

The hydrogen-bond distances are all in good agreement with the corresponding distances in hydrogen-bonded compounds containing donor ring-NH groups and acceptor carbonyl oxygen atoms while the hydro-

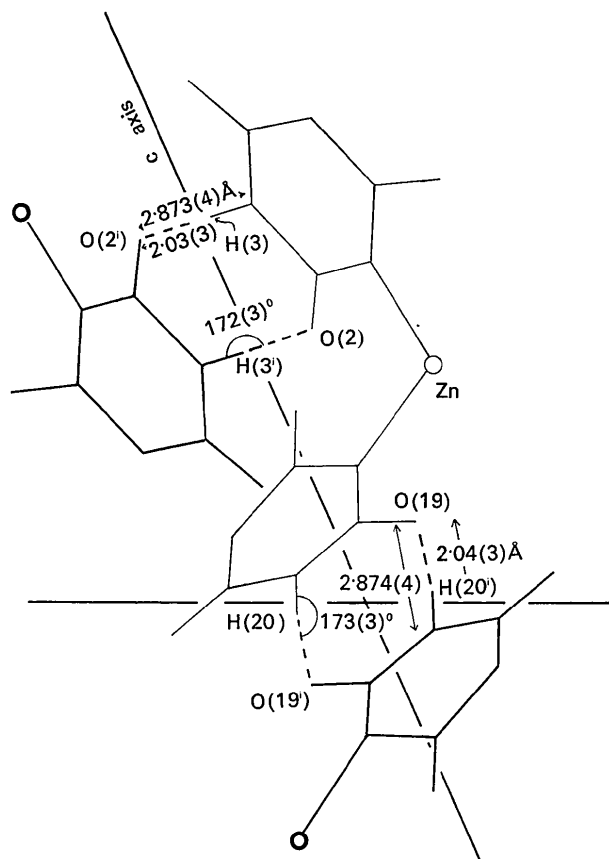


Fig. 5. The geometry of the hydrogen-bonding interactions.

Table 8. Bond lengths (Å) and angles (°) and their *e.s.d.*'s involved in the hydrogen bonding

N(3)-O(2')	2.873 (4)	N(20)-O(19')	2.874 (4)
H(3)-O(2')	2.03 (3)	H(20)-O(19')	2.04 (3)
N(3)-H(3)-O(2')	172 (3)	N(20)-H(20)-O(19')	173 (3)

gen-bond angles are well within the maximum allowed deviation from 180° (Donohue, 1968).

We thank the South African CSIR for the diffractometer data collection. The work was supported by the CSIR and the University of Cape Town's research grants.

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*Acta Cryst.* (1974). B30, 1961

## Crystallographic Studies of Metal-Nucleotide Base Complexes.

### III. Dichlorobis-(9-methyl-6-oxypurine)diaquocopper(II) Trihydrate

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(Received 6 April 1974; accepted 8 April 1974)

$[(C_6H_6N_4O)_2CuCl_2 \cdot 2H_2O] \cdot 3H_2O$  crystallizes as deep-blue prisms from an acidic solution. The space group is  $C2/c$  with  $a = 16.858$ ,  $b = 8.541$ ,  $c = 14.293$  Å,  $\beta = 91.02^\circ$ ,  $Z = 4$ . The structure determination is based on diffractometer data measured with Nb-filtered Mo  $K\alpha$  radiation. Final  $R$  is 0.027 for the 2029 observed reflexions. The copper ion is located at a centre of symmetry and binds to the purine ring through nitrogen N(7); Cu-N = 2.054 Å. The copper coordination is (4+2) with a pair of centrosymmetrically related water molecules completing the equatorial coordination, Cu-O = 1.972 Å, and the axial sites occupied by chloride ions, Cu-Cl = 2.787 Å. The water molecules in the coordination sphere form intramolecular hydrogen bonds to the carbonyl substituent on C(6).

### Introduction

The purine bases incorporated in the nucleic acids have several potential coordination sites. The nitrogen

atoms N(1), N(3) and N(7) are more or less exposed, and so is the substituent in the 6-position. In the reversible unwinding and rewinding of DNA strands caused by certain transition elements, the coordination

of the metal may also involve phosphate groups.

