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The Crystal Structure of Atacamite and the Crystal Chemistry of Cupric Compounds

By A. F. Wells

Imperial Chemical Industries Limited, Research Laboratories, Hexagon House, Manchester 9, *England*

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The co-ordinates assigned in an earlier study of the crystal structure of atacamite, $Cu_2Cl(OH)_3$ or $CuCl_2 . 3Cu(OH)_2$, have been revised. Each Cu atom is shown to have four nearest OH neighbours (mean Cu–OH distance 2·01 A.), and in addition two more neighbours completing distorted octahedral co-ordination groups. For one-half of the Cu atoms these are one OH (at 2·36 A.) and one Cl (at 2·75 A.), and for the remainder, two Cl (at 2·76 A.). A comparison is made of the structures of $CuCl_2$, $Cu_2Br(OH)_3$ and $Cu_2Cl(OH)_3$.

Introduction

The crystal structure of atacamite, $Cu_2Cl(OH)_3$ or $CuCl_2 . 3Cu(OH)_2$, has been previously studied (Brasseur & Toussaint, 1942) with the following results. Atacamite is orthorhombic, $a = 6·01$ A., $b = 9·13$ A. and $c = 6·84$ A.; space group $Pnam$–D_{2h}^{16} with 4 $Cu_2Cl(OH)_3$ in the unit cell. No evidence for the mirror plane was presented, and the atoms were assigned the co-ordinates given in Table 1.

Table 1. *Co-ordinates for atacamite according to Brasseur & Toussaint* (1942)

	x	y	z
4 Cu_I in (a)	0	0	0
4 Cu_{II} in (c)	0·185	0·25	0·25
4 Cl in (c)	0·333	0·044	0·75
4 OH_I in (c)	0·25	0·00	0·25
8 OH_{II} in (d)	0·435	0·25	0·00

The nomenclature is that of the *International Tables*. Fig. 1 shows the projection of the structure on (001). The good general agreement between calculated and observed structure amplitudes shows that the structure is essentially correct, but there are two reasons for suspecting that the lighter atoms may not have been very precisely located. First, there are a number of pairs of reflexions for which $F'_{obs.} > F''_{obs.}$ but $F'_{calc.} < F''_{calc.}$ (e.g. 370 and 390, 520 and 540, 530 and 550, etc.). In particular, the calculated value of F_{380} is exactly zero for the above structure, whereas this reflexion is observed to be stronger than 370, for which $F_{calc.} = 40·8$. The special value 0·25 assigned to the y co-ordinates of Cu_{II} and OH_{II} and to the x co-ordinate of OH_I, and the value 0·00 assigned to the y co-ordinate of OH_I are not required by the space group. This is also true of the value 0·00 for the z co-ordinate of OH_{II}, irrespective of whether the space group is $Pnam$ or Pna. Secondly, the environments of the two types of copper atom are not those to be expected for divalent copper atoms. With the co-ordinates of Table 1 each Cu is surrounded by a somewhat distorted octahedral arrangement of nearest neighbours at the following distances:

Cu_I	2 OH_I	2·25 A.	Cu_{II}	4 OH_{II}	2·25 A.
	2 OH_{II}	2·30 A.		OH_I	2·30 A.
	2 Cl	2·70 A.		Cl	2·70 A.

In all other halogen compounds of divalent copper so far studied copper atoms are found to have four nearest neighbours, coplanar with Cu, and two more at a distance somewhat greater than that corresponding to covalent bonding, completing a distorted octahedron around Cu. Moreover, the interatomic distance Cu–OH of 2·25–2·30 A. is not acceptable. Brasseur & Toussaint state that the interatomic distances in their structure are consistent with the following ionic radii: Cu^{2+}, 0·90 A.; Cl^-, 1·80 A.; and OH^-, 1·35 A., which they describe as generally accepted values. Apart from the fact that it is doubtful if the structures of cupric compounds other than CuF_2 should be interpreted as ionic

