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poly-Di-μ-chloro-tetrachloro(purinium)dicopper(II)

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Abstract. $C_5H_5Cl_6Cu_2N_4$, monoclinic, $P2_1/c$, a = 12·723 (3), b = 6·110 (1), c = 17·234 (4) Å, β = 100·11 (1)°, M_r = 460·9, Z = 4, D_x = 2·32 Mg m^{-3}, R = 0·049 for 2302 reflections. The compound is polymeric with individual units linked by asymmetric Cu—Cl—Cu bridges. It contains one pentacoordinated and one hexacoordinated Cu atom linked by two symmetric Cl bridges. N(3) of the purine base adopts an axial position in the octahedral coordination sphere of the latter Cu atom. N(9) is not a binding site.

Introduction. Adenine (=Ade) forms various compounds with cupric chloride in acid solution (Weiss & Venner, 1963). The structures of compounds of the stoichiometries $Cu(AdeH)_2.4H_2O$ (1) (Sletten, 1969), $[Cu(Ade)_2Cl_2]Cl_2.6H_2O$ (2) (de Meester, Goodgame, Price & Skapski, 1971) and $Cu_3Cl_8(AdeH)_2.4H_2O$ (3) (de Meester, Goodgame, Price & Skapski, 1970) have been established by X-ray analysis. Both the adenine N(3) and N(9) are Cu binding sites in all three complexes. Unsubstituted purine ($C_5H_4N_4$) is also known to form three different complexes with cupric chloride (Weiss & Venner, 1965), for which the following stoichiometries were reported, $[(C_5H_4N_4)CuCl_2].HCl$, $[(C_5H_4N_4)Cu(H_2O)Cl]Cl$ and $[(C_5H_6N_4)CuCl_2]^{2+}$-$[CuCl_4]^{2-}$ (4). In view of the fact that Cl bridges are observed in the trinuclear complex (3), prepared under similar conditions to (4) (2*M* HCl solution), it seemed improbable that the formulation of (4) as a tetrachlorocuprate could be correct. We have, therefore, carried out an X-ray analysis on (4) to clarify the nature of the bonding.

(4) was prepared by the method of Weiss & Venner (1965). 1·5 g of $CuCl_2.2H_2O$ in 2 ml of H_2O were added to a solution of 108 mg of purine in 1 ml of hot 1*M* HCl. After boiling the mixture for 10 min, the precipitate which had formed was dissolved by the addition of a minimum of 1*M* HCl. Brown prismatic crystals of (4) were obtained on slow cooling. These turn green in the presence of water.

For the X-ray analysis, crystals were sealed in Lindemann-glass capillary tubes. Cell dimensions were determined by a least-squares fit to settings for 15 reflections $\pm(hkl)$ on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation, λ = 0·71069 Å). Data collection was carried out in the θ–2θ mode ($2\theta \leq 55°$). An empirical absorption correction, based on azimuthal scan data, was performed [μ(Mo $K\alpha$) = 4·29 mm^{-1}]. The calculated maximum and minimum transmission factors were 0·344 and 0·161. After application of the observation criterion $F^2 \geq 2{\cdot}0\sigma(F^2)$, 2302 independent reflections (from 3034 recorded) were retained for use in the analysis. The structure was solved by direct methods (*SHELX*, G. M. Sheldrick) and refined by full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms. The H-atom positional parameters were refined with individual isotropic temperature factors under the bond-length constraints C—H = 1·08 ± 0·02, N—H = 1·01 ± 0·02Å. Terminal values of R and R_w were respectively 0·049 and 0·047. Weights were given by $w = k[\sigma^2(F_o) + 0{\cdot}0002F_o^2]^{-1}$. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Table 1 lists the final atom coordinates, with equivalent isotropic temperature factors $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ (Willis & Pryor, 1975) for the non-hydrogen atoms.† Table 2 gives

