lyse par diffractométrie de poudre met en évidence l'analogie d'organisation de ces deux composés [Figs. 13(a) et 14]. La déshydratation s'accompagne donc d'un réarrangement des molécules dans le cristal guidé par la redistribution des liaisons hydrogène:

– Les empilements moléculaires de direction [0 1 0], les feuillets qu'ils constituent par l'intermédiaire des liaisons H dirigées suivant [0 0 1] sont à peu près inchangés.

– Les feuillets 'glissent' les uns par rapport aux autres parallèlement au plan (1 0 0); faiblement au niveau des forces de dispersion, de $(b+c)/2$ au niveau des liaisons de solvatation. Ce dernier mouvement substitue aux axes binaires une ligne de centres $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ et remplace les centres $0,0,0$ par des axes hélicoïdaux: la maille cristalline passe donc de la symétrie $C2/c$ à la symétrie $P2_1/c$. Elle est obtenue en conservant les axes y et z et en adoptant pour nouvel axe X la rangée [1 0 1] du groupe $C2/c$.

Si nous retenions comme seule modification le glissement n, on calculerait des valeurs de paramètres de maille (a) très proches de celles de la maille de l'amino-2-naphtoquinone-1,4 (b):

$a=16,65$ Å	$a=17,03$ Å
$b=\ 4,67$	$b=\ 3,99$
$c=14,08$	$c=14,72$
$\beta=130°$	$\beta=125°$.
(a)	(b)

Les différences observées entre les valeurs des tableaux

(a) et (b), celles observées entre les températures de fusion (266 et 206° respectivement) indiquent que si les organisations cristallines sont analogues, elles diffèrent assez nettement par la qualité des relations intermoléculaires. La détermination précise de la structure de l'amino-4 naphtoquinone-1,2 anhydre, s'impose donc comme prochaine étape de cette analyse.

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Crystallographic Studies of Metal–Nucleotide Base Complexes. II. Bis-(6-hydroxypurine)copper(II) Chloride Trihydrate*

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A deep-turquoise complex, bis-(6-hydroxypurine)copper(II) chloride trihydrate, crystallizes from an acidic solution containing hypoxanthine and cupric chloride in molar proportions 2:1. The crystals are triclinic, space group $P\bar{1}$, with cell dimensions $a=9\cdot858$ (2), $b=10\cdot259$ (4), $c=9\cdot717$ (3) Å, $\alpha=102\cdot53$ (3)°, $\beta=89\cdot36$ (2)°, $\gamma=102\cdot21(3)°$. 2313 independent reflexions were measured on a diffractometer using Mo $K\alpha$ radiation. The final R from full-matrix least-squares refinement is $0\cdot11$. The complex is a centrosymmetric dimer, in which each copper atom has square-pyramidal coordination. Two of the ligand atoms in the basal plane are the N(9) nitrogen atoms in the imidazole rings and the other two the N(3) nitrogen atoms in the pyrimidine rings. The apical position is occupied by a chlorine atom, $Cu–Cl=2\cdot431$ Å. The copper–copper distance in the dimer is $3\cdot024$ Å. The molecular dimensions of the hypoxanthine ligands are not determined precisely because of disorder in the crystal.
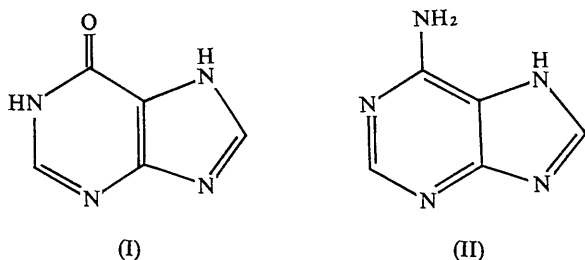
Introduction

The first paper in this series described the crystal structure of a neutral 2:1 adenine–copper(II) complex (later

referred to as AdCu) obtained from a slightly alkaline solution (Sletten, 1969). A similar neutral complex between hypoxanthine and copper could not be isolated due to gel formation (Weiss & Venner, 1965). In hypoxanthine (I) and adenine (II) the proton attached to one of the imidazole nitrogen atoms is dissociated in slightly alkaline solution, thus making it possible for the metal

to bind to either side of the imidazole ring. In the adenine complex the copper ion coordinates only to the

(I)   (II)

amino group since a chelate involving N(7) and the amino group is sterically less favourable. The coordination sites O(6) and N(7) in the hypoxanthine cation do not possess a similar sterical hindrance, and metal binding on either side of the molecule is thus more likely. The gel formation at high pH may be explained by the occurrence of an intermolecular chain structure where bridges between metal atoms are formed simultaneously at N(3), N(9) and O(6), N(7). At lower pH a 2:1 complex is obtained with both adenine and hypoxanthine ligands. To retain a dimer structure similar to the one found in the neutral 2:1 AdCu complex, N(7) rather than N(9) must be protonated. This would be in accordance with the findings in the hypoxanthine analog, 6-mercaptopurine where the imidazole nitrogen atom N(7) is protonated (Sletten, Sletten & Jensen, 1969).

