Crystal Structure of the Dimeric 6-Mercaptopurine Copper(I) Chloride Complex

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The structure of $[C_5H_3N_4S.CuCl_2.H_2O]_2$ has been elucidated by Patterson and Fourier methods and refined by full-matrix least-squares calculations to a final R of 0·051 for 1704 reflexions. The triclinic cell, space group $P1$, with $a=10·067$ (5), $b=7·697$ (5), $c=6·771$ (5) Å, $\alpha=89·7$ (2), $\beta=105·6$ (2) and $\gamma=100·4$ (2)° contains two formula units which are associated by long Cu-S bonds (mean 2·74 Å) into S-bridged dimers. Within the units the Cu-S lengths average 2·25 Å. The Cu atoms have distorted tetrahedral geometry. N(9) of the 6-mercaptopurine ligand is protonated and pairs of hydrogen bonds of the type N–H$\cdots$N link the dimers in infinite chains. The latter are cross-linked by hydrogen bonds of type N–H$\cdots$O and O–H$\cdots$Cl involving bridging water molecules.

Introduction

We are studying the metal adduction to S-containing purines some of which are known to be anticarcinogenic (Sletten, Sletten & Jensen, 1969; Brown, 1969; Kirschner, Wei, Francis & Bergman, 1966).

Recently we have elucidated the structure of a polymeric 1:1 8-mercaptopurine copper(I) chloride complex (Caira & Nassimbeni, 1974) in which the S atom is bonded to Cu. The title compound is of interest because the powerful drug 6-mercaptopurine, whose structure is known (Sletten *et al.*, 1969; Brown, 1969) is of biological significance. In 6-mercapto-9-benzylpurine where both four- and five-membered chelate structures are possible, the larger ring with coordination *via* S and N(7) has been found in the Pd complex (Heitner, Lippard & Sunshine, 1972).

Experimental

The synthesis of a compound of composition [(6-mercaptopurine)CuCl₂] has been reported by Weiss & Venner (1966). Following their procedure, we did not obtain suitable material for X-ray analysis. Crystals of the title compound were isolated from the slow evaporation of a mixture of solutions of 6-mercaptopurine and copper(II) chloride dihydrate in 20% aqueous HCl in a 1:1 ligand-metal ratio. Deep red crystals formed after several weeks. Microanalysis indicated the presence of water molecules of crystallization. Measurement of the magnetic moment of the complex yielded a value of $\mu=0·21$ B.M. indicating that reduction of the metal to Cu(I) had occurred (Evans & Wilkinson, 1974). Preliminary X-ray data, obtained with Ni-filtered Cu $K\alpha$ radiation, showed that the crystals were triclinic. With a single crystal cut to a block of dimensions $0·3 \times 0·3 \times 0·2$ mm the cell parameters were obtained from a least-squares analysis of the settings of 25 reflexions measured on a four-circle diffractometer. Crystal data are listed in Table 1. The density was measured by flotation in a CH_2I_2–C_6H_5Cl mixture.

Table 1. *Crystal data*

$C_5H_5N_4S.CuCl_2.H_2O$	
M.W.	305·5
Space group	$P1$
$a=10·067$ (5) Å	$D_m=2·03$ g cm^{-3}
$b=7·697$ (5)	$D_c=2·04$ for $Z=2$
$c=6·771$ (5)	
$\alpha=89·7$ (2)°	
$\beta=105·6$ (2)	$\mu(Mo\ K\alpha)=28·2$ cm^{-1}
$\gamma=100·4$ (2)	$F(000)=304·0$
$V=496·45$ Å^3	

Intensities were measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0·7107$ Å). The ω–2θ scan mode was employed (scan width $1·8°\theta$, speed $0·06°\theta$ s^{-1}) to measure 1740 reflexions in the θ-range 3° to 25°. A background count was taken for half the total integration time on each side of the peak. Three reference reflexions were measured every hour. The intensities of two of these were constant to within 4% of their respective mean values. The third showed a maximum deviation of 9% from the mean value indicating slow crystal decomposition.