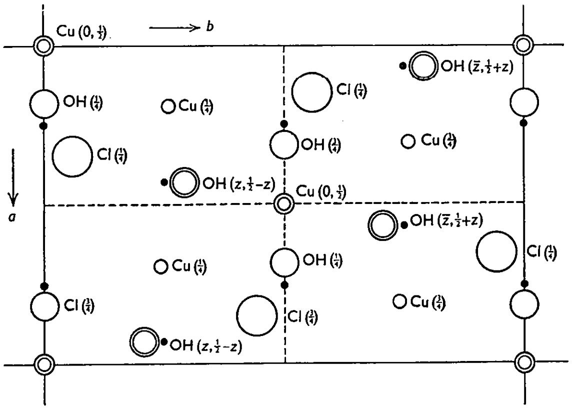

Fig. 1. Projection of the structure of atacamite on (001). The open circles show the positions determined in the present study. The small black circles show the positions of OH_I and OH_{II} given in Table 1. Only small alterations have been made in the positions of the other atoms.

structures, there is no generally accepted value of the radius of the cupric ion, and in any case it is certainly less than 0·90 A. (Goldschmidt, 1946). The distance Cu–Cl observed in this structure does not correspond to a normal Cu–Cl bond, the length of which is known to be 2·30 A. in $CuCl_2$ (Wells, 1947 *a*) and other compounds, but to the weak bonding of the two additional neighbours in the (4+2)-co-ordination characteristic of divalent copper. The Cu–OH distances of 2·25–2·30 A. are much larger than the value to be expected. In $CuCl_2.2H_2O$ (Harker, 1936) and $K_2CuCl_4.2H_2O$ (Chrobak, 1934; Gottfried, 1938), the Cu–H_2O distance was found to be close to 2·0 A., and similar values have recently been found for Cu–OH in $Cu_2Br(OH)_3$ (Aebi, 1948). A value around 2·0 A. would also be expected by analogy with the Cd–OH and Cd–Cl distances in Cd(OH)Cl, viz. 2·34 and 2·71 A. respectively (Hoard & Grenko, 1934).

Revision of the structure

It was decided to check the co-ordinates by preparing projections of the structure on (001) and (100). Weissenberg photographs about the *c* and *a* axes were taken with Cu $K\alpha$ radiation, using very small crystals to eliminate errors due to absorption. (The maximum length in the cross-section of the needle used for the *c*-axis photograph was 0·05 mm.) Atacamite from Mina Resvaloza, Gatica, Bolivia, was used in the investigation.

Since no reason was given for adopting the higher space group *Pnam* rather than *Pna*, the (001) projection was studied first, because the x and y co-ordinates of the (general) fourfold position in *Pna* are the same as those of the positions (*c*) and (*d*) in *Pnam*. The space group *Pnam* has a centre of symmetry at the origin; in *Pna* there is a centre in the (001) projection. The signs of some thirty F_{hk0}'s were determined unambiguously by the contributions from the copper atoms, and an electron-density projection on (001) was made using $F\exp[-2\sin^2\theta]$. The 'artificial' temperature factor was introduced because the series was only slowly convergent. Peaks appeared on the projection corresponding to Cl, OH_I and OH_{II} in positions close to, but in the case of OH_I and OH_{II} significantly different from, those of the structure of Brasseur & Toussaint. In the space group *Pna* there is only a fourfold position. The fact that only four peaks appeared for 8 OH_{II}, as for 4 OH_I, confirms that pairs of OH_{II} are superposed in this projection, and supports the choice of the space group *Pnam*. (It does not conclusively eliminate *Pna*, in which two sets of 4 OH_{II} could have exactly the same x and y co-ordinates.) Refinement of this projection proceeded by determination of the signs of more F_{hk0}'s and resummation of the Fourier series. For the final (001) projection (Fig. 2), 49 terms were used. This projection shows that rather large changes are required in the x co-ordinate of OH_I and the y co-ordinate of OH_{II}, in addition to smaller changes in other co-ordinates (see Table 2). There is some uncertainty as to the value of y of OH_I, since this peak is not well resolved, probably owing to its proximity on the projection to Cu_I. The value $y=0·00$ is subject to a probable error of $\pm 0·01$.

