644. *The Crystal Structure of Anhydrous Copper*(II) *Formate.*

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The crystal structure of royal-blue anhydrous copper(II) formate has been determined by X-ray diffraction techniques involving three-dimensional Fourier syntheses. There are eight molecules in the orthorhombic unit cell (space group *Pbca*) with dimensions a = 14·195 ± 0·005, b = 8·955 ± 0·005, and c = 6·218 ± 0·005 Å. There are no discrete molecules in the crystal; it consists of a three-dimensional array or copper atoms joined together by formate groups in an "*anti-syn*" bridging arrangement. Each copper atom has a distorted tetragonal-pyramidal co-ordination of four oxygen atoms, at a distance of 1·95 Å in a plane containing the copper atom, and a fifth oxygen atom at 2·40 Å along a line which makes an angle of 31° with the normal to this plane.

Three different anhydrous copper(II) formates have been identified by measurements of their magnetic susceptibilities and X-ray diffraction powder patterns.[1] Two of these, which are formed as powders by the dehydration of the di- and tetra-hydrates, exhibit unusual magnetic properties (μ = 1·75 and 1·61 B.M. respectively). The third is obtained as well-formed royal-blue crystals from concentrated formic acid solution kept at 100° for several hours. The magnetic moment of this modification shows no unusual features (μ = 1·90 B.M.). Because of the interest in the stereochemistry of these and related copper(II) salts of carboxylic acids,[2] the crystal structure of royal-blue anhydrous copper(II) formate was determined.

Experimental

The orthorhombic crystals are thin plates lying on their 010 faces. Accurate cell dimensions were obtained by using a Hägg focusing powder camera. The systematically absent reflections ($0kl$, with $k = 2n + 1$; $h0l$, with $l = 2n + 1$; $hk0$, with $h = 2n + 1$) indicate the space group *Pbca* unambiguously. Intensities were estimated visually from equi-inclination Weissenberg photographs by the multiple-film technique. They were corrected for the Lorentz and polarisation factors; no allowance was made for absorption or extinction. The intensities were placed on a common arbitrary scale by internal correlation and eventually the observed structure amplitudes were scaled to the calculated values.

Crystal Data: $Cu(H{\cdot}COO)_2$; M = 153·61; orthorhombic; a = 14·195 ± 0·005, b = 8·955 ± 0·005, c = 6·218 ± 0·005 Å; U = 709·41 Å^3; D_m = 2·58 ± 0·01 g. cm.$^{-3}$ (by flotation); Z = 8; D_c = 2·580 g. cm.$^{-3}$; $F(000)$ = 600; space group — *Pbca* (D_{2h}^{15}, No. 61). Radiation copper, unfiltered; single-crystal rotation, oscillation and equi-inclination Weissenberg photographs. Data for structure analysis from $hk0 \longrightarrow hk4$, $h0l \longrightarrow h4l$, $0kl \longrightarrow 4kl$.

Table 1. *Atomic parameters.*

Atom	x/a	y/b	z/c	σ (Å)
Cu	0·1152	0·0588	0·0065	0·002
O(1)	0·0893	0·2427	0·1621	0·009
O(2)	0·2223	0·0262	0·1950	0·009
O(3)	0·0067	0·0781	−0·1902	0·008
O(4)	0·1493	−0·1207	−0·1459	0·010
C(1)	0·0184	0·3226	0·1613	0·010
C(2)	0·2778	0·1353	0·2336	0·011

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[1] Martin and Waterman, *J.*, 1959, 1359.

[2] Martin and Waterman, *J.*, 1957, 2545.

