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The Crystal Structure of the Thiamine Hydrochloride Copper(II) Complex

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(*Received* 7 *March* 1974; *accepted* 11 *March* 1974)

The structure of the 1:1 thiamine hydrochloride–$CuCl_2$ complex, $C_{12}H_{18}N_4OSCl_2.CuCl_2$, has been elucidated by Patterson and Fourier methods and refined by full-matrix least-squares computations to $R=0{\cdot}029$ for 1607 independent reflexions. The monoclinic unit cell, space group $P2_1/c$, with $a=9{\cdot}488$ (5), $b=16{\cdot}871$ (7), $c=12{\cdot}940$ (5) Å and $\beta=117{\cdot}2$ (2)°, contains four complex units. There is no direct bonding between the metal atom and the organic molecule. Instead each thiamine cation is associated with a tetrachlorocuprate anion. The four Cu–Cl bond lengths average 2·25 Å, but the Cl–Cu–Cl angles deviate significantly from ideal tetrahedral geometry. All the hydrogen atoms were located in difference syntheses. In addition to an N–H···O hydrogen bond, the presence of short intermolecular H···Cl distances is taken as evidence of N–H···Cl and C–H···Cl interactions.

Introduction

The crystal structures of several molecules containing the thiamine entity have been reported. Among these are thiamine hydrochloride (vitamin B_1: Kraut & Reed, 1962), thiamine monophosphate (Karle & Britts, 1966), thiamine pyrophosphate (Carlisle & Cook, 1969), thiamine pyrophosphate hydrochloride (Pletcher & Sax, 1971) and bis(protonated thiamine)-tetrachlorodioxouranium(VI) (Marzotto, Bandoli, Clemente, Benetollo & Galzigna, 1973).

As part of a programme investigating the interaction of metal ions and biological molecules, we have elucidated the crystal structure of the thiamine hydrochloride Cu(II) complex (Marzotto, Nicolini, Signor & Galzigna, 1970). Interactions of copper with thiamine are important because it has been shown (Kobayashi, 1972) that copper specifically promotes reactions involving the thiazole ring either by breaking the ring to form thiamine disulphide or by linking with the amino group to form thiochrome. This analysis was undertaken in order to establish whether or not there is direct bonding between the copper atom and thiamine in the solid state of the complex, and if so, which of the rings, thiazolium or pyrimidine, is involved. It has been suggested (Marzotto *et al.*, 1970) that in solution the thiamine molecule is bonded to the metal by a pyrimidine nitrogen atom.

Experimental

Single yellow-orange crystals of the compound were prepared according to the method of Marzotto *et al.* (1970). Microanalysis showed that the crystals had the composition $C_{12}H_{18}N_4OSCl_2.CuCl_2$ corresponding to a 1:1 adduct of thiamine hydrochloride and copper(II) chloride. Preliminary X-ray data were obtained by rotation and Weissenberg methods with Ni-filtered Cu $K\alpha$ radiation. The space group $P2_1/c$ was indicated by systematic absences $h0l$ $l=2n+1$ and $0k0$ $k=2n+1$. A single crystal selected for intensity measurements was ground into a rough sphere of average radius 0·2 mm. The lattice constants were obtained from a least-squares analysis of the settings of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). The crystal data are listed in Table 1. The density was determined by flotation in a mixture of chlorobenzene and methylene iodide.

Table 1. *Crystal data*

Molecular formula	$CuC_{12}H_{18}N_4OSCl_4$
M.W.	471·8
Space group	$P2_1/c$ (monoclinic, 2nd setting)
a = 9·488 (5) Å	
b = 16·871 (7)	$D_m = 1{\cdot}72$ g cm^{-3}
c = 12·940 (5)	$D_c = 1{\cdot}70$ g cm^{-3} for $Z=4$
β = 117·2 (2)°	μ(Mo $K\alpha$) = 19·2 cm^{-1}
V = 1841·85 Å^3	$F(000)=956$

The intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the ω–2θ scan mode (scan width 1·0°, scan speed 0·04° s^{-1}). With Zr-filtered Mo $K\alpha$ radiation, 1808 reflexions up to $2\theta=40°$ were measured. With the criterion $I_{rel} > 1{\cdot}65\sigma(I_{rel})$ for an observed reflexion, 201 reflexions including systematic absences were omitted as unobserved. The remaining 1607 reflexions were employed in the structural analysis. Throughout the data collection, three reference reflexions were recorded after every 68 measured reflexions; their intensities remained constant to within ±2%. The data were corrected for Lorentz-polarization effects. Since the crystal was closely spherical and the value of μR was only 0·38 absorption corrections were neglected (*International Tables for X-ray Crystallography*, 1967).

