pas possible de justifier la longueur des liaisons de l'anneau des carbones par ces seules structures, et probablement il faut admettre une contribution de structures ionisées, dont on peut concevoir un grand nombre, compatibles avec la formule chimique.

Tableau 3. *Distances interatomiques*

	Piasélénol (±0,04A.)	Piazthiol (±0,03A.)	Benzofurazane (±0,07A.)	*A—B* (Pauling)	*A═B* (Pauling)
Se–N	1,83	—	—	1,87	1,67
S–N	—	1,60	—	1,74	1,54
O–N	—	—	1,20	1,36	1,15
C–N	1,30	1,34	1,35	1,47	1,265
C_1–C_6	1,42	1,46	1,43	1,54	1,33
C_1–C_2	1,30	1,29	1,43	—	—
C_2–C_3	1,42	1,46	1,43	—	—
C_5–C_6	1,46	1,41	1,43	—	—

Piazthiol

L'importance des structures (*b*) et (*c*) semble être égale. En réalité, les distances C–N et N–S sont très courtes, plus voisines à la double liaison qu'à la simple, et la distance C_1–C_2 est légèrement plus courte que celle correspondant à la double liaison (quoique la différence soit à la limite de l'erreur expérimentale). Ceci amènerait à discuter la contribution de structures ionisées, qui devraient justifier, au même temps, la longueur des liaisons de l'anneau des carbones, et rendre compte de la différence des anneaux des carbones du piazthiol et du piasélénol. Cette différence a certainement une signification réelle, quoique à la limite des erreurs expérimentales. Probablement la plus faible densité électronique des atomes C_2 et C_3 (voir ci-dessus), par rapport aux autres atomes de carbone, correspond aussi à une anomalie réelle.

Benzofurazane

La valeur des erreurs expérimentales ne permet pas une discussion détaillée de la structure électronique. L'anneau des carbones paraît néanmoins plus régulier que celui du piasélénol et du piazthiol. Toutes les liaisons, d'autre part, ont une longueur intermédiaire entre celles correspondant à la simple et la double liaison.

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Malachite: Re-examination of Crystal Structure

By A. F. Wells

Imperial Chemical Industries Ltd., Research Laboratories, Hexagon House, Manchester 9, England

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The crystal structure of malachite, $Cu_2(OH)_2CO_3$, has been re-examined in order to check the environment of the copper atoms, one-half of which, according to a previous study, have five nearest neighbours at the apices of a trigonal bipyramid. The cell constants are: $a = 9{\cdot}48$, $b = 12{\cdot}03$, $c = 3{\cdot}21$ A., $\beta = 98 \pm \frac{1}{2}°$. The space group is $P2_1/a$ and there are 4 $Cu_2(OH)_2CO_3$ in the unit cell. With the revised atomic co-ordinates each of the two types of crystallographically non-equivalent copper atoms has four (coplanar) nearest neighbours and two more at a greater distance completing a distorted octahedral group.

Introduction

The formation of four coplanar (square) bonds by divalent copper atoms has now been established in a number of crystals. In the halogen compounds which have been studied the cupric atom also has two more neighbours, at distances appreciably greater than those expected for normal covalent bonding, completing a distorted octahedral co-ordination group. Examples are: $CuCl_2.2H_2O$ (Harker, 1936), $K_2CuCl_4.2H_2O$ (Chrobak, 1934; Gottfried, 1936), $CuBr_2$ (Helmholz, 1947), $CuCl_2$ (Wells, 1947*a*), $CsCuCl_3$ (Wells, 1947*b*), and $Cu_2(OH)_3Cl$ (Wells, 1949). In CuO (Tunell, Posnjak & Ksanda, 1935) the cupric atom forms four coplanar bonds ($Cu–O = 1{\cdot}95$ A.), but its next nearest neighbours are four Cu at 2·88 A. In this crystal the co-ordination numbers of Cu and O must necessarily be the same, so that the formation of two more (weaker) bonds by Cu would require that O formed $4+2$ bonds. The inability of O to form six bonds in an essentially covalent crystal is presumably the reason why Cu forms only four bonds

Table 1. *Interatomic distances in cupric hydroxy-oxy salts* (A.)

