685. *The Crystal Structure of Copper*(II) *Ethyl Acetoacetate*

By G. A. Barclay and A. Cooper

The crystal structure of copper(II) ethyl acetoacetate has been determined by *X*-ray diffraction methods, refined by a least-squares procedure with anisotropic thermal parameters and three-dimensional data. There are two molecules in the monoclinic unit cell (space-group $P2_1/n$) with dimensions $a = 11{\cdot}578 \pm 0{\cdot}006$, $b = 4{\cdot}527 \pm 0{\cdot}002$, $c = 13{\cdot}791 \pm 0{\cdot}006$, $\beta = 104{\cdot}5 \pm 0{\cdot}4°$. The copper atom is surrounded by four oxygen atoms at distances of 1·91 and 1·94 Å in a square-planar arrangement. The next nearest neighbours to the copper atom are the carbon atoms of the –CH– groups of adjacent molecules at distances of 3·10 Å in approximately "octahedral" sites. The environment of the copper atom is similar to that in bis(acetylacetonato)copper(II).

The results of a single projection of copper(II) ethyl acetoacetate have been reported.[1] As the stereochemistry of the molecule and the environment of the copper atom were not determined, the crystal structure has been investigated through three-dimensional data.

[1] E. A. Shugam, *Zhur. fiz. Khim.*, 1954, **28**, 643.

Experimental

Thin, green, tabular crystals of copper(II) ethyl acetoacetate were obtained by evaporation of a dilute benzene solution.

Single-crystal oscillation and Weissenberg photographs about the *a*- and *b*-axes indicated that the crystals were monoclinic. The systematic absences (*h*0*l* absent if $h + l = 2n + 1$ and 0*k*0 absent if $k = 2n + 1$) uniquely determined the space-group as $C_{2h}^5 - P2_1/n$. The density of the crystals was measured by flotation in a mixture of cyclohexane and ethylene dibromide. Accurate cell-dimensions were determined from zero-layer Weissenberg photographs about the *b*- and *c*-axes with silicon-powder lines for calibration; least-square procedures were used to obtain the final parameters. The errors given are twice the estimated standard deviations.

The intensities of 575 independent reflexions were estimated visually from equi-inclination Weissenberg photographs of the layers *h*0*l* ⟶ *h*2*l*, *hk*0 ⟶ *hk*4 and 0*kl* ⟶ 1*kl*. Lorentz and polarisation corrections were applied but no allowance was made for absorption or extinction.

Calculations were made using UTECOM (a Deuce electronic digital computer) with programmes written by Drs. J. S. Rollett and J. Sime. Scattering factors of Berghuis *et al.*[2] were used for all atoms, the values for copper being corrected for anomalous dispersion.[3]

Crystal data. $C_{12}H_{18}CuO_6$: M, 321·7; monoclinic; $a = 11{\cdot}578 \pm 0{\cdot}006$, $b = 4{\cdot}527 \pm 0{\cdot}002$, $c = 13{\cdot}791 \pm 0{\cdot}006$ Å, $\beta = 104{\cdot}5 \pm 0{\cdot}4°$; $U = 699{\cdot}7$ Å^3; $D_m = 1{\cdot}51 \pm 0{\cdot}02$ g. cm.$^{-3}$ (by flotation); $Z = 2$; $D_c = 1{\cdot}53$ g. cm.$^{-3}$; $F(000) = 334$; space-group $P2_1/n$ (C_{2h}^5). Radiation, copper, unfiltered; single-crystal oscillation and Weissenberg photographs.