Solution and refinement of the structure

The position of the copper atom was determined from a Patterson map. From a Fourier synthesis phased on the copper atom, four large peaks surrounding the copper at 2–2·4 Å were located and on the basis of their peak heights were assumed to be chlorine atoms. Structure factors based on the positions of the five atoms yielded an R of 0·46. A subsequent Fourier synthesis revealed the positions of all 23 non-hydrogen atoms. Before refinement R was 0·28. The scattering factors used were those obtained from the HFS model (Hanson, Herman, Lea & Skillman, 1964). The copper was treated as Cu^0 and the anomalous dispersion correction ($\Delta f'=0{\cdot}3$ for Mo $K\alpha$ radiation) was applied to the scattering curve. Each reflexion was assigned unit weight. After five cycles of least-squares refinement (*ORFLS*: Busing, Martin & Levy, 1963) in which all atoms were treated isotropically, R was reduced to

Table 2. *Fractional atomic coordinates and thermal parameters and their e.s.d.'s for the thiamine hydrochloride copper*(II) *compound*

(*a*) Heavy atoms. Coordinates are $\times 10^4$. Thermal parameters are of the form

$$T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{23}kl+2\beta_{31}lh)\times 10^4\right].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
Cu	845 (1)	2200 (0)	756 (1)	33 (2)	18 (0,4)	42 (1)	5 (1)	19 (1)	7 (1)
Cl(1)	2406 (2)	1267 (1)	1981 (1)	45 (3)	28 (1)	56 (2)	15 (2)	21 (2)	20 (1)
Cl(2)	2393 (2)	2542 (1)	−102 (1)	64 (3)	17 (1)	55 (2)	−2 (1)	41 (2)	1 (1)
Cl(3)	−49 (2)	3409 (1)	922 (1)	68 (4)	18 (1)	58 (2)	7 (1)	41 (2)	0 (1)
Cl(4)	−1473 (2)	1567 (1)	64 (1)	39 (3)	21 (1)	50 (2)	−3 (1)	12 (2)	7 (1)
S(1)	−3458 (2)	3764 (1)	991 (1)	83 (4)	16 (1)	61 (2)	12 (2)	48 (3)	7 (1)
C(2)	−3039 (6)	2855 (3)	1551 (5)	54 (11)	18 (3)	47 (6)	−0 (5)	32 (7)	−2 (4)
C(4)	−4598 (5)	3314 (3)	2320 (4)	17 (10)	17 (3)	26 (6)	45 (4)	−2 (6)	−5 (4)
C(5)	−4603 (6)	3946 (3)	1691 (4)	31 (10)	17 (3)	29 (6)	4 (4)	4 (6)	−9 (4)
C(6)	−5424 (7)	3242 (4)	3062 (5)	68 (12)	31 (3)	46 (7)	10 (5)	32 (7)	−2 (4)
C(7)	−5455 (7)	4728 (3)	1497 (5)	66 (12)	17 (3)	41 (7)	6 (5)	12 (8)	−7 (4)
C(8)	−7187 (6)	4668 (4)	570 (5)	48 (13)	20 (3)	54 (8)	5 (5)	27 (8)	7 (4)
C(10)	−3448 (7)	1929 (3)	2861 (5)	48 (11)	15 (3)	27 (6)	−2 (5)	11 (7)	−1 (3)
C(12)	−1407 (6)	108 (3)	1732 (4)	59 (13)	12 (3)	26 (6)	1 (5)	16 (7)	6 (3)
C(14)	−3629 (6)	811 (3)	1471 (4)	51 (12)	13 (3)	22 (6)	−1 (5)	21 (7)	5 (3)
C(15)	−2731 (6)	1300 (3)	2458 (4)	37 (11)	9 (3)	21 (6)	−0 (4)	5 (7)	0 (3)
C(16)	−1138 (6)	1147 (3)	3024 (5)	56 (13)	13 (3)	22 (6)	−6 (5)	4 (7)	−3 (3)
C(17)	−611 (8)	−501 (4)	1367 (6)	67 (11)	21 (3)	63 (7)	12 (5)	29 (7)	−13 (4)
N(3)	−3701 (4)	2691 (2)	2230 (3)	36 (8)	15 (2)	19 (4)	1 (4)	12 (5)	−3 (3)
N(11)	−511 (5)	566 (3)	2657 (4)	33 (9)	16 (2)	29 (5)	1 (4)	1 (6)	−4 (3)
N(13)	−2949 (4)	203 (2)	1170 (3)	25 (9)	14 (2)	22 (4)	1 (4)	4 (5)	−3 (3)
N(18)	−5172 (5)	909 (3)	819 (4)	20 (10)	26 (3)	35 (5)	4 (4)	1 (6)	−2 (3)
O(9)	−7300 (4)	4431 (2)	−525 (3)	66 (8)	26 (2)	34 (4)	1 (3)	2 (4)	−7 (2)

