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The Crystal Structure of Di-μ-hydroxo-bis-(*N*, *N*, *N*′, *N*′-tetramethylethylenediamine)-dicopper(II) Bromide

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Crystals of $[Cu_2\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2(OH)_2]Br_2$ are orthorhombic, space group *Fddd*, with eight formula units in a unit cell of dimensions $a = 17{\cdot}072$, $b = 18{\cdot}482$ and $c = 12{\cdot}825$, all $\pm 0{\cdot}005$ Å. The structure was determined by three-dimensional Patterson syntheses from data taken with Ni-filtered Cu $K\alpha$ radiation using the equi-inclination, multiple-film Weissenberg technique. The formula unit was found to have a dimeric structure with a Cu–Cu distance of 3·000 Å. Anisotropic refinement was carried out by the method of block-diagonal least-squares to obtain a final *R* index of 0·082.

Introduction

A large number of copper(II) complexes having subnormal magnetic moments (*i.e.* moments lower than the 1·73 BM expected for $3d^9$) have been postulated to be dimeric (Kato, Jonassen & Fanning, 1964; Lewis, 1965), largely on the basis of magnetic susceptibility measurements and by analogy with dimeric copper(II) acetate monohydrate (van der Marel, van der Broek, Wasscher & Gorter, 1955; van Niekerk & Schoening, 1953; Chidambaram & Brown, 1965). In the copper(II) acetate type of complexes, which are also characterized by an additional electronic absorption band reportedly arising from the π-system of the alkanoate, the low magnetic moments are thought to arise from direct metal–metal interaction (δ-bonding) (Dubicki & Martin, 1966), since the 2·61 Å Cu–Cu distance in $Cu_2(C_2H_3O_2)_4.2H_2O$ (van der Marel *et al.*, 1955; van Niekerk & Schoening, 1953; Chidambaram & Brown, 1965) is only slightly greater than the interatomic distance of 2·56 Å in metallic copper. With *N*, *N*, *N*′, *N*′-tetraalkyl-substituted diamines, copper(II) forms complexes formulated as $[Cu_2(OH)_2(\text{diamine})_2](ClO_4)_2$ with bridging hydroxide ions (Pfeiffer & Glaser, 1938; Mann & Watson, 1958; Hatfield, Piper & Klabunde, 1963; Meek & Ehrhardt, 1965). The antiferromagnetic and conductivity behavior of these compounds has been used to support the postulated structures. These hydroxy-bridged compounds have room-temperature magnetic moments of about 1·5 BM (Hatfield *et al.*, 1963; Meek & Ehrhardt, 1965; Wasson, Mitchell & Bernard, 1968). Since the low magnetic moments of copper(II) compounds can also arise from a superexchange mechanism, we have undertaken electron spin resonance (Wasson, Shyr & Trapp, 1968) and structural studies of dimeric copper(II) compounds in order to discover criteria for distinguishing between the two metal–metal interaction mechanisms and to provide further structural information about dimeric copper(II) complexes. While the nitrate and perchlorate salts containing the di-μ-hydroxo-bis-(*N*, *N*, *N*′, *N*′-tetramethylethylenediamine) dicopper (II) ion, $[Cu_2(OH)_2(\text{tmen})_2]^{2+}$, have been known for several years (Mann & Watson, 1958; Meek & Ehrhardt, 1965), the preparation of the bromide salt from the reaction of tmen with $Cu_2(OH)_3Br$ or saturated aqueous solutions of copper(II) bromide has been described only recently (Wasson, Mitchell & Bernard, 1968). A subsequent structure analysis reported here has confirmed the dimeric structure of the bromide salt which was initially postulated on the basis of magnetic susceptibility data.

Crystal data

Burgundy colored, bipyramidal {111} crystals of $[Cu_2\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2(OH)_2]Br_2$ were obtained by evaporating an aqueous solution of the compound at room temperature. The crystals begin to decompose at about 42°C. The cell parameters were determined by Cohen's method of least-squares using 24 lines of a Debye–Scherrer powder photograph taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Sodium chloride ($a_0 = 5{\cdot}63869$ Å) was used as a standard in these powder photographs. The crystal density was determined by flotation in a mixture of carbon tetrachloride and iodomethane. The crystal data are given in Table 1.

Table 1. *Crystal data*

$C_{12}H_{34}Br_2Cu_2N_4O_2$
Formula weight 553·3
Space group *Fddd*
$Z = 8$
$a = 17{\cdot}072 \pm 0{\cdot}005$ Å (one standard deviation)
$b = 18{\cdot}482 \pm 0{\cdot}005$
$c = 12{\cdot}825 \pm 0{\cdot}005$
Volume of unit cell 4047 Å^3
$D_m = 1{\cdot}824 \pm 0{\cdot}015$ g.cm^{-3}
$D_x = 1{\cdot}816$ g.cm^{-3}
$\mu(\text{Cu } K\alpha) = 78{\cdot}1$ cm^{-1}

Experimental

Equi-inclination Weissenberg photographs were taken using the three crystals listed in Table 2. The multiple-film technique was employed using four films. A total of 907 independent reflections were recorded out of a possible 1166 non-extinct reflections. Of the 907 reflections recorded 307 were too weak to be observed. The intensities were estimated visually using a calibrated intensity strip. The data collected about the *a* and *b* axes were used to scale the different layers taken about the *c* axis.