		Environment of Cu			
Crystal	Chemical formula	Cu_I	Cu_{II}	Notes	Reference
Azurite	$Cu_3(OH)_2(CO_3)_2$	2 O 2·09 2 O 2·15 2 OH 2·43	3 O 2·04–2·10 OH 2·32 OH 2·37	C–O in CO_3^{2-} = 1·18, 1·22, and 1·32	Brasseur (1932)
Malachite	$Cu_2(OH)_2CO_3$	2 O 2·0 4 OH 2·2	3 O 2·0 2 OH 2·2	—	Brasseur & Toussaint (1938)
Libethenite	$Cu_2(OH)PO_4$	4 O 2·05, 2·28 2 OH 2·10	4 O 1·91, 2·08 OH 1·84	P–O in PO_4^{3-} from 1·44 to 1·73	Heritsch (1939)
Olivenite	$Cu_2(OH)AsO_4$	2 OH 1·96 2 O 2·12 2 O 2·34	4 O 1·92–2·16 OH 1·99	As–O in AsO_4^{3-} = 1·45, 1·49, and 1·81 (2)	Heritsch (1938)

in this crystal. Factors of this sort must always be borne in mind when discussing the stereochemistry of a particular atom either in a crystal or in a molecule. Neglecting for the present any differences in the number or arrangement of next nearest neighbours, it is certain that in all the crystals mentioned above divalent copper forms four covalent primary bonds. However, in the published structures of a number of hydroxy-oxy-salts ('basic' salts) this is not the case (Table 1). For example, in malachite, $Cu_2(OH)_2CO_3$, one-half of the copper atoms were found to have three nearest oxygen neighbours (of CO_3 groups) at 2·0 A. and two OH at 2·2 A., these five neighbours being arranged approximately at the apices of a trigonal bipyramid. It seemed possible that some of the relatively light oxygen atoms might not have been very precisely located in some of these crystals. For this reason the crystal structure of malachite has been re-examined.

The unit cell and space group

Malachite crystallizes with holohedral monoclinic symmetry, and two alternative sets of axes have been used:

$$a : b : c = 0{\cdot}8809 : 1 : 0{\cdot}4012,\ \beta = 61^\circ\ 50'$$

(Descloiseaux, 1862–93, vol. 2, p. 186),

$$a : b : c = 0{\cdot}7823 : 1 : 0{\cdot}4036,\ \beta = 91^\circ\ 03'$$

(Goldschmidt, 1913–22, vol. 5).

In their X-ray study Brasseur & Toussaint adopted the latter axes and found

$$a = 9{\cdot}38,\quad b = 11{\cdot}98,\quad c = 3{\cdot}18\text{ A.},$$

so that $a : b : c = 0{\cdot}7845 : 1 : 0{\cdot}2653$,

the length of the c axis being two-thirds that of Goldschmidt. This unit cell contains 4 $Cu_2(OH)_2CO_3$ and the space group was given as $P2_1/a$.

On re-examining single crystals of malachite (locality unknown) it is found that the cell dimensions of Brasseur & Toussaint are not consistent with the angle $\beta = 91^\circ\ 03'$ which they adopted. With this value of β the cell is B face-centred with $a = 18{\cdot}72 \pm 0{\cdot}05$ A. and $c = 3{\cdot}21 \pm 0{\cdot}02$ A. There is a choice between two cells, one having $a = 9{\cdot}48$ A. and $\beta = 98 \pm \frac{1}{2}^\circ$, the other, $a = 9{\cdot}51$ A. and $\beta = 100 \pm \frac{1}{2}^\circ$, with c as before. The unit cell adopted in this investigation has

$$a = 9{\cdot}48,\quad b = 12{\cdot}03,\quad c = 3{\cdot}21\text{ A.},\quad \beta = 98 \pm \tfrac{1}{2}^\circ,$$

the space group being $P2_1/a$. Referred to these axes the prominent cleavage is $(20\bar{1})$. The relations between the various cells and axes are shown in Fig. 1.