Structure Determination.—As there are four equivalent positions and only two copper atoms in the unit cell, the copper atoms were placed at the centres of symmetry (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; these atoms then only contribute to reflexions of the type $h + k + l = 2n$. A three-dimensional electron-density distribution was computed, taking the structure amplitudes with $h + k + l = 2n$. All the atoms in the asymmetric unit were clearly resolved but false mirror planes occurred parallel to the *xz*-plane and passing through the copper atoms. This resulted in two possible orientations of the molecules about the *y*-axis. The correct orientation was chosen by attempting to refine the two possible sets of co-ordinates by differential syntheses; the incorrect set did not refine beyond $R = 0{\cdot}30$. Overall scale and temperature factors, which were calculated by Wilson's method, were adopted at first, but as the refinement progressed individual isotropic temperature factors for each atom were introduced. When R had fallen to 0·19, refinement was continued by a least-squares method which minimised $\Sigma w(|F_o| - |F_c|)^2$. Individual anisotropic thermal parameters were introduced and reflexions were weighted as follows (unobserved reflexions not included): $|F_o| \leqslant 8F_{min.}$, $w = 1$; $|F_o| > 8F_{min.}$, $w = (8F_{min.}/|F_o|)^2$. The refinement converged after eight cycles and R fell to 0·12.

The final atomic co-ordinates, together with their estimated standard deviations, are given in Table 1. Table 2 contains the thermal parameters of the atoms; the temperature factor for each atom was calculated from the expression 2^{-x}, where $x = (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$. The calculated structure amplitudes are given in Table 3.

Table 1

Atomic co-ordinates (estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Cu	0·0000(———)	0·0000(———)	0·0000(———)
O(1)	0·1437(0·0010)	−0·2143(0·0029)	0·0149(0·0009)
O(2)	−0·0323(0·0009)	−0·2054(0·0029)	0·1123(0·0008)
O(3)	−0·0005(0·0010)	−0·5236(0·0036)	0·2417(0·0008)
C(1)	0·2990(0·0015)	−0·5469(0·0048)	0·0725(0·0014)
C(2)	0·1814(0·0016)	−0·4241(0·0037)	0·0818(0·0014)
C(3)	0·1360(0·0013)	−0·5305(0·0051)	0·1525(0·0011)
C(4)	0·0318(0·0016)	−0·4049(0·0039)	0·1662(0·0013)
C(5)	−0·1112(0·0015)	−0·4183(0·0041)	0·2597(0·0014)
C(6)	−0·1068(0·0016)	−0·4980(0·0080)	0·3628(0·0014)

[2] J. Berghuis, I. M. Hannappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[3] C. H. Dauben and D. H. Templeton, *Acta Cryst.*, 1955, **8**, 841.

Discussion

The crystal is composed of units of composition $(C_2H_5{\cdot}O{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CH_3)_2Cu$ arranged as illustrated in Figure 1. The copper atom is surrounded by four oxygen atoms [O(1) and O(2)] in a square-planar arrangement. The whole molecule with the exception of atoms C(5) and C(6) lies in a plane which makes an angle of 46° with the *xz*-plane. The equation of this plane is $0{\cdot}362x + 0{\cdot}699y + 0{\cdot}617z - 0{\cdot}007 = 0$; (deviations from the plane are: Cu, 0·007 Å; O(1), 0·02; O(2), 0·01; O(3), 0·02; C(1), 0·02; C(2), 0·02; C(3), 0·05; C(6), 0·01 Å). In bis(acetylacetonato)copper(II), the entire molecule lies in a plane which makes angles of 52° to the *a*-axis and 54° to the *b*-axis.[2]

Table 2

Thermal parameters

Atom	10^4b_{11}	10^4b_{22}	10^4b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}
Cu	125	422	109	167	106	162
O(1)	101	637	121	316	68	−10
O(2)	106	714	91	−113	69	20
O(3)	165	615	97	−100	81	66
C(1)	148	802	142	438	116	333
C(2)	112	453	107	70	2	−28
C(3)	110	735	97	−298	113	−53
C(4)	145	589	74	53	9	218
C(5)	120	619	160	154	175	128
C(6)	172	1505	136	122	182	294