Table 2 (*cont.*)

(*b*) Fractional atomic coordinates ($\times 10^3$) and their e.s.d.'s for the hydrogen atoms.

	x	*y*	*z*
H(23)	−775 (8)	433 (4)	81 (5)
H(24)	−769 (7)	521 (4)	49 (5)
H(25)	−543 (7)	489 (4)	226 (6)
H(26)	−494 (7)	519 (4)	132 (5)
H(27)	−588 (8)	369 (4)	316 (6)
H(28)	−620 (8)	287 (4)	294 (6)
H(29)	−479 (8)	305 (4)	394 (6)
H(30)	−253 (7)	247 (4)	123 (5)
H(31)	−443 (7)	174 (4)	283 (5)
H(32)	−273 (7)	204 (4)	368 (6)
H(33)	−51 (7)	147 (4)	370 (5)
H(34)	36 (7)	50 (4)	292 (5)
H(35)	−64 (8)	−95 (4)	154 (6)
H(36)	−106 (7)	−56 (4)	43 (6)
H(37)	46 (8)	−33 (4)	139 (6)
H(38)	−575 (7)	63 (4)	23 (6)
H(39)	−583 (7)	127 (4)	89 (5)
H(40)	−727 (8)	388 (4)	−46 (6)

0·08. This was followed by three cycles of refinement in which anisotropic temperature factors were introduced and *R* decreased to 0·05. In the last cycle of non-hydrogen atom refinement, the average e.s.d. in the positional and anisotropic temperature parameters was at least 50 times the average parameter shift. All the hydrogen atoms were located in difference syntheses and were assigned the temperature factors of the atoms to which they were bonded. After the last refinement cycle in which the hydrogen atomic positions were varied, the average e.s.d. in these parameters was about 20 times the average parameter shift. The last cycle of refinement yielded an *R* of 0·029. As a final check of the correctness of the structure, a difference synthesis with the structure factors calculated in the last cycle of refinement was computed. This map was practically featureless. Final atomic positional and thermal parameters are listed in Table 2. Observed and calculated structure factors are listed in Table 3.

Description of the structure and discussion

Bond lengths and their e.s.d.'s for heavy atoms are listed in Table 4 and those involving hydrogen atoms in Table 5. Table 6 lists the bond angles. All calculations were performed with the X-RAY (1972) program system. Fig. 1 is a schematic diagram of the asymmetric unit showing the bond lengths and angles. For clarity, hydrogen atoms of the methyl and methylene groups have not been included in the figure but bond lengths involving these atoms are listed in Table 5.