Of the reflexions recorded, 156 had $I<1·65\sigma(I)$. Lorentz–polarization corrections were applied to all the data. For the crystal selected, the maximum μR was 0·6 and A^* varied from 2·63 to 2·69 for the θ-range covered. This variation was considered negligible and no absorption corrections were applied (*International Tables for X-ray Crystallography*, 1968).

Solution and refinement of the structure

Several attempts to solve the structure in the space group $P\bar{1}$ failed. The six largest vector peaks in a Patterson map (X-RAY program system, 1972) had

heights corresponding to doubly weighted Cu–S and Cu–Cl interactions. This indicated that the heavy-atom positions were possibly related by a centre (or pseudocentre) of symmetry. Assuming a non-centrosymmetric structure, one Cu was fixed at the origin and the second assigned a position from the Patterson analysis. An electron density map phased on the two Cu atoms revealed the Cl and S atoms in tetrahedral coordination to the metal atoms. Structure factors based on the positions of the eight Cu, S and Cl atoms yielded an R of 0·33 and all the atoms of the mercaptopurine ligands were revealed in a subsequent electron density map. Five cycles of full-matrix least-squares refinement of all the atoms (including hydrate O atoms) with isotropic temperature factors reduced R to 0·141. After several cycles of refinement with anisotropic temperature factors assigned to the Cu, S and Cl atoms, R was 0·055. The ten H atoms of the ligands were located in a difference map. Theoretical positions (at 1·08 Å from their parent atoms) were calculated for the H atoms. The final cycles of refinement were carried out with constraints on the H atom positions as previously calculated and with the same isotropic temperature factors as the atoms to which they are bonded. In the last cycle of refinement the average Δ/σ was 0·3 and a final difference map showed evidence of anisotropic motion of the light atoms but no prominent peaks. With the option that reflexions would be included if they calculated greater than the observed, 1704 reflexions contributed in the final cycle and the terminal R was 0·051 with unit weights applied throughout.* The hydrate H atoms were not located and determination of the absolute configuration was not attempted. Scattering factors for the heavy atoms were those of Cromer & Mann (1968) and for H that of Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections were applied to the Cu, Cl and S curves (*International Tables for X-ray Crystallography*, 1968). Table 2 lists the final atomic coordinates and thermal parameters.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30851 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Description of the structure and discussion

Copper coordination

Interatomic distances and bond angles are listed in Tables 3 and 4 respectively. All calculations were performed with the X-RAY program system (1972). The structure consists of protonated 6-mercaptopurine ligands complexed with Cu(I) chloride *via* Cu–S bonds of normal length (mean 2·25 Å). Two such crystallographically independent units (labelled A and B) are associated by longer Cu–S distances (mean 2·74 Å) into S-bridged dimers. Bond distances and atomic nomenclature are shown in Fig. 1. Although the structure possesses no crystallographic symmetry, the midpoint of the line joining the Cu atoms is very nearly a centre of molecular symmetry, which accounts for the doubling of Cu–Cl and Cu–S vectors in the Patterson map. This pseudo-symmetry is also reflected in the fact that the two independent mercaptopurine moieties are almost coplanar. A least-squares plane calculation (Table 5) shows that the four-membered ring involving Cu and
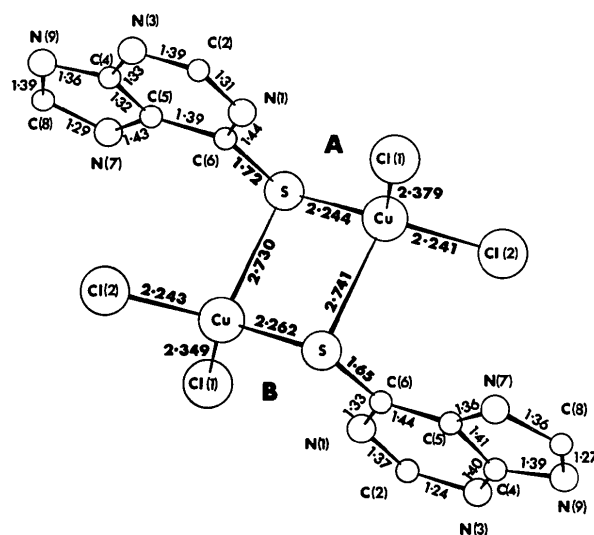

Fig. 1. Molecular configuration of the dimer with bond lengths (Å) and atomic nomenclature.

