Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a packing diagram, have been deposited with the IUCr (Reference: FG1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Low-Temperature Structure of Two Copper-Based Precursors for MOCVD: Aquabis(*tert*-butyl acetoacetato)copper(II) and Bis(dipivaloylmethanido)copper(II)

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(*Received 11 July 1994; accepted 30 August 1995*)

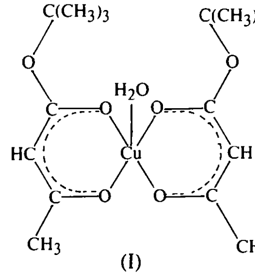
Abstract

The Cu atoms in aquabis(*tert*-butyl acetoacetato)-copper(II), $[Cu(C_8H_{13}O_3)_2(H_2O)]$, and bis(dipivaloylmethanido)copper(II), $[Cu(C_{11}H_{19}O_2)_2]$, adopt square-pyramidal and planar conformations, respectively, with average Cu—O distances of 1.933 Å in the former (not including the water ligand) and 1.892 Å in the latter. It is interesting to note that the lability of the *tert*-butyl and methyl groups in both structures, which renders even the location of the terminal C atoms difficult, is reduced at $T = 130$ K, enabling location of all the protons in the difference Fourier map.

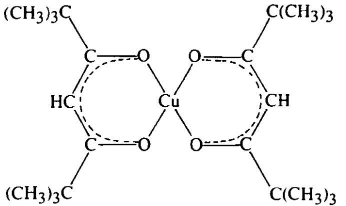
Comment

The structure determinations of aquabis(*tert*-butyl acetoacetato)copper(II), (I), and bis(dipivaloylmethanido)-copper(II), (II), which are used as copper-containing precursors for the metal-organic chemical vapour deposition (MOCVD) of thin film of $YBa_2Cu_3O_{(7-\delta)}$ (Harima, Ohnishi, Hanaoka, Tachibana & Goto, 1990), were undertaken to study their structural stability and the coordination geometry around their respective Cu atoms.

Compound (I) is hydrated and is different from bis(ethyl acetoacetato)copper(II) (Barclay & Cooper, 1965). Compound (II) is isostructural with bis(dipivoloylmethanido)nickel(II) (Cotton & Wise, 1966) and there are no significant differences in the bond parameters in the comparable portion of the two structures. An earlier report on the structure of compound (II) at room temperature (Watson & Holley, 1984) has an *R* factor of 0.107 and there are large displacement ellipsoids on the terminal groups, obscuring the location of H atoms. It was also reported that the compound is X-ray sensitive; however, there was no deterioration of the crystal in the present study.



(I)

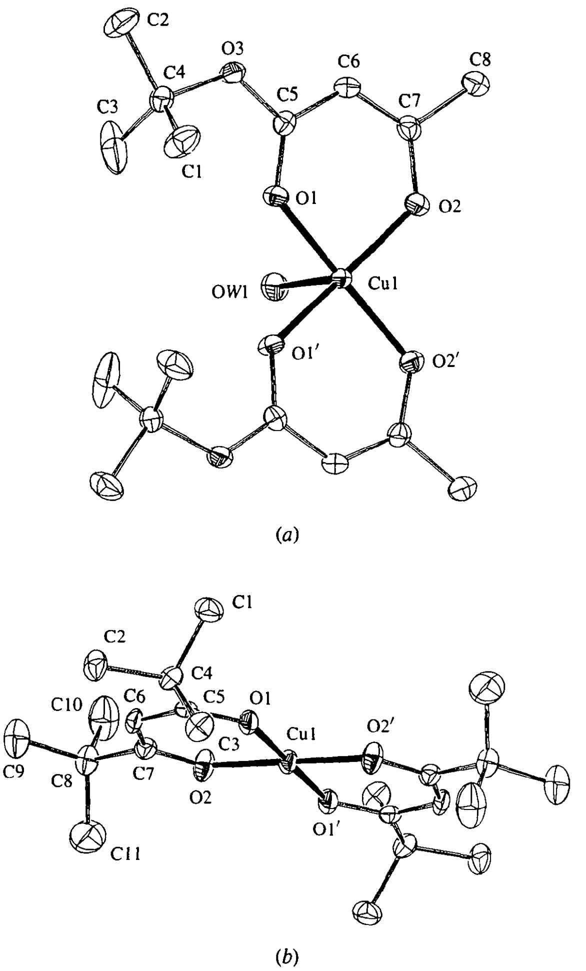


(II)