This is the third in a series of papers dealing with the crystal structures of copper complexes of nucleic

acid components. The two previous papers present the structures of copper complexes with unsubstituted adenine and hypoxanthine ligands (Stetten, 1969, 1970).

Table 1. Observed and calculated structure factors multiplied by 10

h	k	l	F <sub>o</sub>	F <sub>c</sub>	Phase	h	k	l	F <sub>o</sub>	F <sub>c</sub>	Phase
1	0	0	100	100	0	1	0	0	100	100	0
2	0	0	400	400	0	2	0	0	400	400	0
3	0	0	900	900	0	3	0	0	900	900	0
4	0	0	1600	1600	0	4	0	0	1600	1600	0
5	0	0	2500	2500	0	5	0	0	2500	2500	0
6	0	0	3600	3600	0	6	0	0	3600	3600	0
7	0	0	4900	4900	0	7	0	0	4900	4900	0
8	0	0	6400	6400	0	8	0	0	6400	6400	0
9	0	0	8100	8100	0	9	0	0	8100	8100	0
10	0	0	10000	10000	0	10	0	0	10000	10000	0
11	0	0	12100	12100	0	11	0	0	12100	12100	0
12	0	0	14400	14400	0	12	0	0	14400	14400	0
13	0	0	16900	16900	0	13	0	0	16900	16900	0
14	0	0	19600	19600	0	14	0	0	19600	19600	0
15	0	0	22500	22500	0	15	0	0	22500	22500	0
16	0	0	25600	25600	0	16	0	0	25600	25600	0
17	0	0	28900	28900	0	17	0	0	28900	28900	0
18	0	0	32400	32400	0	18	0	0	32400	32400	0
19	0	0	36100	36100	0	19	0	0	36100	36100	0
20	0	0	40000	40000	0	20	0	0	40000	40000	0
21	0	0	44100	44100	0	21	0	0	44100	44100	0
22	0	0	48400	48400	0	22	0	0	48400	48400	0
23	0	0	52900	52900	0	23	0	0	52900	52900	0
24	0	0	57600	57600	0	24	0	0	57600	57600	0
25	0	0	62500	62500	0	25	0	0	62500	62500	0
26	0	0	67600	67600	0	26	0	0	67600	67600	0
27	0	0	72900	72900	0	27	0	0	72900	72900	0
28	0	0	78400	78400	0	28	0	0	78400	78400	0
29	0	0	84100	84100	0	29	0	0	84100	84100	0
30	0	0	90000	90000	0	30	0	0	90000	90000	0
31	0	0	96100	96100	0	31	0	0	96100	96100	0
32	0	0	102400	102400	0	32	0	0	102400	102400	0
33	0	0	108900	108900	0	33	0	0	108900	108900	0
34	0	0	115600	115600	0	34	0	0	115600	115600	0
35	0	0	122500	122500	0	35	0	0	122500	122500	0
36	0	0	129600	129600	0	36	0	0	129600	129600	0
37	0	0	136900	136900	0	37	0	0	136900	136900	0
38	0	0	144400	144400	0	38	0	0	144400	144400	0
39	0	0	152100	152100	0	39	0	0	152100	152100	0
40	0	0	160000	160000	0	40	0	0	160000	160000	0
41	0	0	168100	168100	0	41	0	0	168100	168100	0
42	0	0	176400	176400	0	42	0	0	176400	176400	0
43	0	0	184900	184900	0	43	0	0	184900	184900	0
44	0	0	193600	193600	0	44	0	0	193600	193600	0
45	0	0	202500	202500	0	45	0	0	202500	202500	0
46	0	0	211600	211600	0	46	0	0	211600	211600	0
47	0	0	220900	220900	0	47	0	0	220900	220900	0
48	0	0	230400	230400	0	48	0	0	230400	230400	0
