cu(2)–O(5)–C(5)	123.4(4)
Cu(3)–O(S)–C(S)	131.9(4)	Cu(1)–O(6)–Cu(3′)	81.9(1)
Cu(1)–O(6)–C(17′)	144.3(4)	Cu(3′)–O(6)–C(17′)	133.5(4)
Cu(2)–O(7)–C(9)	126.2(4)	Cu(3)–O(8)–C(9)	131.2(4)
Cu(3)–O(9)–C(15′)	129.3(4)		
O(4)–C(1)–C(2)	108.0(5)	O(4)–C(1)–C(3)	109.5(6)
C(2)–C(1)–C(3)	109.4(6)	O(4)–C(1)–C(4)	110.2(6)
C(2)–C(1)–C(4)	109.4(6)	C(3)–C(1)–C(4)	110.3(6)
O(5)–C(5)–C(6)	108.2(5)	O(5)–C(5)–C(7)	109.8(5)
C(6)–C(5)–C(7)	110.3(5)	O(5)–C(5)–C(8)	107.7(5)
C(6)–C(5)–C(8)	109.3(6)	C(7)–C(5)–C(8)	111.4(6)
O(7)–C(9)–O(8)	125.4(6)	O(7)–C(9)–C(10)	117.0(6)
O(8)–C(9)–C(10)	117.6(6)	O(2)–C(11)–C(12)	107.5(5)
O(2)–C(11)–C(13)	107.9(5)	C(12)–C(11)–C(13)	109.4(5)
O(2)–C(11)–C(14)	109.3(5)	C(12)–C(11)–C(14)	111.7(5)
C(13)–C(11)–C(14)	111.0(6)	O(3)–C(15)–C(16)	115.3(6)
O(3)–C(15)–O(9′)	127.7(6)	C(16)–C(15)–O(9′)	117.0(6)
O(1)–C(17)–C(18)	116.9(6)	O(1)–C(17)–O(6′)	122.1(6)
C(18)–C(17)–O(6′)	121.0(6)		

RESULTS AND DISCUSSION

$Cu(O_2CCH_3)_2(pyridine)_3$, 2

Copper acetate dissolves in pyridine to form a violet-blue solution. $Cu(O_2CCH_3)_2(pyridine)_3$, **2**, can be isolated in greater than 90% yield as violet-blue crystals by recrystallization from pyridine and was characterized by elemental analysis, infrared spectrocopy, and X-ray diffraction. Monometallic **2** contrasts with the bimetallic monopyridine copper acetate complexes $[Cu(O_2CCH_3)_2(pyridine)]_2$, **4**,[14,15] whose structures were reported without any preparative details as dark green crystals in both monoclinic and orthorhombic space groups.[14,15] Loss of two pyridine ligands per copper atom in **2** could generate the bimetallic complexes **4**.

The structure of **2**, which has molecular C_{2v} symmetry, is shown in Figure 1. The copper atom is in a square-pyramidal coordination environment, which is common for five-coordinate Cu(II).[16] The two acetate ligands occupy *trans* basal positions as monodentate ligands. The square-pyramidal structure in **2** is similar to that in $[Cu(OCH_2CH^{i}_{2}Pr)(O_2CCH_3)]_4$,[17] $Cu(O_2CCH_2OC_6H_5)_2(H_2O)_3$,[18] and $CuCl(PhCO_2)(pyridine)_2$,[19] and to both the orthorhombic and monoclinic forms of **4**.[14,15] The (donor atom)–Cu–(donor atom) angle for the atoms in the *trans* basal

