Crystal Structure of Octachlorobis(adeninium)tricopper(II) Tetrahydrate: A Trinuclear Complex with Bridging Adenine

By **P. de Meester** and **A. C. Skapski,*** Chemical Crystallography Laboratory, Imperial College, London SW7 2AY

The structure of the title compound has been determined from three-dimensional X-ray diffractometer data. The crystals are monoclinic, with a = 11·134, b = 12·726, c = 10·404 Å, β = 119° 30′, Z = 2, space group $P2_1/c$. Full-matrix least-squares refinement, using 1187 independent reflections, has reached R 0·051.

The complex, which has $\bar{1}$ crystallographic symmetry, is trinuclear with two adenine molecules bridging three copper atoms *via* N(3) and N(9). Each adenine molecule spans a Cu $\cdots$ Cu separation of 3·479 Å. The central copper atom is six-co-ordinate, with two N(3) atoms at 2·027 Å, and four chlorine bridging atoms forming two strong (2·313 Å) and two weak bonds (2·766 Å). The two terminal copper atoms are five-co-ordinate: Cu–N(9) 2·028 Å, Cu–Cl(terminal) 2·272 and 2·291 Å, and Cu–Cl(bridge) 2·324 and 2·743 Å. The co-ordination geometry is based on a square pyramid. A chlorine atom from an adjacent trinuclear unit occupies the sixth pseudo-octahedral position at 3·274 Å.

Molecules of water of solvation, all non-donor nitrogen atoms of adenine and the chlorine atoms take part in a network of hydrogen bonds in which linkages of the type N–H $\cdots$ O, N–H $\cdots$ Cl, and probably O–H $\cdots$ Cl are involved. The adenine molecule is protonated at N(1).

CERTAIN transition-metal ions are known to denature DNA reversibly.[1,2] Most studies on the binding of metals to nucleotides, nucleosides, and nucleotide bases have been carried out for solutions, and only a few X-ray structural determinations on such compounds have been undertaken. The structures of three copper–adenine (ade) complexes have been reported recently. They are those of the inner complex $[Cu(C_5H_4N_5)_2(H_2O)]_2,6H_2O$,[3] $[Cu(ade)_2Cl]_2Cl_2,6H_2O$,[4] in both of which adenine acts as a bridging ligand, and $[Cu(adeH)_2Br_2]Br_2$,[5] in which adenine acts as a unidentate ligand. In an attempt to crystallise $Cu(ade)Cl_2$ [6,7] a new complex was obtained from dilute hydrochloric acid.[8] An X-ray structure determination has shown that its formula is $Cu_3Cl_8(adeH)_2,4H_2O$, and that this trinuclear complex contains both adenine and chlorine bridges and five- and six-co-ordinate copper(II). A preliminary account of this work has appeared.[9]

EXPERIMENTAL

Octachlorobis(adeninium)tricopper(II) tetrahydrate crystallises from *ca.* 2M-hydrochloric acid as green elongated prisms. All crystals examined were found to be twinned and the intensity data were collected from a fragment broken off a twinned crystal.

Crystal Data.—$C_{10}H_{20}Cu_3Cl_8N_{10}O_4$, M = 818·2, Monoclinic, a = 11·134(4) b = 12·726(2), c = 10·404(3) Å, β = 119·49(3)°, U = 1283·1 Å^3, D_m = 2·10, Z = 2, D_c = 2·12, $F(000)$ = 810. Space group $P2_1/c$ from systematic absences:[10] $h0l$, $l = 2n + 1$; and $0k0$, $k = 2n + 1$. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 110·3 cm^{-1}.

Cell data were determined from preliminary Weissenberg photographs. The single-crystal fragment used to collect

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[1] G. L. Eichhorn, *Adv. Chem. Ser.*, 1967, No. **62**, 378, and references therein.

[2] G. L. Eichhorn and Yong Ae Shin, *J. Amer. Chem. Soc.*, 1968, **90**, 7323.

[3] E. Sletten, *Acta Cryst.*, 1969, **B25**, 1480.

[4] P. de Meester, D. M. L. Goodgame, K. A. Price, and A. C. Skapski, *Nature*, 1971, **229**, 191; P. de Meester and A. C. Skapski, *J. Chem. Soc.* (*A*), 1971, 2167.

[5] P. de Meester, D. M. L. Goodgame, K. A. Price, and A. C. Skapski, *Biochem. Biophys. Res. Comm.*, 1971, **44**, 510.

