1037. *The Crystal Structure of Monopyridinecopper*(II) *Acetate.*

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The structure of monopyridinecopper(II) acetate has been determined by Patterson and Fourier syntheses from three-dimensional *X*-ray diffraction spectra. The copper atoms are bridged in pairs by four acetate groups to form binuclear molecules, $Cu_2(CH_3{\cdot}CO_2)_4,2C_5H_5N$, similar to those found in copper acetate monohydrate. The copper atom is 0·22 Å out of the plane of the four oxygen atoms to which it is joined by covalent bonds (1·98 Å in length). The nitrogen atom of a pyridine molecule is attached to the copper atom by a slightly elongated covalent bond (2·13 Å long), giving the copper atom a distorted tetragonal-pyramidal co-ordination. The sixth, "octahedral," site is occupied by the second copper atom to which a δ-bond is formed (Cu–Cu distance 2·63 Å). The binuclear molecule as a whole possesses a two-fold axis of symmetry which passes through the copper atoms and the pyridine molecules.

Copper acetate monohydrate is a binuclear molecule, $Cu_2(CH_3{\cdot}CO_2)_4,2H_2O$, in which the copper atoms are bridged in pairs by four acetate groups.[1] The close approach of

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[1] van Niekerk and Shoening, *Acta Cryst.*, 1953, **6**, 227.

the two copper atoms (2·64 Å) is consistent with the formation of a δ-bond between them.[2,3] The low magnetic moment at room temperature (μ = 1·40 B.M.) and the antiferromagnetic behaviour in the variation of magnetic susceptibility with temperature are considered to result from the binuclear molecules.[2] On the basis of magnetic susceptibility, absorption spectra, and other physical quantities, several simple and complex copper alkanoates are claimed to have similar binuclear molecules.[4] The structure of one such compound, monopyridinecopper(II) acetate, has now been determined.

EXPERIMENTAL

Monopyridinecopper(II) acetate, in the form of dark-green acicular crystals, was supplied by Dr. R. L. Martin and Miss H. Waterman. Oscillation and Weissenberg photographs showed them to be monoclinic. Systematically absent spectra (hkl with $k + 1 = 2n + 1$; $h0l$ with $h = 2n + 1$) indicated that the space group was either Aa or $A2/a$. Accurate cell dimensions were determined from photographs taken on a Guinier focusing powder camera. The intensities of 1200 independent reflections were estimated visually from equi-inclination Weissenberg photographs by the multiple-film technique. The usual Lorentz and polarisation factors were applied to the intensities of the observed reflections; no allowance was made for absorption or extinction. The resulting intensities were correlated so that all observed data were on the same relative scale. The observed structure amplitudes were placed on an absolute scale by comparison with the calculated values.

Crystal Data.—$Cu(CH_3{\cdot}CO_2)_2,C_5H_5N$; M = 265·64; monoclinic; a = 12·542 ± 0·010, b = 17·314 ± 0·010, c = 9·955 ± 0·005 Å, β = 96° 43′ ± 10′; U = 2144 Å^3; D_m = 1·62 ± 0·01 g. cm.$^{-3}$ (by flotation); Z = 8; D_c = 1·615 g. cm.$^{-3}$; $F(000)$ = 1064; space group, $A2/a$ (C_{2h}^6, No. 15); radiation, copper, unfiltered; single-crystal oscillation and Weissenberg photographs; data for structure analysis from $hk0 \longrightarrow hk7$, $h0l \longrightarrow h8l$.

Structure Determination.—A statistical analysis of the 1200 three-dimensional intensities by the method of Howells, Phillips, and Rogers [5] indicated that the space group was probably centrosymmetric. Hence, the space group $A2/a$ was assumed and was confirmed by the subsequent satisfactory refinement.

There is no requirement for any atom to be in special positions in the unit cell as there are eight equivalent general positions whose fractional co-ordinates are $\pm(x,y,z;\ \tfrac{1}{2}+x,\bar{y},z;\ x,\tfrac{1}{2}+y,\tfrac{1}{2}+z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{1}{2}+z)$. However, if the structure is similar to that of copper acetate monohydrate, the binuclear unit must possess a two-fold axis of rotation or a centre of symmetry.

A three-dimensional Patterson function was interpreted to indicate that the copper atoms were not in general positions but lay on the two-fold axes in two independent sets of special positions of the type $\pm(\tfrac{1}{4},y,0;\ \tfrac{1}{4},\tfrac{1}{2}+y,\tfrac{1}{2})$. Structure factors were calculated with y_1 = 0·056 and y_2 = 0·202 for the two copper atoms; the R factor was 0·40. This interpretation of the Patterson map strongly suggests the binuclear arrangement, in which case the nitrogen atom

TABLE 1.

Atomic parameters.