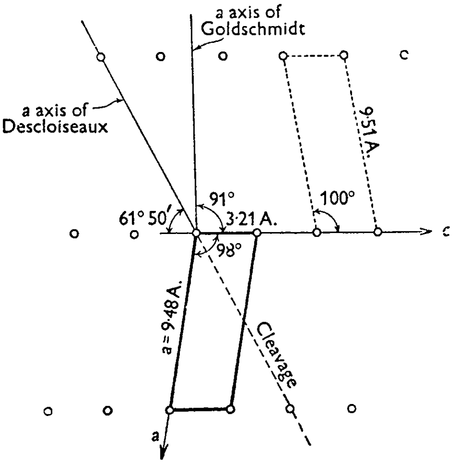

Fig. 1. The relation between the various axes and the lattice of malachite. The circles represent points in a (010) section of the lattice and the heavy lines outline the plan of the unit cell adopted here.

Revision of the crystal structure

All atoms lie in fourfold general positions, so that x, y and z co-ordinates have to be determined for Cu_I, Cu_{II}, OH_I, OH_{II}, C, O_I, O_{II} and O_{III}. Brasseur & Toussaint determined the x and y co-ordinates of the atoms by trial and error followed by a Fourier projection. They did not state how the z co-ordinates were obtained and gave no data for planes involving l indices, so that the accuracy of their z co-ordinates could not be checked. A translation of the carbonate group along the c axis would, of course, entirely change the environment of the Cu atom with the trigonal bipyramidal co-ordination group.

In the present investigation intensity data were obtained from Weissenberg photographs (equatorial and layer lines) about the three principal axes, taken with Cu $K\alpha$ radiation. Intensities were estimated visually using the multiple-film technique. The general nature of the $x\,y$ projection was confirmed by means of an F^2 projection. Refinement of the x and y co-ordinates was carried out in the usual way, using progressively larger numbers of terms in Fourier summations when their signs could be determined unambiguously. The z co-ordinates were determined by three-dimensional line syntheses, using data for hkl reflexions up to $\sin\theta = 0{\cdot}60$. It is difficult to estimate the accuracy of the z co-ordinates because of the arbitrary termination of the series at this point, which was done to avoid the rather laborious determination of further F_{hkl}'s. Some 115 F_{hk1} and F_{hk2} terms were used in the final summations. The atomic co-ordinates are given in Table 2. The observed and calculated values of F_{hk0} and F_{hkl} are compared in Tables 3 and 4. In Table 3 the values of $F_{\text{calc.}}$ of Brasseur & Toussaint are given for comparison purposes. The f curves used were those of the *International Tables...* (1935, vol. 2, pp. 571–2) for Cu, O, and C atoms, that for OH being taken as 9/8 times that of O.

Table 2. *Revised co-ordinates for malachite*

	x	y	z
$\mathrm{Cu_I}$	0·00	0·21	0·89
$\mathrm{Cu_{II}}$	$0{\cdot}23_5$	0·39	0·38
$\mathrm{O_I}$	0·14	0·13	0·28
$\mathrm{O_{II}}$	0·34	0·24	0·50
$\mathrm{O_{III}}$	0·33	0·05	0·63
$\mathrm{OH_I}$	0·09	0·36	0·92
$\mathrm{OH_{II}}$	0·39	0·43	0·86
C	0·27	0·13	0·47