[6] R. Weiss and H. Venner, *Z. physiol. Chem.*, 1963, **333**, 169.

[7] D. M. L. Goodgame and K. A. Price, Proc. XII Internat. Conf. Co-ordination Chem., Sydney, 1969, 131.

[8] D. M. L. Goodgame and K. A. Price, to be published.

[9] P. de Meester, D. M. L. Goodgame, K. A. Price, and A. C. Skapski, *Chem. Comm.*, 1970, 1573.

[10] D. L. Sales, M.Sc. Thesis, University of London, 1969.

intensity data was of size *ca.* 0·03 × 0·10 × 0·09 mm. It was mounted about the *a* axis on a Siemens off-line automatic four-circle diffractometer, and Cu-K_{α} radiation at a take-off angle of 4·5°, a Ni β filter and a Na(Tl)I scintillation counter were used. Accurate unit-cell dimensions were obtained by the method of least squares by use of 62 θ values measured on the diffractometer for high-angle α_1 and α_2 reflections. The intensities of 1187 independent reflections (to θ = 50°) were measured by use of the θ—2θ scan technique with a 'five-value' measuring procedure.[11] Of these 171 reflections were judged to be unobserved as the net count was $<2{\cdot}58\sigma$. The 040 reflection was measured as a reference every 20 reflections, and its net count did not vary noticeably during the data collection (*ca.* 7 days). The data were scaled by use of the reference reflection and the Lorentz and polarisation corrections were applied. At a later stage an absorption correction was calculated according to the method of Busing and Levy,[12] using an 8 × 8 × 8 grid with crystal pathlengths determined by the vector analysis procedure of Coppens *et al.*[13]

Solution and Refinement of the Structure.—The crystal structure calculations system '*X*-ray '63' was used in the solution and refinement of the structure.[14] Calculations were carried out on the Imperial College IBM 7094 and the University of London CDC 6600 computers. Full-matrix least-squares refinement was used throughout and the function minimised was $\Sigma w(F_o - F_c)^2$. Atomic scattering factors were taken from ref. 15 and the real and the imaginary parts of the anomalous dispersion correction for copper and chlorine were taken from ref. 16.

A Patterson synthesis indicated that the copper atoms were located on a centre of symmetry at 0,0,0 and in a general position of *ca.* ¼,0,0. Because of these special or pseudo-special positions of the heaviest atoms considerable difficulty was experienced in correctly locating the chlorine atoms. Eventually a refinement with two copper and two chlorine atoms gave *R* 0·42. A difference-Fourier synthesis showed the positions of the two remaining chlorine atoms. Although *R* dropped only marginally to 0·40 when these were included, the complete adenine molecule and water molecules of hydration could now be located. Isotropic refinement of all non-hydrogen atoms reduced *R* to 0·086, and, when these atoms were allowed to refine with anisotropic temperature factors, *R* was further reduced to 0·060. At this stage all the hydrogen atoms attached to the adeninium ligand and to one water oxygen were located, and were included in subsequent refinement as a fixed-atom contribution with isotropic temperature factors of the parent atom (*R* 0·057). An absorption correction was now applied, and refinement as previously gave *R* 0·051. In the final stages a weighting scheme of the type suggested by Hughes [17] was used, where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 35$ found to be optimum. Although *R* remained unchanged the standard deviations decreased by *ca.* 15%.

The final fractional co-ordinates of the non-hydrogen atoms and their estimated standard deviations are listed in Table 1, while Table 2 shows the coefficients in the expression for the anisotropic temperature factors exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and also the last isotropic temperature factors *B*. Table 3 lists the co-ordinates of the hydrogen atoms, and the observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20488 (2 pp., 1 microfiche).†

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

	x	*y*	*z*
Cu(1)	0·28560(12)	0·00629(9)	−0·05191(13)
Cu(2)	0	0	0
Cl(1)	0·0526(2)	0·1227(2)	−0·1288(2)
Cl(2)	0·1964(2)	−0·1379(2)	0·0101(2)
Cl(3)	0·4249(2)	0·1253(2)	−0·0808(2)
Cl(4)	0·2022(2)	−0·0575(2)	−0·2845(2)
N(1)	0·2074(8)	0·1151(6)	0·4334(8)
C(2)	0·1181(10)	0·0830(7)	0·2985(10)
N(3)	0·1497(7)	0·0597(5)	0·1937(7)
C(4)	0·2871(9)	0·0768(6)	0·2369(8)
C(5)	0·3822(9)	0·1106(6)	0·3753(10)
C(6)	0·3462(10)	0·1292(7)	0·4841(10)
N(7)	0·5071(7)	0·1159(6)	0·3787(8)
C(8)	0·4810(9)	0·0878(7)	0·2452(9)
N(9)	0·3499(7)	0·0628(5)	0·1541(7)
N(10)	0·4327(9)	0·1554(7)	0·6223(8)
O(1)	0·1031(7)	0·1884(5)	0·5980(7)
O(2)	0·7036(7)	0·1871(6)	0·6461(7)