49	0	0	240100	240100	0	49	0	0	240100	240100	0
50	0	0	250000	250000	0	50	0	0	250000	250000	0
51	0	0	260100	260100	0	51	0	0	260100	260100	0
52	0	0	270400	270400	0	52	0	0	270400	270400	0
53	0	0	280900	280900	0	53	0	0	280900	280900	0
54	0	0	291600	291600	0	54	0	0	291600	291600	0
55	0	0	302500	302500	0	55	0	0	302500	302500	0
56	0	0	313600	313600	0	56	0	0	313600	313600	0
57	0	0	324900	324900	0	57	0	0	324900	324900	0
58	0	0	336400	336400	0	58	0	0	336400	336400	0
59	0	0	348100	348100	0	59	0	0	348100	348100	0
60	0	0	360000	360000	0	60	0	0	360000	360000	0
61	0	0	372100	372100	0	61	0	0	372100	372100	0
62	0	0	384400	384400	0	62	0	0	384400	384400	0
63	0	0	396900	396900	0	63	0	0	396900	396900	0
64	0	0	409600	409600	0	64	0	0	409600	409600	0
65	0	0	422500	422500	0	65	0	0	422500	422500	0
66	0	0	435600	435600	0	66	0	0	435600	435600	0
67	0	0	448900	448900	0	67	0	0	448900	448900	0
68	0	0	462400	462400	0	68	0	0	462400	462400	0
69	0	0	476100	476100	0	69	0	0	476100	476100	0
70	0	0	490000	490000	0	70	0	0	490000	490000	0
71	0	0	504100	504100	0	71	0	0	504100	504100	0
72	0	0	518400	518400	0	72	0	0	518400	518400	0
73	0	0	532900	532900	0	73	0	0	532900	532900	0
74	0	0	547600	547600	0	74	0	0	547600	547600	0
75	0	0	562500	562500	0	75	0	0	562500	562500	0
76	0	0	577600	577600	0	76	0	0	577600	577600	0
77	0	0	592900	592900	0	77	0	0	592900	592900	0
78	0	0	608400	608400	0	78	0	0	608400	608400	0
79	0	0	624100	624100	0	79	0	0	624100	624100	0
80	0	0	640000	640000	0	80	0	0	640000	640000	0
81	0	0	656100	656100	0	81	0	0	656100	656100	0
82	0	0	672400	672400	0	82	0	0	672400	672400	0
83	0	0	688900	688900	0	83	0	0	688900	688900	0
84	0	0	705600	705600	0	84	0	0	705600	705600	0
85	0	0	722500	722500	0	85	0	0	722500	722500	0
86	0	0	739600	739600	0	86	0	0	739600	739600	0
87	0	0	756900	756900	0	87	0	0	756900	756900	0
88	0	0	774400	774400	0	88	0	0	774400	774400	0
89	0	0	792100	792100	0	89	0	0	792100	792100	0
90	0	0	810000	810000	0	90	0	0	810000	810000	0
91	0	0	828100	828100	0	91	0	0	828100	828100	0
92	0	0	846400	846400	0	92	0	0	846400	846400	0
93	0	0	864900	864900	0	93	0	0	864900	864900	0
94	0	0	883600	883600	0	94	0	0	883600	883600	0
95	0	0	902500	902500	0	95	0	0	902500	902500	0
96	0	0	921600	921600	0	96	0	0	921600	921600	0
97	0	0	940900	940900	0	97	0	0	940900	940900	0
98	0	0	960400	960400	0	98	0	0	960400	960400	0
99	0	0	980100	980100	0	99	0	0	980100	980100	0
100	0	0	1000000	1000000	0	100	0	0	1000000	1000000	0

