Redetermination of Crystal Structure of
Bis(2,4-pentanedionato)copper(II)

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The crystal structure of *bis*(2.4-pentanedionato)copper(II) has been redetermined at the low-temperature. The results confirmed the reported data, but with significant improvement in precision.

Key Words: Crystal structure, Acetylacetonato ligand, Copper complex.

INTRODUCTION

The structure of *bis*(2,4-pentanedionato)copper(II) was redetermined as part of continued investigations on the synthesis and characterization of mixed-chelate complexes of copper(II)[1,2]. One of the interests is to make mixed-chelate complex and then condense them to a macrocyclic complex. To determine the effect of mixed-chelate formation on the bond distances and angles and also to obtain more information about the effect of these bond lengths and angles on the condensation of mixed-chelate complex we persu-aded to have information concerning with the equivalent homo *bis*-chelate complexes. The structure of *bis*(2,4-pentanedionato)copper(II) have been previously investigated by three-dimentional X-ray diffraction[3] and single crystal X-ray diffraction[4] but these early surveys do not have enough precision for this purpose (R = 0.151 and 0.056, respectively). Thus, the crystal structure of *bis*(2,4-pentanedionato)copper(II) (**I**) at 100 K is reported.
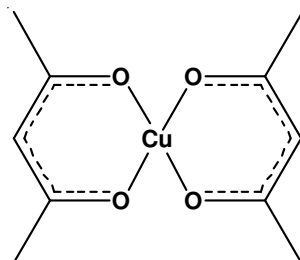
Structure of *bis*(2,4-pentanedionato)copper(II) (**I**)

EXPERIMENTAL

The complex Cu(acac)$_2$ was prepared by procedure given by Peacock[5]. A blue crystal with approximate dimensions of 0.55 mm × 0.18 mm × 0.04 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension (b axis) was approximately parallel to the fiber axis.

Unit cell parameters and orientation matrix were determined on a Bruker SMART APEX II CCD diffractometer with graphic monochromated MoM$_\alpha$ radiation (λ = 0.71073 Å). The technique used was ω-scan with θ limits 2.63 ≤ θ ≤ 28.00 at temperature of 100 K. The crystallographic data is summarized in Table-1. Data were collected on an APEX2 diffractometer.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR Cu(acac)$_2$

Crystal data:	
Empirical formula	$C_{10}H_{14}O_4Cu$
Formula weight	261.75
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 10.2714(9) Å $\alpha = 90°$
	b = 4.6283(4) Å $\beta = 92.384(2)°$
	c = 11.2908(11) Å $\gamma = 90°$
Volume	536.29(8) Å^3
Z	2
Density (calculated)	1.621 Mg/m^3
Absorption coefficient	2.026 mm^{-1}
F(000)	270
Crystal size	0.55 × 0.18 × 0.04 mm^3
Data collection:	
θ-Range for data collection	2.63 to 28.00°.
Index ranges	-13 ≤ h ≤ 13, -6 ≤ k ≤ 6, -14 ≤ l ≤ 14
Reflections collected	5065
Independent reflections	1272 [R(int) = 0.0240]
Observed reflections [I > 2σ(I)]	1131
Completeness to theta = 28.00°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9233 and 0.4020
Refinement:	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1272/0/72
Goodness-of-fit on F^2	1.075
Final R indices [I > 2σ(I)]	R1 = 0.0220, wR2 = 0.0551
R indices (all data)	R1 = 0.0261, wR2 = 0.0575
Largest diff. peak and hole	0.481 and -0.384 e.Å^{-3}

Three standard reflections were checked every 200 reflections. Empirical absorption correction was carried out by using the Bruker APEX II program[6]. A total of 5065 reflections were measured, of which 1131 were uniques [I > 2σ(I)]. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using the SHELXS-97 software package[7,8]. All hydrogen atoms were treated in riding model with the $U_{iso}(H)$ parameters equal to 1.2 $U_{eq}(Ci)$ and 1.5 $U_{eq}(Cii)$, where $U_{eq}(Ci)$ and $U_{eq}(Cii)$ are the equivalent thermal parameters of, respectively, methylene and methyl groups to which corresponding H-atoms are bonded.

The O-bound H atoms were located in a difference map and refined as riding in their as-found relative positions, with $U_{iso}(H) = 1.5U_{eq}(O)$. The C-bound H atoms were placed in idealized locations (C-H = 0.98 Å) and refined as riding, with $U_{iso}(H) = 1.5U_{eq}C$.

The final conventional R = 0.0220 and wR = 0.0551 for I > 2σ(I) with weighing scheme, $w = 1/[\sigma^2(Fo^2) + (0.0264P)^2 + 0.3586P]$ where $P = (Fo^2 + 2Fc^2)/3$. The molecular graphic were plotted using Bruker SHELXTL[9] Atomic scattering factors and anomalous dispersion correction were taken from international tables for X-ray crystallography[10].