Table 3. *Observed and calculated structure factors*

The values listed are 10 F_o and 10 F_c.

h	k	F_o	F_c
[illegible]	[illegible]	[illegible]	[illegible]

Table 4. *Bond lengths and their e.s.d.'s for bonds not involving hydrogen atoms*

Cu–Cl(1)	2·245 (4) Å	C(7)—C(8)	1·533 (8) Å
Cu–Cl(2)	2·283 (3)	C(8)—O(9)	1·427 (8)
Cu–Cl(3)	2·257 (2)	N(3)—C(10)	1·482 (7)
Cu–Cl(4)	2·231 (3)	C(10)–C(15)	1·478 (9)
		N(11)–C(12)	1·349 (7)
S(1)–C(2)	1·664 (6)	C(12)–N(13)	1·313 (7)
S(1)–C(5)	1·731 (7)	N(13)–C(14)	1·360 (7)
C(2)–N(3)	1·323 (9)	C(14)–C(15)	1·430 (7)
N(3)–C(4)	1·391 (7)	C(15)–C(16)	1·369 (7)
C(4)–C(5)	1·339 (8)	N(11)–C(16)	1·342 (8)
C(4)–C(6)	1·50 (1)	C(12)–C(17)	1·48 (1)
C(5)–C(7)	1·508 (8)	C(14)–N(18)	1·323 (7)

Table 5. *Bond lengths involving hydrogen atoms*

Standard deviations are approximately 0·1 Å.

C(8)–H(23)	0·9 Å	C(10)–H(31)	1·0 Å
C(8)–H(24)	1·0	C(10)–H(32)	1·0
C(7)–H(25)	1·0	C(16)–H(33)	1·0
C(7)–H(26)	1·0	N(11)–H(34)	0·7
C(6)–H(27)	0·9	C(17)–H(35)	0·8
C(6)–H(28)	0·9	C(17)–H(36)	1·1
C(6)–H(29)	1·1	C(17)–H(37)	1·0
C(2)–H(30)	1·0	N(18)–H(38)	0·9
O(9)–H(40)	0·9	N(18)–H(39)	0·9

In Fig. 2, the molecular structure is viewed down **a** (*ORTEP*: Johnson, 1965). The asymmetric unit consists of a tetrachlorocuprate anion and a thiamine cation so that the compound is better formulated as (protonated thiamine)$^{2+}$($CuCl_4$)$^{2-}$. The copper atom is tetrahedrally surrounded by four chlorine atoms at an average distance of 2·25 Å but the deviation of the bond angles from ideal tetrahedral geometry is considerable. Four of these angles are roughly equal, their

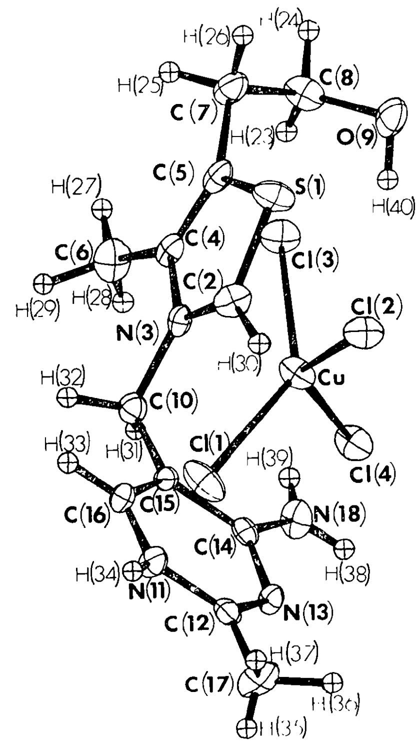

Fig. 2. The molecular structure viewed down **a** (*ORTEP*: Johnson, 1965).