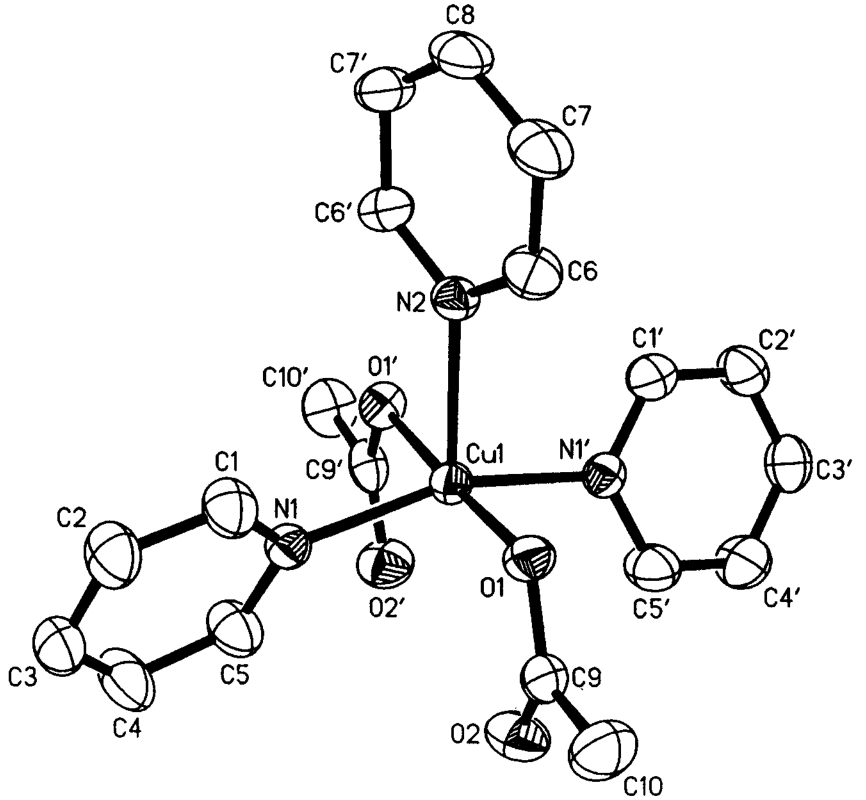

FIGURE 1 Thermal ellipsoid plot of $Cu(O_2CCH_3)_2(pyridine)_3$, **2**, drawn at the 40% probability level.

positions is larger for the acetates, 175.9(1)°, than for the pyridines, 160.4(2)°. Correspondingly, the 88.0(1)° N(2)–Cu–O(1) angle is smaller than the 99.8(1)° N(2)–Cu–N(1) angle.

As is typical with square-pyramidal Cu(II) complexes, the axial Cu(1)–N(2) distance in **2**, 2.298(4) Å, is significantly larger than the Cu(1)–N(1) basal distance, 2.049(3) Å.[16,20] The axial Cu(1)–N(2) distance in **2** is also significantly larger than the distances of 2.186(8) and 2.126(4) Å found in the orthorhombic and monoclinic forms of **4**, respectively.[14,15] The Cu–O bond distance, 1.952(2) Å, is in the 1.955(8)–2.03(1) Å range which is typical for Cu(II) acetate complexes.[17] The other oxygen atom of each acetate ligand is not coordinated to copper: the Cu(1) ⋯ O(2) distance is 2.933 Å.

Hence, isolation of crystalline **2** before loss of pyridine to form **4** provides a monometallic complex with two monohapto acetate groups. This leaves two pendant oxygen donor atoms which could complex an additional metal. Indeed, in the absence of other reagents, these oxygen atoms apparently displace pyridine from another copper complex to form bimetallic **4**.

$Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, 3

In an attempt to make a mixed-metal bismuth–copper complex, $Bi(OCMe_3)_3$ was added to anhydrous $[Cu(O_2CMe)_2]_2$ in THF. This system proved to be complicated,[8] but single crystals of the unusual hexametallic copper(II) alkoxide acetate complex, $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, **3**, shown in Figures 2 and 3, were isolated. Since structural details were not previously reported, they are described here.

The six copper atoms of **3** are planar to within 0.01 Å and form a hexagon with 2.989, 3.027, and 3.073 Å Cu···Cu distances. The copper atoms are connected by six doubly-bridging tert-butoxide ligands, four

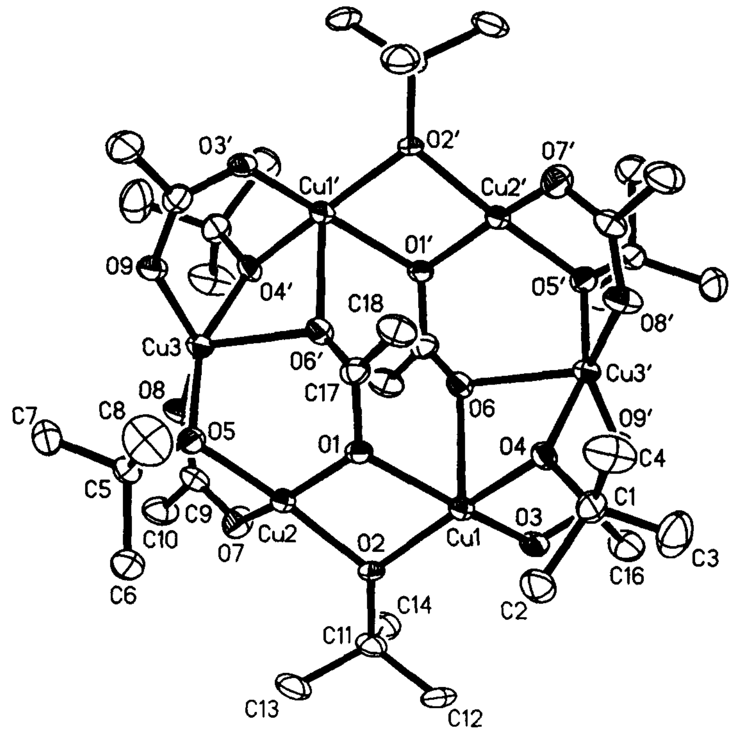

FIGURE 2 Thermal ellipsoid plot of $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, **3**, drawn at the 40% probability level.