TABLE 2. *Calculated structure factors and observed structure amplitudes.* (Scale: ½ absolute values.)

h	F_c	$\lvert F_o \rvert$
	h,0,0	
2	19	18
4	−51	45
6	−19	22
8	85	74
10	46	43
12	−20	23
14	−5	10
18	22	20
	h,0,2	
0	11	11
1	−17	16
2	15	17
3	−6	4
4	−107	67
5	−33	35
6	−25	26
7	19	21
8	37	35
9	15	16
10	16	19
11	−15	14
12	−32	31
13	−7	8
14	−36	33
16	21	20
	h,0,4	
0	45	41
1	10	12
2	−6	6
3	−12	13
4	−35	37
5	22	22
6	−25	24
8	35	33
9	−9	8
10	23	22
12	−29	28
14	−17	17
15	10	9
	h,0,6	
0	54	47
1	−18	14
2	15	16
4	−31	28
6	−5	7
7	9	7
8	28	27
10	17	17
	h,1,0	
2	−44	40
4	−51	41
6	18	23
8	23	25
10	−12	15
12	−29	27
18	−7	7
	h,1,1	
1	81	53
2	9	12
3	−58	47
4	4	5
5	−59	46
6	−6	7
7	28	26
8	23	24
9	55	43
11	−7	9
13	−27	27
16	7	8
17	19	21
	h, 1,2	
1	−34	31
2	−25	25
3	13	15
4	10	12
5	15	16
6	22	23
8	10	13
10	−17	18
14	10	12
15	5	7
16	11	12
17	8	9
	h,1,3	
1	31	29
2	−3	5
3	−28	29
4	−6	8
5	−66	47
7	11	14
9	32	31
13	−40	35
15	−5	6
	h,1,4	
1	8	9
2	−18	18
3	−4	6
5	−7	9
6	24	23
10	−7	9
14	10	11
	h,1,5	
1	38	35
2	−13	13
3	−18	20
5	−22	22
6	12	10
7	11	12
8	−8	7
9	37	30
12	−4	5
13	−14	16
	h,1,6	
2	−17	18
4	−10	8
8	12	9
10	−10	10
	h,1,7	
1	16	14
2	−8	7
3	−19	16
5	−23	19
7	8	7
8	10	8
	h,2,0	
0	72	41
2	−21	22
4	−28	29
6	−5	5
8	50	48
10	18	21
12	−30	30
14	−10	15
16	14	17
	h,2,1	
0	−19	19
1	−32	29
2	57	45
3	−39	39
4	26	27
5	11	11
6	18	21
7	48	41
8	6	9
10	15	17
11	−33	32
12	9	9
15	22	23
16	11	13
17	5	6
	h.2,2	
0	51	37
2	19	18
3	27	27
4	−71	50
6	−23	25
8	30	31
10	19	21
12	−17	21
13	11	13
14	−22	22
15	6	8
16	8	11
17	5	6
	h,2,3	
1	−35	29
2	−15	16
3	−47	38
4	13	13
5	33	29
6	−10	12
7	25	26
8	−7	8
9	−16	18
11	−19	22
15	12	14
	h,2,4	
0	52	39
2	10	13
3	−25	25
4	−36	34
6	−16	17
8	26	26
10	19	20
12	−12	14
13	−10	11
14	−12	14
	h,2,5	
1	−26	24
3	−19	19
4	−11	11
5	9	10
7	22	21
10	−11	9
11	−18	18
	h,2,6	
0	20	18
1	−22	21
4	−16	16
8	18	20
10	6	8
	h,2,7	
3	−14	13
4	12	12
5	6	8
6	5	7
7	15	15
	h,3,0	
2	−40	46
4	−10	12
6	42	39
8	20	22
10	−44	44
12	−27	27
14	24	24
16	20	21
	h,3,1	
1	31	28
2	−22	22
3	−9	9
4	19	21
5	−17	19
6	−17	18
7	4	6
8	5	7
9	30	32
10	−19	18
12	9	9
13	−15	19
14	−10	9
17	11	12
	h,3,2	
1	16	19