Intensities were corrected for absorption using a modified form of an IBM 1620 program by Bernard & Langhammer (1966). They were then corrected for Lorentz and polarization effects and converted to structure factors using an IBM 1620 program by Shiono (1966).

Table 2. *Crystals used for intensity data collection*

Dimensions are lengths in *x*, *y* and *z* directions respectively.

Rotation axis	Dimensions (mm)	Data collected
a	0·49 × 0·56 × 0·39	0*kl*, 1*kl*
b	0·34 × 0·36 × 0·26	*h*0*l*, *h*1*l*
c	0·46 × 0·60 × 0·34	*hk*0 thru *hk*9

Structure determination

Because there are but eight formula units in the unit cell, the point symmetry of the formula unit must be 222. The bromine and copper atoms were located from suitable Patterson peaks for Br–Br, Br–Cu and Cu–Cu on the three-dimensional Harker section $V=0$. These Patterson peaks correspond to Wyckoff positions (*e*) for the bromine atoms and (*g*) for the copper atoms (*International Tables for X-ray Crystallography*, 1952). A preliminary R index ($R=\sum||F_o|-|F_c||/\sum|F_o|$) calculated with bromine and copper only was 0·238 using 314 observed reflections. The form factors used were those given in *International Tables for X-ray Crystallography* (1962) for Br^{1-} and Cu^{2+}.

The nitrogen and carbon atom positions were calculated on the basis of a molecular model. Adding N, C(1), C(2) and C(3) to the structure factor calculations, an R index of 0·169 was obtained using 314 observed reflections.

At this point a Patterson peak for Br–O located the oxygen atom. The R index was reduced to 0·135 using 314 observed reflections. The form factors used for carbon, nitrogen and oxygen were those given in *International Tables for X-ray Crystallography* (1962).

Refinement

Refinement was carried out using a block-diagonal least-squares program by Mair & Ahmed (1966) for the IBM 1620 computer. The quantity minimized was $\sum w(F_o-F_c)^2$. The weighting scheme used was $w=1/\{1+[(F_o-5F_{\min})/8F_{\min}]^2\}$. After five cycles of least-squares using isotropic temperature factors, the R index for all 600 observed reflections was 0·163. At this stage the isotropic temperature factors were converted to anisotropic temperature factors and the form factors for Br and Cu were corrected for the real part of the anomalous scattering. In one cycle of least-squares the R index was 0·123. Six cycles of least-squares and one cycle of layer-to-layer rescaling of the data reduced R to 0·085, using 581 observed reflections. The symmetry-related reflections from the five sets of planes 4 . 4*n* . 4 on the $l=4$ equi-inclination photograph showed large unexplained variations. Since a flat cone photograph of the $l=4$ layer showed no such variations, it was concluded that the large enhancement of some of these inherently weak reflections was due to multiple diffraction (Santoro & Zocchi, 1966) and very slight crystal misalignment. These reflections were therefore omitted from the final refinement calculations, as was the only reflection (111) which had been estimated from powder data. Also omitted at this stage were thirteen reflections which were suspected of being reduced in intensity by secondary extinction. These reflections are indicated in Table 3 by E for reflections suspected of being affected by extinction, M for multiple diffraction, P for powder data and U for reflections too weak to be observed. All reflections too weak to be observed are given an F_o of zero in Table 3; most of them are of the type $(h+k+l)=4n+2$, to which the Br, Cu and O atoms do not contribute.

At this point, a difference map indicated the positions of several hydrogen atoms. Eight hydrogen atom positions were calculated and refined isotropically, holding all other atoms fixed. The R index was reduced to 0·0806; however, the resulting positions, temperature factors and large standard deviations were unsatisfactory. New hydrogen positions, suggested by this refinement but adjusted to make the C–H bonds 1·07 Å and the angles tetrahedral, were then calculated. The hydrogen atoms of the bridging O–H groups were not located. With the hydrogen atoms fixed, three cycles of least-squares were used to refine the other atoms anisotropically. The final parameters are listed in Table 4 along with their standard deviations. The final shifts in all coordinates were less than the standard deviations in the coordinates. The final R index was 0·082, using 581 observed reflections.

Discussion

One formula unit viewed along the y axis is shown in Fig. 1 along with neighboring atoms from other formula units. The atoms drawn with solid lines make up one formula unit; Br″ and Br‴ are respectively above and below this formula unit by $\frac{1}{4}b$. The formula unit has 222 point symmetry. This requires the copper, oxygen and bromine atoms to all lie in the same plane; however, the two ethylenediamine rings are in a *gauche* configuration. The N–Cu–N′ plane makes an angle of

Table 3. *Observed and calculated structure factors*

E: extinction, M: multiple diffraction, P: powder data, U: too weak to be observed.