Table 3

Observed structure amplitudes and calculated structure factors for copper(II) ethyl acetoacetate

l	$\lvert F_o\rvert$	F_c	*l*	$\lvert F_o\rvert$	F_c	*l*	$\lvert F_o\rvert$	F_c	*l*	$\lvert F_o\rvert$	F_c	*l*	$\lvert F_o\rvert$	F_c	*l*	$\lvert F_o\rvert$	F_c
	0,0,*l*			0,4,*l*			1,1,*l*			1,3,*l*			2,0,*l*			2,2,*l*	
2	14	17	0	13	13	−8	6	6	−15	1	0	−16	4	3	−7	11	13
4	13	16	2	9	9	−7	5	5	−12	3	3	−14	3	2	−6	6	6
6	7	9	3	3	−4	−6	21	20	−11	3	4	−12	4	4	−4	23	22
8	23	23	4	7	7	−5	8	9	−10	6	7	−10	7	8	−2	16	17
10	3	3	6	4	5	−4	11	12	−7	1	−3	−8	30	33	−1	2	−3
12	10	10	8	6	8	−2	26	23	−6	11	11	−6	13	15	0	16	17
14	2	2	10	3	3	−1	8	−6	−5	2	−2	−4	10	12	2	4	−3
						0	13	−12	−4	10	10	−2	16	17	3	5	3
	0,1,*l*					1	22	23	−2	11	11	0	42	45	4	29	29
1	10	10				2	71	69	2	19	18	2	25	−23	5	6	4
2	16	17		0,5,*l*		3	19	18	3	8	−6	4	20	22	6	19	18
3	28	28	1	6	8	4	19	18	4	12	11	6	10	10	8	9	9
4	6	5	3	3	5	5	5	4	5	4	−5	8	11	11	13	5	−1
5	16	18	5	1	4	6	13	13	6	11	9	12	6	5			
6	5	−5	7	3	4	7	2	−1	8	3	2					2,3,*l*	
7	20	18				8	5	4	10	6	5		2,1,*l*		−4	3	−4
8	4	0				9	2	2				−15	3	3	−3	13	15
9	15	14				10	9	10				−13	4	2	−1	15	13
11	4	4		1,0,*l*		12	2	−2		1,4,*l*		−11	8	9	1	11	11
15	3	3	−13	1	6				−11	3	2	−9	11	12	3	11	11
			−11	7	6				−9	6	7	−7	4	7	4	8	−10
	0,2,*l*		−9	9	10				−7	6	6	−6	17	15			
0	33	34	−7	23	27		1,2,*l*		−5	7	7	−5	12	14		2,4,*l*	
2	3	3	−5	22	26	−13	5	5	−3	7	8	−4	9	10	−4	8	8
4	14	14	−3	31	36	−10	4	−5	−1	8	10	−3	19	18	−2	7	7
6	5	5	3	6	−7	−8	6	6	1	8	9	−2	4	3	0	10	10
8	8	8	5	13	13	−7	6	6	2	6	−7	−1	42	34	1	5	−5
11	2	1	7	9	10	−6	3	4	3	8	9	0	7	7	2	6	7
12	7	7	9	12	13	−5	14	16	4	3	−4	1	29	27	3	6	−7
			11	8	9	−4	4	6	5	5	6	2	29	25	4	7	8
	0,3,*l*		13	6	3	−3	19	20	7	4	5	3	25	27			
1	4	5				−1	11	12	9	4	5	4	6	6		2,5,*l*	
3	11	11				0	4	4				6	2	0	−3	2	4
4	3	−3		1,1,		1	6	6		1,5,*l*		7	10	10	−1	4	5
5	11	11	−15	3	1	3	5	5				9	5	5	1	5	5
10	5	−6	−14	3	2	4	5	6	−6	4	6	11	5	4			
11	3	4	−12	4	3	5	16	18	−4	3	4					3,0,*l*	
12	2	−1	−10	17	17	7	10	9	−2	4	6		2,2,*l*		−13	4	4
14	2	0	−9	8	2	9	7	6	0	7	8	−8	12	13	−11	4	3
						11	6	5	2	3	5						