Least-squares calculations involving Cu and its neighbouring O atoms showed that the Cu—O groups are

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

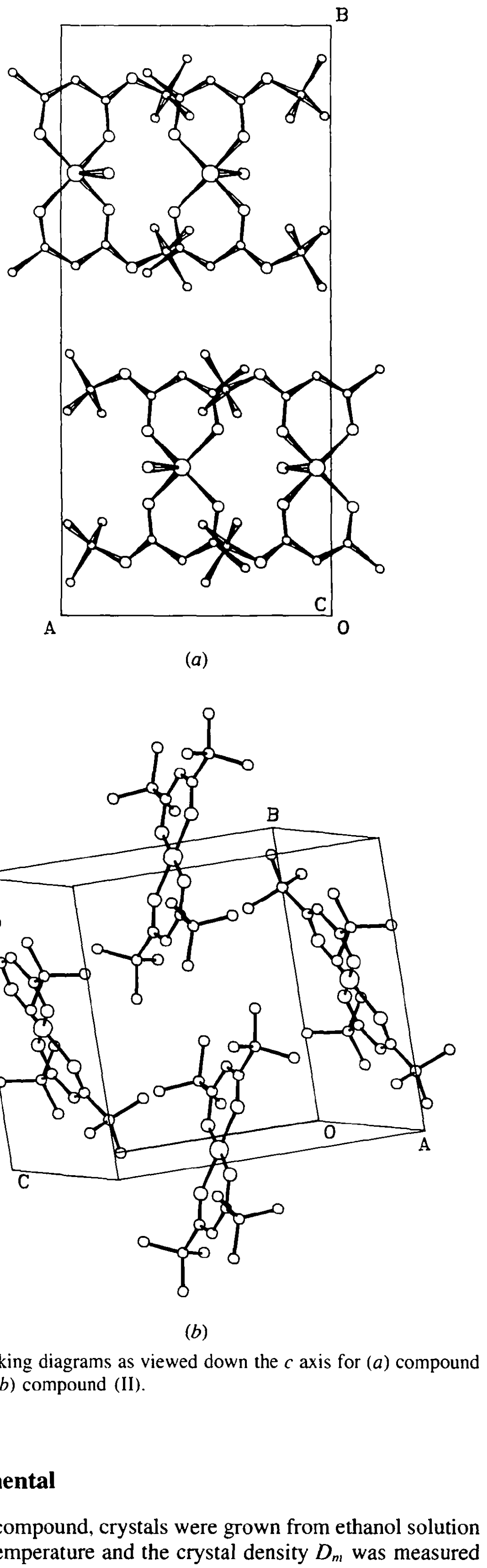
coplanar in compound (II), while in compound (I) the Cu atom is pulled out of the plane formed by the chelated O atoms leading to square-pyramidal geometry around the Cu atom. The Cu—O distance in (I) is slightly longer than that in (II). An increase in the Cu—O distance resulting from the hydration effect decreases its covalent character and hence its stability. The terminal *tert*-butyl and methyl groups, being stable (as shown in Fig. 1), sterically block the axial coordination sites and eliminate intermolecular interactions. The six-membered chelate ring adopts a planar conformation in compound (II) and a slightly puckered conformation (maximum deviation from the plane 0.06 Å for Cu1) in (I) as a result of the extra coordination of the Cu atom with the water molecule. The average C—O and C—C distances within the chelate ring in (I) are 1.272 and 1.386 Å, respectively, and in (II) these values are 1.271 and 1.394 Å, respectively, which are in agreement with the reported values of 1.293 and 1.405 Å.



(*a*)

(*b*)

Fig. 1. Molecular structures showing 50% probability displacement ellipsoids of (*a*) compound (I) and (*b*) compound (II).



(*a*)

(*b*)

Fig. 2. Packing diagrams as viewed down the *c* axis for (*a*) compound (I) and (*b*) compound (II).

Experimental

For each compound, crystals were grown from ethanol solution at room temperature and the crystal density D_m was measured by flotation.