Copper complexes of other simple purines have been described (de Meester & Skapski, 1971, 1973; Carabine & Sundaralingam, 1970; Terzis, Beauchamp & Rivest, 1973). None of the compounds referred to above is directly related to biological systems of nucleic acids where N(9) carries a ribosyl residue. The present paper describes the crystal structure of a copper-purine complex in which N(9) is blocked by a methyl group. It is expected that the methyl-substituted hypoxanthine molecule will have the same ligand properties at neutral pH as the corresponding nucleoside, inosine. A preliminary account of this work has been published (Sletten, 1971).

### Experimental

The compound was synthesized by dissolving 9-methylhypoxanthine in water and adding a 1M solution of  $\text{CuCl}_2$  in excess (Weiss & Venner, 1965). Blue prisms crystallized from the solution the next day. Weissenberg films indicated space group  $Cc$  or  $C2/c$ . Subsequent refinement confirmed space group  $C2/c$ .

#### Crystal data

$[(\text{C}_6\text{H}_6\text{N}_4\text{O})_2\text{CuCl}_2 \cdot 2\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$ , F.W. 515.8,  $a = 16.858(4)$ ,  $b = 8.541(4)$ ,  $c = 14.293(11)$  Å,  $\beta = 91.02(5)^\circ$ ,  $D_m = 1.64$ ,  $D_x = 1.65$  g cm $^{-3}$ ,  $V = 2090$  Å $^3$ ,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 13.85$  cm $^{-1}$ .

Cell dimensions were obtained from a least-squares treatment of  $2\theta$  settings of 13 reflexions as measured

on a Siemens AED diffractometer. None of the differences between observed and calculated  $2\theta$  values was greater than  $0.02^\circ$ .

The crystal used for data collection had dimensions approximately  $0.20 \times 0.27 \times 0.32$  mm, and was mounted along  $a^*$ . Integrated intensities were recorded by the moving-crystal moving-counter technique with Nb-filtered Mo  $K\alpha$  radiation at 40 kV and 20 mA. From a preliminary peak count the instrument selects scan rate and attenuation filter. The scan rates and filters are chosen so as to measure all reflexions, except the very weakest, with approximately the same statistical error. The use of attenuation filters also prevents counting losses which appear at high counting rates. The scan ranges were determined according to the tangent relationship (Alexander & Smith, 1964). Within the sphere of reflexion limited at  $\sin \theta/\lambda = 0.64$ , 2242 unique reflexions were measured. Of these, 228 were less than the threshold value of  $2\sigma_c$ , where  $\sigma_c$  is the estimated error due to counting statistics.

During data collection three standard reflexions were measured every 100 reflexions to check the stability of crystal and electronics. The averages of the three standards were plotted and showed fluctuations less than  $\pm 1\%$ . The expression used for calculating the random error in any one reflexion is:  $\sigma_I = [\sigma_c^2 + (0.02\sigma_c^2)^2]^{1/2}$ . Here both counting statistics and errors due to instrumental instability are taken into account.

The data were corrected for Lorentz and polarization effects, but not for absorption. The standard deviations in structure factors were calculated from  $\sigma_F = \sigma_I/2(I \text{ Lp})^{1/2}$ .

### Structure determination

If the space group is  $C2/c$ , the copper ion must be located on a special position. From a Patterson map the copper coordinates were tentatively chosen as (0,0,0).  $R$  based on copper alone was 0.67 ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ). Even at this high  $R$  value all the non-hydrogen atoms were easily located in the subsequent Fourier map. Refinement proceeded by full-matrix least-squares calculations, minimizing  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/\sigma_F^2$ . The unobserved reflexions were included in the refinement only when  $|F_c| > |F_o|$ . Anisotropic temperature factors were introduced for all atoms, and at an  $R_{\text{of}} 0.043$  the 11 hydrogen atoms were located from a difference map. Two cycles of refinement on all atoms, with isotropic temperature factors for the hydrogen atoms, lowered  $R$  to 0.030.

The data were corrected for secondary extinction according to  $F_{\text{corr}} = KF_{\text{obs}}[1 + \beta(2\theta)CI_{\text{obs}}]$  (Zachariasen, 1963). The constants  $K$  and  $C$  were determined as 0.99 and  $0.155 \times 10^{-5}$  by a least-squares procedure. The extinction correction lowered the  $R$  value 0.2%. During two final cycles the refinement converged at an  $R$  of 0.028. The weighted  $R$  is 0.033 and the 'goodness of fit',  $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ , is 1.14.