TABLE 2

Final anisotropic thermal parameters and the last isotropic temperature factors (at *R* 0·086)

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$	B/Å^2
Cu(1)	78(2)	59(1)	85(2)	−6(1)	59(1)	−4(1)	2·93(6)
Cu(2)	66(2)	59(1)	71(2)	−8(1)	45(2)	−2(1)	2·69(7)
Cl(1)	88(3)	62(2)	95(3)	−4(2)	66(1)	0(2)	3·16(9)
Cl(2)	98(3)	59(2)	106(3)	−1(2)	72(2)	0(2)	3·39(9)
Cl(3)	115(3)	62(2)	105(3)	−15(2)	78(2)	−1(2)	3·59(9)
Cl(4)	78(3)	79(2)	94(3)	−4(2)	59(2)	−15(2)	3·40(9)
N(1)	92(10)	61(6)	69(11)	−7(6)	62(8)	−6(6)	2·9(3)
C(2)	101(13)	60(7)	99(14)	0(7)	71(12)	−8(7)	3·4(3)
N(3)	54(9)	55(6)	77(10)	−3(5)	50(7)	2(5)	2·2(3)
C(4)	89(13)	45(7)	75(12)	−1(6)	48(10)	9(7)	3·0(3)
C(5)	98(13)	47(7)	109(15)	−11(7)	70(11)	−8(7)	2·6(3)
C(6)	111(15)	52(7)	136(17)	−18(7)	85(12)	7(8)	3·2(4)
N(7)	46(9)	70(6)	86(12)	−7(6)	47(8)	1(6)	2·7(3)
C(8)	76(12)	57(7)	82(13)	−8(7)	40(10)	1(7)	3·4(4)
N(9)	61(9)	45(5)	82(10)	−4(5)	54(8)	−4(5)	2·5(3)
N(10)	147(13)	83(7)	55(12)	−41(7)	58(10)	−19(6)	4·2(3)
O(1)	159(10)	70(5)	130(10)	27(6)	110(8)	15(5)	4·1(3)
O(2)	112(9)	82(6)	109(10)	−34(6)	19(7)	20(6)	4·8(3)

TABLE 3

Fractional co-ordinates of the hydrogen atoms

	x	*y*	*z*
H(1)[N(1)] *	0·185	0·150	0·510
H(2)[C(2)]	0·025	0·067	0·256
H(7)[N(7)]	0·611	0·125	0·466
H(8)[C(8)]	0·555	0·070	0·213
H(101)[N(10)]	0·541	0·162	0·653
H(102)[N(10)]	0·402	0·137	0·683
H(21)[O(2)]	0·708	0·262	0·633
H(22)[O(2)]	0·805	0·150	0·733

* The atom in square brackets is that to which the hydrogen is attached.

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[11] A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, **B26**, 716.

[12] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[13] P. Coppens, L. Leiserowitz, and D. Rabinovitch, *Acta Cryst.*, 1965, **18**, 1035.

[14] '*X*-Ray '63,' J. M. Stewart, University of Maryland Technical Report, TR 64 6.

[15] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[16] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[17] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure contains trinuclear units of formula $Cu_3Cl_8(adeH)_2$ and water molecules of solvation, held together by a network of hydrogen bonds. Figure 1 shows the geometry of this trinuclear group and also the thermal vibration ellipsoids[18] of all the non-hydrogen atoms. The more important interatomic distances and bond angles are given in Table 4.