As regards the z co-ordinates, only that of OH_{II} is variable in this structure, and this may readily be determined by projecting the structure on (100). The approximate value of z for OH_{II}, to which Brasseur & Toussaint assigned the special value 0·00, may be determined from the structure amplitudes of weak planes (e.g. 024, 028, 042, etc.), for which the contributions from the copper atoms are very small. A value of about 0·06 is required. The signs of the structure amplitudes of all the observed 0*kl* reflexions are determined by the contributions from Cu, Cl and OH_I, so that the z co-ordinate of OH_{II} is determined directly by projecting the electron density on (100). From this projection (Fig. 3) the value of z for OH_{II} was found to be 0·065. The revised co-ordinates are given in Table 2. The observed and calculated values of F_{hk0} and F_{0kl} are given in Tables 3 and 4. The observed values were obtained by visual estimation using the multiple-film technique. The f curves used were those of the *International Tables* (2, pp. 571–2) for Cu, Cl and O atoms.

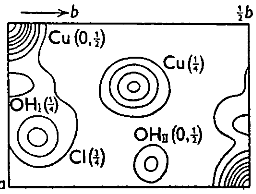

Fig. 2. Electron density of atacamite projected on to (001).

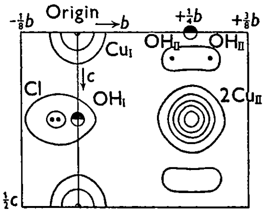

Fig. 3. Electron density of atacamite projected on (100). The small black circles indicate the positions assigned to Cl, OH_I and OH_{II}; the half-black circles show the positions given in Table 1.

Table 2. *Revised co-ordinates for atacamite*

	x	y	z
Cu_I	0	0	0
Cu_{II}	0·192	0·258	0·25
Cl	0·35	0·058	0·75
OH_I	0·185	0·00	0·25
OH_{II}	0·43	0·292	0·065

Description of the structure

The structure is illustrated in Fig. 4 to show the sixfold co-ordination of Cu and the threefold co-ordination of Cl and OH. Other features are accentuated in Fig. 6.

Table 3. *Observed and calculated values of* F_{hk0}

		$F_{\text{calc.}}$	
*hk*0	$F_{\text{obs.}}$	A. F. W.	B. & T.
200	31	22	9
400	37	40	54
600	90	109	90
020	32	23	19
040	130	210	236
060	<10	-3	19
080	87	78	120
0,10,0	<8	4	33
110	61	95	67
120	15	-7	26
130	71	65	66
140	59	-62	33
150	95	106	64
160	<9	7	31
170	52	69	63
180	32	-34	21
190	55	76	60
1,10,0	20	35	8
1,11,0	36	63	55
210	6	-8	12
220	75	103	60
230	59	67	50
240	33	19	18
250	<9	-5	8
260	90	107	69
270	48	59	47
280	16	13	28
290	30	-43	7
2,10,0	70	92	68
2,11,0	16	18	22
310	90	102	109
320	<8	5	0
330	49	51	91
340	38	-27	0
350	55	65	64
360	<10	6	0
370	<10	0	41
380	10	-6	0
390	24	10	24
3,10,0	<10	2	0
410	76	85	82
420	28	42	69
430	82	-99	94
440	48	60	56
450	45	42	48
460	50	63	66
470	45	-53	88
480	60	76	56
490	23	34	37
510	48	61	40
520	32	28	14
530	55	87	42
540	23	20	23
550	36	38	50
560	34	33	24
570	50	81	53
580	<7	0	18
610	32	-42	19
620	45	55	42
630	11	22	40
640	70	81	70
650	37	-52	18
660	8	13	17
670	15	29	21
710	21	20	30
720	<8	-1	12
730	30	39	34
740	16	-15	20