H	K	FOBS	FCAL
L = 0			
4	0	416	-443
8	0	486	493
12	0	271	-250
16	0	149	135
20	0	0	0U
2	2	222	-179
6	2	168	-141
10	2	0	-12U
14	2	171	159
18	2	62	-69
0	4	772	-1184E
4	4	654	714
8	4	331	-320
12	4	300	287
16	4	102	-99
2	6	142	135
6	6	216	206
10	6	92	72
14	6	114	-105
18	6	82	87
0	8	513	595E
4	8	605	-614
8	8	197	194
12	8	284	-273
16	8	66	64
2	10	59	-41
6	10	130	-111
10	10	71	-57
14	10	97	89
18	10	65	-66
0	12	483	-457
4	12	300	292
8	12	236	-201
12	12	171	157
16	12	65	-68
2	14	0	-12U
6	14	0	26U
10	14	0	21U
14	14	81	-77
0	16	232	271
4	16	154	-135
8	16	162	144
12	16	82	-82
16	16	0	53U
2	18	0	9U
6	18	0	-13U
10	18	0	-20U
14	18	0	42U
0	20	98	-103
4	20	97	94
8	20	73	-60
12	20	0	54U
L = 1			
1	1	388	189P
3	1	193	268E
5	1	56	52
7	1	289	-282
9	1	76	-74
11	1	302	265
13	1	0	20U
15	1	219	-214
17	1	34	-24
19	1	94	97
21	1	20	15
1	3	168	218E
3	3	199	-219
5	3	0	4U
7	3	227	218
9	3	41	-46
11	3	269	-261
13	3	0	22U
15	3	192	188
17	3	0	-20U
19	3	94	-107
21	3	19	20
1	5	134	-151
3	5	250	-290
5	5	54	-61
7	5	246	255
9	5	56	61
11	5	256	-236
13	5	34	-29
15	5	199	193
17	5	0	19U
19	5	75	-81
1	7	124	-137
3	7	185	200
5	7	64	71
7	7	162	-153
9	7	61	61
11	7	221	219
13	7	0	-6U
15	7	150	-147
17	7	32	24
19	7	85	91
1	9	121	125
3	9	206	223
5	9	47	59
7	9	174	-176
9	9	0	-25U
11	9	184	184
13	9	36	39
15	9	134	-136
17	9	0	-9U
19	9	58	69
1	11	115	115
3	11	110	-103
5	11	37	-40
7	11	138	133
9	11	38	-39
11	11	141	-134
13	11	0	7U
15	11	101	111
17	11	0	-15U
19	11	43	-58
1	13	64	-61
3	13	154	-143
5	13	0	-10U
7	13	109	114
9	13	0	29U
11	13	115	-116
13	13	0	-15U
15	13	79	90
17	13	0	15U
1	15	91	-90
3	15	50	49
5	15	0	5U
7	15	98	-93
9	15	0	8U
11	15	83	80
13	15	0	-15U
15	15	60	-64
17	15	0	2U
1	17	0	28U
3	17	94	87
5	17	0	-7U
7	17	68	-62
9	17	0	-16U
11	17	53	62
13	17	0	4U
15	17	44	-55
1	19	0	40U
3	19	40	-36
5	19	0	-9U
7	19	44	47
9	19	0	-8U
11	19	48	-50
13	19	0	5U
1	23	0	-11U
L = 2			
2	0	416	526E
6	0	322	-301
10	0	144	129
14	0	0	-24U
18	0	80	-76
0	2	101	-112E
2	2	0	-13U
4	2	549	619
6	2	33	-42
8	2	200	-168
10	2	0	10U
12	2	136	120
14	2	0	0U
16	2	39	-24
18	2	0	0U
20	2	0	-10U
2	4	360	-444E
4	4	38	-51
6	4	225	233
8	4	0	20U
10	4	150	-141
12	4	0	-18U
14	4	0	4U
16	4	0	-7U
18	4	57	53
20	4	0	0U
0	6	456	520
2	6	0	-22U
4	6	208	-230
6	6	0	41U
8	6	280	275
10	6	0	-26U
12	6	38	-29
14	6	0	-1U
16	6	60	54
18	6	0	3U
20	6	26	25
2	8	316	325
4	8	0	25U
6	8	116	-124
8	8	0	-39U
10	8	151	141
12	8	0	6U
14	8	0	10U
16	8	0	2U
18	8	31	-28
20	8	0	-5U
0	10	292	-306
2	10	0	26U
4	10	196	197
6	10	0	-18U
8	10	191	-180
10	10	0	25U
12	10	0	23U
14	10	0	1U
16	10	31	-32
18	10	0	-4U
2	12	181	-177
4	12	0	-12U
6	12	120	116
8	12	0	27U
10	12	81	-71
12	12	0	-3U
14	12	0	12U
16	12	0	-1U
18	12	29	28
0	14	128	113
2	14	0	3U
4	14	206	-188
6	14	0	20U
8	14	71	63
10	14	0	-8U
12	14	40	-43
14	14	0	3U
16	14	0	2U
2	16	96	93
4	16	0	7U
6	16	82	-70
8	16	0	-6U
10	16	33	36
12	16	0	8U
14	16	0	-13U
16	16	0	4U
0	18	81	-72
2	18	0	-4U
4	18	111	94
6	18	0	-6U
8	18	38	-39
10	18	0	4U
12	18	0	20U
2	20	45	-46
4	20	0	0U
6	20	32	30
8	20	0	2U
10	20	19	-22
0	22	56	51
2	22	0	-1U
4	22	22	-28
L = 3			
1	1	100	-101
3	1	99	-110
5	1	191	195
7	1	0	-17U
9	1	305	-293
11	1	61	-60
13	1	232	208
15	1	57	46
17	1	125	-122
19	1	30	-27
21	1	60	73
1	3	49	63
3	3	41	-40
5	3	204	-217
7	3	0	-1U
9	3	284	280
11	3	57	-57
13	3	224	-198
15	3	44	40
17	3	112	117
19	3	35	-31
21	3	55	-70
1	5	43	45
3	5	33	-31
5	5	226	-246
7	5	42	-45
9	5	260	232
11	5	0	16U
13	5	186	-184
15	5	74	-66
17	5	109	111
19	5	0	13U
21	5	49	-61
1	7	62	-63
3	7	68	-56
5	7	174	178
7	7	34	-38
9	7	233	-235
11	7	33	33
13	7	143	146
15	7	53	-46
17	7	98	-100
19	7	21	19
1	9	62	-63
3	9	30	24
5	9	197	195
7	9	30	27
9	9	154	-151
11	9	0	-20U
13	9	139	144
15	9	50	51
17	9	79	-79