Table 3. *Observed and calculated structure factors* F_{hk0}

	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{calc.}}$ (B. & T.)
200	40	−47	−20
400	88	85	136
600	24	17	6
800	96	110	104
10,0,0	18	20	38
020	56	−66	−46
040	68	−81	−34
060	84	−74	−72
080	30	42	−6
0,10,0	60	53	100
0,12,0	64	−90	−48
0,14,0	20	15	—
110	20	20	24
120	64	79	84
130	52	−50	−72
140	40	36	65
150	68	75	128
160	68	−65	−68
170	76	−84	−60
180	64	−51	−67
190	56	41	20
1,10,0	<8	17	—
1,11,0	8	−6	—
1,12,0	64	52	—
1,13,0	<6	−2	—
1,14,0	12	−3	—
1,15,0	18	30	—
210	4	−6	−18
220	88	−112	−112
230	20	−24	−31
240	112	123	104
250	80	98	64
260	52	57	76
270	4	23	24
280	76	−76	−84
290	20	−39	18
2,10,0	<6	8	—
2,11,0	14	−33	—
2,12,0	24	−25	—
2,13,0	<8	5	—
2,14,0	68	92	—
2,15,0	<6	−4	—
310	52	48	40
320	56	−36	−64
330	60	−56	−76
340	36	−16	4
350	68	71	60
360	44	50	40
370	84	−79	−96
380	44	51	44
390	48	58	68
3,10,0	20	−36	—
3,11,0	24	−29	—
3,12,0	36	−62	—
3,13,0	<4	−19	—
3,14,0	4	6	—
410	12	−12	64
420	64	−59	−58
430	24	27	4
440	<6	−15	−32
450	16	−16	−28
460	28	−21	−83
470	24	−24	−13
480	20	18	—
490	20	−25	−8
4,10,0	64	100	115
4,11,0	24	27	28
4,12,0	44	−79	−50
4,13,0	16	14	—
4,14,0	<5	−8	—
510	28	−32	−35
520	76	87	84
530	28	−48	−46
540	20	23	28
550	96	101	92
560	22	−47	−57
570	38	−36	−60
580	40	−30	−62
590	8	27	40
5,10,0	24	44	—
5,11,0	24	−23	—
5,12,0	14	28	—
5,13,0	10	12	—
610	8	−16	−8
620	64	−78	−96
630	44	−26	−28
640	92	114	116
650	16	−18	0
660	<6	9	32
670	32	27	29
680	40	−59	−52
690	24	20	10
6,10,0	<6	−4	—
6,11,0	16	−13	—
6,12,0	22	−30	—
6,13,0	24	−19	—
710	60	64	80
720	36	−74	−52
730	60	−88	−60
740	32	−38	−44
750	<6	4	16
760	12	21	16
770	24	−26	−74
780	24	27	44
790	56	78	60
7,10,0	<8	−17	—
7,11,0	8	−20	—
7,12,0	14	−20	—
810	40	36	36
820	32	−39	−36
830	26	20	36
840	22	−23	−12
850	<6	−2	−12
860	20	−27	0
870	24	−33	−38
880	<6	9	−14
890	<6	14	−9
8,10,0	36	73	—
8,11,0	14	21	—
910	<6	−4	−6
920	8	14	36
930	<6	−1	−32
940	16	20	20
950	64	88	92
960	<5	−8	−6
970	60	−82	−40
980	30	−28	−14
990	<5	−11	4
9,10,0	<5	2	—
10,10	18	−29	−28
10,20	36	−41	−52
10,30	22	−28	−32
10,40	28	46	48
10,50	<5	−1	8
10,60	8	16	16
10,70	24	36	48
10,80	36	−51	−44
11,10	18	32	32
11,20	<4	−10	0
11,30	22	−45	−52
11,40	<4	5	−10
11,50	<4	9	8
11,60	14	29	16