Table 2. *Fractional atomic coordinates and thermal parameters and their e.s.d.'s*

(a) Heavy atoms. Coordinates are $\times 10^4$. Anisotropic temperature factors are of the form

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^3\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu A	10000	0	0	23 (2)	50 (2)	25 (2)	17 (1)	−7 (1)	−17 (1)
Cl(1) A	10222 (6)	1495 (9)	3173 (9)	25 (3)	37 (3)	22 (3)	16 (2)	−4 (2)	−21 (2)
Cl(2) A	12179 (5)	−255 (8)	−17 (9)	16 (2)	28 (3)	19 (3)	5 (2)	5 (2)	−6 (2)
S A	8130 (5)	243 (7)	−2612 (9)	12 (2)	23 (3)	19 (3)	9 (2)	2 (2)	−9 (2)
Cu B	6940 (2)	−3067 (3)	−1818 (3)	21 (2)	45 (2)	32 (2)	15 (1)	−6 (1)	−18 (1)
Cl(1) B	6719 (6)	−4562 (9)	−4939 (10)	25 (3)	37 (3)	17 (3)	16 (2)	−16 (2)	−15 (2)
Cl(2) B	4754 (6)	−2852 (9)	−1775 (9)	20 (2)	35 (3)	20 (3)	5 (2)	−2 (2)	−3 (2)
S B	8808 (6)	−3310 (8)	842 (9)	18 (3)	28 (3)	16 (3)	6 (2)	−5 (2)	−9 (2)

Table 2 (cont.)

	x	y	z	$U_{iso}(\times 10^3)$
N(1)A	7337 (19)	1851 (22)	396 (27)	22 (2)
C(2)A	6549 (26)	2665 (31)	1186 (39)	26 (4)
N(3)A	5237 (23)	2929 (26)	63 (32)	19 (4)
C(4)A	4873 (24)	2178 (29)	−1819 (37)	19 (4)
C(5)A	5627 (21)	1392 (24)	−2740 (30)	12 (4)
C(6)A	6990 (20)	1229 (24)	−1716 (30)	11 (3)
N(7)A	4866 (23)	919 (28)	−4826 (35)	20 (3)
C(8)A	3662 (22)	1337 (27)	−4990 (33)	14 (3)
N(9)A	3643 (19)	2272 (22)	−3247 (27)	17 (3)
OA	11380 (15)	−1901 (19)	−4467 (23)	33 (3)
N(1)B	9553 (17)	−5028 (21)	−1974 (26)	11 (3)
C(2)B	10433 (22)	−5795 (27)	−2763 (32)	13 (3)
N(3)B	11659 (20)	−5970 (24)	−1911 (29)	15 (3)
C(4)B	12064 (22)	−5347 (26)	137 (32)	11 (3)
C(5)B	11230 (22)	−4497 (26)	1035 (31)	15 (4)
C(6)B	9849 (23)	−4276 (28)	−105 (34)	17 (4)
N(7)B	12082 (18)	−3923 (22)	2933 (28)	13 (3)
C(8)B	13309 (26)	−4524 (30)	3241 (31)	25 (4)
N(9)B	13366 (20)	−5221 (23)	1568 (29)	19 (3)
OB	5823 (14)	−951 (18)	2678 (22)	30 (3)

(b) Hydrogen atom theoretical positions ($\times 10^3$)

	x	y	z
H(1)A	832	163	140
H(2)A	694	315	277
H(7)A	522	34	−600
H(8)A	277	100	−632
H(9)A	282	294	−306
H(1)B	851	−503	−297
H(2)B	1001	−632	−433
H(7)B	1182	−312	402
H(8)B	1411	−443	468
H(9)B	1427	−564	131