19	9	18	-13
1	11	72	70
3	11	50	38
5	11	121	-116
7	11	0	22U
9	11	162	157
11	11	34	-33
13	11	104	-99
15	11	34	33
17	11	63	68
1	13	91	90
3	13	0	16U
5	13	109	-99
7	13	0	13U
9	13	113	109
11	13	34	38
13	13	74	-83
15	13	23	-23
17	13	49	57
1	15	58	-43
3	15	38	-31
5	15	89	81
7	15	0	-7U
9	15	84	-82
11	15	31	28
13	15	66	68
1	17	73	-59
3	17	0	-2U
5	17	60	56
7	17	0	-4U
9	17	62	-63
11	17	0	-15U
13	17	36	43
1	19	0	24U
3	19	29	25
5	19	43	-43
7	19	0	6U
9	19	42	47
1	21	0	20U
3	21	0	-11U
5	21	39	-38
L = 4			
0	0	461	-494
4	0	207	-215
8	0	0	24U
12	0	91	-65
16	0	71	66
20	0	103	-121
2	2	503	-650E
4	2	0	27U
6	2	621	688
8	2	0	-4U
10	2	316	-322
12	2	0	16U
14	2	109	94
16	2	0	10U
18	2	76	-82
20	2	0	2U
0	4	203	222
2	4	0	-12U
4	4	83	13M
6	4	49	-49
8	4	122	-102
10	4	0	18U
12	4	56	18
14	4	0	2U
16	4	99	-87
18	4	0	-1U
20	4	82	102
2	6	395	506E
4	6	0	-26U
6	6	511	-564
8	6	0	32U
10	6	270	256
12	6	0	-12U
14	6	106	-106
16	6	0	-8U
18	6	54	59
0	8	102	-80
2	8	0	-26U
4	8	113	76M
6	8	0	16U
8	8	141	129
10	8	0	-35U
12	8	0	13U
14	8	0	-7U
16	8	98	95
2	10	316	-346
4	10	0	7U
6	10	343	391
8	10	36	-42
10	10	178	-188
12	10	0	-1U
14	10	92	87
16	10	0	1U
18	10	41	-46
0	12	109	101
2	12	0	5U
4	12	53	-4M
6	12	0	-18U
8	12	57	-43
10	12	0	19U
12	12	0	27U
14	12	0	1U
16	12	61	-54
2	14	227	221
4	14	0	-5U
6	14	216	-222
8	14	0	18U
10	14	138	134
12	14	0	-7U
14	14	48	-51
16	14	0	-6U
0	16	93	-78
2	16	0	16U
4	16	47	-21M
6	16	0	20U
8	16	0	7U
10	16	0	-3U
12	16	48	-34
2	18	142	-120
4	18	0	2U
6	18	120	120
8	18	0	-3U
10	18	72	-75
0	20	0	18U
2	20	0	0U
4	20	0	-1U
6	20	0	1U
8	20	0	-16U
10	20	0	7U
2	22	67	60
4	22	0	4U
6	22	52	-59
L = 5			
1	1	99	103
3	1	179	173
5	1	377	-386
7	1	59	-46
9	1	283	264
11	1	0	-22U
13	1	179	-163
15	1	90	74
17	1	126	129
19	1	0	7U
21	1	0	-78U
1	3	102	142
3	3	103	-99
5	3	349	-347
7	3	78	58
9	3	298	292
11	3	68	59
13	3	163	-156
15	3	57	-51
17	3	118	122
1	5	112	-143
3	5	82	-85
5	5	254	270
7	5	101	98
9	5	252	-227
11	5	53	40
13	5	197	150
15	5	47	-47
17	5	112	-114
1	7	132	-152
3	7	34	30
5	7	221	232
7	7	86	-71
9	7	255	-266
11	7	76	-80
13	7	130	129
15	7	51	17
17	7	96	-99
1	9	104	110
3	9	40	42
5	9	194	-191
7	9	85	-86
9	9	162	166
11	9	39	-30
13	9	123	-122
15	9	34	28
17	9	86	90
1	11	84	75
3	11	60	-56
5	11	171	-173
7	11	0	11U
9	11	166	178
11	11	0	27U
13	11	94	-100
15	11	0	-19U
17	11	64	73
1	13	68	-61
3	13	42	-39
5	13	125	127
7	13	0	35U
9	13	113	109
11	13	0	0U
13	13	74	82
15	13	0	-23U
17	13	52	-66
1	15	42	-26
3	15	60	55
5	15	113	113
7	15	0	9U
9	15	94	-99
11	15	0	0U
13	15	63	71
15	15	0	14U
1	17	45	42
3	17	0	16U
5	17	69	-68
7	17	0	-18U
9	17	63	67
11	17	0	3U
13	17	39	-47
1	19	0	26U
3	19	0	-19U
5	19	47	-48
7	19	0	10U
9	19	49	57
1	21	0	-24U
3	21	0	-4U
5	21	32	37
L = 6			
2	0	251	-349E
6	0	279	259
10	0	268	-223
14	0	117	86
18	0	0	9U
0	2	180	251E
2	2	23	23
4	2	386	-349
6	2	0	15U
8	2	69	62
10	2	0	3U
12	2	0	-4U
14	2	0	-1U
16	2	43	-36
18	2	0	0U
20	2	0	40U
2	4	272	333
4	4	0	0U
6	4	264	-258
8	4	0	6U
10	4	219	200
12	4	0	12U
14	4	81	-71
16	4	0	13U
18	4	0	-4U
20	4	0	5U
0	6	240	-276
2	6	0	-6U
4	6	170	180
6	6	0	4U
8	6	117	-116
10	6	0	14U
12	6	40	-31
14	6	0	11U
16	6	0	5U
18	6	0	0U
2	8	263	-282
4	8	0	16U
6	8	205	198
8	8	0	18U
10	8	150	-157
12	8	0	6U
14	8	45	45
16	8	0	-1U
18	8	0	0U
0	10	178	180
2	10	0	-2U
4	10	111	-112
6	10	0	-10U
8	10	98	93
10	10	0	-17U
12	10	0	17U
14	10	0	-9U
16	10	0	0U
18	10	0	4U
2	12	197	198
4	12	0	-12U
6	12	153	-136
8	12	0	-16U
10	12	95	98
12	12	0	-3U
14	12	30	-27
16	12	0	3U
0	14	66	-64
2	14	0	-19U
4	14	96	94
6	14	0	-11U
8	14	39	-30
10	14	0	1U
12	14	0	13U
14	14	0	0U
16	14	0	11U
2	16	135	-120
4	16	0	4U
6	16	89	86
8	16	0	3U
10	16	44	-50
12	16	0	-6U
14	16	0	19U
0	18	0	25U
2	18	0	13U
4	18	43	-50
6	18	0	7U
8	18	0	14U