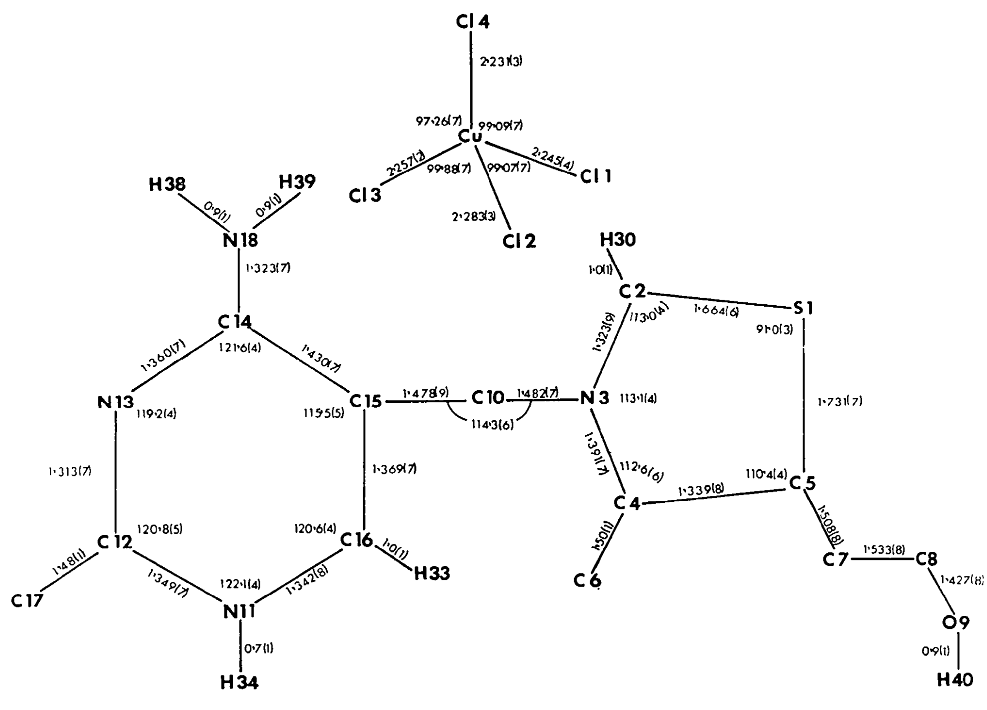

Fig. 1. Bond lengths and angles and their e.s.d.'s.

Table 6. *Bond angles and their e.s.d.'s (°) for angles not involving hydrogen atoms*

Cl(1)–Cu–Cl(2)	99·07 (7)	C(4)–C(5)–C(7)	130·5 (6)
Cl(1)–Cu–Cl(4)	99·09 (7)	C(5)–C(7)–C(8)	111·9 (5)
Cl(2)–Cu–Cl(3)	99·88 (7)	C(7)–C(8)–O(9)	111·3 (6)
Cl(3)–Cu–Cl(4)	97·26 (7)	N(3)–C(10)–C(15)	114·3 (6)
Cl(1)–Cu–Cl(3)	136·20 (7)		
Cl(2)–Cu–Cl(4)	131·40 (7)	C(12)–N(11)–C(16)	122·1 (4)
		N(11)–C(12)–N(13)	120·8 (5)
C(2)–S(1)–C(5)	91·0 (3)	N(11)–C(12)–C(17)	118·4 (5)
S(1)–C(2)–N(3)	113·0 (4)	N(13)–C(12)–C(17)	120·8 (4)
C(2)–N(3)–C(4)	113·1 (4)	C(12)–N(13)–C(14)	119·2 (4)
C(2)–N(3)–C(10)	122·8 (5)	N(13)–C(14)–C(15)	121·6 (4)
C(4)–N(3)–C(10)	124·1 (5)	N(13)–C(14)–N(18)	116·3 (4)
N(3)–C(4)–C(5)	112·6 (6)	C(15)–C(14)–N(18)	122·1 (5)
N(3)–C(4)–C(6)	120·8 (5)	C(14)–C(15)–C(16)	115·5 (5)
C(5)–C(4)–C(6)	126·6 (5)	C(10)–C(15)–C(16)	121·4 (4)
S(1)–C(5)–C(4)	110·4 (4)	C(10)–C(15)–C(14)	123·2 (4)
S(1)–C(5)–C(7)	119·1 (5)	N(11)–C(16)–C(15)	120·6 (4)

mean being about 99° (Fig. 1) and the remaining two, Cl(1)–Cu–Cl(3) and Cl(2)–Cu–Cl(4) are 136·2 (1) and 131·4 (1)° respectively. The tetrachlorocuprate tetrahedron is therefore 'squashed'. This distortion is similar to that observed in the structure of $[(C_2H_5)_3NH]_2CuCl_4$ (Lamotte-Brasseur, Dupont & Dideberg, 1973) in which four of the Cl–Cu–Cl angles in the $CuCl_4^{2-}$ unit average about 98° while the remaining two are 136·75 (0·10) and 132·91 (0·10)°. The average Cu–Cl distance is 2·24 Å as compared with 2·25 Å in the compound reported here.