Experimental

Deep-turquoise crystals of bis-(6-hydroxypurine)copper(II) chloride trihydrate were obtained from a hydrochloric acid solution ($pH \simeq 4$) of hypoxanthine and cupric chloride in molar proportions 2:1 (Weiss & Venner, 1965). At lower pH a yellow 1:1 complex is formed. The turquoise crystals disintegrate when exposed to air and had to be mounted in a capillary. Several crystals were tested on the Weissenberg camera; however, all of them had very high mosaic spread. The crystal chosen for data collection had dimensions of approximately $0.22 \times 0.34 \times 0.40$ mm. The crystals belong to the triclinic system with two formula units per unit cell. Density measurements in a mixture of chloroform and tetrabromoethane indicated a variable water content for different crystals, averaging 3 to 4 water molecules per formula unit. The chemical analysis of the compound dried over silica gel corresponds to one molecule of hydration (Weiss & Venner, 1965).

Crystal data

$[(C_5H_4N_4O)_2Cu]Cl_2.3H_2O$ F.W. 460·7
Triclinic: $P\bar{1}$
$a = 9.858$ (2), $b = 10.259$ (4), $c = 9.717$ (3) Å,
$\alpha = 102.53$ (3)°, $\beta = 89.36$ (2)°, $\gamma = 102.21$ (3)°
$D_m = 1.66$ g.cm^{-3}, $D_x = 1.63$ g.cm^{-3}, $V = 936$ Å^3, $Z = 2$,
λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 14.1$ cm^{-1}

Cell dimensions were obtained from a least-squares treatment of 2θ settings of 18 reflections as measured on a Picker four-circle diffractometer. The cell dimensions changed slightly during data collection, resulting in a decrease in volume from 942 to 936 Å^3. The intensities of the three standard reflections monitored during data collection decreased 15% on an average. The crystal moved slightly in the capillary, giving rise to a 5% fluctuation in intensities compared with the usual 1% fluctuation observed for crystals mounted on glass fibers. 2313 unique reflections were measured within a sphere limited at sin $\theta/\lambda = 0.54$ using the θ–2θ scan technique and niobium filtered Mo $K\alpha$ radiation. The scan ranges were calculated according to the relation $\varDelta 2\theta = A + B$ tan θ (Alexander & Smith, 1964). The constant A had to be set equal to $2.5°$ to cover the broad mosaic peak. B was taken as 1.0, a value which has been found to be satisfactory for Mo radiation. A background count was made at each end of the scan range for half the time of the total scan, and the net count deduced by subtracting the two backgrounds from the peak scan. 243 reflexions had net count less than the threshold value of $2\sigma_c$ where $\sigma_c = (N_{B1} + N_{pk} + N_{B2})^{1/2}$. These reflections were given the value $2\sigma_c$ and were included in the refinement only if F_c was greater than the F_o corresponding to the threshold value. The data were corrected for Lorentz and polarization effects. Also, an empirical cor-
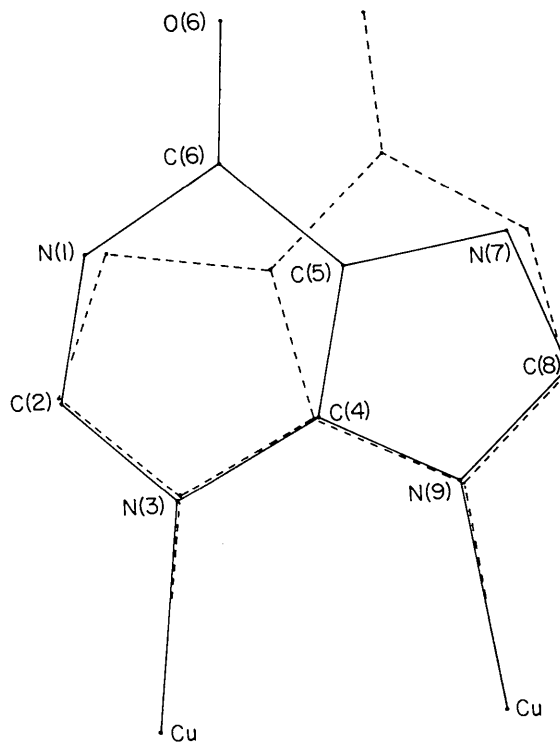