A difference map based on all atoms did not show maxima or minima greater than  $0.15$  e Å $^{-3}$ . The few

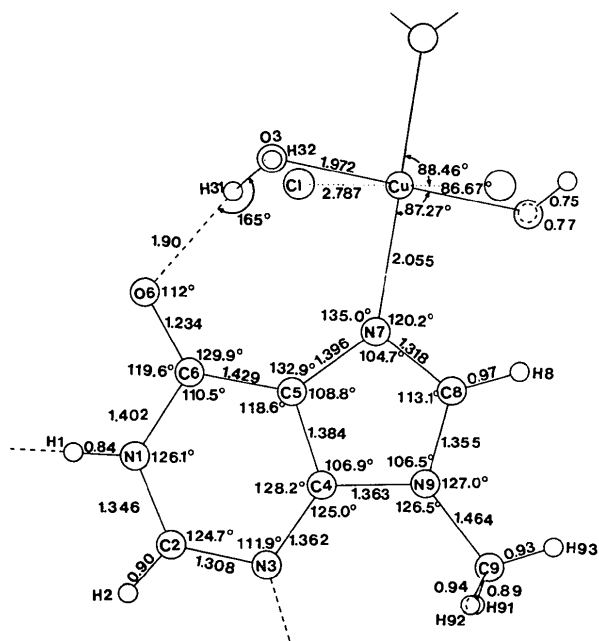


Fig. 1. Interatomic distances and angles. The  $\sigma$ 's in bond distances are: Cu-Cl 0.001, Cu-N(O) 0.002, C-X (=C, N, O) 0.003, H-X 0.02-0.03 Å. The  $\sigma$ 's for angles involving only non-hydrogen atoms are in the range 0.05-0.14°, and for those involving hydrogens 0.8-2.5°.

Table 2. *The final atomic parameters*(a) Non-hydrogen atoms (coordinates  $\times 10^5$  and 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	0	0	147 (1)	354 (2)	264 (2)	-25 (1)	47 (1)	11 (1)
Cl	4243 (3)	29144 (6)	42892 (4)	241 (2)	361 (3)	406 (3)	-28 (2)	-20 (2)	-10 (2)
N(1)	19212 (9)	52749 (19)	571 (12)	153 (7)	332 (9)	384 (9)	32 (6)	5 (7)	-11 (6)
C(2)	15883 (10)	43263 (25)	6920 (15)	173 (8)	367 (10)	386 (11)	-5 (8)	-68 (9)	33 (7)
N(3)	19822 (9)	33716 (19)	12448 (12)	195 (7)	337 (9)	354 (9)	-42 (6)	-19 (6)	62 (6)
C(4)	27790 (10)	34578 (21)	11113 (13)	197 (8)	257 (9)	275 (9)	-15 (7)	-32 (7)	18 (7)
C(5)	31817 (9)	43898 (21)	4852 (13)	151 (7)	254 (8)	282 (9)	-17 (7)	-22 (7)	21 (6)
C(6)	27348 (10)	54156 (21)	-1128 (13)	186 (8)	293 (10)	291 (9)	15 (6)	-47 (8)	2 (7)
O(6)	29615 (8)	63201 (16)	-7256 (10)	238 (6)	395 (8)	387 (8)	38 (6)	113 (7)	31 (6)
N(7)	39930 (8)	40870 (18)	5778 (11)	162 (7)	274 (8)	303 (8)	10 (6)	17 (7)	12 (6)
C(8)	40423 (11)	30117 (23)	12376 (13)	193 (8)	307 (10)	332 (10)	-10 (7)	45 (8)	10 (7)
N(9)	33350 (9)	25866 (18)	15796 (11)	213 (7)	291 (8)	312 (8)	-21 (6)	59 (7)	20 (6)
C(9)	31883 (14)	14379 (31)	23164 (18)	346 (11)	447 (13)	392 (12)	-37 (10)	158 (11)	28 (10)
O(1)	11235 (11)	12666 (22)	24816 (13)	490 (10)	475 (10)	392 (10)	-97 (8)	-29 (8)	99 (8)
O(2)	0	50793 (36)	25000	531 (16)	506 (16)	614 (19)	0	0	-118 (14)
O(3)	44319 (8)	43784 (20)	38408 (11)	193 (77)	405 (8)	301 (7)	5 (6)	-14 (7)	4 (5)

Table 2 (cont.)