Atom	x/a	y/b	z/c	σ (Å)	Atom	x/a	y/b	z/c	σ (Å)
Cu(1) ...	0·2500	0·0529	0·0000	0·002	C(4)	0·2244	0·4488	0·1126	0·014
Cu(2) ...	0·2500	0·2049	0·0000	0·002	C(5)	0·0395	0·1278	0·2801	0·019
O(1)	0·3621	0·1906	0·1558	0·011	C(6)	0·4857	0·1278	0·3116	0·019
O(2)	0·1404	0·1923	0·1272	0·010	C(7)	0·3484	−0·1921	−0·0203	0·016
O(3)	0·1500	0·0657	0·1391	0·010	C(8)	0·3420	−0·1108	−0·0161	0·011
O(4)	0·3719	0·0645	0·1431	0·010	C(9)	0·2500	−0·2302	0·0000	0·014
C(1)	0·4012	0·1274	0·1962	0·011	C(10) ...	0·2500	0·4916	0·0000	0·012
C(2)	0·1157	0·1291	0·1694	0·018	N(1) ...	0·2500	−0·0696	0·0000	0·009
C(3)	0·2234	0·3691	0·1096	0·012	N(2) ...	0·2500	0·3279	0·0000	0·011

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[2] Figgis and Martin, *J.*, 1956, 3837.

[3] Ross, *Trans. Faraday Soc.*, 1959, **55**, 1057.

[4] Martin and Waterman, *J.*, 1957, 2545; Martin and Whitley, *J.*, 1958, 1394; Martin and Waterman, *J.*, 1959, 1359; Graddon, *Nature*, 1960, **186**, 715.

[5] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

TABLE 2.

Calculated structure factors and observed structure amplitudes. (Scale: $\frac{1}{2}$ absolute values.)