10	18	0	-2U
12	18	0	-8U
2	20	65	63
4	20	0	-2U
6	20	42	-44
8	20	0	-3U
0	22	0	-20U
L = 7			
1	1	0	8U
3	1	146	156
5	1	29	11
7	1	154	-134
9	1	103	86
11	1	188	170
13	1	68	-65
15	1	116	-110
17	1	25	26
19	1	72	86
1	3	17	12
3	3	180	152
5	3	0	15U
7	3	154	-157
9	3	107	-99
11	3	162	162
13	3	60	59
15	3	106	-110
17	3	28	-25
19	3	74	76
1	5	62	65
3	5	78	-78
5	5	36	28
7	5	168	161
9	5	35	-33
11	5	133	-102
13	5	64	69
15	5	122	126
17	5	29	-25
19	5	48	-63
1	7	52	-54
3	7	81	-87
5	7	40	-44
7	7	168	182
9	7	79	74
11	7	103	-106
13	7	53	-52
15	7	109	105
17	7	26	22
1	9	46	-48
3	9	69	69
5	9	32	-11
7	9	114	-115
9	9	34	23
11	9	71	72
13	9	51	-50
15	9	96	-98
17	9	24	25
1	11	37	34
3	11	71	73
5	11	0	21U
7	11	113	-120
9	11	49	-55
11	11	102	87
13	11	38	40
15	11	60	-64
17	11	0	-14U
1	13	0	9U
3	13	90	-78
5	13	0	-13U
7	13	48	46
9	13	31	-23
11	13	73	-70
13	13	28	29
15	13	45	49
1	15	0	-14U
3	15	53	-54
5	15	0	-1U
7	15	58	62
9	15	32	35
11	15	64	-63
13	15	23	-23
1	17	0	-6U
3	17	54	47
5	17	0	6U
7	17	30	-29
9	17	0	11U
11	17	33	40
1	19	0	16U
3	19	25	22
5	19	0	2U
7	19	27	-37
9	19	16	-13
1	21	16	12
3	21	16	-14
L = 8			
0	0	494	603E
4	0	437	-346M
8	0	354	301
12	0	244	-203
16	0	100	104
2	2	26	41
4	2	0	9U
6	2	128	-96
8	2	0	-13U
10	2	75	-57
12	2	0	-3U
14	2	134	112
16	2	0	-6U
18	2	74	-71
0	4	369	-515E
2	4	27	23
4	4	347	358
6	4	0	-13U
8	4	257	-255
10	4	0	6U
12	4	197	203
14	4	0	-7U
16	4	91	-84
18	4	0	-3U
2	6	46	-31
4	6	0	-26U
6	6	68	69
8	6	0	13U
10	6	52	43
12	6	0	-3U
14	6	105	-95
16	6	0	5U
18	6	45	62
0	8	337	376
2	8	0	-8U
4	8	322	-316
6	8	35	33
8	8	169	179
10	8	0	5U
12	8	158	-175
14	8	0	13U
16	8	52	56
2	10	0	15U
4	10	37	31
6	10	48	-47
8	10	0	2U
10	10	39	-35
12	10	0	14U
14	10	67	64
16	10	0	1U
0	12	266	-261
2	12	0	18U
4	12	211	214
6	12	0	-12U
8	12	121	-131
10	12	0	2U
12	12	121	111
14	12	0	-4U
2	14	0	-3U
4	14	0	-16U
6	14	0	23U
8	14	0	1U
10	14	0	24U
12	14	0	0U
14	14	29	-39
0	16	196	175
2	16	0	-22U
4	16	138	-112
6	16	0	-4U
8	16	86	95
10	16	0	-3U
12	16	38	-55
2	18	0	-1U
4	18	0	6U
6	18	0	-3U
8	18	0	0U
0	20	75	-89
2	20	0	4U
4	20	69	63
L = 9			
1	1	181	248
3	1	227	183
5	1	0	6U
7	1	254	-189
9	1	0	-4U
11	1	162	163
13	1	0	5U
15	1	148	-150
17	1	23	-13
1	3	154	196
3	3	217	-205
5	3	31	-24
7	3	179	159
9	3	44	-29
11	3	203	-174
13	3	0	-11U
15	3	128	134
17	3	22	-16
1	5	160	-169
3	5	209	-191
5	5	31	21
7	5	128	134
9	5	0	11U
11	5	166	-174
13	5	0	0U
15	5	117	122
17	5	0	11U
1	7	129	-121
3	7	177	186
5	7	40	37
7	7	108	-105
9	7	38	30
11	7	164	175
13	7	0	17U
15	7	89	-94
17	7	13	9
1	9	107	99
3	9	163	157
5	9	35	-30
7	9	80	-88
9	9	0	-10U
11	9	139	147
13	9	0	-8U
15	9	85	-95
1	11	100	98
3	11	109	-103
5	11	0	-7U
7	11	102	101
9	11	0	-4U
11	11	106	-114
13	11	0	-9U
15	11	62	79
1	13	74	-72
3	13	85	-80
5	13	0	11U
7	13	80	79
9	13	0	-6U
11	13	75	-85
13	13	0	7U
1	15	72	-64
3	15	40	48
5	15	0	1U
7	15	79	-79
9	15	0	-1U
11	15	52	63
1	17	46	42
3	17	40	44
5	17	0	-5U
7	17	49	-48
9	17	0	9U
1	19	23	27
3	19	25	-32
5	19	0	-7U
L = 10			
2	0	125	131
6	0	79	-82
10	0	0	46U
14	0	49	46
0	2	288	-290
0	6	270	266
0	10	240	-212
0	14	121	130
0	18	54	-61
L = 11			
1	1	111	-88
3	1	0	-22U
5	1	58	64
7	1	0	47U
9	1	107	-102
11	1	70	-68
13	1	72	84
15	1	49	42
1	3	93	84
1	5	41	45
1	7	40	-33
1	9	0	-35U
1	11	0	21U
1	13	33	35
1	15	0	-23U
1	17	0	-16U
L = 12			
0	0	101	-104
4	0	43	40
8	0	37	20
12	0	36	-42
0	4	104	97
0	8	56	-58
0	12	0	18U
0	16	0	-10U
L = 13			
1	1	65	56
3	1	91	77
5	1	190	-176
7	1	0	-41U
9	1	129	133
11	1	0	3U
13	1	74	-92
1	3	68	71
1	5	59	-65
1	7	68	-67
1	9	73	66
1	11	37	41
1	13	36	-36
L = 14			
2	0	212	-205
6	0	186	167
10	0	113	-110
0	2	48	47
0	6	27	-30
0	10	36	32
L = 15			
1	1	0	11U
3	1	51	41
5	1	0	-7U
7	1	41	-46
9	1	0	51U
L = 16			
0	0	152	150
4	0	136	-141
0	4	143	-148