TABLE 3 (*Continued*)

l	$\|F_o\|$	F_c	l	$\|F_o\|$	F_c	l	$\|F_o\|$	F_c	l	$\|F_o\|$	F_c	l	$\|F_o\|$	F_c	l	$\|F_o\|$	F_c
	3,0,*l*			4,1,*l*			5,1,*l*			6,1,*l*			8,0,*l*			9,4,*l*	
−9	13	13	−15	2	4	1	9	−11	9	3	4	−16	3	3	−1	3	4
−7	25	21	−9	8	8	2	16	15	10	4	−2	−14	5	5	1	3	5
−3	6	−5	−7	12	13	4	5	6				−12	6	6			
−1	7	7	−6	13	13	5	3	−2		6,2,*l*		−8	22	23		10,0,*l*	
1	34	30	−5	10	12	6	10	10				−6	18	19			
3	7	7	−4	8	5	8	5	6	−12	10	11	−4	17	17	−16	3	4
5	11	11	−3	17	17	9	4	−6	−10	4	6	0	15	16	−14	4	5
9	6	6	−2	16	−14				−8	6	5	4	9	10	−12	4	2
			−1	16	16		5,2,*l*		−6	5	5	6	4	3	−8	11	11
	3,1,*l*		0	16	−14				−4	15	15	8	4	3	−6	3	1
−13	4	2	1	16	14	−13	6	6	−3	5	5				−4	4	4
−12	4	5	3	15	16	−11	7	7	−2	7	6		8,1,*l*		0	8	6
−10	7	7	5	5	7	−9	11	11	−1	12	−11				4	6	7
−8	6	7	6	5	−2	−7	9	9	0	15	13	−15	4	3			
−7	4	5	7	10	10	−5	18	18	1	7	−6	−13	4	4		10,1,	
−6	25	25	9	5	4	−4	3	2	2	5	5	−11	9	9	−12	3	2
−5	22	23	11	3	4	−3	17	15				−9	5	5	−7	7	7
−4	14	14				−2	5	3		6,3,*l*		−7	7	7	−1	3	4
−3	4	1		4,2,*l*		−1	16	15				−6	4	3	1	3	4
−2	14	14	−13	6	2	0	9	−9	−3	10	10	−5	9	9			
−1	1	−2	−12	7	7	1	10	10	−1	7	7	−4	9	6			
0	19	17	−10	8	9	2	2	−4	0	9	9	−3	9	9		10,2,*l*	
1	5	5	−8	10	10	3	8	9	3	3	3	−2	6	1	−10	3	5
2	31	31	−6	9	9	5	9	9				−1	6	5	−8	8	8
3	6	6	−5	10	−10	6	6	−7		6,4,*l*		1	16	16	−4	6	6
4	6	−5	−4	34	32				−4	7	8	3	9	9	−2	8	9
5	6	−4	−3	5	6		5,3,*l*		−3	4	3	4	4	4	0	8	9
6	8	8	−2	21	24	−4	6	5	2	7	7				5	3	−1
7	8	−3	−1	11	−7	−3	6	−8	4	5	5		8,2,*l*				
8	9	9	0	17	15	−2	16	17				−8	8	8		10,3,*l*	
10	7	7	2	9	9	−1	3	5		6,5,*l*		−6	4	4	−3	4	5
			4	21	20	0	10	8	1	3	3	−4	9	9	−1	4	6
	3,2,*l*		6	7	9	1	3	1				−2	4	4	1	4	5
−12	6	2	7	8	−10	2	6	5		7,0,*l*		0	8	8			
−11	6	5	8	6	5	4	4	3				3	3	3		10,4,*l*	
−9	9	8							−13	8	7				−2	2	3
−8	9	9		4,3,*l*			5,4,*l*		−9	11	10		8,3,*l*				
−7	11	10	−3	13	14	−3	5	5	−7	15	15	1	4	5			
−5	19	17	−1	13	14	−2	6	6	−5	20	20	2	4	−5		11,0,*l*	