Table 4. *Observed and calculated values of* F_{0kl}

0*kl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$
002	55	-87
004	174	200
006	60	-38
008	110	133
011	87	-107
013	45	31
015	82	-73
017	54	37
022	90	94
024	64	44
026	90	92
028	40	39
031	110	146
033	102	-89
035	135	103
037	73	-72
042	10	-7
044	143	142
046	28	-18
048	91	91
051	53	-38
053	20	24
055	32	-29
057	21	20
062	140	132
064	<14	-4
066	99	107
071	82	73
073	80	-76
075	73	61
077	70	-57
082	28	18
084	103	80
086	29	27
091	54	-47
093	73	61
095	30	-36
0,10,2	131	118
0,10,4	21	-10
0,11,1	23	14
0,11,3	36	-31

Each Cu is surrounded by a (distorted) octahedral group of six nearest neighbours, and each OH or Cl is bonded to 3 Cu atoms. The lengths of the Cu–OH and Cu–Cl bonds are as follows:

Cu_I	2 OH_I	2·04 A.	Cu_{II}	2 OH_{II}	1·94 A.
	2 OH_{II}	2·00 A.		2 OH_{II}	2·07 A.
	2 Cl	2·76 A.		OH_I	2·36 A.
				Cl	2·75 A.

(The distance Cu_{II}–OH_{II} is less certain than the others; it may be slightly less than 2·36 A. if y of $OH_I > 0$.) The mean Cu–OH bond length, 2·01 A., may be compared with those in Table 5; it is the normal length of a Cu^{II}–O bond. The fifth hydroxyl group is at an appreciably greater distance from Cu_{II}, and also the Cu–Cl distances are considerably greater than the length of a single covalent Cu–Cl bond (2·30 A.). They may be compared with the longer Cu–Cl distances listed in Table 5. It is clear that in atacamite, as in crystals of other cupric compounds, the divalent copper atoms are forming four strong and two additional weak bonds, for which a theoretical explanation is at present lacking. It is interesting that the structure of $Cu_2Cl(OH)_3$ is quite different from that of $Cu_2Br(OH)_3$; these structures are compared later.

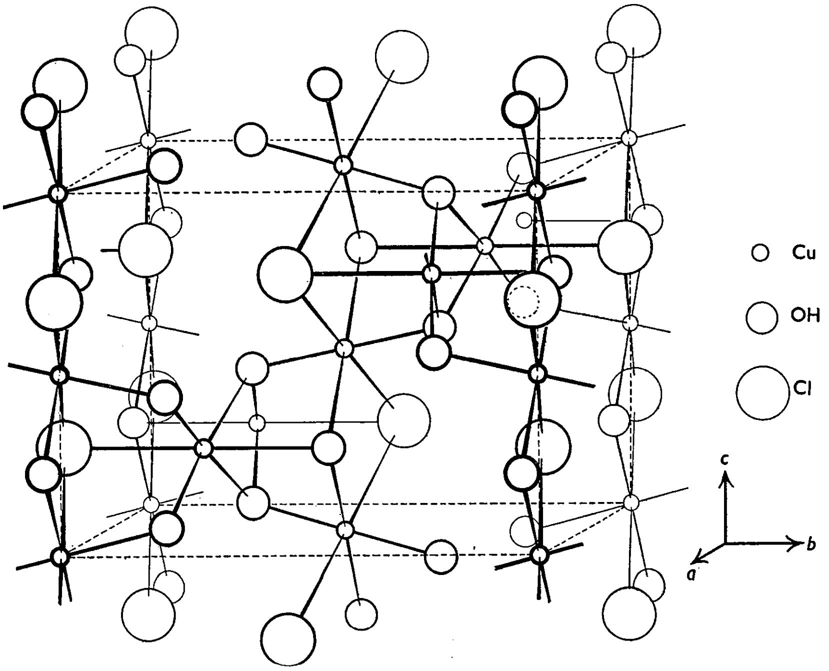

Fig. 4. Unit cell of the structure of atacamite.

