Crystal and Molecular Structure of *catena*-[Dichloro(8-mercaptopurine)-copper(I)]

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The title compound, $C_5H_5N_4S{\cdot}CuCl_2$, crystallises as monoclinic needles, with a = 9.464(5), b = 6.119(3), c = 19.69(1) Å, β = 124.78(5)°, Z = 4, space group $P2_1/c$. The structure was determined by the heavy-atom method from diffractometer data and refined by full-matrix least-squares methods to a final R of 0.050 for 1 253 reflections. The structure is polymeric, consisting of infinite columns of 8-mercaptopurine units which are bonded to copper chloride *via* their sulphur atoms. The chains of –S–Cu–S–Cu– bonds form a helix around the two-fold crystallographic axis.

WE are studying the metal addition complexes of various sulphur-containing purines some of which are known to be anticarcinogenic.[1-3] We have prepared copper chloride complexes of both the 6- and 8-mercaptopurines in order to elucidate their binding sites to the metal. Pyridine-2-thiol complexes have been prepared [4-8] and even with the short bite of the ligand a chelate structure is formed. In 6-mercapto-9-benzylpurine where both four- and five-membered chelate structures are possible, it is the larger ring with co-ordination *via* S and N(7) which has been found in the palladium complex.[9] Copper(II) halide complexes have been shown to be easily reduced to the corresponding copper(I) complexes.[8]

EXPERIMENTAL

Preparation.—The crystals were prepared by mixing heated solutions of $CuCl_2{\cdot}2H_2O$ and 8-mercaptopurine in HCl(1M), with 1 : 1 metal–ligand. On cooling the resulting brown solution, long (*ca.* 3 mm) orange needles were obtained. The formulation (8-mercaptopurine)$\cdot CuCl_2$ was consistent with microanalytical data. Magnetic measurements yielded a value of 0.24 B.M. indicating that the compound is diamagnetic, *i.e.* the metal is copper(I), and the mercaptopurine ligand must therefore be protonated.

Crystal Data.—$C_5H_5N_4S{\cdot}CuCl_2$, M = 287.5, Monoclinic, a = 9.464(5), b = 6.119(3), c = 19.690(10) Å, β = 124.78(5)°, U = 936.57 Å^3, D_m (by flotation) = 2.04, Z = 4, D_c = 2.03. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 31.5 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5).

Preliminary cell dimensions and space-group symmetry were determined from rotation and Weissenberg photographs. Accurate cell parameters were obtained from a least-squares analysis of the settings of 25 reflections measured on a Philips PW 1 100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Three-dimensional intensity data were collected by the ω—2θ scan technique (scan width 1°θ, scan speed 0.03°θ s^{-1}) in the range 6° ⩽ 2θ ⩽ 50°. A crystal of dimensions 0.2 × 0.2 × 0.1 mm was used. The intensities of three reference reflections monitored after every 52 measured reflections remained constant to within ±3%. A total of 1 776 reflections were collected, 164 of these being systematically absent while of the remaining 1 612 reflections, 1 253 had $I > 2.0\sigma(I)$ and were considered observed. Lorentz-polarisation corrections were applied. No absorption corrections were made (μR *ca.* 0.32) but anomalous dispersion corrections were applied to the heavy-atom scattering curves.

Structure Determination and Refinement.—Analysis of a three-dimensional Patterson map [10] yielded the positions of the copper atom and the remaining three heavy atoms, the latter being tetrahedrally arranged at a mean distance of 2.4 Å from the Cu atom. All light atom positions were revealed in a subsequent electron-density map. The assignment of the pyrimidine ring nitrogens was facilitated by the relative map peak-heights. After four cycles of full-matrix least-squares refinement [10] with anisotropic temperature factors, R was 0.056 and a difference electron-density map was then prepared and enabled location of five hydrogen atoms bonded to atoms N(1), C(2), C(6), N(7), and N(9). During the final four cycles of refinement,[11] the H atoms were constrained to ride on their parent atoms with both C–H and N–H distances 1.08 Å. Their isotropic temperature factors were refined as one common parameter. The refinement converged to R 0.050 and R' [$= \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$] 0.051, with a weighting scheme $w = 1/(\sigma^2F + gF^2)$. The final value of g (0.000 813) was chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F. An analysis of variance computed after the final cycle is shown in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21486 (9 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The final mean estimated standard deviation in the parameters of the non-hydrogen atoms was > 100 times the average parameter shift. A final difference electron-density map was practically featureless. The copper, chlorine, and sulphur scattering factors [12] were corrected for anomalous dispersion.[13] The final atomic positional