Bond lengths and angles in the thiamine moiety compare favourably with those found in the structure of thiamine hydrochloride (Kraut & Reed, 1962). An important feature is the site of protonation in the pyrimidine ring. As in thiamine hydrochloride, the atom N(11) opposite the amino group is protonated in the copper compound. The region around N(13), the other possible protonation site, was scanned in difference maps but the electron density was found to be slightly negative. In both compounds the N(11)–H(34) distance is 0·7 (1) Å. A possible explanation for the preferred N(11) protonation site in the case of the parent hydrochloride has been offered by Kraut & Reed in terms of qualitative resonance theory. Bond lengths for C–H and N–H bonds in the cation are normal.

Table 7. *Least-squares planes*

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

Plane I: through the atoms of the pyrimidine ring

Equation: $0{\cdot}47455I+0{\cdot}63898J-0{\cdot}6054K=-2{\cdot}2231$

Atoms included in the calculation	Distance from plane	Atoms not included in calculation	Distance from plane
C(15)	−0·007 Å	C(10)	−0·047 Å
C(16)	−0·009	H(33)	−0·039
N(11)	0·006	H(34)	0·069
C(12)	0·013	C(17)	0·071
N(13)	−0·030		
C(14)	0·026	N(18)	0·074

Plane II: through the atoms of the thiazolium ring

Equation: $0{\cdot}50087I+0{\cdot}35636J+0{\cdot}78876K=1{\cdot}22196$

Atoms included in the calculation	Distance from plane	Atoms not included in calculation	Distance from plane
N(3)	−0·0002 Å	C(10)	0·048 Å
C(4)	0·0031	C(6)	0·021
C(5)	−0·0038	C(7)	−0·056
S(1)	0·0030		
C(2)	−0·002	H(30)	−0·186

Least-squares planes for the pyrimidine and thiazolium rings were calculated (Table 7). In the pyrimidine ring, the greatest deviation from the least-squares plane is that of atom N(13), 0·03 Å. The standard deviation of the six atoms defining the plane is 0·02 Å from the least-squares plane. The thiazolium ring is planar; the standard deviation of the five atoms from the plane is 0·003 Å and the maximum deviation, that of atom C(5), is 0·0038 Å. The acute angle between the pyrimidine and thiazolium ring planes is 89·3°. The dihedral angles for related structures, *i.e.* the angles between the normals to the planes of the two rings, are 76° for thiamine–HCl (Kraut & Reed, 1962), 83° for thiamine pyrophosphate–HCl (Pletcher & Sax, 1971) and 90° for thiamine monophosphate (Karle & Britts, 1966). The flexibility in the orientations of these ring planes in different structures has been pointed out (Carlisle & Cook, 1969). In addition, the structural relationship between the pyrimidine amino group and the thiazolium dimethylene side chain is *cis* (Pletcher &

Table 8. *Interatomic distances (Å) and angles (°) for hydrogen bonds,* N–H···Cl, O–H···Cl and C–H···Cl *interactions*

Symmetry operations: The atoms without superscripts refer to the asymmetric unit whose coordinates (x,y,z) are given in Table 2.

i	$x+1,\ \frac{1}{2}-y,\ \frac{1}{2}+z$
ii	$x-1,\ y,\ z$
iii	$x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

H(34)···O(9^i)	2·2 (1)	N(11)···O(9^i)	2·87 (1)	N–H···O	148 (7)
H(39)···Cl(1^ii)	2·6 (1)	N(18)···Cl(1^ii)	3·33 (1)	N–H···Cl	133 (7)
H(39)···Cl(2^ii)	2·7 (1)	N(18)···Cl(2^ii)	3·44 (1)	N–H···Cl	144 (6)
H(40)···Cl(2^ii)	2·35 (7)	O(9)···Cl(2^ii)	3·27 (1)	O–H···Cl	166 (7)
H(23)···Cl(3^ii)	2·7 (1)	C(8)···Cl(3^ii)	3·64 (1)	C–H···Cl	164 (7)
H(30)···Cl(4)	2·64 (8)	C(2)···Cl(4)	3·64 (1)	C–H···Cl	171 (4)
H(31)···Cl(1^ii)	2·8 (1)	C(10)···Cl(1^ii)	3·73 (1)	C–H···Cl	162 (5)
H(33)···Cl(3^iii)	2·7 (1)	C(16)···Cl(3^iii)	3·49 (1)	C–H···Cl	137 (5)