Table 4. *Observed and calculated structure factors* F_{hkl}

	$F_{\text{obs.}}$	$F_{\text{calc.}}$
001	30	−19
011	24	24
021	57	−54
031	60	−66
041	75	59
051	51	64
061	42	40
071	60	79
081	60	−67
111	75	58
121	9	2
131	18	−28
141	60	−25
151	9	19
161	99	101
171	105	−86
181	21	−17
$11\bar{1}$	< 6	3
$12\bar{1}$	21	−27
$13\bar{1}$	30	−23
$14\bar{1}$	< 7	19
$15\bar{1}$	72	85
$16\bar{1}$	15	−17
$17\bar{1}$	66	−74
$18\bar{1}$	108	91
201	114	118
211	93	73
221	93	−74
231	39	38
241	< 10	−13
251	15	−16
261	21	−14
271	54	−46
281	27	28
$20\bar{1}$	186	259
$21\bar{1}$	114	−133
$22\bar{1}$	30	−22
$23\bar{1}$	33	13
$24\bar{1}$	51	−51
$25\bar{1}$	12	9
$26\bar{1}$	63	−59
$27\bar{1}$	27	43
$28\bar{1}$	21	21
311	87	−85
321	102	106
331	< 12	− 5
341	24	−20
351	111	121
361	12	9
371	27	−40
$31\bar{1}$	54	48
$32\bar{1}$	72	47
$33\bar{1}$	90	−76
$34\bar{1}$	84	76
$35\bar{1}$	18	12
$36\bar{1}$	90	95
$37\bar{1}$	24	−28
401	33	28
411	20	16
421	52	−61
431	135	−105
441	66	81
451	48	43
461	< 6	10
$40\bar{1}$	40	−60
$41\bar{1}$	22	−18
$42\bar{1}$	105	−85
$43\bar{1}$	69	65
$44\bar{1}$	138	132
$45\bar{1}$	27	33
$46\bar{1}$	22	18
$47\bar{1}$	24	−25
511	75	77
521	< 5	− 2
531	85	−96
541	69	−53
551	18	−19
$51\bar{1}$	18	8
$52\bar{1}$	138	−91
$53\bar{1}$	45	−35
$54\bar{1}$	12	27
$55\bar{1}$	72	74
$56\bar{1}$	9	14
601	60	51
611	67	67
621	28	−29
$60\bar{1}$	60	56
$61\bar{1}$	40	−43
$62\bar{1}$	42	−32
$63\bar{1}$	< 6	9
$64\bar{1}$	21	−30
002	54	34
012	162	134
022	36	−33
032	18	27
042	< 15	15
052	12	−20
112	84	−89
122	36	42
132	12	30
142	30	−32
152	69	81
$11\bar{2}$	72	66
$12\bar{2}$	30	−26
$13\bar{2}$	< 10	−17
$14\bar{2}$	42	37
$15\bar{2}$	48	−51
202	15	27
212	30	47
222	< 9	− 7
232	90	−103
242	< 10	10
$20\bar{2}$	33	−29
$21\bar{2}$	12	15
$22\bar{2}$	15	6
$23\bar{2}$	92	−139
$24\bar{2}$	42	27
312	42	42
322	30	50
332	36	−55
$31\bar{2}$	21	− 9
$32\bar{2}$	15	−17
$33\bar{2}$	< 15	− 4
$34\bar{2}$	55	59
$35\bar{2}$	60	50

Description of the structure

The crystal structure of malachite is illustrated in Fig. 2 (projection on (001)) and Fig. 3 (two unit cells). The structure is not of the chain or layer type, the good ($20\bar{1}$) cleavage being practically parallel to the planes of the carbonate groups. The two types of non-equivalent copper atoms have different environments, viz.:

Cu_{I}	O_{I}	1·95 A.	Mean, 1·98 A.,
	O_{II}	1·97 A.	
	OH_{I}	2·00 A.	
	OH_{II}	1·98 A.	
	O'_{I}	2·69 A.	Mean, 2·71 A.,
	O'_{II}	2·73 A.	
Cu_{II}	O_{II}	2·07 A.	Mean, 2·01 A.,
	O_{III}	2·02 A.	
	OH_{I}	2·04 A.	
	OH_{II}	1·91 A.	
	OH'_{I}	2·42 A.	Mean, 2·41 A.
	OH'_{II}	2·39 A.	

In each case, however, the spatial arrangement of the six nearest neighbours is the same, that is, four approximately coplanar with the copper atom at the corners of a square, and two more at a greater distance completing a distorted octahedral group. Each OH forms three (pyramidal) bonds, of which two are normal covalent Cu–O bonds (length ≈ 2 A.) and one is a longer bond (2·4–2·7 A.). The stereochemistry of divalent copper atoms in malachite is, therefore, similar to that in the halogen compounds already mentioned.