5·8° with the O–Cu–O′ plane and the C(1)–C(1′) bond makes an angle of 35·3° with the O–Cu–O′ plane. The formula unit is shown in Fig. 2 viewed along the x axis and in Fig. 3 viewed along the z axis. Fig. 4 shows the unit cell viewed along the y axis. The unit cell is made up of four layers each containing two formula units. The formula units drawn with open circles are located between $y=0$ and $y=\frac{1}{4}$; the formula units drawn with a bar are located between $y=\frac{1}{4}$ and $y=\frac{1}{2}$; the formula units half shaded are located between $y=\frac{1}{2}$ and $y=\frac{3}{4}$ and the formula units fully shaded are located between $y=\frac{3}{4}$ and $y=\frac{4}{4}$.

Table 4. *Atomic positions and thermal parameters* ($\times 10^5$)

Origin at center of symmetry (*International Tables for X-ray Crystallography*, 1952, p. 162)
Standard deviations are in parenthesis.* Hydrogen positions ($\times 10^3$).

$$f=f_o \exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk)\right].$$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Br	39074 (6)	12500	62500	276	383	366	−2	0	0
Cu	12500	12500	50805 (15)	209	314	189	0	0	3
O	19355 (12)	12500	62500	227	512	476	39	0	0
N	20620 (58)	11732 (62)	39299 (71)	293	372	270	−59	−197	−48
C(1)	15930 (97)	10266 (91)	29570 (115)	407	482	438	214	221	−41
C(2)	25303 (86)	18359 (85)	39065 (120)	379	374	546	154	119	−69
C(3)	25972 (92)	05404 (90)	40465 (138)	368	339	809	−265	277	61
H(1)	141	047	293						
H(2)	196	114	229						
H(3)	215	230	389						
H(4)	287	188	462						
H(5)	291	183	324						
H(6)	308	058	352						
H(7)	284	053	483						
H(8)	227	006	391						

$B=6{\cdot}0$ for all hydrogen atoms.

* The computer program used does not compute standard deviations for the thermal parameters.