Fig. 1. The molecule drawn with a full line is a hypoxanthine ligand connected to the copper ions as viewed normal to the ligand plane. The molecule in dashed lines is arrived at by a 180° rotation around a line lying in the plane of the ligand and going through the centre of symmetry, normal to the Cu–Cu 'bond'.

Table 1. *Observed and calculated structure factors*

rection for absorption as a function of φ was applied. A more accurate absorption correction was difficult to obtain because of the uncertainty in calculating the absorption of glass capillary and mother liquor surrounding the crystal.

Structure determination

A sharpened Patterson map gave the positions of the copper atom and one of the chlorine atoms. A Fourier synthesis based on these two atoms revealed the hypoxanthine molecules. It was not possible to distinguish between water molecules and the second chlorine atom at this stage. The hypoxanthine ligands show the same kind of disorder as that found in AdCu where in some of the unit cells the ligands are rotated 180° so as to interchange the donor atoms N(3) and N(9) (Fig.1) All the atoms except C(5), C(6) and O(6) overlap almost completely in the two orientations.

A structure factor calculation based on Cu, Cl (1) and 30 light atoms (C, N and O) gave an agreement factor of 0·25 $(R=\sum(||F_o|-|F_c||)/\sum|F_o|)$. Atoms C(5), C(6) and O(6) were assigned fractional multiplicity factors. Two cycles of isotropic least-squares refinement lowered R to 0·15. At this stage the distances from three of the oxygen atom sites to the nitrogen atom were in the range 2·7 to 2·9 Å, which is the range of a normal N–H···O hydrogen bond. The distance from the fourth oxygen atom site to the closest nitrogen atom [N(12)] was 3·2 Å and this corresponds to a normal N–H···Cl hydrogen bond. Accordingly, this site was chosen as the position of the second chlorine atom in the succeeding refinement. The thermal parameters of this chlorine atom were found in the final refinement to be exceptionally high. The temperature factors for the three water molecules were also found to be unreasonably large. This apparent thermal motion is probably induced by the disorder in the crystal.

Two cycles of least-squares refinement with anisotropic thermal parameters on atoms with unit multiplicities lowered R to 0·12. Fractional atoms were refined by simultaneously adjusting occupancy and temperature factors. This procedure gave a satisfactory result for ligand (1), where the relative amount of the two rotamers are approximately 2:3. For ligand (2) one of the orientations is dominant (about 90%) and the fractional atoms with low multiplicities (0·1) could not be refined by least-squares. Since the electron densities of these sites were only slightly above the noise level, the coordinates were determined with low precision and were thus omitted from the coordinate table. Two more least-squares cycles did not improve the results significantly, and the refinement was terminated at an R of 0·11. The atomic positions in the hypoxanthine ligands could not be determined to a precision suitable for discussing the influence of the metal bonding on the purine skeleton. The lack of precision in coordinates is mainly due to the disorder in the crystal and the poor quality of the data. Observed and calculated structure factors

are listed in Table 1 and atomic parameters are found in Table 2.

All the above calculations were carried out on an IBM 7094 computer with programs from *X-ray 63* (Stewart, 1964). Structure factor calculations were based on the scattering curves in *International Tables for X-ray Crystallography* (1962).

Results and discussion

Environment of the copper ion

The coordination of the copper ion is established with reasonable precision in spite of the disorder and is shown in Fig. 2. A least-squares plane calculated through the four nitrogen atoms in the basal plane of the square pyramid shows that the diagonal atom pair N(31), N(91) is 0·005 Å below the plane and N(32), N(92) is 0·005 Å above the plane. The copper ion is displaced from this plane by 0·29 Å in a direction toward the apical chlorine atom. A similar displacement (0·27 Å) is found in AdCu where the apical ligand is a water molecule. The average of the Cu–N bond lengths is 2·00 Å, with the Cu–N(3) bonds systematically longer than Cu–N(9) bonds, which is consistent with a larger amount of s-character in the coordinating orbital of the imidazole nitrogen atom, N(9). The same trend is observed in AdCu where the average Cu–N(9) bond is 2·007 Å and the average Cu–N(3) bond is 2·032 Å. The fact that Cu–N bonds in the present structure are shorter than corresponding bonds in AdCu is somewhat surprising since a neutral 'inner' complex is expected to form stronger dative bonds than a charged complex.