Table 5. *Environments of* Cu^{II} *atoms in crystals*

Compound		Distances to nearest neighbours (A.)			
$CuCl_2$		4 Cl	2·30	2 Cl	2·95
$CuCl_2.2H_2O$		2 O 2 Cl	2·01 2·31	2 Cl	2·98
$CsCuCl_3$		4 Cl	2·30	2 Cl	2·65
$K_2CuCl_4.2H_2O$		2 O 2 Cl	1·97 2·32	2 Cl	2·95
$Cu_2Br(OH)_3$		4 OH	~2·0	2 Br	~3·0
	or	4 OH	~2·0	Br OH	2·8 2·3
$Cu_2Cl(OH)_3$		4 OH	2·02	2 Cl	2·76
	or	4 OH	2·00	Cl OH	2·75 2·36

The $(4A+2B)$ and $(5A+B)$ co-ordination in a compound M_2A_3B is a consequence of the ratio of A to B atoms and of the co-ordination numbers of M, A and B (6, 3 and 3 respectively). It is not possible for all the M atoms in such a structure to have the same numbers of A and B neighbours, as will be apparent shortly. If we assume the minimum of two kinds of crystallographically non-equivalent M atoms, present in equal numbers, and having co-ordination groups of $(aA+bB)$ and $(cA+dB)$, then it follows from the relative numbers of A and B atoms that $a+c=3\ (b+d)$. Since

$$a+b+c+d=12,$$

therefore $b+d=3$ and $a+c=9$. The only integral solutions are

$$a=6,\ b=0 \quad \text{and} \quad c=3,\ d=3$$

or

$$a=5,\ b=1 \quad \text{and} \quad c=4,\ d=2$$

(and of course, the solutions with a and c, b and d, interchanged). There is no integral solution for $a=c$ and $b=d$, i.e. it is not possible for all the M atoms to have the same type of co-ordination group. The first solution corresponds to a structure in which one half the metal atoms have $6A$ neighbours and the other half $3A+3B$. It could be realized in a structure with the sequence of layers shown below, for a hydroxy-chloride, at (a), the metal atoms between the layers having the co-ordination groups shown. The analogous structure for a compound M(OH)Cl is that shown at (b); it is the structure of Cd(OH)Cl, in which all metal atoms have 3 OH and 3 Cl neighbours:

Close-packed layer	Metal co-ordination group	Close-packed layer	Metal co-ordination group
Cl		OH	
	$M(OH)_3Cl_3$		$M(OH)_3Cl_3$
OH		Cl	
OH		OH	
	$M(OH)_6$		$M(OH)_3Cl_3$
OH		Cl	
Cl			
	(a)		(b)

The second solution corresponds to structures in which equal numbers of metal atoms have $(5A+B)$- and $(4A+2B)$-co-ordination, as in $Cu_2Cl(OH)_3$ and $Cu_2Br(OH)_3$.

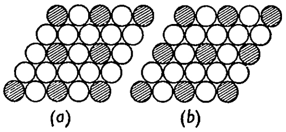

Fig. 5. The two simplest types of close-packed layer AX_3 (A atoms represented by shaded circles).