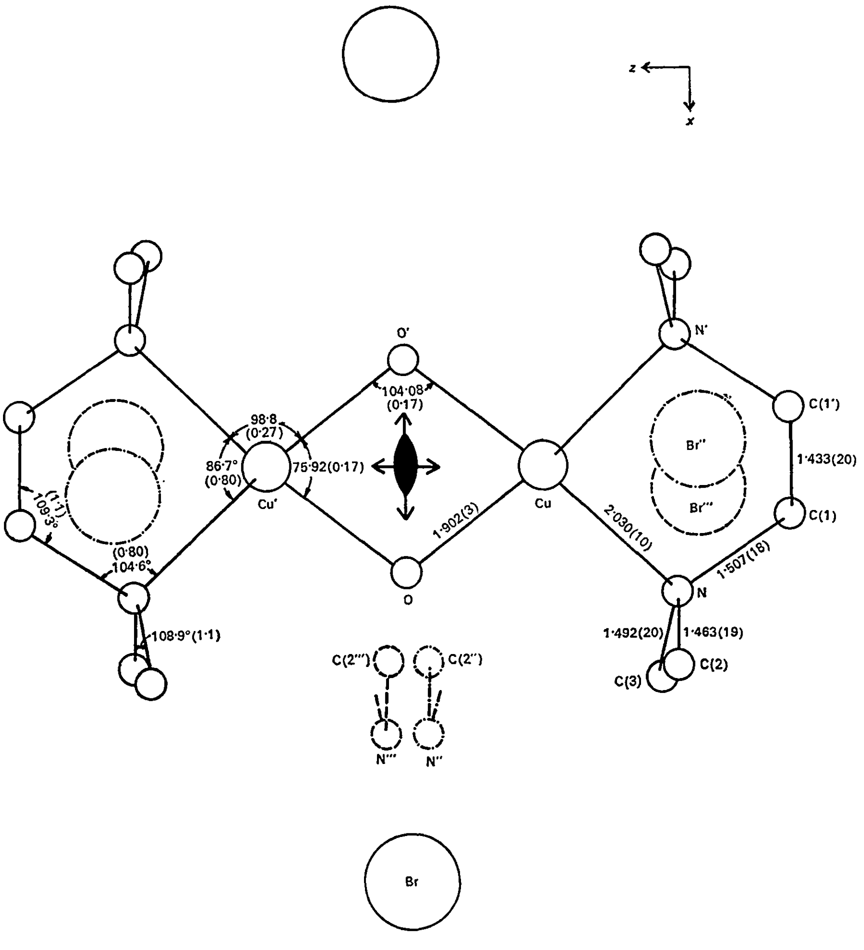

Fig. 1. Formula unit viewed along the y axis with some nearest neighbors.

Bond lengths and angles along with their standard deviations are shown in Fig. 1 and non-bonded interatomic distances and their standard deviations are listed in Table 5. The Cu–O bond length of 1·902 Å in $[Cu_2(OH)_2(tmen)_2]Br_2$ is comparable with those found in $[Cu(C_5H_5NO)Cl_2]_2$ (Schlafer, Morrow & Smith, 1965; Sager, Williams & Watson, 1967) and $Cu_4Cl_6O.4C_5H_5N$ (Kilbourn & Dunitz, 1967) which also have bridging oxygen atoms, and is shorter than the Cu–O distances in $Cu_2(OH)_3Br$ (2·00 and 2·02 Å), $CuCl_2.2H_2O$ (1·93 Å), $K_2CuCl_4.2H_2O$ (1·97 Å) (Wells, 1962) and anhydrous copper(II) formate (1·99 Å) (Barclay & Kennard, 1961).

Table 5. *Non-bonded interatomic distances and estimated standard deviations*

Cu—Br	4·778 ± 0·002 Å
Cu—Br″	4·933 ± 0·002
Cu—Cu′	3·000 ± 0·004
O—Br	3·366 ± 0·003
O—C(2″)	3·659 ± 0·02
N—Br″	5·047 ± 0·02
N—Br‴	4·622 ± 0·02
C(1)–Br″	5·205 ± 0·02
C(1)–Br‴	4·340 ± 0·02
C(2)–Br	3·966 ± 0·02
C(2)–Br″	4·310 ± 0·02
C(2)–C(2″)	3·729 ± 0·02
C(3)–Br	3·835 ± 0·02
C(3)–Br‴	3·901 ± 0·02
C(3)–C(2‴)	3·764 ± 0·02

The Cu–N bond length of 2·030 Å and N–Cu–N angle of 86·7° are normal for ethylenediamine complexes (Brown & Lingafelter, 1964; Komiyama & Lingafelter, 1964) and for complexes with ligands based on an ethylenediamine type of linkage (Llewellyn & Waters, 1966). In the copper(II) ethylenediamine complexes which have been studied, ethylenediamine has a *gauche* configuration (Brown & Lingafelter, 1964; Komiyama & Lingafelter, 1964).