RESULTS AND DISCUSSION

The fractional atomic coordinates of complex is given in Table-2. ORTEP drawing for bis(2,4-pentanedionato)copper(II) (**I**) is presented in Fig. 1.
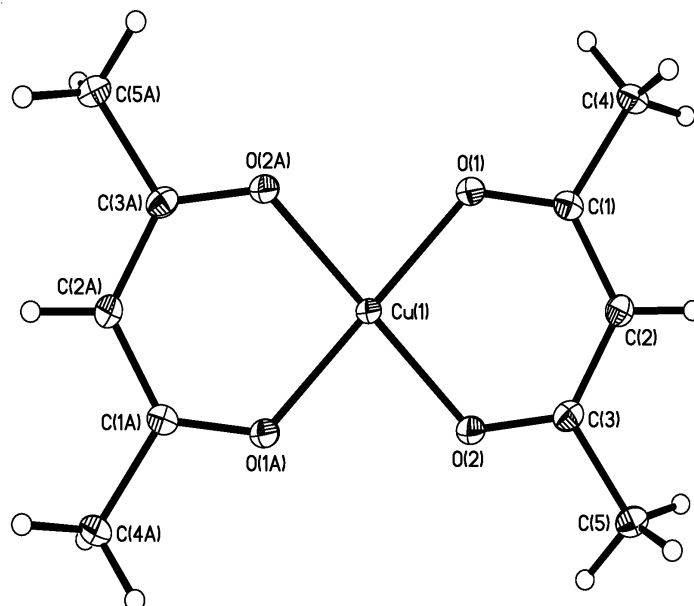

Fig. 1. ORTEP drawing of **I** at the 50 % probability level

TABLE-2
ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC
DISPLACEMENT PARAMETERS ($\text{Å}^2 \times 10^3$) FOR COMPOUND **I**

Atom	x	y	z	U(eq)*
Cu(1)	5000	0	0	12(1)
O(1)	3376(1)	2066(2)	-58(1)	15(1)
O(2)	5654(1)	2022(2)	-1340(1)	15(1)
C(1)	3097(1)	4197(3)	-727(1)	13(1)
C(2)	3890(2)	5311(3)	-1601(1)	15(1)
C(3)	5111(2)	4152(4)	-1864(1)	14(1)
C(4)	1812(2)	5653(4)	-528(2)	17(1)
C(5)	5858(2)	5525(4)	-2837(2)	19(1)

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

The copper atom lies on a center of inversion and adopts a square planar geometry. The selected bond lengths and angles are given in Table-3. The two bite distances for Cu-O are 1.9214(11) and 1.9234(116) Å. These distances are longer than to those observed by Lebrun *et al.*[4] and Lingafelter *et al.*[11] for 13 three-dimensionally determined acetylacetonato complexes. The O-Cu-O bite angle is 93.58(5)° and slightly wider that those reported before. The chemically unique acetylacetonato ligand mean bond lengths C-O, C-H and C-CH$_3$ are 1.268(2) Å, 1.404(2) Å and 1.507(2) Å and do not differ significantly from those reported by Lebrun *et al.*[4]. The dihedral angle between two CuO$_2$ are 180(3)° and 180(9)°. The torsion angle of Cu-O1-C1-C2, O1-C1-C2-C3 and Cu-O1-C1-C4 are 4.4(2)°, 1.1(3)° and -170.09(10)°, respectively. Molecules stack in a face-to-face mode to form a molecular column along the b axis (Fig. 2) and there is no interaction between molecules.

TABLE-3
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND **I***

Cu(1)-O(1)#1	1.9214(11)	O(2)-C(3)	1.268(2)
Cu(1)-O(1)	1.9214(11)	C(2)-C(3)	1.407(2)
Cu(1)-O(2)	1.9234(11)	C(1)-C(2)	1.404(2)
Cu(1)-O(2)#1	1.9234(11)	C(1)-C(4)	1.507(2)
O(1)-C(1)	1.268(2)	C(3)-C(5)	1.507(2)
O(1)#1-Cu(1)-O(1)	180.00(3)	C(3)-O(2)-Cu(1)	125.74(10)
O(1)#1-Cu(1)-O(2)	86.42(5)	O(1)-C(1)-C(2)	125.51(14)
O(1)-Cu(1)-O(2)	93.58(5)	O(1)-C(1)-C(4)	115.89(13)
O(1)#1-Cu(1)-O(2)#1	93.58(5)	C(2)-C(1)-C(4)	118.58(15)
O(1)-Cu(1)-O(2)#1	86.42(5)	C(1)-C(2)-C(3)	123.84(15)
O(2)-Cu(1)-O(2)#1	180.00(9)	O(2)-C(3)-C(2)	125.25(14)
C(1)-O(1)-Cu(1)	125.60(10)	O(2)-C(3)-C(5)	116.14(14)

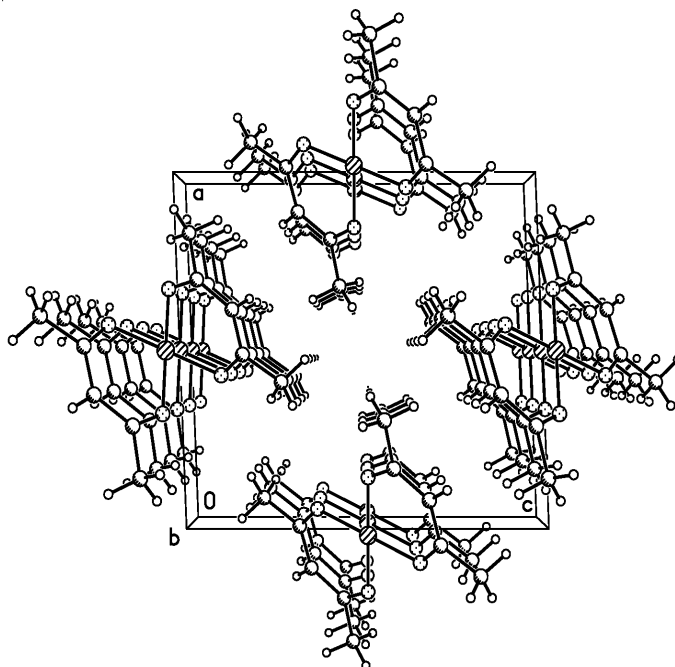*Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z

Fig. 2.   Fragment of crystal packing of compound **I** (projection along b crystal axis)

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