The apical Cu–Cl(1) bond length of 2·431 Å is approximately half way between an ionic (2·62 Å) and a

$\angle$N(31)–Cu–N(32) = 87·6°

$\angle$N(32)–Cu–N(91) = 87·6°

$\angle$N(91)–Cu–N(92) = 90·2°

$\angle$N(92)–Cu–N(31) = 89·9°

$\angle$Cl(1)–Cu–N(31) = 98·0°

$\angle$Cl(1)–Cu–N(32) = 99·2°

$\angle$Cl(1)–Cu–N(91) = 98·3°

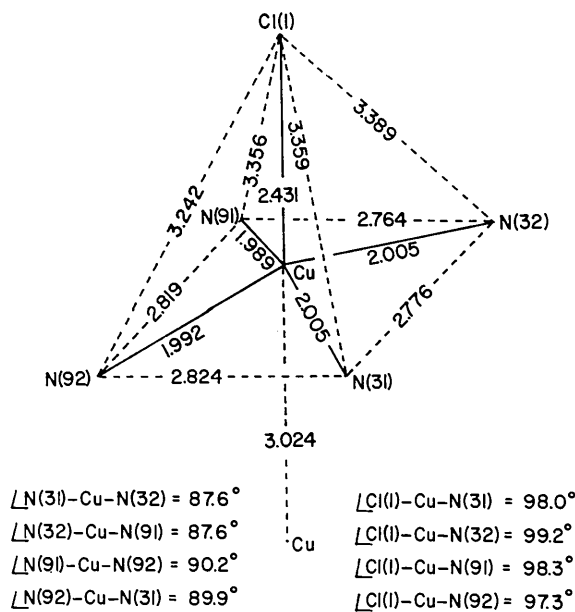$\angle$Cl(1)–Cu–N(92) = 97·3°

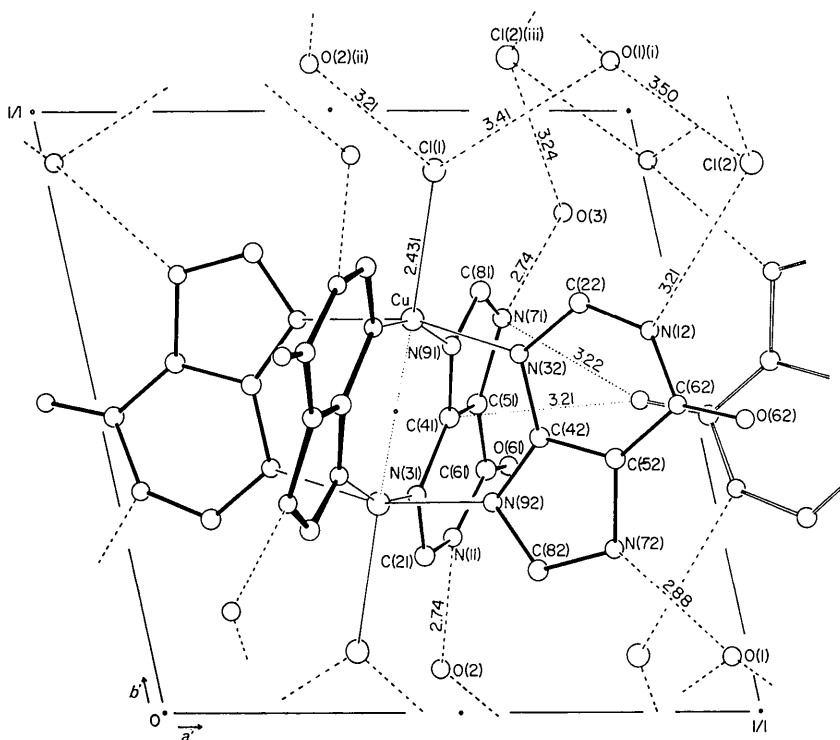Fig. 2. Environment of the copper ion.

