sight into these distances must await the magnetic anisotropy studies (Boyd, Davies & Gerloch, 1977).

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Crystallographic Studies on Metal–Nucleotide Base Complexes. VIII. Tetraaquabis(9-methylhypoxanthine)copper(II) Sulphate

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Abstract. $[(C_6H_6N_4O)_2Cu(H_2O)_4]SO_4$, monoclinic, space group $P2_1/c$, $a = 8.709$ (3), $b = 13.348$ (3), $c = 16.778$ (1) Å, $\beta = 105.44$ (2)°, $Z = 4$, $D_m = 1.879$ (7), $D_x = 1.85$ (3) g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å. The structure was refined by full-matrix least squares to an R of 0.040. The complex unit has both a pseudo two-fold axis and a pseudo mirror plane. The Cu ion is octahedrally surrounded, the guanine bases binding equatorially through N(7) with four water molecules completing the coordination sphere.

Introduction. The compound was synthesized according to a procedure described by Weiss & Venner (1965). Single crystals suitable for X-ray work appeared overnight. The experimental procedure for data collection and processing is described elsewhere (Sletten, 1974). Within the sphere of reflexion limited at $\sin\theta/\lambda = 0.56$, 4144 unique reflexions were recorded. Of these, 1107 were less than the threshold value. The least-squares refinement converged slowly owing to pseudosymmetry, to an R of 0.040. Atomic parameters are listed in Table 1.*

Discussion. The molecular dimensions of the complex and the sulphate ion are shown in Fig. 1. The hypoxanthine ligands are coordinated equatorially and arranged in an *anti* configuration while in the analogous guanine complex the purine ligands are *syn* (Sletten & Fløgstad, 1976). Apart from the metal–nucleic acid interaction it is also of interest to elucidate the role of anions in these systems. In the present compound the sulphate serves as a hydrogen-bond bridge between crystallographically independent hypoxanthine ligands (Fig. 2). Guanine is the only purine able to establish a true di-hydrogen bond to oxyanions; however, the connexion between sulphate and hypoxanthine ligand A is similar in nature, regarding C(2)–H $\cdots$ O(5) as a hydrogen bond. The interaction between sulphate and ring B is through a bifurcated hydrogen bond involving N(1)–H

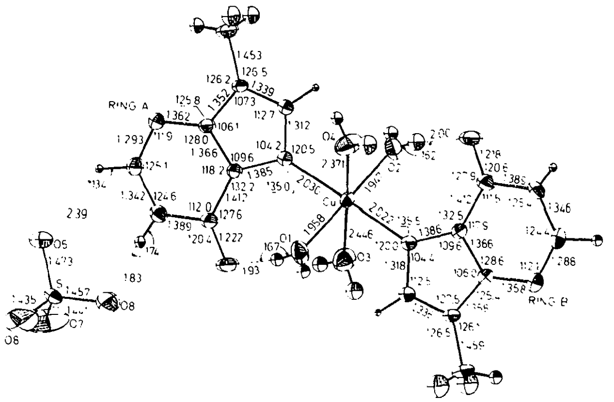

Fig. 1. Interatomic distances and angles in the complex unit. The σ's in bond lengths are: Cu–O(N) 0.002 Å, C–C(N)(O) 0.003–0.004 Å. The σ's for angles involving non-hydrogen atoms are in the range 0.04–0.4°. The thermal spheres of the H atoms correspond to $\frac{1}{4}$ of the U values.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31994 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *The final atomic parameters*

(*a*) Non-hydrogen atoms (temperature parameters $\times 10^4$). Standard deviations are in parentheses. Anisotropic temperature factor: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.