S is accurately planar with C(6)A 1·63 Å above and C(6)B 1·57 Å below the plane. Fig. 2 shows the coordination geometry around the Cu and bridging S atoms. The Cu–Cl and short Cu–S distances are within the expected ranges. The relatively small angles within the ring are evidence of strain in the structure, resulting in considerable distortion from tetrahedral geometry

around Cu. Of interest also are the short CuA···CuB and SA···SB distances, 3·456 (3) and 3·629 (9) Å respectively. A similar Cu···Cu distance has been observed in the Cl⁻ bridged trinuclear adenine–copper complex (De Meester, Goodgame, Price & Skapski, 1970). The relatively short S···S distance does not necessarily imply any interaction as the effective van der Waals radius for S can vary from 1·65 to 1·85 Å (Sletten et al., 1969). The resultant flattening of the tetrahedron and its orientation are such that the Cu and its bonded Cl atoms lie close to the plane of the mercaptopurine ligand with the CuA–SB bond approximately normal to this plane. The distortions reflect the different environments of the Cl atoms, one being involved in an intramolecular hydrogen bond with a ring N atom while the other participates in hydrogen bonding with a hydrate O atom. These interactions are discussed below. In the structure of the polymeric 8-mercaptopurine copper(I) chloride analogue (Caira & Nassimbeni, 1974) the short C–S distance of 1·69 (1) Å indicated that the thione form, C=S,

Table 3. Interatomic distances (Å) and their e.s.d.'s

Cu A—Cl(1)A	2·379 (7)	Cu B—Cl(1)B	2·349 (7)
Cu A—Cl(2)A	2·241 (6)	Cu B—Cl(2)B	2·243 (7)
Cu A—S A	2·244 (5)	Cu B—S B	2·262 (6)
Cu A—S B	2·741 (6)	Cu B—S A	2·730 (6)
C(6)A–S A	1·72 (2)	C(6)B–S B	1·65 (3)
N(1)A–C(2)A	1·31 (4)	N(1)B–C(2)B	1·37 (3)
C(2)A–N(3)A	1·39 (3)	C(2)B–N(3)B	1·24 (3)
N(3)A–C(4)A	1·33 (3)	N(3)B–C(4)B	1·40 (3)
C(4)A–C(5)A	1·32 (4)	C(4)B–C(5)B	1·41 (3)
C(5)A–C(6)A	1·39 (3)	C(5)B–C(6)B	1·44 (3)
C(6)A–N(1)A	1·44 (3)	C(6)B–N(1)B	1·33 (3)
C(5)A–N(7)A	1·43 (3)	C(5)B–N(7)B	1·36 (2)
N(7)A–C(8)A	1·29 (3)	N(7)B–C(8)B	1·36 (3)
C(8)A–N(9)A	1·39 (3)	C(8)B–N(9)B	1·27 (4)
N(9)A–C(4)A	1·36 (3)	N(9)B–C(4)B	1·39 (3)