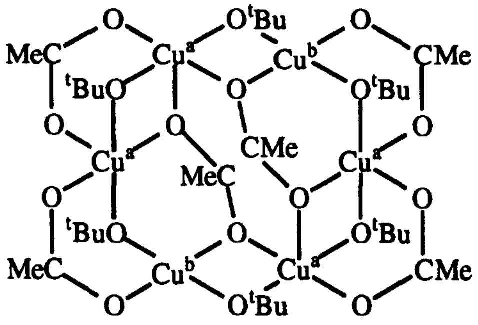

FIGURE 3 The molecular structure of $Cu_6(\mu\text{-}O_2CCH_3)_4(\mu_4\text{-}O_2CCH_3)_2(\mu\text{-}OCMe_3)_6$, **3**.

doubly-bridging bidentate acetate groups, and two quadruply-bridging bidentate acetate ligands. Four of the copper sites are surrounded by five oxygen atoms which have very distorted square-pyramidal geometries [$Cu^a = Cu(1), Cu(1'), Cu(3), Cu(3')$]. The remaining two copper sites are ligated by four oxygen atoms which have an irregular geometry [$Cu^b = Cu(2), Cu(2')$]. Unlike $Cu(O_2CCH_3)_2(pyridine)_3$, **2**, all of the oxygen atoms in the acetate ligands in **3** are coordinated to copper.

The Cu–O bond lengths in **3** are within the range of bonding distances previously reported for Cu(II)–O complexes.[16,17] The Cu–O(μ-$OCMe_3$) distances fall in a narrow 1.895(4)–1.942(4) Å range, average 1.914(7) Å, and are the shortest Cu–O distances in the structure. The doubly-bridging acetates which have only one copper attached to each oxygen atom have a slightly larger Cu–O range of 1.935(5)–1.960(4) Å for oxygen atoms 3, 7, 8, and 9. The quadruply-bridging acetates which have two copper atoms attached to each oxygen atom have irregular bond lengths. O(1) is asymmetrically bonded to Cu(1) and Cu(2) with 2.164(4) and 2.001(4) Å bond distances, respectively. O(6) has nearly identical bond lengths to Cu(1), 2.344(4) Å, and Cu(3), 2.345(4) Å.

CONCLUSION

Copper(II) acetate is readily converted by pyridine to a monometallic species which can function as a copper-containing chelating ligand *via* two pendant acetate oxygen atoms. Copper(II) acetate also readily transforms in the presence of tert-butoxide ligands to a hexametallic complex containing extensive acetate and alkoxide bridging in which every oxygen atom coordinates to copper.

Supplementary Material

Figures and tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and structure factors are available from W.J.E.

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References

[1] L.G. Hubert-Pfalzgraf, *New J. Chem.* **19**, 727 (1995).
[2] K.G. Caulton and L.G. Hubert-Pfalzgraf, *Chem. Rev.* **93**, 969 (1993).
[3] D.C. Bradley, *Chem. Rev.* **89**, 1317 (1989).
[4] D.C. Bradley, *Polyhedron* **13**, 1111 (1994).
[5] J.G. Bednorz, K.A. Muller and M. Takashige, *Science* **236**, 73 (1987).
[6] M.B. Maple, Ed., *Bull. Mater. Res. Soc.* **14**, 20 (1989) and references therein.
[7] H.S. Horowitz, S.J. McLain, A.W. Sleight, J.D. Druliner, P.L. Gai, M.J. Vankavelaar, J.L. Wagner, B.D. Biggs and S.J. Poon, *Science* **243**, 66 (1989).
[8] W.J. Evans and J.H. Hain, Jr., *Mat. Res. Soc. Symp. Proc.* **180**, 39 (1990).
[9] W.J. Evans, L.R. Chamberlain, T.A. Ulibarri and J.W. Ziller, *J. Am. Chem. Soc.* **110**, 6423 (1988).
[10] M.R. Churchill, R.A. Lashewycz and F.J. Rotella, *Inorg. Chem.* **16**, 265 (1977).
[11] *UCLA Crystallographic Computing Package*, University of California Los Angeles, 1981; C. Strouse; personal communication.
[12] Nicolet Instrument Corporation, Madison, WI, 1988.
[13] *International Tables for X-Ray Crystallography* (Kynoch Press, Birmingham, England, 1974) (a) pp. 99–101; (b) pp. 149–150.
[14] G.A. Barclay and C.H.L. Kennard, *J. Chem. Soc.* 5244 (1961).
[15] F. Hanic, D. Stempelova and K. Hanicova, *Acta Cryst.* **17**, 633 (1964).
[16] R.J. Doedens, *Prog. Inorg. Chem.* **21**, 209 (1976).
[17] C. Sirio, O. Poncelet, L.G. Hubert-Pfalzgraf, J.C. Daran and J. Vaissermann, *Polyhedron* **11**, 177 (1992).
[18] C.V. Goebel and R.J. Doedens, *Inorg. Chem.* **10**, 2607 (1971).
[19] G. Speier and V. Fülöp, *J. Chem. Soc., Chem. Commun.* 905 (1990).
[20] J.N. van Niekerk and F.R.L. Schoening, *Acta Cryst.* **6**, 227, (1953).