	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu	−0·01210 (4)	0·12482 (4)	0·243804 (18)	192 (2)	254 (2)	156 (2)	−47 (1)	−26 (1)	83 (1)
S	0·47005 (7)	0·37272 (8)	0·24696 (4)	135 (3)	282 (3)	227 (3)	14 (4)	7 (3)	−7 (3)
O(6*A*)	0·25778 (22)	0·12797 (21)	0·45152 (12)	146 (9)	785 (17)	278 (10)	16 (12)	68 (14)	72 (8)
O(6*B*)	−0·27731 (23)	0·10947 (23)	0·03334 (13)	145 (9)	1048 (23)	274 (11)	−27 (13)	56 (14)	60 (8)
N(1*A*)	0·15465 (25)	0·12544 (21)	0·56213 (13)	166 (10)	311 (13)	185 (10)	−6 (12)	16 (12)	13 (9)
N(3*A*)	−0·11680 (24)	0·12353 (21)	0·55596 (12)	205 (10)	332 (13)	166 (10)	−15 (12)	−6 (12)	69 (8)
N(7*A*)	−0·09175 (23)	0·11533 (18)	0·34682 (13)	151 (10)	249 (13)	170 (10)	6 (10)	−3 (10)	39 (8)
N(9*A*)	−0·27720 (23)	0·11491 (19)	0·41440 (13)	121 (9)	296 (14)	186 (10)	14 (10)	10 (10)	47 (8)
N(1*B*)	−0·16849 (28)	0·12078 (23)	−0·07491 (14)	189 (11)	461 (16)	166 (11)	−29 (13)	−9 (13)	−10 (9)
N(3*B*)	0·10278 (27)	0·12998 (22)	−0·06596 (13)	271 (12)	417 (15)	187 (10)	−5 (13)	−14 (13)	90 (9)
N(7*B*)	0·06952 (23)	0·13181 (19)	0·14181 (12)	149 (9)	264 (12)	167 (10)	−13 (11)	−3 (11)	46 (8)
N(9*B*)	0·25828 (24)	0·13554 (20)	0·07638 (13)	138 (10)	348 (15)	209 (10)	−13 (11)	−2 (11)	59 (8)
C(2*A*)	0·0320 (3)	0·12471 (26)	0·59646 (15)	231 (13)	285 (15)	184 (12)	7 (14)	28 (14)	64 (10)
C(4*A*)	−0·13639 (27)	0·12099 (23)	0·47271 (15)	150 (11)	213 (13)	190 (11)	−7 (12)	12 (13)	54 (9)
C(5*A*)	−0·02130 (27)	0·12100 (23)	0·43108 (14)	151 (11)	201 (13)	162 (11)	−8 (12)	21 (13)	40 (9)
C(6*A*)	0·13954 (28)	0·12537 (25)	0·47759 (15)	154 (12)	305 (14)	201 (12)	14 (13)	17 (14)	41 (10)
C(8*A*)	−0·24491 (29)	0·11148 (22)	0·34077 (16)	148 (11)	241 (17)	180 (12)	2 (11)	−1 (11)	31 (10)
C(9*A*)	−0·4342 (4)	0·1158 (4)	0·42909 (22)	155 (13)	670 (28)	315 (16)	4 (18)	41 (21)	101 (12)
C(2*B*)	−0·0442 (3)	0·12629 (27)	−0·10817 (16)	312 (14)	345 (16)	168 (12)	−14 (16)	−31 (15)	84 (11)
C(4*B*)	0·11823 (29)	0·13074 (24)	0·01671 (15)	191 (12)	226 (14)	192 (12)	9 (13)	−16 (13)	71 (10)
C(5*B*)	0·00150 (27)	0·12692 (23)	0·05723 (14)	167 (11)	210 (13)	176 (11)	12 (13)	−7 (13)	59 (9)
C(6*B*)	−0·1580 (3)	0·11922 (26)	0·00917 (16)	179 (12)	389 (17)	207 (12)	5 (14)	28 (15)	33 (10)
C(8*B*)	0·2239 (3)	0·13658 (23)	0·14941 (16)	159 (11)	282 (17)	196 (12)	−11 (12)	−4 (12)	53 (10)
C(9*B*)	0·4170 (4)	0·1382 (4)	0·06289 (23)	160 (14)	730 (30)	369 (18)	−40 (18)	−71 (21)	153 (13)
O(1)	0·1583 (3)	0·21548 (22)	0·30122 (16)	401 (15)	400 (17)	189 (12)	−177 (12)	−7 (11)	75 (11)
O(2)	−0·1820 (3)	0·03460 (24)	0·18736 (17)	373 (14)	450 (18)	202 (13)	−212 (13)	−45 (12)	77 (11)
O(3)	0·1847 (4)	−0·00715 (22)	0·29414 (19)	371 (15)	465 (18)	307 (15)	79 (13)	64 (13)	118 (13)
O(4)	−0·1979 (3)	0·25582 (22)	0·19658 (20)	360 (16)	434 (18)	446 (17)	144 (13)	120 (14)	201 (14)
O(5)	0·31029 (21)	0·37410 (18)	0·26122 (12)	192 (9)	315 (11)	408 (11)	4 (10)	−11 (11)	100 (8)
O(6)	0·5626 (3)	0·45606 (26)	0·28756 (22)	446 (17)	909 (26)	1161 (27)	−394 (17)	−679 (22)	307 (19)
O(7)	0·5486 (4)	0·27917 (28)	0·27484 (23)	609 (19)	891 (27)	1350 (30)	527 (20)	694 (24)	534 (21)
O(8)	0·45284 (26)	0·38089 (27)	0·15843 (13)	264 (12)	1337 (28)	275 (12)	−84 (17)	32 (17)	19 (9)