2	−75	59
3	29	29
4	−18	19
6	55	59
7	−6	7
8	26	26
9	8	10
10	−27	28
11	18	18
12	−19	21
14	14	17
16	16	18
	h,3,3	
1	16	18
3	−26	26
4	−7	9
5	−39	35
6	13	16
7	16	16
8	−11	11
9	4	7
10	5	6
12	−6	6
13	−14	15
	h,3,4	
1	−22	21
2	−56	48
3	−12	15
4	−13	15
6	42	37
8	13	15
9	−13	13
10	−20	19
11	−13	14
12	−16	18
14	8	10
	h,3,5	
1	18	19
3	−12	12
5	−5	8
8	12	11
9	20	16
13	−4	6
	h,3,6	
2	−19	20
3	6	7
5	10	9
6	16	16
7	6	6
8	10	10
10	−20	19
	h,3,7	
1	7	8
5	−9	9
	h,4,0	
4	−9	12
6	−35	36
8	−7	12
10	15	16
14	−8	12
	h,4,1	
1	−51	46
2	15	17
3	−55	48
5	23	28
6	7	11
7	48	56
9	−15	17
11	−43	36
12	8	12
15	21	23
16	5	5
	h,4,2	
0	9	10
1	−26	27
3	−13	15
5	6	9
6	10	12
7	6	11
8	9	13
15	−9	11
	h,4,3	
0	−11	13
1	−32	31
2	−8	13
3	−48	45
5	32	35
7	47	50
8	−8	9
11	−23	24
15	26	22
	h,4.4	
1	13	14
4	−9	11
6	11	16
	h,4,5	
1	−28	26
3	−26	25
4	10	12
5	11	14
7	26	27
10	−4	14
11	−25	27
	h,4,7	
0	−7	9
1	−12	14
3	−18	20
5	8	12
	h,5,0	
2	−90	70
4	−7	9
6	43	39
8	39	37
10	−35	33
12	−11	17
16	16	16
	h.5,1	
1	−23	23
2	−14	16
3	7	8
4	12	13
5	9	10
7	−17	17
9	−10	10
12	10	10
	h,5,2	
2	−43	40
3	10	12
4	−18	20
5	16	19
6	51	44
7	22	23
8	7	10
10	−21	23
12	−25	23
14	21	21
15	5	5
	h,5,3	
3	16	17
5	18	21
7	17	17
9	−11	12
11	5	8
13	10	10
	h,5,4	
1	−8	10
2	−33	33
3	−7	9
4	−5	9
6	22	24
7	−20	19
8	17	17
10	−29	29
12	−14	16
13	5	5
	h,5,5	
1	−11	11
	h,5,6	
2	−30	24
3	10	9
4	−8	7
	h,5,7	
1	−6	5
3	7	5
	h,6,0	
0	−43	43
2	−22	24
4	40	36
6	9	13
8	−24	25
10	−20	21
14	9	10
	h,6,1	
0	7	8
1	−38	33
3	−35	32
5	22	20
6	13	14
7	33	30
9	−9	9
11	−21	22
15	13	12
	h,6,2	
0	−27	27
2	9	10
3	11	11
4	23	26
6	13	14
7	−11	12
8	−17	18
9	−11	13
10	−6	9
12	19	21
14	10	12
	h,6,3	
1	−10	14
3	−29	28
5	9	14
7	24	24
11	−24	25
	h,6,4	
0	−17	20
2	−7	9
4	15	17
8	−16	18
9	9	11
10	−8	7
11	8	8
12	10	11
	h,6,5	
1	−18	17
3	−16	17
4	10	9
	h,6,6	
0	−18	16
4	16	13
	h,7,0	
2	−29	31
4	10	10
6	11	11
10	−27	27
	h,7,1	
1	−32	30
2	8	9
3	15	15
5	29	28
7	−10	14
9	−29	29
12	−4	6
	h,7,2	
2	−20	20
3	−10	10
4	−13	14
5	−14	14
6	24	26
8	7	9
9	−9	10
12	−13	15
	h,7,3	
1	−17	19
3	28	25
5	28	29
7	−7	9
9	−16	18
11	9	11
	h,7,4,	
2	−15	18
3	7	10
4	−6	8
5	15	17
6	11	16
8	16	18
10	−7	9