Table 4. Bond angles (°) and their e.s.d.'s

Cl(1)A–Cu A—Cl(2)A	106·1 (2)	Cl(1)B–Cu B—Cl(2)B	106·1 (2)
Cl(1)A–Cu A—S A	117·1 (2)	Cl(1)B–Cu B—S B	117·5 (3)
Cl(2)A–Cu A—S A	130·2 (2)	Cl(2)B–Cu B—S B	129·0 (3)
Cl(2)A–Cu A—S B	104·3 (2)	Cl(2)B–Cu B—S A	105·0 (2)
Cl(1)A–Cu A—S B	98·7 (2)	Cl(1)B–Cu B—S A	99·7 (2)
S A——Cu A—S B	92·9 (2)	S B——Cu B—S A	92·8 (2)
Cu A——S A——Cu B	87·5 (2)	Cu A—S B——Cu B	86·8 (2)
Cu A—S A——C(6)A	109·4 (7)	Cu B—S B——C(6)B	106·4 (8)
Cu B—S A——C(6)A	92·9 (7)	Cu A—S B——C(6)B	92·9 (8)
S A——C(6)A–N(1)A	121 (1)	S B——C(6)B–N(1)B	127 (2)
S A——C(6)A–C(5)A	128 (2)	S B——C(6)B–C(5)B	124 (2)
N(1)A–C(6)A–C(5)A	111 (2)	N(1)B–C(6)B–C(5)B	109 (2)
C(6)A–N(1)A–C(2)A	125 (2)	C(6)B–N(1)B–C(2)B	126 (2)
N(1)A–C(2)A–N(3)A	122 (2)	N(1)B–C(2)B–N(3)B	128 (2)
C(2)A–N(3)A–C(4)A	112 (2)	C(2)B–N(3)B–C(4)B	111 (2)
N(3)A–C(4)A–C(5)A	129 (2)	N(3)B–C(4)B–C(5)B	124 (2)
C(4)A–C(5)A–C(6)A	121 (2)	C(4)B–C(5)B–C(6)B	121 (2)
C(6)A–C(5)A–N(7)A	129 (2)	C(6)B–C(5)B–N(7)B	134 (2)
C(4)A–C(5)A–N(7)A	110 (2)	C(4)B–C(5)B–N(7)B	104 (2)
C(5)A–N(7)A–C(8)A	104 (2)	C(5)B–N(7)B–C(8)B	110 (2)
N(7)A–C(8)A–N(9)A	112 (2)	N(7)B–C(8)B–N(9)B	110 (2)
C(8)A–N(9)A–C(4)A	106 (2)	C(8)B–N(9)B–C(4)B	109 (2)
N(9)A–C(4)A–C(5)A	107 (2)	N(9)B–C(4)B–C(5)B	107 (2)
N(9)A–C(4)A–N(3)A	123 (2)	N(9)B–C(4)B–N(3)B	129 (2)

was retained in the complex. In the structure of chloro-bis-(2-thiouracil)copper(I) dimethylformamide solvate (Hunt & Amma, 1973) the analogous bond lengths are 1·70 (1) and 1·68 (1) Å. For the complex presented here, there are again two such C–S bonds with lengths 1·72 (2) and 1·65 (3) Å (Fig. 1). There is no significant lengthening of this bond on complexation with the Cu(I) ion relative to the parent compound (Brown, 1969). The angles C(6)–S–Cu of 109·4 (7)° and 106·4 (8)° for units A and B respectively compare favourably with the analogous angles, 109·8° and 108·6°, observed in the 2-thiouracil complex.

There are significant differences in chemically equivalent bond lengths and angles in the two complexed mercaptopurine ligands. Comparison with the parent 6-mercaptopurine monohydrate structure (Brown, 1969) again shows significant differences in these parameters but several factors e.g. presence of metal and halogen atoms, ligand protonation, hydrogen bonding, would have to be considered for detailed comparison of individual features. Corrections due to anisotropic motion of the light atoms were not applied in our analysis owing to inferior reflexion data quality and this may account for the scatter in these bond lengths and
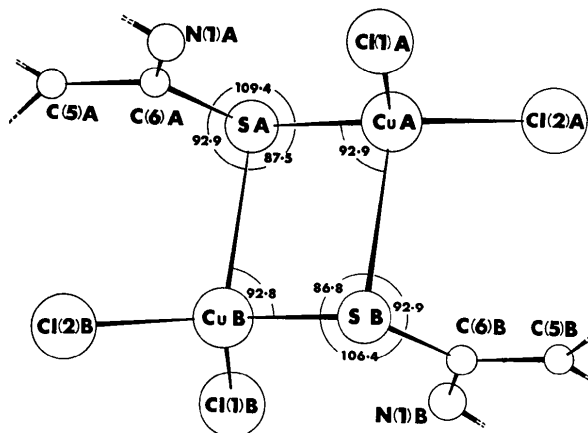
Table 5. Least-squares planes

The equations of the planes are expressed in orthogonalized space as $PI + QJ + RK = S$.