Table 1. *Positional parameters* (×10^4)

	x	y	z	U_{eq} (Å^2)
Cu(1)	7704 (1)	10795 (1)	719 (1)	24
Cu(2)	7542 (1)	6017 (1)	1730 (1)	24
Cl(1)	8908 (1)	12149 (2)	27 (1)	27
Cl(2)	6571 (1)	13661 (2)	439 (1)	25
Cl(3)	6474 (1)	9070 (2)	1393 (1)	28
Cl(4)	8781 (1)	7903 (2)	1179 (1)	30
Cl(5)	6424 (1)	4758 (2)	2521 (1)	26
Cl(6)	8774 (1)	3446 (3)	2158 (1)	40
N(1)	5560 (4)	6420 (8)	−1213 (3)	26
C(2)	5944 (5)	7971 (10)	−679 (3)	27
N(3)	6970 (4)	8470 (7)	−493 (3)	21
C(4)	7586 (4)	7289 (9)	−882 (3)	20
C(5)	7249 (5)	5643 (9)	−1425 (3)	22
C(6)	6163 (5)	5218 (10)	−1610 (3)	26
N(7)	8121 (4)	4883 (8)	−1702 (3)	28
C(8)	8962 (5)	5950 (12)	−1330 (4)	35
N(9)	8668 (4)	7468 (9)	−841 (3)	29
H(1)	4779 (16)	6399 (118)	−1326 (38)	54 (22)
H(2)	5377 (38)	8706 (88)	−370 (29)	32 (17)
H(6)	5876 (51)	4062 (80)	−2062 (27)	47 (20)
H(8)	9760 (28)	5942 (138)	−1474 (43)	76 (26)
H(9)	9147 (47)	8495 (92)	−475 (33)	58 (23)

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35837 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Bond lengths* (Å) *and angles* (°)

Cl(1)–Cu(1)	2·257 (2)	Cl(2)–Cu(1)	2·265 (2)
Cl(3)–Cu(1)	2·355 (2)	Cl(4)–Cu(1)	2·291 (2)
Cl(6)′–Cu(1)	3·072 (2)	N(3)–Cu(1)	2·563 (4)
Cl(2)′–Cu(2)	2·754 (1)	Cl(3)–Cu(2)	2·321 (2)
Cl(4)–Cu(2)	2·290 (2)	Cl(5)–Cu(2)	2·270 (2)
Cl(6)–Cu(2)	2·250 (2)	C(2)–N(1)	1·351 (8)
C(6)–N(1)	1·333 (8)	N(3)–C(2)	1·324 (8)
C(4)–N(3)	1·330 (7)	C(5)–C(4)	1·390 (7)
N(9)–C(4)	1·370 (8)	C(6)–C(5)	1·388 (9)
N(7)–C(5)	1·364 (8)	C(8)–N(7)	1·318 (8)
N(9)–C(8)	1·350 (9)		

Cl(2)–Cu(1)–Cl(1)	94·0 (1)	Cl(3)–Cu(1)–Cl(1)	174·8 (1)
Cl(3)–Cu(1)–Cl(2)	89·9 (1)	Cl(4)–Cu(1)–Cl(1)	92·6 (1)
Cl(4)–Cu(1)–Cl(2)	171·7 (1)	Cl(4)–Cu(1)–Cl(3)	83·9 (1)
Cl(6)–Cu(1)–Cl(1)	89·3 (1)	Cl(6)–Cu(1)–Cl(2)	86·6 (0)
Cl(6)–Cu(1)–Cl(3)	94·4 (1)	Cl(6)–Cu(1)–Cl(4)	88·5 (1)
N(3)–Cu(1)–Cl(1)	87·5 (1)	N(3)–Cu(1)–Cl(2)	97·3 (1)
N(3)–Cu(1)–Cl(3)	88·6 (1)	N(3)–Cu(1)–Cl(4)	88·0 (1)
N(3)–Cu(1)–Cl(6)	175·1 (1)	Cl(3)–Cu(2)–Cl(2)	93·3 (0)
Cl(4)–Cu(2)–Cl(2)	99·9 (1)	Cl(4)–Cu(2)–Cl(3)	84·7 (1)
Cl(5)–Cu(2)–Cl(2)	94·0 (1)	Cl(5)–Cu(2)–Cl(3)	91·3 (1)
Cl(5)–Cu(2)–Cl(4)	165·8 (1)	Cl(6)–Cu(2)–Cl(2)	95·0 (1)
Cl(6)–Cu(2)–Cl(3)	170·7 (1)	Cl(6)–Cu(2)–Cl(4)	89·8 (1)
Cl(6)–Cu(2)–Cl(5)	92·3 (1)	Cu(2)–Cl(2)′–Cu(1)	93·1 (0)
Cu(2)–Cl(3)–Cu(1)	94·2 (1)	Cu(2)–Cl(4)–Cu(1)	96·8 (1)
Cu(2)–Cl(6)′–Cu(1)	85·4 (1)	C(6)–N(1)–C(2)	124·3 (5)
N(3)–C(2)–N(1)	123·4 (6)	C(2)–N(3)–Cu(1)	121·9 (4)
C(4)–N(3)–Cu(1)	123·3 (3)	C(4)–N(3)–C(2)	113·3 (5)
C(5)–C(4)–N(3)	126·4 (5)	N(9)–C(4)–N(3)	127·3 (5)
N(9)–C(4)–C(5)	106·3 (5)	C(6)–C(5)–C(4)	117·8 (5)
N(7)–C(5)–C(4)	108·0 (5)	N(7)–C(5)–C(6)	134·1 (5)
C(5)–C(6)–N(1)	114·8 (5)	C(8)–N(7)–C(5)	107·6 (5)
N(9)–C(8)–N(7)	110·7 (6)	C(8)–N(9)–C(4)	107·4 (5)