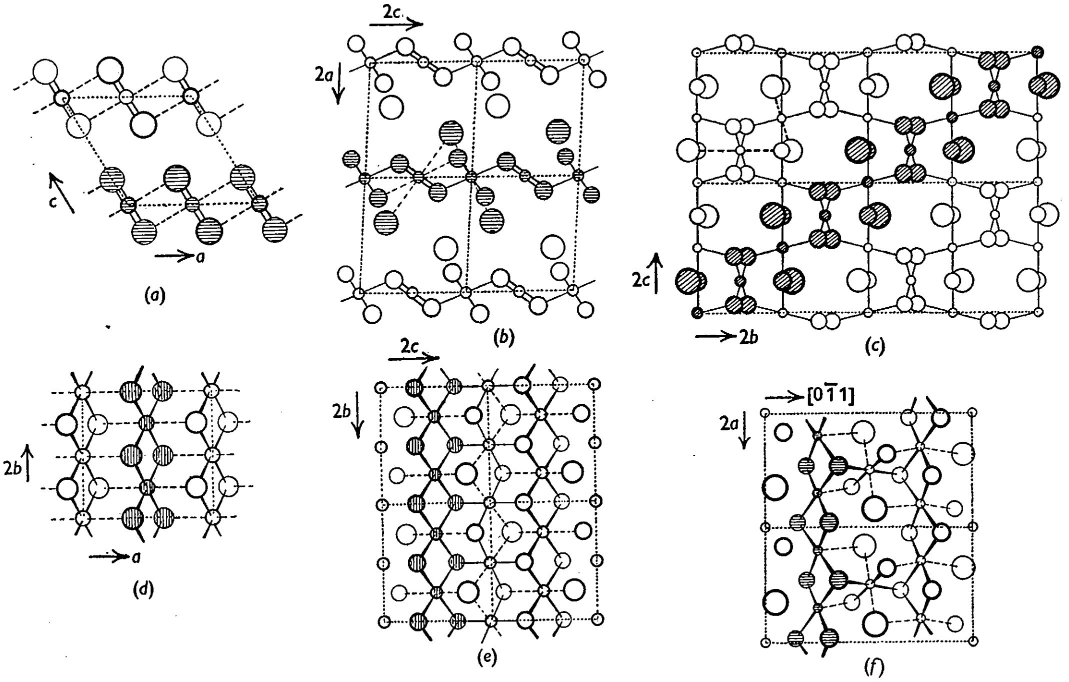

Fig. 6. (a), (b), (c) Elevations of the crystal structures of $CuCl_2$, $Cu_2Br(OH)_3$ and $Cu_2Cl(OH)_3$. (d), (e), (f) Projections of layers of these structures, showing a layer of metal atoms (smallest circles) in the plane of the paper, and close-packed layers of halogen atoms (or halogen atoms and OH groups) above and below the plane of the paper. The largest circles represent halogen atoms. Full lines indicate short, and broken lines long, Cu–OH or Cu–halogen bonds.

In connexion with the crystal chemistry of cupric compounds it is instructive to compare the structures of $Cu_2Cl(OH)_3$, $Cu_2Br(OH)_3$ and $CuCl_2$ (with which $CuBr_2$ is isomorphous). In crystals of many complex halides $A_mB_nX_{3m}$ in which A and X are large monovalent ions of comparable size (K^+ and F^-, or Cs^+ and Cl^-) the A and X ions together form a close-packed array with the small B ions in the interstices. The simplest close-packed layers in which the ratio of X to A atoms is 3 : 1 are shown in Fig. 5. In the complex halides $A_mB_nX_{3m}$ layers of type (b) are commonly found (e.g. in $KMgF_3$, $CsCuCl_3$, $Cs_3Tl_2Cl_9$, etc.). In the structures of a number of hydroxy-halides of the type $M_nX(OH)_3$ there is close packing of X and OH, but it is interesting that the layers are of type (a). In Fig. 6 are shown elevations (a), (b) and (c), and plans (d), (e) and (f), of the structures of $CuCl_2$, $Cu_2Br(OH)_3$ and $Cu_2Cl(OH)_3$. In the plans are shown two adjacent close-packed layers together with the metal atoms between them, i.e. the atoms shown as shaded circles in (a), (b) and (c). If the difference between the four strong and the two weak bonds formed by a Cu atom is disregarded, then the structure of $CuCl_2$ is a layer structure with close-packed layers of the same type as in $CdCl_2$. The individual layers are, however, superposed in such a way as to give each Cu atom four nearest (coplanar) neighbours, and this leads to the formation of chains as shown in Fig. 6 (d). (A similar small relative translation of the layers is found in $CsCuCl_3$ (Wells, 1947b), and is due to the same cause.) The hydroxy-bromide, $Cu_2Br(OH)_3$, has a simple layer structure (Fig. 6 (b)), in which the layers are a slightly distorted form of the 3 : 1 layer of Fig. 5 (a). If we consider the strong