l	F_c	$\lvert F_o \rvert$
	0,0,l	
2	53	56
4	22	27
6	57	59
8	34	31
10	17	15
12	9	9
	0,1,l	
1	54	49
3	12	19
5	27	28
7	28	28
9	7	6
11	6	5
	0,2,l	
0	−2	4
2	−4	6
4	−8	10
6	−3	4
	0,3,l	
3	−1	5
5	−7	9
7	−9	10
	0,4,l	
0	−29	28
2	34	38
4	11	13
6	5	5
8	10	12
	0,5,l	
1	22	24
3	4	4
5	7	5
7	9	10
9	8	8
	0,6,l	
0	−6	8
2	−6	10
6	−4	5
8	−4	6
	0,7,l	
1	−61	58
3	−20	22
5	−23	28
7	−27	28
9	−15	13
11	−6	4
	0,8,l	
0	−43	45
2	−36	35
4	−4	3
6	−23	25
8	−22	22
	0,9,l	
1	−9	10
3	5	8
7	−6	8
	0,10,l	
0	1	4
2	5	7
4	5	7
	0,11,l	
1	−6	7
3	−17	18
5	−15	18
7	−7	9
9	−3	3
	0,12,l	
0	−36	37
2	−13	14
4	−13	13
6	−14	14
8	−9	7
10	−9	7
	0,13,l	
1	−15	17
3	−10	11
5	−11	13
7	−8	9
	0,14,l	
0	10	13
6	5	7
8	4	4
	0,15,l	
1	17	20
3	4	5
5	10	11
7	11	11
9	4	3
	0,16,	
0	22	25
4	−2	4
6	7	8
8	4	4
	0,17,l	
3	−3	5
7	1	3
	0,18,l	
2	6	6
4	5	6
6	3	4
	0,19,l	
1	9	9
3	12	11
5	8	6
	0,20,l	
0	7	8
2	11	10
4	7	5
	0,21,l	
1	2	3
3	2	3
	0,22,l	
0	−2	2
	1,1,l	
−11	−7	6
−9	−10	8
−7	−28	27
−5	−11	12
−3	14	19
−1	−50	45
1	−45	46
3	10	17
5	−11	14
7	−14	14
	1,2,l	
−12	−5	3
−10	−5	5
−8	−6	6
−6	−27	30
−2	13	16
0	−34	44
2	14	16
6	−16	20
	1,3,l	
−7	−6	7
−5	5	7
−3	16	18
−1	−20	22
1	−19	19
3	16	16
	1,4 l	
−4	−9	10
−2	−8	9
	1,5,l	
−9	−10	8
−7	−13	13
−5	−10	11
−3	−13	12
−1	−24	24
1	−24	24
3	−13	14
5	−10	10
7	−16	16
	1,6,l	
−12	−7	5
−10	−7	4
−8	−26	22
−6	−24	23
−4	−12	9
−2	−38	36
0	−46	35
2	−32	30
4	−18	20
6	−25	26
8	−17	20
10	−12	12
	1,7,l	
−9	−12	10
−7	−20	21
−5	−15	18
−3	−15	17
−1	−39	40
1	−38	39
3	−18	19
5	−15	20
7	−17	20
9	−9	11
11	−6	6
	1,8,l	
−8	5	5
−4	−3	3
0	9	11
2	3	3
4	−3	5
	1,9,l	
−9	5	4
−7	11	11
−5	5	6
−1	13	13
1	10	10
5	4	6
7	8	12
	1,10,l	
−10	−4	4
−8	6	6
−4	−14	15
0	6	9
4	−10	12
	1,11,l	
−7	−4	4
−5	−6	7
−3	−5	7
−1	−4	5
1	−3	4
3	−5	7
5	−4	6
9	−3	4
	1,12,l	
−6	5	7
−4	9	10
−2	8	8
0	8	9
2	8	9
4	9	11
6	9	11
8	5	6
	1,13,l	
−9	8	5
−7	14	12
−5	12	10
−3	9	9
−1	25	24
1	26	27
3	11	11
5	12	12
7	12	13
9	10	10
	1,14,l	
−8	9	7
−6	19	16
−4	14	13
−2	14	16
0	24	26
2	13	15
4	14	17
6	15	20
8	9	11
	1,15,l	
−9	3	2
−7	6	6
−3	−2	4
−1	8	9
1	7	8
	1,16,l	
0	−6	7
	1,17,l	
−5	4	4
−3	9	10
3	8	10
5	4	4
	1,18,l	
−6	5	4
−4	11	11
−2	12	11
0	6	7
2	12	14
4	10	12
6	6	6
	1,19,l	
−3	4	3
1	3	4
3	4	4
	1,20,l	
−4	−3	3
−2	−5	5
0	−4	5
2	−4	5
4	−3	3
	1,21,l	
−3	−7	6
−1	−7	7
1	−7	8
3	−6	6
	1,22,l	
0	−3	4
	2,0,l	
−12	−8	6
−10	−14	11
−8	−31	31
−6	−41	48
−4	−22	25
−2	−79	97
0	−87	75
2	−98	101
4	−48	54
6	−29	34
8	−33	52
	2,1,l	
−11	−6	4
−9	−6	6
−7	−14	15
−5	−28	29
−3	−23	22
−1	−29	30
1	−25	25
3	−26	24
5	−32	33
7	−15	15
	2,2,l	
0	−5	6
4	9	8
	2,3,l	
−5	5	7
−3	−7	9
−1	9	11
1	12	15
5	10	13
	2,4,l	
−8	−8	7
−6	−10	11
−4	−22	25
−2	−6	3
0	−30	30
2	2	6
4	−16	16
6	−14	12
	2,5,l	
−9	−7	6
−7	−13	12
−3	−7	8
−1	−15	15
1	−13	11
3	−16	15
5	−7	7
7	−6	6
9	−6	5
11	−6	7
	2,6,l	
−4	6	4
−2	4	5
0	8	6
2	3	4
6	4	5
12	1	2
	2,7,l	
−11	7	4
−9	14	10
−7	25	24
−5	21	23
−3	32	30
−1	44	41
1	41	39
3	36	35
5	25	26
7	19	19
9	13	11
	2,8,l	
−10	6	5
−8	17	13
−6	20	21
−4	19	18
−2	20	20
0	44	38
2	19	19
6	21	23
8	8	7
10	12	10
	2,9,l	
−7	6	6
−3	7	7
−1	6	7
3	4	4
5	4	6
7	3	4
	2,10,l	
4	−7	8
6	−3	5
	2,11,l	
−9	5	3
−7	5	5
−5	18	17
−3	19	19
−1	11	12
1	10	9
3	11	12
5	14	15
7	8	10
9	4	5
	2,12,l	
−10	7	5
−8	10	8
−6	12	11
−4	9	8
−2	19	19
0	17	17
2	24	23
4	12	12
6	8	7
8	13	11
10	7	6
	2,13,l	
−7	5	6
−5	8	9
−3	7	8
−1	10	11
1	9	10
3	11	12
5	11	12
7	6	6
9	6	5
	2,14,l	
−8	−4	4
−6	−5	6
−4	−6	5
−2	−7	7
0	−6	8
2	−7	11
6	−3	4
8	−4	5
	2,15,l	
−9	−4	3
−7	−8	7
−5	−11	12
−3	−9	9
−1	−12	13
1	−11	12
3	−10	12
5	−10	13
7	−7	7
	2,16,l	
−8	−3	3
−2	−6	6
0	−5	7
2	−8	8
4	−3	4
6	−1	3
	2,18,l	
−4	−5	5
−2	−5	5
0	−6	6
2	−4	5
4	−4	5
6	−4	6
	2,19,l	
1	−10	9
3	−9	9
5	−8	8
	2,20,l	
−4	−7	5
−2	−7	7
0	−10	9
2	−7	6
4	−8	7
	2,21,l	
−3	−2	2
3	−2	6
	3,1,l	
−11	8	5
−9	17	12
−7	18	15
−5	25	27
−3	36	35
−1	20	21
1	27	30
3	44	45
5	11	9