(*b*) Hydrogen atoms (temperature parameters $\times 10^3$). Isotropic temperature factor: $\exp[-8\pi^2 U \sin^2\theta/\lambda^2]$.

	X/a	Y/b	Z/c	U		X/a	Y/b	Z/c	U
H(1*A*)	0·247 (4)	0·1254 (26)	0·5952 (19)	34 (9)	H(92*B*)	0·454 (7)	0·058 (5)	0·071 (4)	154 (25)
H(2*A*)	0·062 (3)	0·1205 (21)	0·6577 (16)	16 (7)	H(93*B*)	0·469 (7)	0·203 (5)	0·087 (4)	158 (25)
H(8*A*)	−0·322 (3)	0·1060 (20)	0·2899 (16)	12 (7)	H(11)	0·198 (4)	0·197 (3)	0·3469 (24)	45 (12)
H(1*B*)	−0·248 (3)	0·1207 (24)	−0·1049 (17)	19 (8)	H(12)	0·206 (5)	0·257 (3)	0·2847 (25)	52 (15)
H(2*B*)	−0·064 (3)	0·1128 (24)	−0·1698 (18)	32 (8)	H(21)	−0·220 (6)	0·045 (4)	0·1446 (29)	87 (19)
H(8*B*)	0·299 (3)	0·1380 (20)	0·1999 (16)	14 (7)	H(22)	−0·216 (5)	−0·015 (4)	0·2037 (26)	52 (16)
H(91*A*)	0·569 (4)	0·115 (3)	0·4820 (26)	60 (12)	H(31)	0·270 (6)	−0·007 (4)	0·281 (3)	90 (18)
H(92*A*)	0·517 (6)	0·057 (4)	0·4074 (28)	94 (17)	H(32)	0·217 (5)	−0·022 (3)	0·3403 (28)	63 (16)
H(93*A*)	0·507 (6)	0·182 (4)	0·401 (3)	133 (21)	H(41)	−0·269 (5)	0·263 (3)	0·2108 (25)	42 (13)
H(91*B*)	0·415 (4)	0·118 (3)	0·0159 (24)	50 (11)	H(42)	−0·214 (6)	0·269 (4)	0·154 (3)	102 (20)

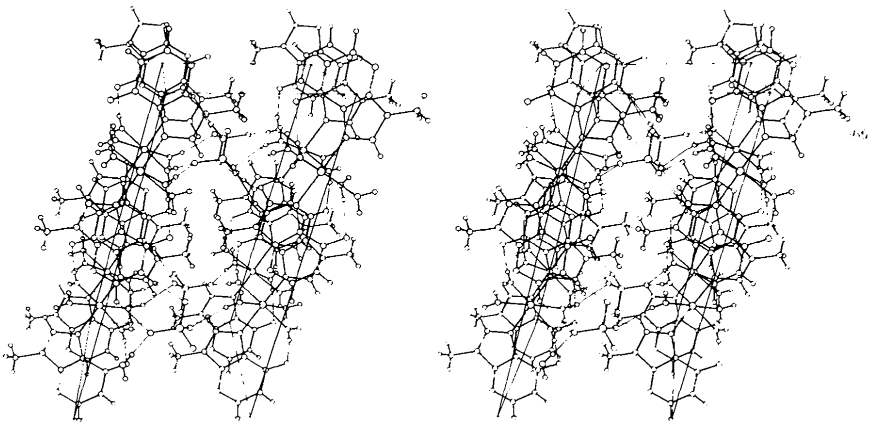

Fig. 2. Stereoscopic drawing of the crystal packing viewed along **b** with **a** parallel to the interocular line.