Sax, 1972) in the copper adduct (Fig. 2) as in thiamine monophosphate and thiamine hydrochloride. In the latter, the rings are oriented so that the amino group of the pyrimidine ring can readily interact with C(2) of the thiazolium ring. The non-bonded distance C(2)··· N(18) is 3·50 Å while in the copper compound reported here it is 3·74 Å. In bis(protonated thiamine)tetrachlorodioxouranium(VI) (Marzotto *et al.*, 1973) one $(UO_2Cl_4)^{2-}$ ion is associated with two thiamine cations. Moreover, the dihedral angle between the ring planes is 74·4° and interaction between the amino group and the thiazolium ring atom C(2) is indicated by the non-bonded N(18)···C(2) separation of 3·48 Å.

Hydrogen bonding is evident in the structure. For a hydrogen bond to exist between the two atoms H and B, we adopt the criterion (Hamilton, 1968) $d(\text{H–B}) < W_{\rm H} + W_{\rm B} - 0{\cdot}2$ Å, where $W_{\rm H}$ and $W_{\rm B}$ are the van der Waals radii for the H atom and the acceptor atom B respectively. In all, we have found two N–H···Cl interactions, one N–H···O intermolecular hydrogen bond, one O–H···Cl and four C–H···Cl interactions. Relevant interatomic distances and angles are listed in Table 8. Atom H(39) of the pyrimidine amino group is involved in interactions with two chlorine atoms giving rise to a system similar to the bifurcated hydrogen bond involving the same atom types observed in glycine hemihydrochloride (Hahn & Buerger, 1957). For all the entries in Table 8 the interatomic distance H···B has a value equal to or below that for which a hydrogen bond may be said to exist (Hamilton, 1968) but it must be noted that the average error in the H···B distances is large (0·1 Å). All the interactions mentioned are represented by dashed lines in Fig. 3 (*ORTEP*: Johnson, 1965) in which the atoms with superscripts are symmetry-related to the atoms of the asymmetric unit. The two $CuCl_4^{2-}$ units drawn are equivalent by translation along x while atom Cl(3^{iii}) is a chlorine of the third $CuCl_4^{2-}$ unit surrounding the thiamine cation. The intermolecular N–H···O hydrogen bond with N(11)···O(9^{i}) = 2·87 (1) Å was also found in bis(protonated thiamine) $(UO_2Cl_4)^{2-}$. Although the proton was not located in the latter analysis, the non-bonded N(11)···O(9) distance was found to be 2·77 Å. The similarity between the copper compound investigated here and thiamine hydrochloride lies in the apparent formation of C–H···Cl hydrogen bonds. In the parent hydrochloride, these bonds involve H(33) and H(30) with H···Cl^- = 2·5 and 2·6 Å respectively. We have found four H···Cl distances less than the normal van der Waals sum of 3·0 Å involving atoms H(33), H(30), H(31) and H(23). These interactions, especially those involving methylene hydrogens, are probably very weak since each hydrogen is interacting not with a full charge of a free chloride ion as in thiamine hydrochloride, but with a Cl of a $CuCl_4^{2-}$ unit. For the same reason, the N–H···Cl interactions are probably much weaker than those reported for the parent hydrochloride. In the structure of $[(C_2H_5)_3NH]_2CuCl_4$,