TABLE 2. (*Continued.*)

l	F_c	$\|F_o\|$
	3,2,l	
−12	8	5
−8	12	10
−6	13	12
−4	33	37
−2	42	42
0	−34	45
2	27	24
4	29	30
	3,3,l	
−9	5	5
−5	2	4
−3	3	3
−1	−2	2
1	11	13
3	10	12
5	−8	12
	3,4,l	
−4	7	9
0	−3	5
4	1	4
6	5	6
	3,5,l	
−11	6	4
−7	9	10
−5	12	13
−3	13	14
−1	13	13
1	14	13
3	13	14
5	16	19
7	7	6
9	7	7
11	7	6
	3,6,l	
−12	7	4
−10	13	9
−8	13	10
−6	23	22
−4	34	30
−2	21	20
0	35	31
2	25	24
4	36	37
6	18	22
8	9	8
10	13	13
	3,7,l	
−11	6	5
−9	9	6
−7	15	14
−5	18	21
−3	24	24
−1	24	24
1	21	22
3	27	29
5	21	23
7	7	8
9	9	10
11	8	8
	3,8,l	
−6	−6	6
−4	−4	7
−2	−4	4
0	−9	12
2	−7	9
4	−4	5
10	−2	3
	3,9,l	
−7	−8	7
−5	−12	12
−3	−16	16
−1	−7	6
3	−13	14
5	−14	16
7	1	6
	3,10,l	
−8	3	5
−2	10	13
2	5	6
4	−1	4
6	4	6
8	5	8
	3,11,l	
−9	6	5
−7	8	6
−5	8	8
−3	9	11
−1	10	11
1	9	10
3	8	9
5	3	4
7	4	5
	3,12,l	
−4	−6	8
−2	−4	6
2	−5	6
4	−5	8
6	−6	8
8	−4	5
	3,13,l	
−9	−10	6
−7	−10	8
−5	−12	10
−3	−15	15
−1	−14	12
1	−19	18
3	−20	22
5	−8	8
7	−9	9
9	−10	7
	3,14,l	
−8	−11	7
−6	−13	12
−4	−22	20
−2	−24	22
0	−8	9
2	−20	21
4	−20	23
6	−10	12
8	−8	8
	3,15,l	
−9	−5	4
−7	−5	4
−5	−4	4
−3	−6	8
−1	−5	6
1	−6	6
3	−7	9
	3,16,l	
2	4	5
4	2	4
	3,17,l	
−1	−6	7
1	−5	6
5	−5	6
	3,18,l	
−6	−8	6
−4	−7	7
−2	−7	8
0	−14	15
2	−7	9
4	−7	8
	3,19,l	
−1	−4	4
1	−4	4
	3,20,l	
−4	4	3
−2	3	3
0	5	5
2	4	4
4	3	4
	3,21,l	
−3	7	6
−1	7	7
1	7	7
	4,0,l	
−12	8	5
−10	17	17
−8	22	24
−6	17	18
−4	59	74
−2	39	39
0	17	26
2	71	63
4	57	55
6	14	14
8	17	14
10	22	15
	4,1,l	
−11	7	5
−9	8	6
−5	19	18
−3	52	48
−1	−10	12
1	−10	17
3	47	48
5	16	12
	4,2,l	
−2	−3	3
0	9	9
2	7	7
	4,3,l	
−5	8	9
−3	−14	16
−1	16	17
1	18	21
3	−17	21
	4,4,l	
−12	5	3
−10	6	5
−6	18	18
−4	14	13
−2	23	24
0	18	15
2	12	13
4	14	14
	4,5,l	
−11	5	3
−9	6	4
−7	7	8
−5	12	14
−3	6	8
−1	12	10
1	12	10
3	9	10
5	14	14
9	6	6
11	5	4
	4,6,l	
−6	−4	4
−4	−7	7
−2	−2	4
0	−4	3
2	−7	7
4	−4	6
8	−2	4
	4,7,l	
−11	−12	7
−9	−11	8
−7	−12	10
−5	−33	35
−3	−34	36
−1	−22	23
1	−29	30
3	−36	37
5	−28	29
7	−8	7
9	−13	13
11	−10	10
	4,8,l	
−10	−12	9
−8	−6	4
−6	−17	20
−4	−33	33
−2	−26	25
0	−4	3
2	−29	26
4	−33	33
6	−9	11
8	−9	10
10	−11	10
	4,9,l	
−11	−5	3
−5	−13	14
−3	−12	13
3	−10	11
5	−9	12
7	2	5
9	−3	3
	4,10,l	
−8	−4	4
0	−10	11
2	−7	7
	4,11,l	
−9	−7	5
−7	−9	7
−5	−11	12
−3	−22	22
−1	−16	16
1	−11	12
3	−15	15
5	−9	11
7	−12	15
9	−4	4
	4,12,l	
−8	−12	9
−6	−8	6
−4	−11	12
−2	−12	14
0	−15	15
2	−17	18
4	−11	15
6	−8	9
8	−8	7
	4,13,l	
−5	−2	5
−3	−10	10
3	−10	12
5	−6	7
7	−5	7
9	−3	4
	4,14,l	
−8	4	3
−6	6	6
−4	10	11
−2	8	9
0	7	7
2	10	11
4	7	9
6	3	4
8	3	4
	4,15,l	
−5	9	9
−3	19	19
1	4	4
3	18	20
5	7	10
7	5	5
	4,16,l	
−4	6	7
0	−3	6
2	7	8
4	6	9
6	−1	3
	4,17,l	
−7	−3	3
−1	−5	6
1	−4	6
	4,18,l	
−6	4	3
−4	3	3
−2	4	4
0	6	8
2	4	5
4	3	3
	4,19,l	
−5	9	6
−3	6	4
−1	11	9
1	11	10
3	6	5
	4,20,l	
−4	6	4
−2	7	6
0	8	6
2	7	6
4	7	7
	5,1,l	
−11	−8	4
−9	−13	8
−7	−13	12
−5	−22	19
−3	−48	53
−1	−16	14
1	−24	23
3	−46	42
5	−18	15
	5,2,l	
−10	−11	6
−6	−5	5
−4	−51	43
−2	−23	22
0	0	3
2	−21	22
4	−30	26
	5,3,l	
−7	−5	5
−3	−6	9
−1	4	6
1	−8	8
3	−14	14
	5,4,l	
−4	−2	4
−2	3	4
0	4	5
	5,5,l	
−11	−7	4
−9	−5	5
−5	−19	19
−3	−10	11
1	−13	11
3	−15	16
5	−9	11
7	−5	8
9	−7	7
	5,6,l	
−10	−12	8
−8	−8	7
−6	−19	19
−4	−32	32
−2	−33	27
0	−6	4
2	−34	29
4	−31	32
6	−12	11
8	−12	13
10	−10	7
	5,7,l	
−11	−8	4
−9	−8	7
−7	−6	5
−5	−22	23
−3	−25	25
−1	−13	12
1	−17	19
3	−25	25
5	−14	14
7	−8	10
9	−8	9
	5,8,l	
−6	5	5
−4	6	9
−2	6	8
0	6	7
2	10	13
4	6	8
8	2	4
	5,9,l	
−11	6	4
−7	−3	6
−5	17	17
−3	20	20
3	16	17
5	11	10
9	4	4
	5,10,l	
−8	−5	7
0	−14	15
2	4	6
4	2	4
6	−7	12
8	−2	3
	5,11,l	
−9	−5	4
−7	−8	8
−5	−5	6
−3	−12	13
−1	−14	15
1	−10	11
3	−7	9
5	−8	9
7	−6	6
	5,12,l	
−4	3	5
	5,13,l	
−9	8	6
−7	11	9
−5	10	10
−3	15	16
−1	11	10
1	15	14
3	18	18
5	9	9
7	6	5
	5,14,l	
−8	7	5
−6	9	9
−4	26	26
−2	19	20
0	12	12
2	17	19
4	19	21
6	13	14
8	7	6
	5,15,l	
−7	4	3
−5	5	6
−3	8	9
−1	4	5
1	7	8
3	9	12
5	4	5
	5,17,l	
−7	4	3
−5	3	3
−1	7	8
1	6	6
5	2	4
	5,18,l	
−6	8	6
−4	4	4
−2	9	10
0	11	11
2	7	8
4	5	7
	5,19,l	
−1	4	4
	5,20,l	
−4	−3	2
−2	−3	3
0	−4	4
2	−5	5
	5,21,l	
−1	−7	4
	6,0,l	
−12	−9	4
−10	−18	18
−8	−18	18
−6	−26	28
−4	−41	46
−2	−32	40
0	−30	32
2	−44	50
4	−32	33