Cu–OH bonds (four from each Cu atom), as shown by the full lines in Fig. 6 (*b*) and (*e*), then it is apparent that these link one-half the Cu atoms into chains which are cross-linked into layers through the remaining Cu atoms. It will be observed that the OH groups lying between these chains have a different environment from those in the chains. An OH group in a chain is attached to 3 Cu by short Cu–OH bonds, whereas an OH group of the other type is attached to 2 Cu by short bonds and to the third by a long Cu–OH bond. The Br atoms serve to link together the two types of Cu atom, but only by secondary Cu–Br bonds (broken lines).

The crystal structure of $Cu_2Cl(OH)_3$ consists of essentially close-packed layers of the same type as in the hydroxy-bromide which are parallel to the (011) and $(0\bar{1}1)$ planes. The structure is therefore not a layer structure, for only three-quarters of the Cu atoms lie in the (011) or $(0\bar{1}1)$ layers, the remainder cross-linking the layers into a three-dimensional complex of a honeycomb type (Fig. 6 (*c*)). If the atoms in a pair of adjacent close-packed layers (the shaded circles in Fig. 6 (*c*)) are projected on to the $(0\bar{1}1)$ plane, as in Fig. 6 (*f*), the similarity of the structure to that of $Cu_2Br(OH)_3$ becomes apparent. The strong Cu–OH bonds lead to chains in the direction of the *a* axis, and these chains are cross-linked by other Cu atoms. One-half of the Cu atoms lie in the chains shown in Fig. 6 (*f*), one-quarter between the chains in the same $(0\bar{1}1)$ plane, and the remainder between the layers. Herein lies the essential difference between the structures of $Cu_2Cl(OH)_3$ and $Cu_2Br(OH)_3$. A comparison of the plans of the layers in $CuCl_2$, $Cu_2Br(OH)_3$ and $Cu_2Cl(OH)_3$ shows the strong resemblance between the crystal structures of these three compounds.

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The Crystal Structure of Hexamethylenediamine Dihydrochloride

By W. P. Binnie and J. Monteath Robertson

The University, Glasgow W. 2, Scotland

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Hexamethylenediamine dihydrochloride is isomorphous with the dihydrobromide (monoclinic, space group $P2_1/c$). Better crystals are available, and a detailed structure analysis is given with Fourier projections along two axes mutually at right angles, from which the co-ordinates of all the atoms are obtained with an accuracy of about $\pm 0{\cdot}04$ A. In the chain molecule there is evidence of alternating long and slightly shorter bonds, but the variations are close to the experimental limits. The shorter N–Cl distances are of two types, averaging 3·11 and 3·24 A. The latter figure is close to the sum of the ionic radii, and the shorter type is probably accounted for by hydrogen bonding between the chlorine and nitrogen atoms. The compact grouping of the halogen ions in the lattice is illustrated in the diagram.

Introduction

The dihydrochloride of hexamethylenediamine is isomorphous with the dihydrobromide, described in an earlier paper (Binnie & Robertson, 1949). Well-formed crystals of the dihydrochloride are readily obtained, and it is possible to carry out a detailed structural investigation, utilizing several different zones of reflexions. Furthermore, the halogen contribution to the total scattering power of this molecule is only 33 %, and so with careful intensity estimates it should be possible to derive reasonably accurate bond-length measurements within the hexamethylenediamine chain. For the dihydrobromide molecule, with a halogen contribution of 51 %, no great accuracy was possible. The present paper gives the results of a detailed investigation of the structure of the dihydrochloride. Two projections of the structure are obtained, along axes mutually at right angles, and after refinement by the double Fourier series method these projections provide excellent resolution of all the atoms. Certain minor bond-length variations which may be significant are detected in the saturated aliphatic chain, but they are close to the limit of possible error.