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

	$X/a$	$Y/b$	$Z/c$	$U$
H(1)	161 (1)	587 (3)	-24 (2)	33 (6)
H(2)	106 (1)	435 (3)	71 (2)	37 (6)
H(8)	453 (1)	252 (2)	145 (2)	29 (5)
H(91)	283 (2)	77 (4)	209 (2)	76 (10)
H(92)	293 (2)	195 (3)	281 (2)	71 (9)
H(93)	366 (2)	91 (4)	246 (2)	75 (9)
H(11)	90 (2)	164 (3)	290 (2)	57 (9)
H(12)	134 (2)	193 (4)	221 (2)	55 (9)
H(21)	8 (2)	460 (3)	292 (2)	53 (9)
H(31)	404 (2)	403 (4)	398 (2)	58 (9)
H(32)	440 (1)	507 (3)	350 (2)	35 (7)

positive regions of  $0.10\text{--}0.15 \text{ e } \text{\AA}^{-3}$  appear in the middle of covalent bonds. These peaks are probably significant, indicating residual bonding electrons.

The observed and calculated structure factors are listed in Table 1. The scattering curves used for Cu, O, N, C are those given in *International Tables for X-ray Crystallography* (1962) and for H that published by Stewart, Davidson & Simpson (1965).

Atomic parameters are listed in Table 2. All cal-

culations were carried out on an IBM 360/50H computer. Some of the programs used have been written by cand. real. K. Maartmann-Moe, and some originate from The Weizmann Institute of Science, Rehovoth, Israel and have been modified by Dr D. Rabinovich, cand. real. K. Åse, and cand. real. L. Milje.

### Description of the structure and discussion

The structure of the complex is shown in Fig. 1. The copper ion is situated at a centre of symmetry with (4+2) coordination. In the equatorial plane the base nitrogen N(7) and water oxygen O(3) are bonded at 2.054(2) and 1.972(2) Å respectively. The axial positions are occupied by chloride ions at 2.787(1) Å. The sum of the relevant ionic radii is 2.62 Å, thus indicating very weak axial coordination. The coordination octahedron is slightly skewed, the angles Cl-Cu-N(7), Cl-Cu-O(3), and N(7)-Cu-O(3) being 88.46(5), 86.67(5), and 87.27(6)°, respectively. The equatorial plane is tilted 25° relative to the plane through the purine ring to accommodate intramolecular hydrogen bonding between the water molecules in the coordination sphere and the carbonyl oxygen O(6).

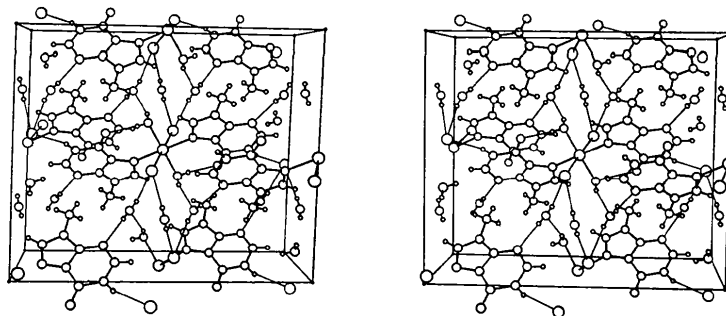


Fig. 2. Stereoscopic illustration of the crystal packing viewed approximately along **b**, with **a** parallel to the interoculuar line. The drawing was made by ORTEP (Johnson, 1970).

The hypoxanthine ligand is unidentate. The coordinating orbital on N(7) is bent, the angles Cu–N(7)–C(5) and Cu–N(7)–C(8) being 135.0 and 120.2° respectively. The copper ion is displaced 0.1 Å from the plane through the purine ring.

The possibility of a chelate structure involving both N(7) and O(6) has been invoked on the basis of spectroscopic results (see *e.g.* Tu & Friedrich, 1968). Recently the structure of a palladium complex of a thionucleoside analogue has been reported where a chelate is formed between S(6), N(7) and Pd (Heitner, Lippard & Sunshine, 1972). The distortion of the ligand geometry to obtain bidentate bonding is appreciable. The donor properties of sulphur far exceed those of oxygen; thus the severely strained five-membered chelate ring is evidently energetically favourable in the case of the palladium complex.