TABLE 2. (*Continued.*)

h	F_c	$\|F_o\|$
	h,7,5	
1	−22	22
3	7	8
	h,7,6	
2	−10	10
	h,8,0	
0	−27	29
2	−20	21
4	20	22
8	−30	31
10	−20	21
12	15	15
	h,8,1	
0	−9	9
1	−7	8
2	7	9
4	−12	9
7	6	9
	h,8,2	
0	−40	36
4	36	32
5	−9	9
6	19	22
8	−20	22
9	11	10
10	−11	15
12	17	15
	h,8,3	
0	8	8
3	−13	14
4	6	7
11	−5	5
	h,8,4	
0	−29	26
2	−5	8
4	34	28
6	7	10
7	−8	8
8	−17	18
9	−5	5
	h,8,5	
1	−7	7
	h,9,0	
8	9	11
10	8	9
	h,9,1	
1	−19	19
3	15	17
5	25	25
7	−6	7
9	−22	23
	h,9,2	
1	−8	9
6	−6	7
9	−4	5
	h,9,3	
1	−26	22
3	17	16
5	21	23
7	−10	12
9	−18	14
	h,9,4	
1	8	7
2	5	6
	h,10,0	
0	−27	28
4	22	21
6	15	16
8	−13	14
	h,10,1	
0	−22	22
1	8	11
3	12	13
4	−10	10
5	−11	12
7	−9	10
8	−7	6
	h,10,2	
0	−17	19
3	5	6
4	19	19
6	3	5
7	−4	4
	h,10,3	
0	6	7
1	10	11
3	6	7
4	5	5
	h,11,0	
2	23	22
4	8	8
	h,11,1	
1	−12	13
3	8	8
4	5	4

STRUCTURE DETERMINATION

All atoms in the unit $Cu(H{\cdot}COO)_2$ are in general positions whose fractional co-ordinates are $\pm\,(x,y,z;\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\bar{z};\ x,\tfrac{1}{2}-y,\ \tfrac{1}{2}+z;\ \tfrac{1}{2}-x,\ \bar{y},\tfrac{1}{2}+z)$. Approximate co-ordinates for the copper and the four oxygen atoms were obtained from a three-dimensional Patterson function. Calculation of structure factors with these co-ordinates gave a discrepancy factor, R, of 0·37. A three-dimensional Fourier synthesis led to positions for the carbon atoms. The structure was refined by successive three-dimensional Fourier syntheses; the co-ordinates of the electron-density maxima were determined by the method of Berghius *et al.*[3] Termination-of-series errors were estimated by the back-shift method.[4] Atomic scattering factors of Berghius *et al.*[5] were used for all atoms, the values for copper being corrected for dispersion.[6] A temperature factor, $\exp\,(-\,B \sin^2 \theta/\lambda^2)$ with $B = 1{\cdot}2$ Å^2 for the copper atom and $B = 1{\cdot}4$ Å^2 for the other atoms, was applied. Structure factors and Fourier syntheses were calculated on UTECOM, a Deuce digital computor, with programmes written by Dr. J. S. Rollett. The estimated standard deviations of the atomic co-ordinates were calculated by Cruickshank's method.[7] The final atomic parameters together with their root-mean-square estimated standard deviations (σ) are given in Table 1. The observed structure amplitudes and the calculated structure factors are listed in Table 2. The final discrepancy factor, R, for the 510 observed reflections was 0·12.

DISCUSSION

The arrangement of the atoms in a unit cell is illustrated in Fig. 1. There are no discrete molecules or ions in the crystal. Both oxygen atoms of the formate group are joined by covalent bonds to copper atoms and, in this way, the formate group acts as a bridge between copper atoms. As each copper atom is linked to four others by four different formate groups, an infinite three-dimensional network is produced.

The possible bridging arrangements of the carboxyl group in copper(II) compounds have been discussed by Martin and Waterman.[1] Because of the strain involved in the formation of a four-membered ring, the chelate structure (I) was considered unlikely. However, a ring system of this type has been found in carbonatotetramminecobalt(III) bromide.[8] The *syn-syn* (II) and the *anti-anti* configuration (III) are known in copper acetate monohydrate [9] and copper formate tetrahydrate [10] respectively. Anhydrous copper formate provides the first example of the *anti-syn*-arrangement (IV).

A correlation between the bridging arrangement of the carboxyl groups and magnetic behaviour is indicated. The close approach (2·64 Å) of the two copper atoms in the

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[3] Berghius, Shoemaker, Donohue, Shomaker, and Corey, *J. Amer. Chem. Soc.*, 1950, **72**, 2328.