TABLE 2. (*Continued.*)

	F_c	$\lvert F_o\rvert$
	6,1,*l*	
−11	−9	6
−9	−7	6
−5	−21	21
−3	−27	31
−1	−11	11
5	−20	18
	6,2,*l*	
−4	4	3
−2	4	10
	6,3,*l*	
−7	−3	5
−3	2	3
−1	−3	4
1	−4	5
3	−9	9
	6,4,*l*	
−8	−6	5
−6	−8	6
−4	−17	18
−2	−17	16
0	−13	13
2	−15	14
6	−10	11
8	−8	7
	6,5,*l*	
−11	−5	3
−9	−7	5
−7	−5	5
−5	−9	8
−3	−16	13
−1	−7	6
1	−8	8
3	−15	15
7	−8	9
9	−5	5
	6,6,*l*	
−6	3	4
−4	3	4
−2	2	4
0	3	8
2	6	6
4	4	4
	6,7,*l*	
−11	10	6
−9	12	10
−7	12	9
−5	24	22
−3	33	35
−1	19	17
1	22	27
3	33	35
5	13	12
7	14	15
9	10	11
	6,8,*l*	
−10	11	7
−8	8	7
−6	12	11
−4	30	26
−2	21	21
0	11	10
2	24	22
4	18	19
6	11	11
8	11	13
10	7	4

l	F_c	$\lvert F_o\rvert$
	6,9,*l*	
−11	3	3
−5	7	7
−3	12	13
1	3	4
3	12	13
5	3	4
7	4	5
9	3	3
	6,10,*l*	
−6	4	5
0	8	8
2	7	8
4	3	4
	6,11,*l*	
−7	8	7
−5	11	11
−3	12	12
−1	17	18
1	12	11
3	7	6
5	15	17
7	7	7
9	4	2
	6,12,*l*	
−10	6	3
−8	9	6
−6	11	9
−4	9	9
−2	11	9
0	15	13
2	13	12
4	10	10
6	7	7
8	5	4
	6,13,*l*	
−5	5	7
−3	7	7
−1	4	8
5	6	7
7	3	4
	6,14,*l*	
−6	−5	5
−4	−6	7
−2	−7	8
0	−8	8
2	−8	9
4	−7	8
6	−4	5
	6,15,*l*	
−5	−10	9
−3	−12	12
−1	−8	8
1	−7	7
3	−7	9
5	−10	10
7	−5	5
	6,16,*l*	
−4	−4	4
2	−3	5
	6,17,*l*	
−1	3	4
3	2	3
	6,18,*l*	
0	−4	5