Table 2. *Fractional atomic coordinates and thermal parameters and estimated standard deviations (in parentheses)*

Anisotropic temperature factor: $T_i = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0·5611 (2)	0·6520 (1)	0·0349 (2)	4·64 (7)	2·19 (6)	4·54 (8)	0·54 (5)	0·38 (6)	1·22 (5)
Cl(1)	0·6522 (4)	0·8975 (3)	0·0846 (4)	6·9 (2)	2·4 (1)	8·3 (3)	0·2 (1)	0·2 (2)	1·5 (1)
Cl(2)	1·1850 (9)	0·9042 (10)	0·2889 (10)	17·1 (7)	19·3 (7)	22·0 (9)	−6·3 (6)	2·1 (6)	−6·5 (7)
C(21)	0·4942 (13)	0·2621 (15)	−0·3428 (17)	5·8 (7)	5·0 (8)	4·4 (9)	2·3 (6)	−0·5 (7)	−0·1 (7)
C(41)	0·5887 (13)	0·4860 (15)	−0·2585 (13)	4·6 (6)	6·5 (8)	3·2 (6)	2·3 (6)	0·8 (5)	2·7 (6)
C(81)	0·6873 (14)	0·6970 (14)	−0·2368 (17)	6·1 (7)	5·9 (7)	5·4 (1·0)	1·1 (6)	1·5 (7)	3·7 (7)
C(22)	0·8489 (18)	0·6769 (19)	0·1392 (19)	5·2 (9)	5·3 (9)	5·5 (1·1)	1·0 (8)	−0·1 (8)	1·7 (8)
C(42)	0·7354 (16)	0·4577 (17)	0·0753 (18)	5·6 (8)	4·7 (9)	5·4 (9)	2·1 (7)	2·4 (7)	2·8 (8)
C(82)	0·6782 (21)	0·2360 (18)	0·0339 (22)	7·7 (1·0)	4·8 (1·0)	7·6 (1·1)	2·7 (8)	2·3 (8)	2·7 (9)
N(11)	0·5499 (11)	0·2861 (11)	−0·4618 (12)	6·8 (6)	4·6 (6)	4·1 (7)	1·7 (5)	0·4 (5)	1·0 (5)
N(31)	0·5087 (9)	0·3622 (10)	−0·2269 (10)	4·4 (4)	4·8 (5)	4·0 (6)	1·4 (4)	0·5 (4)	0·5 (4)
N(71)	0·7147 (11)	0·6512 (12)	−0·3695 (14)	5·7 (5)	4·1 (6)	5·6 (7)	0·7 (5)	−0·3 (5)	2·0 (6)
N(91)	0·6163 (9)	0·6079 (8)	−0·1645 (11)	5·0 (7)	2·6 (4)	5·4 (6)	0·8 (4)	−0·5 (4)	1·5 (4)
N(12)	0·9550 (17)	0·6299 (20)	0·1731 (17)	7·3 (9)	10·7 (9)	5·6 (1·0)	4·3 (7)	1·1 (8)	3·0 (8)
N(32)	0·7303 (10)	0·5919 (9)	0·0833 (11)	6·1 (6)	3·3 (5)	4·4 (6)	1·0 (5)	1·0 (5)	1·4 (4)
N(72)	0·8153 (14)	0·2698 (14)	0·0920 (14)	8·6 (8)	8·3 (8)	7·1 (8)	5·4 (7)	1·1 (7)	3·4 (7)
N(92)	0·6297 (9)	0·3473 (9)	0·0298 (11)	4·8 (4)	3·1 (5)	5·6 (7)	1·0 (4)	1·0 (4)	1·9 (5)
O(1)	0·9840 (19)	0·0851 (22)	0·1399 (27)	12·1 (1·2)	16·1 (1·5)	32·4 (2·9)	0·1 (1·1)	−0·8 (1·5)	5·4 (1·6)
O(2)	0·4814 (15)	0·0729 (12)	−0·6908 (14)	14·4 (1·0)	8·2 (7)	7·7 (8)	3·8 (7)	−0·7 (7)	−1·2 (6)
O(3)	0·8537 (17)	0·8297 (18)	−0·5225 (16)	16·2 (1·2)	15·8 (1·3)	11·0 (1·1)	−0·4 (1·0)	6·1 (9)	5·1 (1·0)