[4] Booth, *Proc. Roy. Soc.*, 1946, *A*, **188**, 77.

[5] Berghius, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[6] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

[7] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

[8] Barclay and Hoskins, unpublished observations.

[9] Van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.

[10] Kiriyama, Ibamoto, and Matsuo, *Acta Cryst.*, 1954, **7**, 482.

syn-syn-configuration (II) is said[9] to rationalise the anomalous magnetic behaviour of copper acetate monohydrate ($\mu = 1{\cdot}40$ B.M.). An explanation of the difference in magnetic susceptibility of the anhydrous and the tetrahydrated copper formate ($\mu = 1{\cdot}90$ and $\mu = 1{\cdot}61$ B.M. respectively) does not appear possible in terms of the distances between copper atoms in these compounds (3·44 and 5·80 Å) respectively.

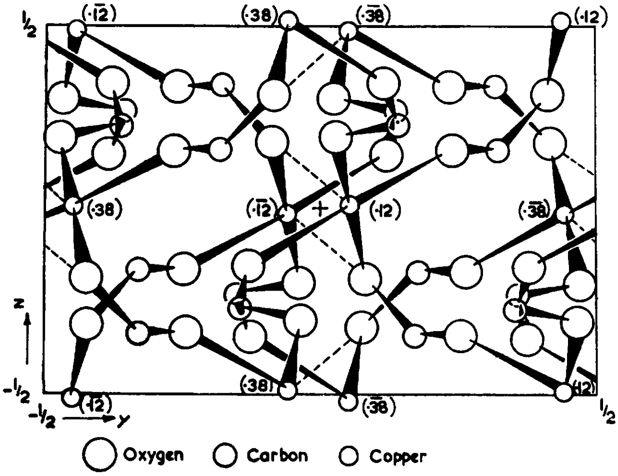


FIG. 1. *Arrangement of the atoms in the unit cell of copper*(II) *formate. The fractional x co-ordinates of the copper atoms are shown in parentheses.*

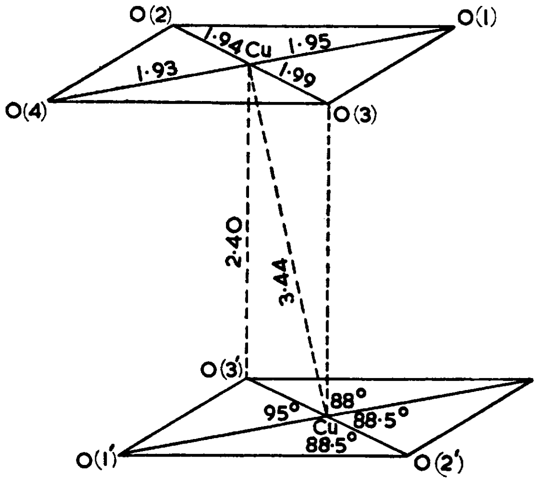


FIG. 2. *Environment of the copper atoms.*

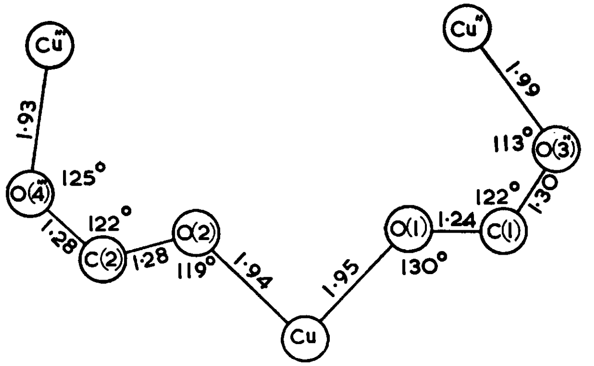
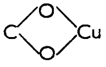
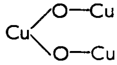