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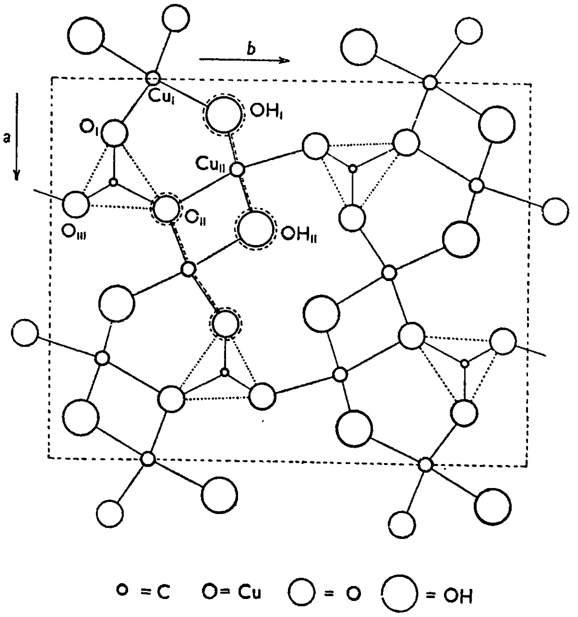

Fig. 2. Projection of the structure of malachite on (001). The broken lines from Cu atoms represent bonds to O or OH in adjacent unit cells (broken circles).

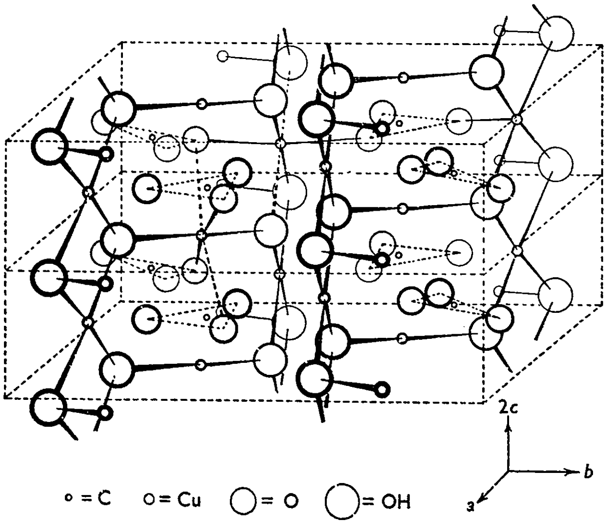

Fig. 3. The crystal structure of malachite (two unit cells).

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The Crystal Structure of Bandylite, $CuCl_2.CuB_2O_4.4H_2O$

By Robert L. Collin

Mellon Institute of Industrial Research, Pittsburgh 13, *Pennsylvania, U.S.A.*

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The crystal structure of bandylite is tetragonal C_{4h}^3–$P4/n$ with one molecule of $CuCl_2.CuB_2O_4.4H_2O$ in a cell of dimensions $a = 6{\cdot}19$ and $c = 5{\cdot}61$ A. The copper atoms are surrounded in a square planar configuration by four hydroxyl groups at a distance of 1·98 A. and two chlorine atoms on a line at right angles to this plane at 2·80 A. These distorted octahedra about copper are joined together into layers by boron atoms that are surrounded tetrahedrally by four hydroxyl groups at a distance of 1·42 A.

Introduction

The nature of the co-ordination of copper in cupric compounds has been the subject of a number of crystal-structure investigations. The type of bonding that occurs is not yet completely understood (Wells, 1947), and more interatomic distance data, of sufficient accuracy to allow deductions as to bond type, are needed. The possibility for studying the bonding of the copper (II) atom as well as the co-ordination of boron makes bandylite a crystal of some interest from a structural point of view.

The cupric atom usually occurs in sixfold co-ordination with four close neighbors in a square planar arrangement and with two more neighbors at a somewhat longer distance on a line at right angles to this plane. Boron commonly has a triangular, threefold co-