				B	M				
C(51)	0·6428 (29)	0·5113 (33)	−0·3795 (35)	5·3 (6)	0·60				
C(51')	0·6103 (39)	0·4326 (48)	−0·4026 (53)	5·2 (9)	0·41				
C(61)	0·6277 (23)	0·4041 (26)	−0·5023 (31)	5·1 (5)	0·58				
C(61')	0·6865 (37)	0·5276 (41)	−0·4748 (49)	5·9 (8)	0·42				
C(52)	0·8524 (21)	0·4198 (41)	0·1166 (27)	5·0 (6)	0·84				
C(62)	0·9761 (23)	0·5075 (19)	0·1741 (21)	5·1 (7)	0·70				
O(61)	0·6687 (19)	0·4083 (22)	−0·6221 (23)	6·4 (4)	0·53				
O(61')	0·7214 (27)	0·5058 (30)	−0·6045 (32)	6·3 (6)	0·37				
O(62)	1·0830 (14)	0·4841 (14)	0·2133 (15)	5·8 (4)	0·68				
O(62')	1·0338 (94)	0·3545 (93)	0·1788 (93)	6·0 (9)	0·09				

Fig. 3. The structure viewed along the c axis. (i), x, $y+1$, z; (ii), x, $y+1$, $z+1$; (iii), $2-x$, $2-y$, $-z$.

covalent bond (2·27 Å), and is thus comparable with the apical copper–water oxygen bond of 2·195 Å in AdCu. The internuclear Cu–Cu distance of 3·024 Å is 0·075 Å longer than the corresponding distance in AdCu. Chemically the 'bite' of hypoxanthine and adenine should be almost identical. The effect of replacing the water molecule as apical ligand with a chlorine atom may result in a stronger axial coordination and thus pull the metal ions further apart. There is probably no incipient covalent bonding between the copper ions that might counteract a larger separation.

Molecular packing

The environment of the complex is shown in Fig. 3. Each hypoxanthine ligand has two hydrogen-bond donors, N(1) and N(7), and one potential hydrogen-bond acceptor, O(6). Donor atoms N(11), N(71) and N(72) participate in hydrogen bonds to water oxygen atoms O(2), O(3) and O(1) respectively, while the fourth donor atom N(12) is hydrogen bonded to a chlorine atom Cl(2). The carbonyl oxygen atoms do not participate in hydrogen bonding. Instead both O(61) and O(62) have close contacts to imidazole rings in neighbouring dimers, with the C=O vector pointing nearly perpendicular to the plane of the imidazole ring. O(61) is situated 3·00 Å from the plane through the imidazole ring of ligand (2) translated one unit along the negative z axis, while O(62) is situated 3·00 Å from the corresponding plane of ligand (1) inverted through the centre of symmetry in (1, $\frac{1}{2}$, 0). The occurrence of identical intermolecular short contacts for the two crystallographically independent carbonyl groups may indicate the existence of a stabilizing interaction between the carbonyl dipole and the π-system of the purine moiety.

The chlorine atom coordinated to copper is hydrogen bonded to two water molecules. The O(9)–H···Cl(1) bond of 3·21 Å is 'normal' while the O(1)(i)–H···Cl(1) bond of 3·41 Å is on the limit of what might be considered a hydrogen bond. The non-coordinated chlorine atom Cl(2) participates in two 'normal' hydrogen bonds [N(12)–H···Cl(2) = 3·21 Å, and O(3)(iii)–H···Cl(2) = 3·24] and one 'long' hydrogen bond [O(1)(i)–H···Cl(2) = 3·50 Å]. The angle ∠Cl(1)–O(1)(i)–Cl(2) = 108·8° is close to an H–O–H bond angle, and is thus consistent with the presence of 'long' hydrogen bonds between water molecule O(1) and the two chlorine ions.

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An Alternative Form for $B_{3,0}$, a Phase Determining Formula

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An alternative form is derived for the phase determining formula $B_{3,0}$ defining cos $(\varphi_{h_1} + \varphi_{h_2} + \varphi_{-h_1-h_2})$ in which improved scaling is achieved by replacing the coefficient in the original formulation of this formula by a ratio of averages over functions of normalized structure factor magnitudes. Subsets of the measured data used with the modified $B_{3,0}$ formula generally give more accurate results for the cosine function than the complete set of data. A method for examining various subsets and choosing an optimum value is presented. The modified $B_{3,0}$ relation readily permits use of limited subsets of the experimental data. It has application as an auxiliary formula for use with the symbolic addition procedure. Used with care, the modified $B_{3,0}$ formula can help to determine which triples, $\varphi_{h_1} + \varphi_{h_2} + \varphi_{-h_1-h_2}$, are close to zero, a basic assumption in the symbolic addition procedure, and which ones may be exceptions. The formula can also help to evaluate symbolic phases.

A form of expression $B_{3,0}$ of sufficient generality for the present purposes is given for centrosymmetric crystals (equation 2.1.3 of Hauptman & Karle, 1958) and for noncentrosymmetric crystals (equation 2.1.3 of