Plane I: through atoms Cu A, SA, Cu B and S B.
      Equation: $0.68316I - 0.40118J - 0.61020K = 6.87083$

Atoms included in calculation	Distance from plane (Å)	Atoms not included in calculation	Distance from plane (Å)
Cu A	0·007		
S A	−0·007	C(6)A	−1·63
Cu B	0·007		
S B	−0·007	C(6)B	1·57

Plane II: through atoms S A, N(1)A, C(2)A, N(3)A, C(4)A, C(5)A, C(6)A, N(7)A, C(8)A and N(9)A of the mercaptopurine ligand A.

      Equation: $0.32081I + 0.88387J - 0.34037K = 3.48986$

Atoms included in calculation	Distance from plane (Å)	Atoms not included in calculation	Distance from plane (Å)
S A	0·023	Cu A	−0·260
N(1)A	−0·054	Cl(1)A	−0·128
C(2)A	−0·013	Cl(2)A	0·286
N(3)A	0·047	O A	0·228
C(4)A	−0·020		
C(5)A	−0·018		
C(6)A	0·031		
N(7)A	0·019		
C(8)A	−0·057		
N(9)A	0·043		

Angle of intersection of planes I and II: 85·9°

Plane III: through atoms S B, N(1)B, C(2)B, N(3)B, C(4)B, C(5)B, C(6)B, N(7)B, C(8)B and N(9)B of the mercaptopurine ligand B.

      Equation: $0.31437I + 0.87814J - 0.36061K = 0.43470$

Atoms included in calculation	Distance from plane (Å)	Atoms not included in calculation	Distance from plane (Å)
S B	0·010	Cu B	0·351
N(1)B	−0·019	Cl(1)B	0·247
C(2)B	0·005	Cl(2)B	−0·217
N(3)B	0·033	O B	0·024
C(4)B	−0·043		
C(5)B	−0·031		
C(6)B	0·005		
N(7)B	0·046		
C(8)B	−0·036		
N(9)B	0·030		

Angles of intersection: planes I and III: 85·3°
              planes II and III: 1·3°

Fig. 2. Coordination geometry around the copper and sulphur-bridging atoms (angles in degrees).
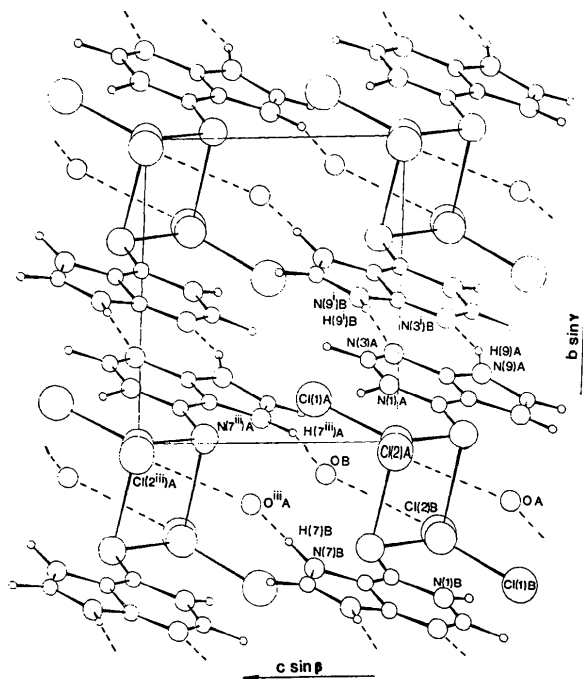

Fig. 3. The structure viewed down the a axis. Hydrogen bonds of the type N–H· · ·N, N–H· · ·O and HO–H· · ·Cl are represented by dashed lines.

angles. The aim of the analysis was the establishment of the binding sites in 6-mercaptopurine rather than the effect of such binding on the ligand geometry.