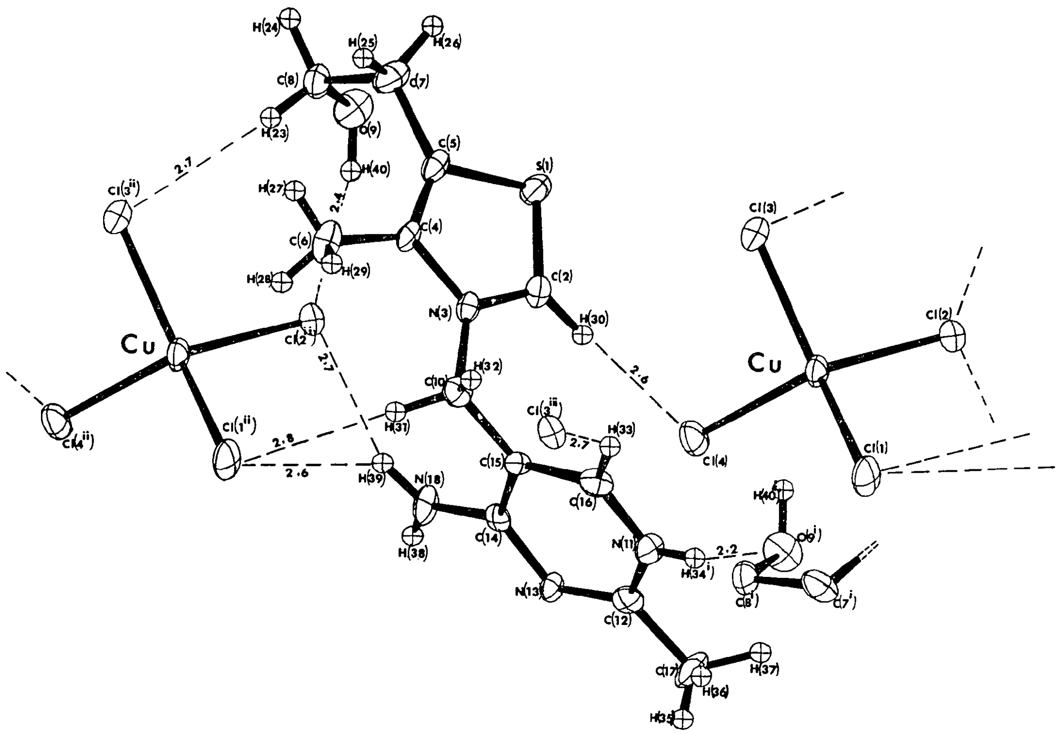

Fig. 3. The structure viewed down **c***. Hydrogen bonds and H···Cl interactions are represented by dashed lines (*ORTEP*: Johnson, 1965).

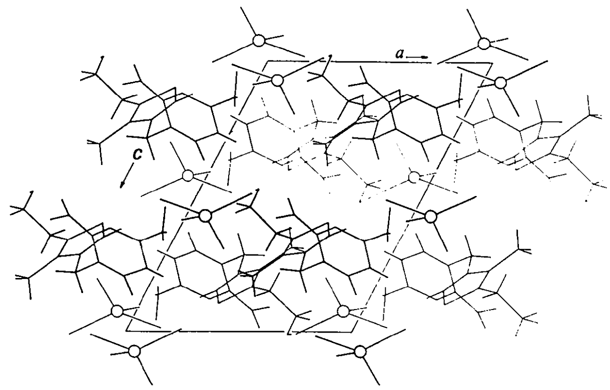

Fig. 4. The (010) projection of the structure.

however, a similar N–H···Cl hydrogen bond involving a Cl atom of the $CuCl_4^{2-}$ anion and the organic cation is reported with N···Cl = 3·11 Å (Lamotte-Brasseur *et al.*, 1973).

Figs. 4 and 5 are projections of the structure down [010] and [001] respectively.

This work was supported by the CSIR and the University of Cape Town's research grants.

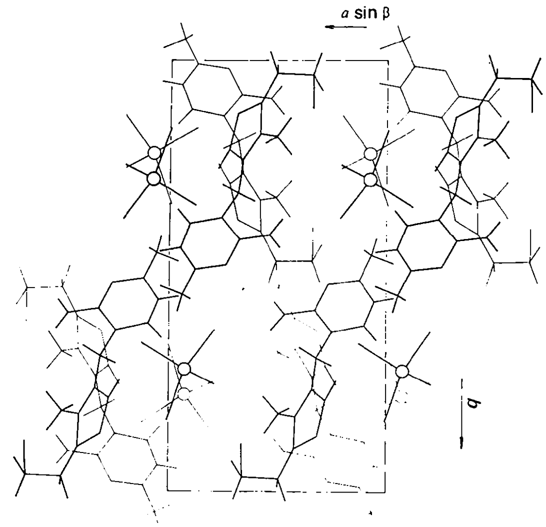

Fig. 5. The (001) projection of the structure.

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