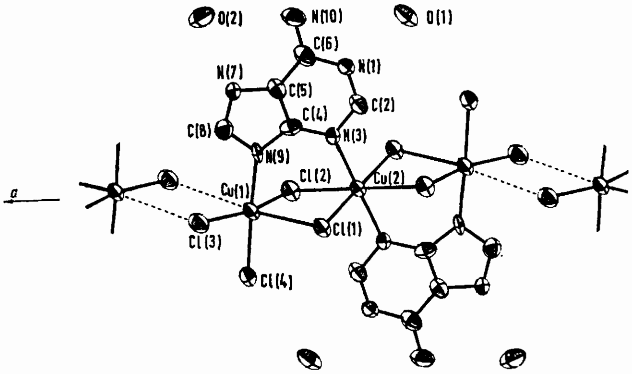

FIGURE 1 The structure of trinuclear $Cu_3Cl_8(adeH)_2$ with the water molecules of solvation also indicated. The thermal vibration ellipsoids are scaled to enclose 50% probability

TABLE 4

Interatomic distances (Å) and bond angles (°) with standard deviations in parentheses

(*a*) Distances			
Cu(1)–N(9)	2·028(7)	Cu(2)–N(3)	2·027(5)
Cu(1)–Cl(1)	2·743(3)	Cu(2)–Cl(1)	2·313(3)
Cu(1)–Cl(2)	2·324(3)	Cu(2)–Cl(2)	2·766(3)
Cu(1)–Cl(3)	2·291(3)	Cu(1) · · · Cu(2)	3·479(2)
Cu(1)–Cl(4)	2·272(3)	Cu(1) · · · Cl(3^{I})	3·274(3)
N(1)–C(2)	1·323(10)	C(6)–N(10)	1·319(11)
C(2)–N(3)	1·334(15)	C(5)–N(7)	1·375(14)
N(3)–C(4)	1·383(12)	N(7)–C(8)	1·320(13)
C(4)–C(5)	1·371(10)	C(8)–N(9)	1·330(10)
C(5)–C(6)	1·394(17)	N(9)–C(4)	1·361(14)
C(6)–N(1)	1·377(13)		
(*b*) Angles			
Cl(1)–Cu(1)–Cl(2)	92·0(1)	Cl(1)–Cu(2)–Cl(2)	91·7(1)
Cl(1)–Cu(1)–Cl(3)	102·1(1)	Cl(1)–Cu(2)–N(3)	90·2(2)
Cl(1)–Cu(1)–Cl(4)	92·9(1)	Cl(2)–Cu(2)–N(3)	87·3(2)
Cl(1)–Cu(1)–N(9)	84·7(2)		
Cl(2)–Cu(1)–Cl(3)	165·4(1)	Cu(1)–N(9)–C(4)	133·7(5)
Cl(2)–Cu(1)–Cl(4)	90·4(1)	Cu(1)–N(9)–C(8)	122·0(7)
Cl(2)–Cu(1)–N(9)	87·9(2)	Cu(2)–N(3)–C(2)	118·5(6)
Cl(3)–Cu(1)–Cl(4)	92·5(1)	Cu(2)–N(3)–C(4)	128·2(6)
Cl(3)–Cu(1)–N(9)	89·7(2)		
Cl(4)–Cu(1)–N(9)	177·0(2)		
C(2)–N(1)–C(6)	124·3(1·0)	N(1)–C(6)–N(10)	122·0(1·2)
N(1)–C(2)–N(3)	124·9(1·0)	C(5)–C(4)–N(9)	109·5(8)
C(2)–N(3)–C(4)	113·3(7)	C(4)–C(5)–N(7)	106·8(1·0)
N(3)–C(4)–C(5)	123·3(1·0)	C(5)–N(7)–C(8)	105·3(7)
C(4)–C(5)–C(6)	121·6(9)	N(7)–C(8)–N(9)	114·2(1·0)
C(5)–C(6)–N(1)	112·5(8)	C(8)–N(9)–C(4)	104·1(7)
C(5)–C(6)–N(10)	125·4(1·0)		

Superscript refers to atom in the following position:
I $1 - x, -y, -z$

The complex has $\bar{1}$ crystallographic symmetry, with Cu(2) located on a centre of symmetry. This central copper atom is joined to the other two by four bridging chlorine atoms and two adeninium groups. The adeninium ligands are co-ordinated to Cu(2) *via* N(3) and to Cu(1) *via* N(9). Thus the central copper atom has an octahedral co-ordination with two Cu(2)–N(3) bonds of 2·027 Å, two strong Cu(2)–Cl(1) bonds (2·313 Å) and two weak Cu(2)–Cl(2) bonds (2·766 Å). The two outer copper atoms are five-co-ordinate with a geometry based on the square pyramid. Thus Cu(1) is bonded to N(9) (2·028 Å), to two terminal chlorine atoms Cl(3) and Cl(4) (2·291 and 2·272 Å), and to two bridging chlorine atoms, Cl(2) and Cl(1) (2·324 and 2·743 Å). This last weak bond is the apical one. The sixth, pseudo-octahedral position is occupied by a chlorine atom from a neighbouring trinuclear unit, but at 3·274 Å.