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

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TABLE 1

Analysis of variance *

(*a*) As a function of sin θ

sin θ	0.00—0.19	0.19—0.24	0.24—0.27	0.27—0.30	0.30—0.32	0.32—0.35	0.35—0.37	0.37—0.39	0.39—0.41	0.41—0.43
N	139	142	117	128	105	173	126	123	112	88
V	223	181	185	169	185	171	173	179	241	224

(*b*) As a function of $\sqrt{(F/F_{\text{max.}})}$

$\sqrt{(F/F_{\text{max.}})}$	0.00—0.24	0.24—0.27	0.27—0.29	0.29—0.31	0.31—0.34	0.34—0.38	0.38—0.41	0.41—0.46	0.46—0.53	0.53—1.00
N	160	143	108	100	124	152	94	129	128	115
V	244	215	204	170	173	172	162	171	171	207

(*c*) By parity groups

	ggg	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	188	180	162	158	124	129	151	161	1 253
V	179	194	192	199	202	197	184	198	193

* N = No. of reflections in the group, $V = 100\,(M\Sigma(w|F_o - F_c|^2)/N\Sigma w)$, M = total no. of reflections.

TABLE 2

Fractional atomic co-ordinates and thermal parameters *, with estimated standard deviations in parentheses, for heavy atoms. Co-ordinates $\times 10^4$

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	1 039(1)	521(1)	8 347(1)	38(1)	31(1)	34(1)	−0(0)	29(0)	−0(0)
Cl(1)	619(2)	−710(2)	9 310(1)	29(1)	23(1)	26(1)	9(1)	20(1)	5(1)
Cl(2)	3 521(2)	2 902(3)	8 946(1)	27(1)	31(1)	26(1)	−11(1)	20(1)	−9(1)
S	1 250(2)	−2 095(2)	7 579(1)	28(1)	19(1)	24(1)	−3(1)	20(1)	−7(1)
N(1)	3 527(6)	1 909(9)	5 511(3)	23(3)	31(3)	22(3)	3(2)	16(2)	1(2)
C(2)	4 092(8)	3 455(11)	6 075(4)	28(3)	27(4)	26(4)	2(3)	17(3)	−1(3)
N(3)	3 895(6)	3 457(9)	6 688(3)	23(3)	23(3)	25(3)	−3(2)	16(2)	−7(2)
C(4)	3 069(7)	1 677(10)	6 692(4)	13(3)	19(3)	16(3)	4(2)	9(2)	2(2)
C(5)	2 453(7)	−26(9)	6 115(4)	19(3)	15(3)	17(3)	0(2)	14(3)	1(2)
C(6)	2 692(7)	101(10)	5 499(4)	17(3)	22(3)	27(3)	−3(3)	12(3)	−0(3)
N(7)	1 705(7)	−1 526(9)	6 348(3)	30(3)	19(3)	25(3)	−6(2)	22(2)	−7(2)
C(8)	1 849(7)	−762(9)	7 034(3)	14(3)	13(3)	13(3)	−2(2)	7(2)	2(2)
N(9)	2 677(6)	1 210(8)	7 241(3)	14(2)	15(2)	17(3)	−6(2)	8(2)	−5(2)

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

and thermal parameters are presented in Tables 2 and 3. Isotropic temperature factors of the H atoms refined to a value U 0.037 Å^2.

Interatomic distances and angles are listed in Table 4. Atom numbering is shown in Figure 1. The bonding around the sulphur atom appears to be tetrahedral; the departure from this co-ordination of the Cu–S–Cu^{II} angle is probably due to repulsion between the metal atoms (Cu · · · Cu^{II} 4.1 Å). The copper atom exhibits tetrahedral co-ordination but there are significant differences in both the Cu–S bond lengths [2.289(2) and 2.375(2) Å] and the Cu–Cl bond lengths [2.276(2) and 2.423(2) Å]. In the analogous 6-mercaptopurine copper(I) chloride complex, which is dimeric, Cu–S distances of 2.252(2) and 2.733(2) Å were found.[14] Differences of up to 0.12 Å were also observed for chemically-equivalent Cu–Cl distances.