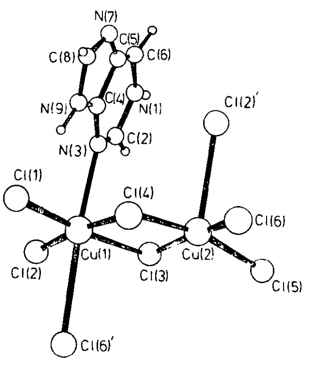

Fig. 1. The structural unit of (4).

bond distances and angles. Fig. 1 was drawn by *RSPLOT* (W. S. Sheldrick).

Discussion. The analysis establishes the constitution of (4) as $(C_5H_5N_4)Cu_2Cl_6$. N(1) of the base is protonated as would be expected from the preparation conditions. No evidence was found in difference syntheses for a further protonation of the base at N(7). For a formal balance of charge in the complex it must, therefore, be assumed that the purine base (=Pu) is present as $(PuH)^{2+}$. In the crystal (4) is polymeric, with individual units linked by asymmetric Cu–Cl–Cu bridges, and contains one pentacoordinated and one hexacoordinated Cu atom. The coordination of Cu(1) is [4 + 2]-octahedral with the terminal equatorial bonds, Cu(1)–Cl(1) and Cu(1)–Cl(2), significantly shorter than the bridging equatorial bonds, Cu(1)–Cl(3) and Cu(1)–Cl(4). The Cu coordination sphere is completed by one N(3) donor atom and Cl(6) of the adjacent structural unit at x, $1 + y$, z. This is the first reported structure of a transition-metal complex of a purine base in which only N(3) is coordinated and in which the N donor atom adopts an axial position to a penta- or hexacoordinated Cu atom. The Cu(1)–N(3) distance of 2·563 (4) Å is 0·528 Å longer than the average equatorial Cu–N(3) distance of 2·035 (7) Å, which has been found for nucleic-acid constituents containing purine bases (Swaminathan & Sundaralingam, 1979). Previous studies of Cu complexes of unsubstituted purine bases have shown N(9) to be the most preferred binding site, either as a unidentate site or in conjunction with N(3) as observed in the adenine complexes (1)–(3).

The coordination of Cu(2) is distorted square pyramidal with Cl(2) of the adjacent structural unit at x, $-1 + y$, z occupying the apical position. The Cu(2)–Cl(2) distance of 2·754 (1) Å is much shorter than the axial Cu(1)–Cl(6) distance of 3·072 (2) Å. As observed for Cu(1), the terminal basal bonds, Cu(2)–Cl(5) and Cu(2)–Cl(6), are shorter than the bridging basal bonds, Cu(2)–Cl(3) and Cu(2)–Cl(4). Cu(2) is displaced 0·218 (1) Å from the least-squares plane through the basal Cl atoms. The distances of the Cl atoms from this plane are: Cl(3) 0·057 (2), Cl(4) −0·059 (2), Cl (5) −0·054 (2) and Cl (6) 0·056 (2) Å.

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