It can be seen that all three copper atoms form four strong bonds. In the case of the central atom these bonds form an exact plane, while for the other two metal atoms the arrangement is nearly planar, and all three ' planes ' are approximately parallel. Figure 2 which is a schematic drawing of the copper co-ordination polyhedra shows this feature also.

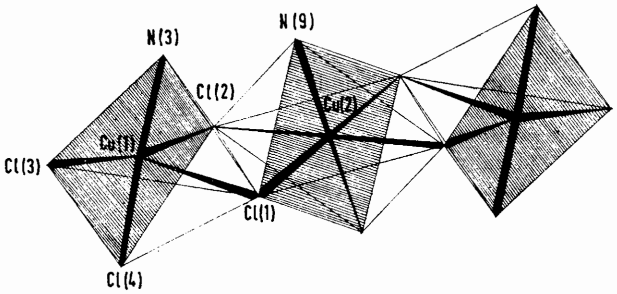

FIGURE 2 A schematic drawing showing the copper co-ordination polyhedra. The shaded planes, which are approximately parallel, contain the four strong bonds about each metal atom

The bridging chlorine atoms form one strong bond of *ca.* 2·3 Å and one weak one of *ca.* 2·75 Å. Such asymmetry is a common feature for halide bridges.[19] The two terminal Cu–Cl distances are as expected slightly shorter than the two strong Cu–Cl bridging bonds. They may be compared with a terminal Cu–Cl distance of 2·28 Å found in the 2 : 1 cytosine–copper chloride complex.[20] The weak Cu–Cl bonds of *ca.* 2·75 Å are again fairly typical of 4 + 2 or 4 + 1 co-ordinated copper(II). For instance, Sletten finds a distance of 2·785 Å in a 9-methylhypoxanthine–copper(II) complex.[21] The distances Cu(1)–N(9) and Cu(2)–N(3) are almost identical, and are very similar to those found in other bridging-adenine[3,4] or -hypoxanthine[22] complexes. The Cu · · · Cu separation (3·479 Å) however, is unusually long and merits further comment.

One can assume that the ideal Cu · · · Cu separation,

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[18] C. K. Johnson, ORTEP thermal ellipsoid plotting program, Oak Ridge National Laboratory Report, 1965, ORNL 3794.

[19] R. Colton and J. H. Canterford, ' Halides of the First-Row Transition Metals,' Wiley–Interscience, New York, 1969, ch. 9.

[20] J. A. Carrabine and M. Sundaralingam, *Chem. Comm.*, 1968, 746.

[21] E. Sletten, *Chem. Comm.*, 1971, 558.

[22] E. Sletten, *Acta Cryst.*, 1970, **B26**, 1609.

from the viewpoint of adenine, is when the angles Cu–N(3)–C(2) and Cu–N(3)–C(4) are equal, and similarly for Cu–N(9)–C(4) and Cu–N(9)–C(8). Cu–N distances of just over 2 Å lead to a Cu · · · Cu separation of 3·0—3·1 Å. The complex $[Cu_2(ade)_4Cl_2]Cl_2,6H_2O$ [4] corresponds very nearly to this 'neutral' situation with Cu · · · Cu of 3·066 Å and the angles at N(3) and N(9) bent outwards by only 0·3°. The inner complex, $[Cu_2(C_5H_4N_5)_4(H_2O)_2],6H_2O$,[3] with Cu · · · Cu 2·947 Å has an average bending inwards of *ca.* 2°, but concentrated mainly at N(3). In case of the title compound the Cu · · · Cu separation enforces an outward distortion in the Cu–N–C angles of 5—6°, without, it seems, any appreciable weakening of the Cu–N bonds. Since the copper atoms are in all these cases at non-bonding distances from each other their separation clearly depends on the atoms co-ordinated to them, and on the detailed co-ordination geometry at the metal atom, for instance in the case of square-pyramidal co-ordination the extent to which the metal atom is above the base of the pyramid depending on the identity of the apical atom. The equilibrium separation is achieved mainly at the expense of angular distortions at the donor nitrogen atoms, rather than of any lengthening of the copper–ligand bonds. In the title compound the dominant feature seems to be the preference of copper(II) for a 4 + 2 or 4 + 1 co-ordination and the resulting asymmetry of the chloride bridge system. Indeed, it seems likely that if one were to substitute bromide bridges in the title complex an even greater Cu · · · Cu separation would result, with a concomitant further slight angular distortion at the N(3) and N(9) atoms.