TABLE 3

Fractional atomic co-ordinates of the hydrogen atoms ($\times 10^3$)

	x	*y*	*z*
H(1)	374	210	503
H(2)	477	482	603
H(6)	225	−115	503
H(7)	111	−305	604
H(9)	297	223	775

Relevant least-squares planes are listed in Table 5. The mercaptopurine ligand is essentially planar. The twist in the ligand to avoid close contacts between the imidazole hydrogens and the metal atoms is reflected by the torsion angles Cu–S–C(8)–N(9) (23.1°) and Cu^{II}-S–C(8)–N(7) (−28.3°). From the C–S distance[1,2] [1.676(2) and 1.678 6(09) Å] in 6-mercaptopurine monohydrate (two independent determinations) it was deduced that the tautomeric form in the crystal is that of the thione. The distance C(8)–S of 1.683(6) Å in this complex therefore suggests a double carbon–sulphur bond.

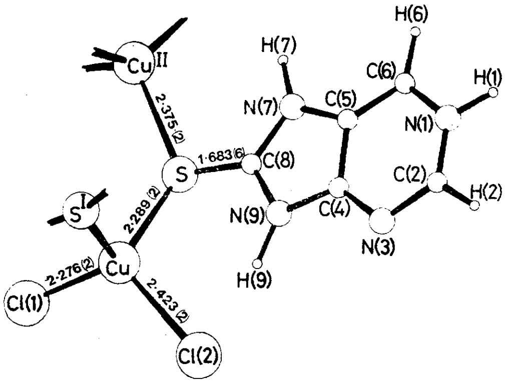

FIGURE 1 Molecular conformation, with crystallographic atom numbering system and principal bond lengths

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[14] M. R. Caira and L. R. Nassimbeni, *Acta Cryst.*, 1975, in the press.

TABLE 4

Bond lengths (Å) angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Cu–Cl(1)	2.276(2)	C(5)–C(4)	1.401(8)
Cu–Cl(2)	2.423(2)	C(4)–N(9)	1.357(7)
Cu–S	2.289(2)	N(1)–C(2)	1.318(9)
Cu^{II}–S	2.375(2)	C(2)–N(3)	1.321(8)
S–C(8)	1.683(6)	N(3)–C(4)	1.343(8)
N(9)–C(8)	1.368(7)	C(5)–C(6)	1.356(9)
N(7)–C(8)	1.359(8)	N(1)–C(6)	1.352(8)
N(7)–C(5)	1.387(7)		

(*b*) Angles

Cl(1)–Cu–Cl(2)	112.0(1)	N(3)–C(4)–C(5)	124.9(5)
Cl(1)–Cu–S	116.2(1)	C(4)–C(5)–C(6)	118.5(5)
Cl(2)–Cu–S	108.4(1)	C(5)–C(6)–N(1)	115.2(6)
S^{I}–Cu–Cl(1)	109.1(1)	N(3)–C(4)–N(9)	126.9(5)
S^{I}–Cu–Cl(2)	102.2(1)	C(6)–C(5)–N(7)	135.3(6)
S^{I}–Cu–S	107.9(1)	C(5)–C(4)–N(9)	108.2(5)
Cu–S–C(8)	105.7(2)	C(4)–N(9)–C(8)	108.6(5)
Cu^{II}–S–C(8)	107.4(2)	N(9)–C(8)–N(7)	108.4(5)
Cu^{II}–S–Cu	123.5(1)	N(9)–C(8)–S	125.6(4)
C(2)–N(1)–C(6)	123.7(5)	N(7)–C(8)–S	125.9(4)
N(1)–C(2)–N(3)	124.7(6)	C(8)–N(7)–C(5)	108.7(5)
C(2)–N(3)–C(4)	113.0(5)	N(7)–C(5)–C(4)	106.2(5)