Compound (I)

Crystal data

$[Cu(C_8H_{13}O_3)_2(H_2O)]$
$M_r = 395.92$
Orthorhombic
Pnma
$a = 9.558\,(2)$ Å
$b = 20.676\,(4)$ Å
$c = 9.591\,(2)$ Å
$V = 1895.4\,(7)$ Å^3
$Z = 4$
$D_x = 1.387$ Mg m^{-3}
$D_m = 1.349$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 29 reflections
$\theta = 9.72\text{–}24.51°$
$\mu = 1.183$ mm^{-1}
$T = 130\,(2)$ K
Plate
0.78 × 0.36 × 0.12 mm
Green

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (Sheldrick, 1990) $T_{\min} = 0.531$, $T_{\max} = 0.663$
1903 measured reflections
1903 independent reflections
1464 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 26.00°$
$h = 0 \rightarrow 11$
$k = -25 \rightarrow 0$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0386$
$wR(F^2) = 0.0924$
$S = 0.985$
1903 reflections
116 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.5660P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.248$
$\Delta\rho_{\max} = 0.366$ e Å^{-3}
$\Delta\rho_{\min} = -0.530$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Cu1	0.0547 (1)	1/4	0.0802 (1)	0.017 (1)
O1	0.1782 (2)	0.3124 (1)	−0.0071 (2)	0.022 (1)
O2	−0.0790 (2)	0.3161 (1)	0.1283 (2)	0.022 (1)
O3	0.2638 (2)	0.4102 (1)	−0.0615 (2)	0.021 (1)
O*W*1	0.1771 (3)	1/4	0.2813 (3)	0.026 (1)
C1	0.3505 (4)	0.3429 (2)	−0.2520 (4)	0.037 (1)
C2	0.4672 (4)	0.4432 (2)	−0.1756 (4)	0.036 (1)
C3	0.4759 (4)	0.3467 (3)	−0.0212 (5)	0.055 (1)
C4	0.3909 (3)	0.3830 (2)	−0.1274 (3)	0.021 (1)
C5	0.1662 (3)	0.3728 (1)	−0.0033 (3)	0.018 (1)
C6	0.0541 (3)	0.4068 (1)	0.0560 (3)	0.019 (1)
C7	−0.0608 (3)	0.3776 (1)	0.1142 (3)	0.019 (1)
C8	−0.1793 (3)	0.4189 (2)	0.1658 (4)	0.028 (1)

Table 2. *Selected geometric parameters (Å, °) for (I)*

Cu1—O1$^{\rm i}$	1.938 (2)	C4—C1	1.504 (5)
Cu1—O2$^{\rm i}$	1.927 (2)	C4—C3	1.504 (5)
Cu1—O*W*1	2.256 (3)	C4—C2	1.514 (4)
O1—C5	1.254 (4)	C5—C6	1.402 (4)
O2—C7	1.291 (4)	C7—C6	1.371 (4)
O3—C5	1.335 (3)	C7—C8	1.503 (4)
O3—C4	1.480 (3)		
O2$^{\rm i}$—Cu1—O2	90.33 (12)	C6—C7—C8	119.2 (3)
O2$^{\rm i}$—Cu1—O1	168.25 (10)	O1—C5—O3	120.1 (3)
O2—Cu1—O1	92.02 (9)	O1—C5—C6	125.5 (3)
O2—Cu1—O1$^{\rm i}$	168.25 (10)	O3—C5—C6	114.4 (3)
O1—Cu1—O1$^{\rm i}$	83.43 (12)	C7—C6—C5	123.8 (3)
O2$^{\rm i}$—Cu1—O*W*1	98.00 (9)	O3—C4—C1	109.8 (3)
O1—Cu1—O*W*1	93.08 (9)	O3—C4—C3	110.1 (3)
C5—O1—Cu1	126.4 (2)	C1—C4—C3	113.6 (3)
C7—O2—Cu1	125.7 (2)	O3—C4—C2	102.3 (2)
C5—O3—C4	122.1 (2)	C1—C4—C2	109.5 (3)
O2—C7—C6	125.7 (3)	C3—C4—C2	11.09 (3)
O2—C7—C8	115.0 (3)		
O2—Cu1—O1—C5	8.7 (3)	Cu1—O2—C7—C6	3.5 (4)
O*W*1—Cu1—O1—C5	−89.5 (3)	Cu1—O1—C5—C6	−5.2 (5)
O1—Cu1—O2—C7	−7.8 (3)	O2—C7—C6—C5	3.4 (5)
O*W*1—Cu1—O2—C7	85.5 (2)	O1—C5—C6—C7	−2.5 (5)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Compound (II)