The 3·000 Å Cu–Cu distance in $[Cu_2(OH)_2(tmen)_2]Br_2$ is rather characteristic of dimeric copper(II) compounds (Schlafer, Morrow & Smith, 1965; Sager, Williams & Watson, 1967; Kilbourn & Dunitz, 1967; Bertrand, 1967; Barclay & Kennard, 1961; Barclay & Hoskins, 1965; Wallwork & Addison, 1965; Schlueter, Jacobsen & Rundle, 1966) not having the copper(II) acetate monohydrate type of structure (van Niekerk & Schoening, 1953; Barclay & Kennard, 1961; Hanic, Štempelová & Hanicová, 1964; Chidambaram & Brown, 1965; O'Connor & Maslen, 1966; Manojlović-Muir, 1967). In the latter structure the Cu–Cu distance of about 2·63 Å is presumably responsible (Figgis & Martin, 1956) for weak δ-bond formation which causes the subnormal magnetic moments observed for such compounds. Qualitative calculations using Slater orbitals show that δ-bonding type interaction between two copper(II) ions is essentially zero at a distance of 2·80 Å. For compounds like $[Cu_2(OH)_2(tmen)_2]Br_2$ where there appears to be no opportunity for direct metal–metal interaction, spin coupling takes place by super-exchange. On the basis of Anderson's theory (Anderson, 1959), super-exchange, *i.e.* exchange *via* the ligand atom, takes place because of overlap of the ligand atom orbitals with the magnetic orbitals of the metal. Exchange results from contact between magnetic wave functions having a common ligand atom orbital

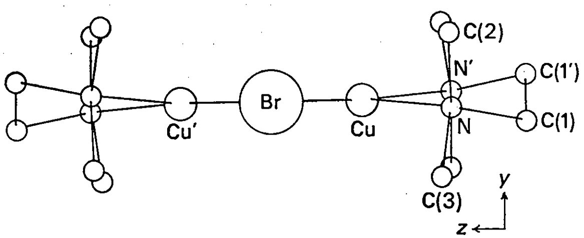

Fig. 2. Formula unit viewed along the *x* axis.

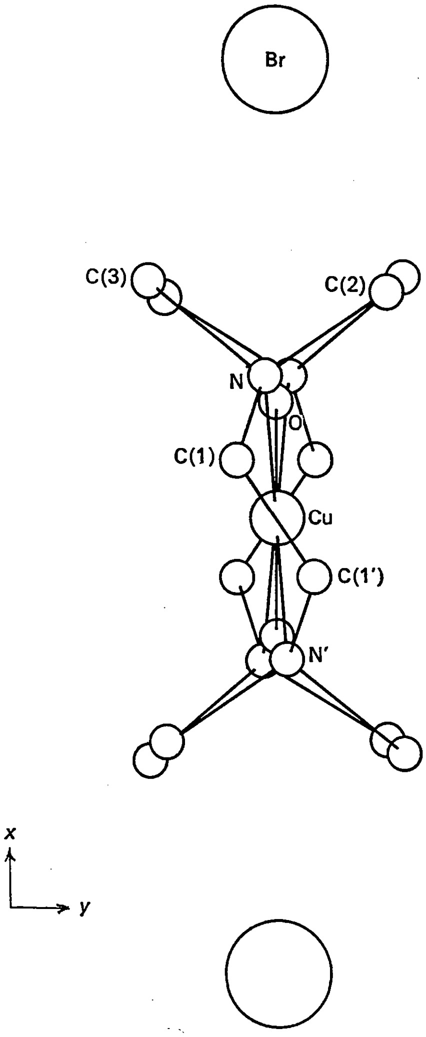

Fig. 3. Formula unit viewed along the *z* axis.

component but different metal atom components. Thus super-exchange can occur over large distances because the magnetic wave functions themselves are spread over long distances.

The O–Br distance of 3·366 Å leads us to believe there is hydrogen bridging O···H···Br. In manganese(II) and cobalt(II) bromide dihydrate, Br–O separations involving hydrogen bonding are 3·39 and 3·37 Å respectively. Several attempts to locate this hydrogen atom have not produced any conclusive results.

This hydrogen bridging requires approximate sp^2 hybridization for the oxygen atoms. $[Cu_2(OH)_2(tmen)_2]Br_2$ exhibits a strong OH stretching band at 3410 cm^{-1}. While the OH band supports hydroxy-bridging between the copper ions (Ferraro & Walker, 1965; McWhinnie, 1964, McWhinnie, 1965), the value of the OH frequency suggests hydrogen bonding, since 'free' OH groups lead to sharp bands around 3620 cm^{-1} while H-bonded OH groups have broad bands around 3320 cm^{-1} (Brand & Eglinton, 1965).

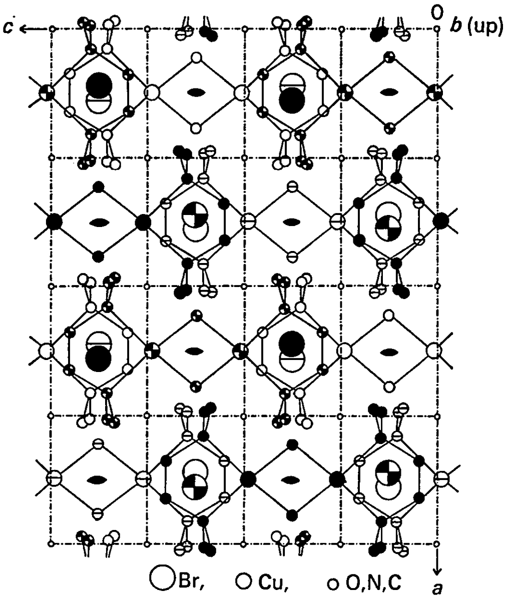

Fig. 4. Unit cell viewed along the y axis. ○: $0<y<\frac{1}{4}$, ⊖: $\frac{1}{4}<y<\frac{1}{2}$, ◔ : $\frac{1}{2}<y<\frac{3}{4}$, ●: $\frac{3}{4}<y<\frac{4}{4}$.

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