(*c*) Hydrogen-bond data

Cl(2) · · · $N(1^{IV})$	3.08(1)	Cl(2) · · · $H(1^{IV})$–$N(1^{IV})$	165(8)
Cl(2) · · · $H(1^{IV})$	2.0(1)		
Cl(1) · · · $N(7^{I})$	3.13(1)	Cl(1) · · · $H(7^{I})$–$N(7^{I})$	154(10)
Cl(1) · · · $H(7^{I})$	2.1(1)		
Cl(2) · · · N(9)	3.15(1)	Cl(2) · · · H(9)–N(9)	156(8)
Cl(2) · · · H(9)	2.1(1)		

(*d*) Short contacts

Cl(1) · · · $C(6^{III})$	3.36(1)
Cl(1) · · · $H(6^{III})$	2.4(1)
Cl(1) · · · $H(6^{III})$–$C(6^{III})$	153(8)

Roman numeral superscripts refer to the following co-ordinate transformations:

I $-x, \frac{1}{2} + y, 1\frac{1}{2} - z$ II $-x, y - \frac{1}{2}, 1\frac{1}{2} - z$
III $x, -\frac{1}{2} - y, \frac{1}{2} + z$ IV $x, \frac{1}{2} - y, \frac{1}{2} + z$

The structure consists of infinite columns of 8-mercaptopurine units bonded to copper chloride *via* their sulphur atoms. This is shown in Figure 2 which illustrates the –S–Cu–S–Cu– bonds forming a helical chain around the two-fold crystallographic axis shown as a broken line. Figure 3 shows the (010) projection of the structure. There are two N–H · · · Cl hydrogen bonds within any polymer chain. For a hydrogen bond to exist between two atoms H and B, we adopt the criterion $d(\text{H–B}) < W_H + W_B - 0.2$ Å, where W_H and W_B are the van der Waals radii for the H atom and the acceptor atom B respectively.[15] The polymer chains are cross-linked by a third N–H · · · Cl hydrogen bond and by short C–H · · · Cl interactions. Data relating to the hydrogen bonds and short contacts are listed in Table 4.

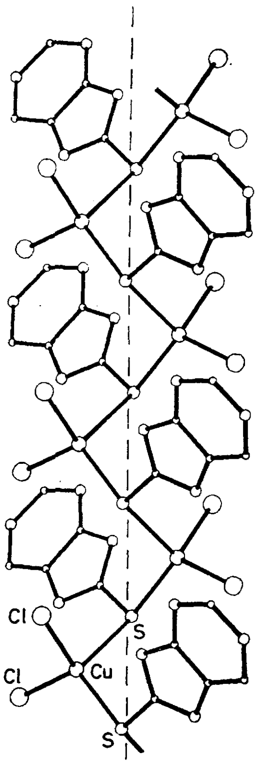

FIGURE 2 A single column of the polymer, illustrating the helical arrangement about the crystallographic two-fold screw axis

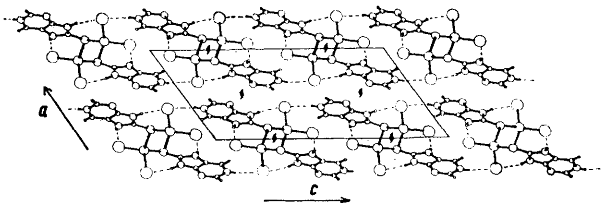

FIGURE 3 (010) Projection of the structure; hydrogen bonds are shown as broken lines

TABLE 5

Equations of least-squares planes, expressed in direct space as $PX + QY + RZ = S$. Distances (Å) of relevant atoms from the plane are given in square brackets

Plane (I): N(1), C(2), N(3), C(4), C(5), C(6), N(7), C(8), N(9), S

$$6.3722X - 2.8718Y + 1.6776Z = 2.6081$$

[N(1) 0.015, C(2) 0.026, N(3) 0.003, C(4) −0.011, C(5) −0.012, C(6) 0.001, N(7) −0.018, C(8) −0.031, N(9) −0.035, S 0.061, Cu −0.696, Cl(1) −0.448, Cl(2) 0.303]

Plane (II): Cu, S, C(8)

$$6.1891X - 0.8729Y + 4.6709Z = 4.4963$$

Angle between normals to planes (I) and (II): 21.3°.

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[4/2470 *Received, 26th November*, 1974]

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