Ultraviolet measurements on *cis*- and *trans*-dichlorodiammineplatinum(II) nucleoside complexes have indicated that the ligands are unidentate in the case of guanosine and inosine, but bind bifunctionally between N(7) and the 6-amino group in adenosine

(Mansy, Rosenberg & Thomson, 1973). Thus the spectroscopic results point towards unidentate binding for 6-oxo compounds and bidentate for 6-amino compounds. However, an X-ray determination of the latter type of complex shows no tendency to bidentate coordination (Sletten, to be published). Instead an indirect chelation *via* a water molecule in the coordination sphere seems to be preferred.

The effect of metal bonding on the purine geometry is minor. The ligand is planar within experimental error. The slight bend around C(4)–C(5) observed in most purine structures is barely detectable in the present compound. A comparison between the dimensions in the analogue inosine and the present compound reveals a slight *trans* effect on the bonds adjacent to the coordination site N(7), the lengthening being 0.022 and 0.012 Å in C(5)–N(7) and N(7)–C(8), respectively (Sletten, 1972).

Apparently the angle C(5)–C(6)–O(6) of 129.9° is appreciably distorted to accommodate both metal and hydrogen bonds. However, the average value of the C(5)–C(6)–O(6) angle obtained from ten 6-oxypurines, is 127.8° with r.m.s. deviation of 0.3° (Sletten, 1972). The angle C(6)–C(5)–N(7) is opened up 3.0° relative to the average structure. The total widening of the ligand 'bite' is approximately 0.1 Å. In the corresponding palladium complex of 6-thiopurine the 'bite' is reduced by 0.3 Å.

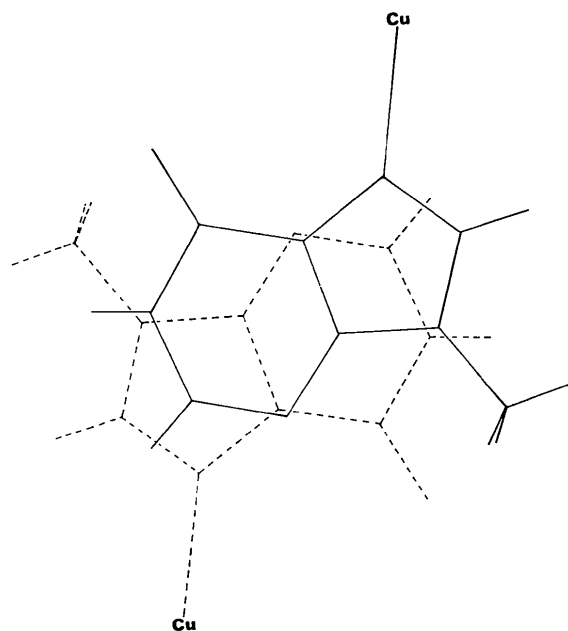


Fig. 3. Base stacking of the hypoxanthine ligands viewed perpendicular to the least-squares plane of the purine ring. Interplanar spacing = 3.41 Å.

### Hydrogen bonding and crystal packing

The molecular packing in the unit cell is shown in a stereo drawing viewed approximately along *b* (Fig. 2). Hydrogen bonds are listed in Table 3 and are also shown as thin lines in Fig. 2.

The chloride ion participates in three relatively strong hydrogen bonds, one directly to the ring, N(1)–H(1)···Cl, one *via* a water molecule to the ring, N(3)···H(12)–O(1)–H(11)···Cl, and one connecting two chloride ions *via* the water molecule located on a twofold axis, Cl···H(21)–O(2)–H(21)···Cl. The water molecule in the coordination sphere forms both an intra- and an intermolecular hydrogen bond. Somewhat unexpectedly the two bonds have identical lengths within the limit of error; O(3)···O(6) = 2.634(2) and O(3)···O(1) = 2.643(2) Å. There are no inter-base hydrogen bonds.