l	F_c	$\lvert F_o\rvert$
2	−5	5
4	−3	3
	7,1,*l*	
−11	6	3
−9	9	9
−7	10	9
−5	20	20
−3	10	13
−1	26	28
1	32	30
3	12	12
5	19	16
	7,2,*l*	
−10	6	4
−6	12	11
−4	10	9
−2	25	21
	7,3,*l*	
−5	5	6
−3	−9	11
−1	6	4
1	11	12
	7,4,*l*	
−2	4	5
	7,5,*l*	
−11	4	2
−9	7	5
−7	11	8
−5	5	5
−3	16	17
−1	10	8
1	8	4
3	15	13
	7,6,*l*	
−10	11	6
−8	13	12
−6	11	9
−4	26	24
−2	20	18
0	23	19
	7,7,*l*	
−11	6	3
−9	8	6
−7	10	9
−5	11	10
−3	19	22
−1	15	16
1	16	18
3	16	18
	7,8,*l*	
−4	−3	6
−2	−3	5
0	−6	6
2	−7	8
	7,9,*l*	
−3	−14	15
−1	−8	8
1	−5	5
3	−8	9
7	−9	11
	7,10,*l*	
−6	5	8
−2	6	7

l	F_c	$\lvert F_o\rvert$
4	5	8
6	2	5
	7,11,*l*	
−5	7	7
−3	5	6
−1	8	10
1	9	9
3	5	6
5	8	9
7	5	4
	7,12,*l*	
−6	−4	4
−4	−2	3
−2	−5	6
	7,13,*l*	
−9	−7	4
−7	−10	8
−5	−13	12
−3	−6	6
−1	−14	14
1	−16	15
3	−9	9
5	−10	9
7	−6	5
	7,14,*l*	
−8	−5	4
−6	−11	9
−4	−12	11
−2	−18	17
0	−16	16
2	−10	10
4	−12	12
6	−13	12
	7,15,*l*	
−5	−5	4
−1	−5	5
1	−8	8
3	−4	4
5	−4	4
	7,17,*l*	
−3	−5	5
3	−5	5
	7,18,*l*	
−4	−8	7
−2	−7	6
0	−6	6
2	−8	8
4	−6	6
	7,19,*l*	
−3	−3	3
	8,0,*l*	
−10	13	11
−8	24	23
−6	36	37
−4	18	19
−2	31	36
0	56	57
2	27	28
4	17	16
6	22	20
	8,1,*l*	
−9	9	6
−7	12	11

	F_c	$\lvert F_o\rvert$
−5	13	13
−3	14	14
−1	31	33
1	14	14
	8,2,*l*	
−2	−1	4
	8,3,*l*	
−5	−7	7
−1	−8	7
	8,4,*l*	
−4	12	14
−2	13	12
0	6	5
	8,5,*l*	
−7	8	7
−5	7	6
−3	8	10
−1	8	7
1	15	13
	8,6,*l*	
−2	−5	5
	8,7,*l*	
−9	−13	9
−7	−18	17
−5	−14	14
−3	−20	21
−1	−27	25
1	−25	25
3	−13	12
7	−14	13
	8,8,*l*	
−10	−8	5
−8	−14	11
−6	−11	12
−4	−13	16
−2	−21	22
0	−24	23
2	−15	16
4	−8	7
6	−14	14
	8,9,*l*	
−3	−4	7
−1	−7	10
1	−5	7
	8,11,*l*	
−5	−8	12
−3	−11	11
−1	−11	12
1	−5	7
3	−9	10
5	−9	9
	8,12,*l*	
−8	−8	6
−6	−13	15
−4	−8	8
−2	−9	8
0	−15	16
2	−12	11
4	−9	9
	8,13,*l*	
−5	−8	9
−3	−6	7

l	F_c	$\lvert F_o\rvert$
−1	−8	10
1	−6	7
	8,14,*l*	
−2	5	6
0	6	8
4	4	5
	8,15,*l*	
−7	6	5
−5	7	7
−3	6	7
−1	13	15
1	8	10
	8,16,*l*	
−6	5	5
0	8	9
	8,18,*l*	
−4	3	4
−2	3	4
2	3	4
	8,19,*l*	
−1	6	5
1	7	5
	9,1,*l*	
−7	−15	16
−1	−20	25
1	−17	18
	9,5,*l*	
1	−12	13
	9,7,*l*	
1	−18	20
	10,0,*l*	
−8	−23	22
−6	−24	25
−4	−20	23
−2	−27	27
0	−35	33
2	−30	29
4	−19	17
6	−16	12
	10,1,*l*	
−3	−17	17
−1	−22	21
1	−14	13
	10,7,*l*	
1	18	16
	12,0,*l*	
−8	12	10
−6	17	18
−4	20	19
−2	18	18
0	15	16
2	24	19
4	20	15
	14,0,*l*	
−6	−12	12
−4	−15	17
2	−13	11
4	−14	10

and one of the carbon atoms of each of the pyridine nuclei must occupy special positions on the two-fold axes. The asymmetric unit would then consist of two copper atoms, two acetate groups, and the nitrogen and three carbon atoms of each of the pyridine molecules.