Hydrogen bonding

In Table 6, all data pertaining to hydrogen bonding and short contacts are presented. From difference maps, N(9) was clearly indicated as the protonation site in both ligands A and B. This permits hydrogen bonding of the type $N(9)A-H(9)A\cdots N(3^i)B$ and $N(9^i)B-H(9^i)B\cdots N(3)A$ between adjacent parallel mercaptopurine planes. Hydrogen bonding of the same type links molecules of trichloroadeniniumzinc(II) in pairs (Taylor, 1973). In contrast, in the Cu complex the dimers are linked by pairs of such bonds to form infinite chains (Fig. 3). The angle of intersection of adjacent hydrogen-bonded purine planes is about 1° (Table 5) and the independent $N\cdots N$ distances are 2·93 (3) and 2·94 (3) Å compared with 2·952 Å for the analogous distance in the Zn complex.

Table 6. *Hydrogen bonds and short contacts*
(*distances in* Å, *angles in degrees*)

E.s.d.'s are not quoted for distances and angles involving H atoms as the latter were assigned theoretical positions. Symmetry code for equivalent positions referred to the asymmetric unit x,y,z.

(i)	$x-1$	$y+1$	z		(iv)	x	$y+1$	$z+1$
(ii)	x	y	$z-1$		(v)	x	$y-1$	$z-1$
(iii)	x	y	$z+1$					

$N(3)A\cdots N(9^i)B$	2·94 (3)	$N(3)A\cdots H(9^i)B—N(9^i)B$	155
$N(3)A\cdots H(9^i)B$	1·92		
$N(9)A\cdots N(3^i)B$	2·93 (3)	$N(3^i)B\cdots H(9)A—N(9)A$	163
$H(9)A\cdots N(3^i)B$	1·88		
$O^{iii}A\cdots Cl(2^{iii})A$	3·12 (2)		
$O^{iii}A\cdots N(7)B$	2·67 (3)	$O^{iii}A\cdots H(7)B—N(7)B$	177
$O^{iii}A\cdots H(7)B$	1·59		
$O\ B\cdots Cl(2)B$	3·18 (1)		
$O\ B\cdots N(7^{iii})A$	2·70 (5)	$O\ B\cdots H(7^{iii})A-N(7^{iii})A$	164
$O\ B\cdots H(7^{iii})A$	1·64		
$N(1)A\cdots Cl(1)A$	3·06 (2)	$N(1)A-H(1)A\cdots Cl(1)A$	174
$H(1)A\cdots Cl(1)A$	2·00		
$N(1)B\cdots Cl(1)B$	3·09 (2)	$N(1)B-H(1)B\cdots Cl(1)B$	169
$H(1)B\cdots Cl(1)B$	2·03		
$Cl(1)A\cdots O^{iii}A$	3·29 (2)		
$Cl(1)A\cdots C(2^{iv})B$	3·40	$Cl(1)A\cdots H(2^{iv})B-C(2^{iv})B$	144
$Cl(1)A\cdots H(2^{iv})B$	2·47		
$Cl(1)B\cdots C(2^v)A$	3·34 (3)	$Cl(1)B\cdots H(2^v)A—C(2^v)A$	141
$Cl(1)B\cdots H(2^v)A$	2·43		

Each hydrate O atom participates in two analogous hydrogen bonds; one is the $N(7)-H(7)\cdots O$ interaction and the other is of the type $HO-H\cdots Cl(2)$. These link the infinite chains of base-paired dimers as shown in Fig. 3. H(1) of each ligand A and B is involved in an intramolecular hydrogen bond of the type $N(1)-H(1)\cdots Cl(1)$ with $N\cdots Cl$ distances of about 3·1 Å. These and other interactions including short $C-H\cdots Cl$ contacts involving C(2) of each ligand are listed. The only H atoms which do not appear to be engaged in any interactions are H(8) and H(8)B.

All calculations were carried out on a Univac 1106 computer system at the University of Cape Town.

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