The familiar stacking pattern found in most purine structures is also retained in the metal complex. The

Table 3. *Hydrogen-bond distances and angles*

Bond	Position of acceptor atom	Distances (Å)		Angle (°)
		D···A	H···A	
N(1)–H(1)···Cl	$x, 1-y, z-\frac{1}{2}$	3.141 (2)	2.35 (2)	159 (2)
O(1)–H(11)···Cl	$x, y, z$	3.186 (2)	2.41 (3)	170 (2)
O(1)–H(12)···N(3)	$x, y, z$	2.923 (2)	2.16 (3)	168 (2)
O(2)–H(21)···Cl	$x, y, z$	3.226 (2)	2.50 (3)	176 (3)
O(3)–H(32)···O(1)	$\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$	2.643 (2)	1.93 (2)	153 (2)
O(3)–H(31)···O(6)	$x, 1-y, z-\frac{1}{2}$	2.634 (2)	1.90 (3)	165 (3)

interplanar distance between pairs of hypoxanthine ligands related by a screw axis is 3.41 Å. The overlap is seen to be extensive (Fig. 3).

The methyl group is found to be almost exactly eclipsed relative to C(8)-H(8), the H(8)···H(93) distance being only 2.3 Å. There are no other short intra- or intermolecular H···H contacts in the structure.

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## Preparation and Single-Crystal Structure of $\beta$ -NH<sub>4</sub>UF<sub>5</sub>, Ammonium Pentafluorouranate(IV)

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(Received 14 January 1974; accepted 1 April 1974)

The single-crystal structure of  $\beta$ -NH<sub>4</sub>UF<sub>5</sub> has been determined by a three-dimensional X-ray study. It belongs to space group *P2<sub>1</sub>/c*, with dimensions  $a = 7.799$  (5),  $b = 7.158$  (5),  $c = 8.762$  (7) Å,  $\beta = 116.45$  (5)°,  $Z = 4$ ,  $V = 437.9$  Å<sup>3</sup>,  $d_{\text{calc}} = 5.32$ ,  $d_{\text{obs}} = 5.3$  g cm<sup>-3</sup>. Full-matrix least-squares treatment of 1325 observed intensities, measured by counting techniques, gave an unweighted *R* value of 0.036, all atoms having anisotropic thermal parameters. The structure is composed of infinite sheets of equivalent UF<sub>5</sub> polyhedra, running parallel to the (100) plane. One fluorine in each polyhedron is unshared, projecting alternatively toward adjacent sheets, but not connecting them. Ammonium ions bind the sheets together. The minimum U-U distances are 3.91 Å within the sheets and 6.33 Å between closest uranium atoms in adjacent sheets. The structure differs greatly from that of isostructural  $\alpha$ -NH<sub>4</sub>UF<sub>5</sub>.

### Introduction

Ten years ago it was established (Benz, Douglass, Kruse & Penneman, 1963) that NH<sub>4</sub>UF<sub>5</sub> exists in  $\alpha$  and  $\beta$  forms. Compounds of 1:1 NH<sub>4</sub>F/UF<sub>4</sub> stoichiometry are actually difficult to prepare. The usual result from aqueous precipitation is formation of 7NH<sub>4</sub>F.6MF<sub>4</sub>. Indeed, many compounds having this special 7:6 molar ratio of alkali fluoride to tetravalent fluoride are known (Thoma, 1962; Penneman, Ryan & Rosenzweig, 1973). The parent structure is that of 7NaF.6ZrF<sub>4</sub> (Burns, Ellison & Levy, 1968). In this structure the tetravalent element is surrounded by eight fluorines in an antiprism, six of which enclose a

large cubo-octahedral cavity which accommodates the 'extra' fluoride. We volatilized NH<sub>4</sub>F from higher NH<sub>4</sub>F/UF<sub>4</sub> complexes and obtained  $\alpha$  and  $\beta$  forms of NH<sub>4</sub>UF<sub>5</sub> in which the molar ratio of NH<sub>4</sub>F to UF<sub>4</sub> was established as unity. The  $\alpha$  form has the same X-ray powder diffraction pattern as that of 7NH<sub>4</sub>F.6UF<sub>4</sub> and is thus presumed to be an NH<sub>4</sub>F-deficient form of it. The structure of the  $\beta$  form was unknown; therefore it was of considerable interest to us that a patent (Allied Chemical Corporation, 1970) disclosed that both  $\alpha$ - and  $\beta$ -NH<sub>4</sub>UF<sub>5</sub> could be selectively precipitated from hot uranium-bearing aqueous ammonium fluoride solutions upon reduction of U(VI) to U(IV).