Table 2. *Hydrogen-bond distances and angles*

	Position of acceptor atom			Distances (Å) $D\cdots A$	$H\cdots A$	Angles (°) D–H$\cdots A$
N(1*A*)–H(1*A*)···O(8)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	2·670 (3)	1·83 (3)	174 (3)
N(1*B*)–H(1*B*)···O(6)	$x-1$,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	2·997 (4)	2·33 (3)	150 (3)
N(1*B*)–H(1*B*)···O(7)	$x-1$,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·302 (4)	2·66 (3)	146 (3)
O(1)–H(11)···O(6*A*)	x,	y,	z	2·704 (3)	1·93 (4)	167 (3)
O(1)–H(12)···O(5)	x,	y,	z	2·676 (4)	1·90 (5)	168 (4)
O(2)–H(21)···O(6*B*)	x,	y,	z	2·688 (4)	2·00 (5)	162 (4)
O(2)–H(22)···O(5)	$\bar{x}$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$	2·664 (4)	1·86 (5)	176 (3)
O(3)–H(31)···O(6)	$1-x$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$	2·928 (5)	2·14 (6)	159 (4)
O(3)–H(32)···N(3*A*)	$\bar{x}$,	$\bar{y}$,	$1-z$	3·143 (4)	2·54 (5)	136 (4)
O(4)–H(41)···O(7)	$x-1$,	y,	z	2·870 (5)	2·15 (5)	170 (3)
O(4)–H(42)···N(3*A*)	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·089 (4)	2·31 (6)	149 (4)
C(2*A*)–H(2*A*)···O(5)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	3·154 (3)	2·39 (2)	134 (2)

and O(6), O(7). In the corresponding adenine–sulphate complex (Sletten & Thorstensen, 1974) the anion is situated in the coordination sphere and hydrogen-bonded to the amino substituent at C(6). Guanine and hypoxanthine do not have the ability to form a corresponding hydrogen bond to oxyanions, and in order to accommodate hydrogen bonds between purine and anion, an axial metal–anion bond is not established.

Three of the atoms in the sulphate show very large thermal motion (Table 1). A difference map shows residual peaks at O(6), O(7) and O(8) indicating disorder brought about by a rotation around S–O(5) which lies in the pseudo mirror plane. The rotational motion tends to shift the sulphate position from the pseudo mirror-plane-symmetry, where O(6), O(7) are symmetry related, to one where O(8), O(6) or O(8), O(7) are symmetry related. The latter arrangement implies that the H atom at N(1) would be bifurcated.

The molecular packing is shown in Fig. 2. The guanine ligands are stacked on top of each other with an approximately equidistant spacing of 3·34 Å. Other significant intermolecular contacts are between methyl groups. The distances between O(6) and the methyl H atoms are in the range 2·63–2·72 Å for ligand *A* and 2·62–2·89 Å for *B*. Hydrogen-bond distances and angles are given in Table 2. Of the possible hydrogen-bond acceptors on the purines, N(3*B*) is the only one not involved in hydrogen bonding.

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Dipiperidine Disulphide

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Abstract. $C_{10}H_{20}N_2S_2$, monoclinic, $P2_1/c$, $a = 10{\cdot}114$ (8), $b = 11{\cdot}158$ (8), $c = 11{\cdot}390$ (8) Å, $\beta = 96{\cdot}08$ (6)°, $U = 1278$ Å^3, $Z = 4$, $D_x = 1{\cdot}34$ g cm^{-3}, μ(Cu $K\alpha$) = 33·67 cm^{-1}. The structure was solved by direct methods and refined to an R of 0·046 for 1308 unique diffractometer data. The S–S distance is 2·067 Å and N–S–S–N dihedral angle 101·1 (4)°.

Introduction. The structure of dipiperidine disulphide has been determined as part of a study of non-metal sulphides. It was prepared by the action of piperidine on S_2Cl_2 (Michaelis & Luxembourg, 1895) and recrystallized from petroleum spirit. Intensities were determined with a Syntex $P2_1$ four-circle diffractometer, Cu $K\alpha$ radiation, a graphite monochromator and a crystal 0·12 × 0·08 × 0·035 mm. 1603 reflexions were measured; after Lp and numerical absorption corrections, equivalent reflexions were merged to give 1308 reflexions with $F > 2{\cdot}5\sigma(F)$ based on counting statistics. The structure was solved by multisolution Σ_2 sign expansion, and refined by full-matrix least squares with an overall isotropic temperature fac-