FIG. 3. *Bond lengths* (Å) *and bond angles in the formate bridging groups.*

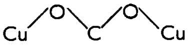
The copper atom has a distorted tetragonal-pyramidal co-ordination. Four oxygen atoms are in a plane containing the copper atom with a fifth at a greater distance along a line which makes an angle of 31° with the normal to this plane. Two copper atoms share oxygen atoms to form a type of bimolecular unit (see Figs. 1 and 2). The distance between these atoms is much shorter (3·44 Å) than between any other pair of copper atoms (greater than 4·6 Å). Similar bimolecular arrangements have been reported for *NN′*-ethylenebis-(salicylideneiminato)copper(II),[11] bis(dimethylglyoximato)copper(II),[12] and dichloro(dimethylglyoxime)copper(II).[13]



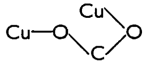
(I)
Chelate



(II)
syn-syn



(III)
anti-anti



(IV)
anti-syn

The bond distances and angles are listed in Table 3 and are shown diagrammatically in Figs. 2 and 3.*

The Cu–O(3) bond is significantly longer (1·99 Å) than the other planar Cu–O bonds (1·94 Å). This might be expected as the O(3) atom is bonded to two copper atoms while the others have only one copper atom as a near neighbour. In Table 4 the copper–oxygen bond lengths are compared with those reported previously. The C(1)–O(1) bond length appears to differ from the other carbon–oxygen distances. However, it is probable

TABLE 3. *Bond distances and angles.*

Bond	Length (Å)	σ (Å)	Angle	Value	σ
Cu–O(1)	1·945	0·009	O(1)–Cu–O(2)	89°	1°
Cu–O(2)	1·942	0·009	O(1)–Cu–O(3)	95	1
Cu–O(3)	1·986	0·008	O(2)–Cu–O(4)	89	1
Cu–O(4)	1·928	0·010	O(3)–Cu–O(4)	88	1
C(1)–O(1)	1·235	0·013	O(1)–C(1)–O(3″)	122	1
C(1)–O(3″)	1·295	0·013	O(2)–C(2)–O(4‴)	122	1
C(2)–O(2)	1·278	0·014			
C(2)–O(4‴)	1·284	0·015	Cu–O(1)–C(1)	130	1
			Cu–O(2)–C(2)	119	1
Cu–O(3′)	2·397	0·008	Cu″–O(3″)–C(1)	113	1
			Cu‴–O(4‴)–C(2)	125	1
Cu–Cu′	3·435	0·004			

TABLE 4. *Copper–oxygen bond lengths.**

Compound	Cu–O bond length (Å)	Compound	Cu–O bond length (Å)
Copper(II) formate	1·94, 1·99	Bisbiuretcopper(II) chloride	1·92
Monopyridinecopper(II) acetate [a]	1·95	Anhydrous copper nitrate [g]	1·9
Linarite [b]	1·93	Copper fluoride dihydrate [h]	1·93
NN′-Propylenebis(salicylideneiminato) copper(II) [c]	1·88, 1·94	Callaghanite [i]	2·00
NN′-Ethylenebis(salicylideneiminato)-copper(II) [c]	1·91, 2·03	Chalkomenite [j]	1·93
Copper salicylate tetrahydrate [d]	1·84, 1·92	Azurite [k]	1·88, 1·98
Meta-zeunerite [e]	2·14	Barium copper formate [l]	1·97, 2·18

* For values reported before 1956 see Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ. No.* 11, London, 1959.

a, Unpublished work. *b*, Bachman and Zemann, *Naturwiss.*, 1960, **8**, 177. *c*, Llewellyn and Waters, *J.*, 1960, 2639. *d*, Hanic and Michalov, *Acta Cryst.*, 1960, **13**, 299. *e*, Hanic, *Czech. J. Phys.*, 1960, **10**, *B*, 169. *f*, Freeman, Smith, and Taylor, *Nature*, 1959, **184**, 707. *g*, Wallwork, *Proc. Chem. Soc.*, 1959, 311. *h*, Geller and Bond, *J. Chem. Phys.*, 1958, **29**, 925. i, Brunton, Steinfink, and Beck, *Acta Cryst.*, 1958, **11**, 169. *j*, Gattow, *ibid.*, p. 377. *k*, Gattow and Zemann, *ibid.*, p. 866. *l*, Rao, Sundarama, and Rao, *Z. Krist.*, 1958, **110**, 231.