−3	25	24	1	10	9	1	6	6	−3	11	11	3	5	5	−15	2	3
−2	4	−6	3	9	9	3	5	6	−1	29	30				−7	3	4
−1	22	18	4	3	−6				1	14	14		8,4,*l*		−5	4	4
1	17	18					5,5,*l*		3	9	10	−4	5	5	−3	6	7
3	19	19		4,4,*l*					5	7	6	0	18	7			
4	9	9				−2	4	6	7	5	4	2	3	5		11,1,*l*	
5	21	21	−11	7	2	−1	4	−1	9	4	4				2	4	5
7	9	8	−4	10	10	0	4	5					9,0,*l*				
9	4	5	−3	3	5	2	4	5		7,1,*l*		−13	5	4		11,2,*l*	
			−2	3	4				−10	15	16	−11	4	4			
	3,3,*l*		−1	3	2		6,0,*l*		−9	7	−6	−9	11	11	−10	5	−1
−4	11	12	2	5	3	−14	4	2	−8	10	10	−7	14	14	−7	4	4
−2	15	16	4	5	5	−12	9	10	−6	14	13	−5	5	7	−5	4	5
−1	1	3				−8	12	13	−5	2	2	−3	4	5	−3	7	9
0	11	10		4,5,*l*		−6	14	15	−4	6	7	−1	3	3	−1	5	6
1	3	−4	−3	2	0	−4	15	15	−2	14	15	3	7	9			
2	13	14	−1	3	4	−2	5	4	0	2	2	5	6	7		11,3,*l*	
3	6	−7	1	4	5	0	31	30	1	6	−3				0	4	5
4	7	8				2	21	23	2	17	17		9,1,*l*				
				5,0,*l*		4	13	14	4	9	9	−14	2	3		12,0,*l*	
	3,4,*l*		−13	4	4	6	4	2	6	6	6	−12	4	4			
−4	4	−3	−9	11	13	8	5	5				−10	8	8	−4	6	6
−3	7	7	−7	14	15	10	5	5		7,2,*l*		−6	12	11			
−1	6	8	−5	13	13	12	3	4	−13	5	6	−5	5	5		12,1,*l*	
1	7	7	−3	12	−10				−7	6	2	−4	10	9	−1	4	5
4	8	2	−1	16	18		6,1,*l*		−5	8	7	−3	5	6			
			1	14	25	−15	3	4	−3	10	9	−2	11	11			
	3,5,*l*		3	13	15	−11	8	7	−1	14	14	0	3	3		12,2,*l*	
0	4	3	5	8	8	−10	6	−5	0	8	−8	2	10	10	−4	5	5
2	4	4	7	4	4	−8	6	−5	1	3	1				0	3	3
			9	6	7	−7	15	17					9,2,*l*				
	4,0,*l*		11	2	4	−6	2	−3		7,3,*l*		−9	7	7		12,3,*l*	
−12	1	3				−5	15	15				−3	7	7	−1	3	4
−10	8	7		5,1,*l*		−4	3	−3	−4	5	3	−1	8	7			
−8	10	13	−10	4	7	−3	23	24	−2	10	10	1	4	3		13,0,*l*	
−6	2	5	−9	7	−4	−2	12	−13	3	4	−5	3	4	4			
−4	10	8	−8	10	11	−1	4	4	4	5	5	6	4	−1	−13	1	4
−2	8	6	−6	15	16	0	5	−6							−7	2	3
0	13	14	−5	7	5	1	13	12		7,4,*l*			9,3,*l*		−5	4	6
2	11	11	−4	7	8	2	2	−3	−3	7	6						
4	15	16	−3	21	−17	3	12	13	−1	4	5	−4	4	7		13,1,*l*	
8	2	3	−2	26	23	5	7	8	1	7	8	−2	7	9	0	2	3
10	6	5	−1	15	−15	7	6	5	3	3	3	2	5	5			
12	4	4	0	18	18	8	3	−4									