By using the phases of those structure factors to which the copper atoms had a reasonable contribution, together with the corresponding observed structure amplitudes, a three-dimensional Fourier synthesis was computed. This electron-density distribution confirmed the binuclear structure and led to co-ordinates for the light atoms (excluding hydrogen atoms). The atomic positions were refined by successive three-dimensional Fourier syntheses.

The maxima in the electron-density distribution were determined by fitting a ten-parameter

Gaussian function to 27 values for the electron density about the maximum value.[6] The co-ordinates were corrected for termination-of-series errors by the back-shift method.[7] Scattering-factor curves of Berghuis *et al.*[8] were used for all atoms; the values for copper were corrected for dispersion from the values given by Dauben and Templeton.[9] A temperature factor, $\exp -(B \sin^2 \theta/\lambda^2)$, with $B = 2{\cdot}1$ Å^2 for the copper atoms and $B = 3{\cdot}6$ Å^2 for the other atoms, was applied. The standard deviations of the atomic co-ordinates were estimated by Cruickshank's method.[10] The final atomic co-ordinates, together with their root-mean-square, estimated standard deviations are listed in Table 1. The calculated structure factors and the observed structure amplitudes are given in Table 2. The final discrepancy factor (R), based on the 1200 observed reflections, was 0·13.

DISCUSSION

The binuclear molecules are arranged along the two-fold axes as shown in Fig. 1. The intermolecular distances (see Fig. 1) indicate that the crystal is truly " molecular " with only van der Waals's forces acting between molecules. These forces operate between the pyridine nuclei of one molecule and methyl groups and pyridine rings of other molecules which lie along neighbouring two-fold axes; there is no contact between molecules on the same two-fold axis (distance of separation 4·82 Å).

TABLE 3.

Bond distances and angles.

Bond	Length (Å)	σ (Å)	Bond	Length (Å)	σ (Å)	Bond	Length (Å)	σ (Å)
Cu(1)–O(3)	1·985	0·010	C(1)–O(1)	1·247	0·016	C(8)–N(1)	1·379	0·014
Cu(1)–O(4)	1·973	0·010	C(1)–O(4)	1·247	0·015	C(3)–N(2)	1·377	0·016
Cu(2)–O(2)	1·985	0·010	C(2)–O(2)	1·231	0·021			
Cu(2)–O(1)	1·982	0·011	C(2)–O(3)	1·231	0·021	C(3)–C(4)	1·381	0·018
						C(7)–C(8)	1·411	0·019
Cu(1)–N(1)	2·122	0·009	C(1)–C(6)	1·467	0·022	C(7)–C(9)	1·433	0·021
Cu(2)–N(2)	2·129	0·011	C(2)–C(5)	1·540	0·026	C(4)–C(10)	1·412	0·018
Cu(1)–Cu(2)	2·630	0·003						

Angle	Value	σ	Angle	Value	σ	Angle	Value	σ
O(3)–Cu(1)–O(4)	89·0°	0·5°	O(3)–C(2)–O(2)	127·3°	0·9°	C(8)–N(1)–C(8′)	117·9°	1·5°
O(1)–Cu(2)–O(2)	88·2	0·5	O(4)–C(1)–O(1)	122·9	0·9	C(3)–N(2)–C(3′)	116·4	1·5
						N(1)–C(8)–C(7)	125·2	0·9
Cu(1)–O(3)–C(2)	122·6	0·7	O(3)–C(2)–C(5)	115·0	0·9	N(2)–C(3)–C(4)	121·5	0·9
Cu(1)–O(4)–C(1)	123·6	0·7	O(1)–C(1)–C(6)	118·1	0·9	C(8)–C(7)–C(9)	113·7	0·9
Cu(2)–O(2)–C(2)	122·6	0·7				C(3)–C(4)–C(10)	120·5	0·9
Cu(2)–O(1)–C(1)	125·0	0·7				C(7)–C(9)–C(7′)	124·2	1·5
						C(4)–C(10)–C(4′)	116·5	1·5

The bond distances and bond angles in the molecule are listed in Table 3 and shown diagrammatically in Fig. 2. The variation in bond length for chemically similar bonds is well within experimental error; the apparently large difference between the two C–CH_3 bond lengths is only twice the estimated standard deviation of their difference. The copper–copper distance (2·63 Å) is the same as that found in copper acetate monohydrate [1] (2·64 Å), and the other bond lengths agree with the values reported for other compounds.[11] There is no significant difference between the carbon–nitrogen and carbon–carbon bond lengths in the pyridine molecules; the bond angles vary from 114° to 125° but the mean value is 119·5°. Since the values found for the same angle in the two pyridine molecules are not consistent, the variations are probably due to experimental error.