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* The co-ordinates of the atoms marked with primes are related to those listed in Table 1 in the following way: A′ $(\bar{x}, \bar{y}, \bar{z})$; A″ $(x, \frac{1}{2} - y, \frac{1}{2} + z)$; A‴ $(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$.

[11] Hall and Waters, *J.*, 1960, 2644.

[12] Frasson, Bardi, and Bezzi, *Acta Cryst.*, 1959, **12**, 201.

[13] Barclay, unpublished observations.

that the estimated standard deviation is too small and that the mean value of 1·273 Å would better represent the carbon–oxygen bond length. The values reported previously for carbon–oxygen bond length and oxygen–carbon–oxygen bond angles in formates are listed in Table 5 for comparison.

The copper atom and its four nearest neighbours are in a plane the equation for which (calculated by the method of least squares) is $0{\cdot}572x + 0{\cdot}521y - 0{\cdot}633z - 1{\cdot}191 = 0$. The deviations of these atoms from the plane [Cu, 0·007; O(1), 0·03; O(2), 0·03; O(3), 0·03; O(4), 0·03 Å] are all within the experimental error. The Cu–O(2)–C(2)–O(4‴)–Cu‴ grouping is planar, but the similar Cu–O(1)–C(1)–O(3″)–Cu″ group is not, presumably owing to the interaction between O(3) and a second copper atom. The equations for the least-squares planes (and the deviations from these planes) are:

$$0{\cdot}556x - 0{\cdot}282y - 0{\cdot}782z - 0{\cdot}732 = 0$$

[Cu, 0·002; O(2), 0·01; C(2), 0·01; O(4‴), 0·01; Cu‴, 0·006 Å]

$$0{\cdot}503x - 0{\cdot}594y - 0{\cdot}628z - 1{\cdot}178 = 0$$

[Cu, 0·07; O(1), 0·12; C(1), 0·04; O(3″), 0·10; Cu″, 0·01 Å]

Orgel and Dunitz [14] have listed three types of stereochemical arrangements found in copper(II) compounds, namely, distorted octahedral with four shorter and two longer bonds, square planar, and tetrahedral. To these types should be added tetragonal-pyramidal (with four shorter and one longer bond) and the binuclear compounds. Anhydrous copper formate and three other examples of tetragonal-pyramidal co-ordination which involve a bimolecular unit have been mentioned above (p. 3293). Callaghanite,[15] chalkomenite,[16] tetramminecopper(II) sulphate monohydrate,[17] and *NN*′-propylenebis-(salicylideneiminato)copper(II) monohydrate [18] have a tetragonal-pyramidal configuration about the copper atom without a bimolecular association. Copper(II) acetate monohydrate [9] and monopyridinecopper(II) acetate [19] are examples of binuclear compounds in which the copper atom has four short and one long bond with a second copper atom in the sixth " octahedral " site. In bis(bipyridine)copper(II) iodide, the copper atom forms five bonds which are directed towards the corners of a trigonal bipyramid.[20] These five bonds are of normal covalent length. In all other cases, the fifth and the sixth atom are at greater distances than expected for covalent bonds.

TABLE 5. *Bond lengths and angles in formates.**

Compound	C–O bond length (Å)	O–C–O bond angle	Compound	C–O bond length (Å)	O–C–O bond angle
Anhydrous copper formate	1·27	122°	Barium copper formate [b] ...	1·23, 1·43	124°
Strontium formate dihydrate [a]	1·21, 1·24	124, 127	Copper formate tetrahydrate [10]	1·25	120

* See footnote * of Table 4.

a, Osaki, *Ann. Reports Sci. Works, Osaka Univ.*, 1958, **6**, 13; *b*, Rao, Sundarama, and Rao, *Z. Krist.*, 1958, **110**, 231.

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[14] Orgel and Dunitz, *Nature*, 1957, **179**, 462.

[15] Ref. *i* of Table 4.

[16] Ref. *j* of Table 4.

[17] Mazzi, *Acta Cryst.*, 1955, **8**, 137.

[18] Ref. *c* of Table 4.

[19] Ref. *a* of Table 4.

[20] Barclay and Kennard, *Nature*, in the press.