The bond lengths and angles within the molecules are shown in Figure 2, and the bond lengths are compared with values reported for bis(acetylacetonato)copper(II) [4,5] in Table 4.

[4] H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytechnics, Osaka City Univ.*, 1953, **4***C*, 43.
[5] E. A. Shugam, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 853.

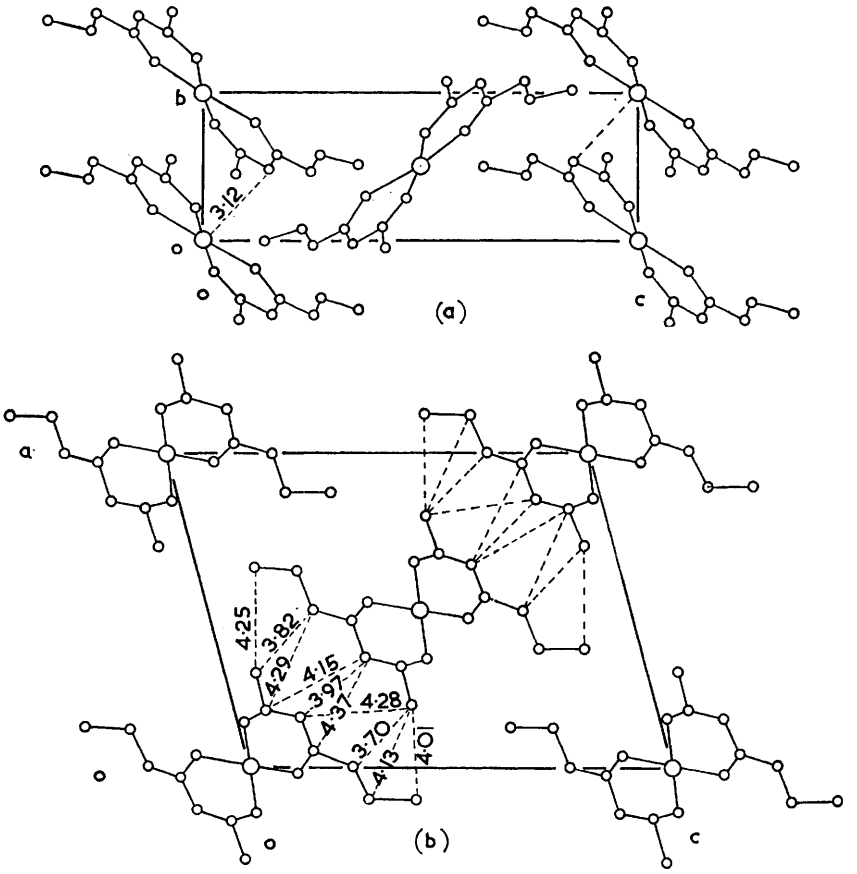

FIGURE 1. The arrangement of the molecules in copper(II) ethyl acetoacetate: (a) Projection down the *a*-axis; (b) projection down the *b*-axis

TABLE 4

Comparison of bond distances in copper(II) ethyl acetoacetate and bis(acetylacetonato)copper(II)

Bond	Distances (Å)		
	Copper(II) ethyl acetoacetate	Bis(acetylacetonato)copper(II)	
Cu–O(1)	1·89	1·96 [4]	1·94 [5]
Cu–O(2)	1·92	1·95	1·88
O(1)–C(2)	1·32	1·24	1·25
O(2)–C(4)	1·28	1·29	1·30
C(1)–C(2)	1·51	1·55	1·60
C(2)–C(3)	1·31	1·45	1·38
C(3)–C(4)	1·39	1·50	1·44

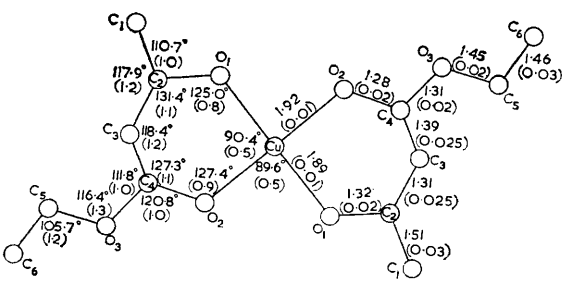

FIGURE 2. Bond lengths (Å) and angles in copper (II) ethyl acetoacetate. Estimated standard deviations are given in parentheses

In the " octahedral sites " of the copper atom, the carbon atoms C(3) of the =CH– groups of other molecules are situated at distances of 3·12 Å. This is similar to the environment of the copper atom in bis(acetylacetonato)copper(II) where the distances between the copper and carbon atoms are 2·84 Å. The greater separation of the molecules in copper(II) ethyl acetoacetate than in bis(acetylacetonato)copper(II) is consistent with the greater solubility of the former in organic solvents. All other intermolecular distances (see Figure 1) have values which are expected for van der Waals contacts.

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School of Chemistry, The University of New South Wales,
Box 1, P.O., Kensington, N.S.W., Australia. [*Received, October 26th*, 1964.]