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

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

[8] Berghuis, Haanapel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

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

[10] Cruickshank, *Acta Cryst.*, 1948, **2**, 65; Cruickshank and Rollett, *ibid.*, 1953, **6**, 705.

[11] " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11; see also Barclay and Kennard, *J.*, 1961, 3289.

Each copper atom is joined by covalent bonds (1·98 Å in length) to four oxygen atoms lying in a plane which is approximately normal to the two-fold axis. The copper atoms are 0·22 Å out of these planes towards the nitrogen atoms of the pyridine rings. The copper–nitrogen bond is slightly longer (2·13 Å) than expected for a covalent bond (1·95—2·04 Å) but is shorter than usually found for the fifth and sixth bonds to copper atoms (2·6—2·8 Å for Cu–N and 2·2—3·0 Å for Cu–O bonds).[11] The four oxygen atoms and the nitrogen atom form a slightly distorted tetragonal-pyramidal co-ordination about the copper atom. The sixth, "octahedral," site is occupied by a second copper atom at 2·63 Å.

The two pyridine nuclei are planar, but the angle between the planes of the two pyridine rings in the one binuclear molecule is 60°. The equations for these planes (calculated by the method of least squares) and the deviations of the atoms from these planes are:

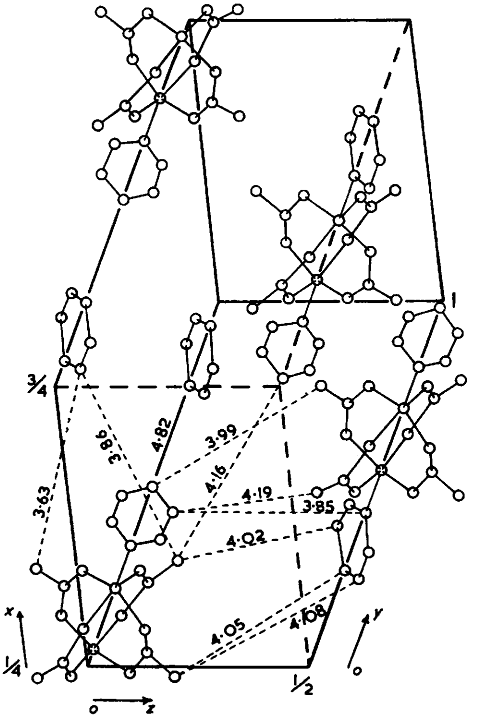

FIG. 1. Arrangement of the molecules in the unit cell of monopyridinecopper(II) acetate.

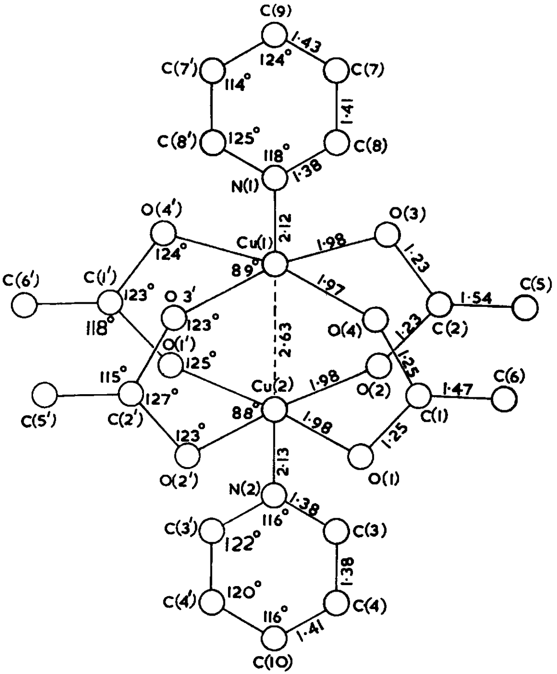

FIG. 2. Bond lengths (Å) and bond angles in the binuclear molecules.

$$0{\cdot}149x - 0{\cdot}004y + 0{\cdot}988z - 0{\cdot}477 = 0$$

[C(9), 0·005; C(7), 0·010; C(8), 0·012; N(1), 0·007 Å]

$$0{\cdot}924x - 0{\cdot}003y + 0{\cdot}383z - 2{\cdot}872 = 0$$

[C(10), 0·004; C(4), 0·008; C(3), 0·008; N(2), 0·004 Å]

The close approach of the two copper atoms in the binuclear unit indicates the presence of a δ-bond between them. The low magnetic moment at room temperature (μ 1·40 B.M.) of monopyridinecopper(II) acetate [12] is the same as that of copper acetate monohydrate and may be explained in the same way as due to an interaction between the copper atoms in the binuclear molecule.[2]

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[12] Waterman, personal communication.

[*Note added October* 17*th*, 1961]. Hanic, Stempelova, and Hanicova (*Chem. Zvesti*, 1961, **15**, 102) have reported the structure of an orthorhombic form of monopyridinecopper(II) acetate. This crystal is built up of binuclear molecules similar to those reported here except that the two pyridine molecules of the binuclear unit lie in the same plane.

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