Crystal data

$[Cu(C_{11}H_{19}O_2)_2]$
$M_r = 430.06$
Monoclinic
$P2_1/c$
$a = 10.175\,(2)$ Å
$b = 10.939\,(2)$ Å
$c = 11.469\,(2)$ Å
$\beta = 112.06\,(3)°$
$V = 1183.1\,(4)$ Å^3
$Z = 2$
$D_x = 1.213$ Mg m^{-3}
$D_m = 1.205$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 29 reflections
$\theta = 5\text{–}25°$
$\mu = 0.945$ mm^{-1}
$T = 130$ K
Plate
0.84 × 0.42 × 0.10 mm
Deep Violet

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (Sheldrick, 1990) $T_{\min} = 0.710$, $T_{\max} = 0.981$
2167 measured reflections
2045 independent reflections
1483 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0724$
$\theta_{\max} = 25.03°$
$h = -11 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = -12 \rightarrow 13$
3 standard reflections monitored every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0462$
$wR(F^2) = 0.1182$
$S = 0.787$
2045 reflections
200 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1074P)^2 + 2.2804P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.004$
$\Delta\rho_{\max} = 0.397$ e Å^{-3}
$\Delta\rho_{\min} = -0.345$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)*

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cu1	1/2	0	1/2	0.0194 (3)
O1	0.5683 (3)	0.1394 (3)	0.4424 (3)	0.0219 (7)
O2	0.3196 (3)	0.0709 (3)	0.4629 (3)	0.0274 (7)
C1	0.6240 (6)	0.2778 (5)	0.2558 (5)	0.0307 (11)
C2	0.5147 (6)	0.4549 (4)	0.3194 (5)	0.0299 (11)
C3	0.7270 (5)	0.3548 (5)	0.4771 (5)	0.0301 (11)
C4	0.5890 (4)	0.3329 (4)	0.3632 (4)	0.0211 (9)
C5	0.5026 (4)	0.2388 (4)	0.4010 (4)	0.0200 (9)
C6	0.3632 (5)	0.2615 (4)	0.3895 (4)	0.0208 (9)
C7	0.2791 (4)	0.1773 (4)	0.4205 (4)	0.0210 (9)
C8	0.1267 (5)	0.2061 (4)	0.4057 (4)	0.0261 (10)
C9	0.0762 (6)	0.3322 (5)	0.3520 (6)	0.0418 (13)
C10	0.0321 (6)	0.1097 (6)	0.3157 (7)	0.052 (2)
C11	0.1201 (7)	0.1922 (8)	0.5342 (6)	0.056 (2)

Table 4. *Selected geometric parameters (Å, °) for (II)*

Cu1—O2	1.888 (3)	C5—C4	1.519 (6)
Cu1—O1	1.895 (3)	C5—C6	1.396 (6)
O1—C5	1.271 (5)	C6—C7	1.391 (6)
O2—C7	1.270 (5)	C7—C8	1.529 (6)
C4—C1	1.529 (6)	C8—C9	1.519 (7)
C4—C2	1.523 (6)	C8—C10	1.536 (7)
C4—C3	1.535 (6)	C8—C11	1.507 (7)
O2—Cu1—O1	92.51 (12)	C5—C4—C2	114.8 (4)
C7—O2—Cu1	127.7 (3)	C1—C4—C2	108.5 (4)
C5—O1—Cu1	127.5 (3)	C5—C4—C3	107.8 (3)
O1—C5—C6	124.1 (4)	C1—C4—C3	109.4 (4)
O1—C5—C4	114.0 (4)	C2—C4—C3	109.0 (4)
C6—C5—C4	121.9 (4)	C11—C8—C9	110.8 (5)
C7—C6—C5	124.0 (4)	C11—C8—C7	106.7 (4)
O2—C7—C6	124.2 (4)	C9—C8—C7	114.0 (4)
O2—C7—C8	113.7 (4)	C11—C8—C10	110.0 (5)
C6—C7—C8	122.1 (4)	C9—C8—C10	108.6 (4)
C5—C4—C1	107.3 (3)	C7—C8—C10	106.7 (4)
O1—Cu1—O2—C7	−2.8 (4)	O1—C5—C6—C7	−0.9 (7)
O2—Cu1—O1—C5	2.1 (3)	Cu1—O2—C7—C6	2.1 (6)
Cu1—O1—C5—C6	−0.8 (6)	C5—C6—C7—O2	0.2 (7)

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLUTO*82 (Motherwell, Sussman & Beebf, 1982), *ORTEP*II (Johnson 1976); software used to prepare material for publication: *SHELXS*86.

We thank the Council of Scientific and Industrial Research (CSIR) [No. 1(1272)/93-EMR-II] and the Department of Science and Technology (DST) (through the National Superconductivity Programme), India, for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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