The adeninium ligand is protonated at N(1), and the hydrogen atom involved, H(1), was clearly visible on a difference-Fourier synthesis. When a trial least-squares calculation was carried out in which H(1) was allowed to refine, this atom remained very close to the position found in the difference Fourier, and a reasonable N(1)–H(1) distance and temperature factor were obtained. Bonding within the adeninium ligand and comparison with that found in other similar complexes will be discussed in a separate publication.[23]

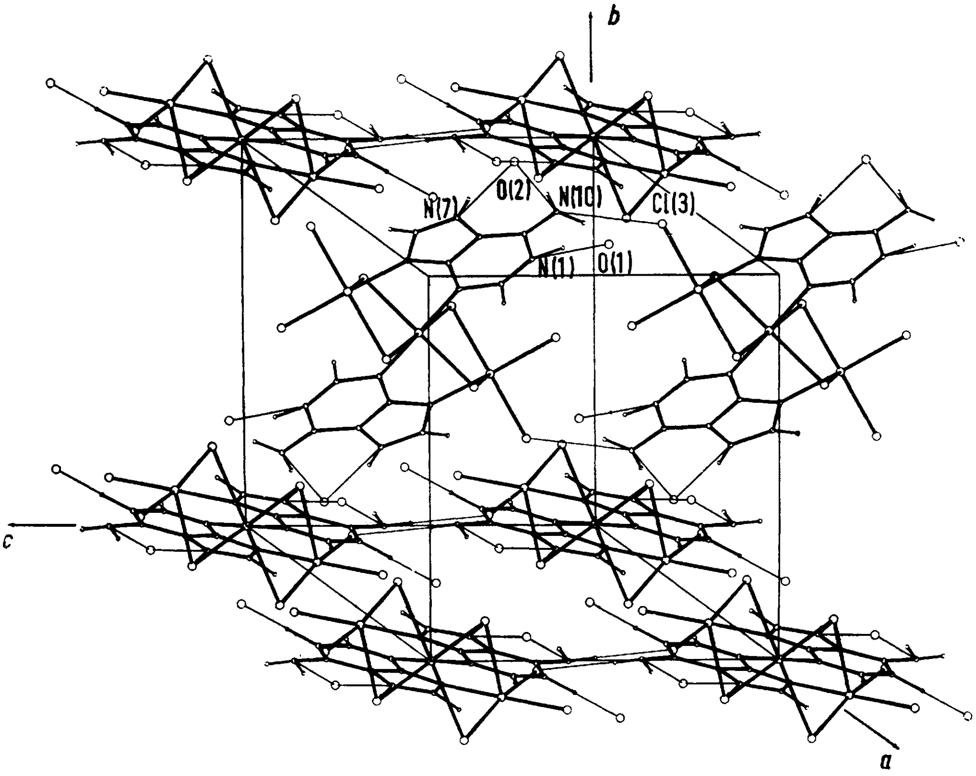

FIGURE 3 A diagram showing the packing of $Cu_3Cl_8(adeH_2)$ trinuclear units and water molecules of solvation. Only definite hydrogen bonds are indicated. (The atom labels show atom type and do not refer to atomic positions listed in Table 1)

A network of hydrogen bonds connects the trinuclear units and the water molecules. The packing of these groups is shown in Figure 3, while all definite or possible hydrogen bonding distances are listed in Table 5. The water molecule centred on O(2) forms two definite hydrogen bonds to N(7) and N(10), both of which have their own hydrogen atoms. There are also two chlorine atoms at distances *ca.* 3·25 Å. These distances are consistent with weak hydrogen bonding, and since the water molecule has its two hydrogen atoms free one would expect these to take part in such bonds. However, the two hydrogen atoms, H(21) and H(22), as located from a

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[23] P. de Meester and A. C. Skapski, *J.C.S. Dalton*, to be published.

difference-Fourier synthesis and whose positions seem in every way reasonable, do not point even approximately in the direction of these chlorine atoms. The other water molecule, centred on O(1), has one definite strong hydrogen bond to the protonated N(1) atom. The water hydrogen atoms could not be located with any confidence, but there are three chlorine atoms in the vicinity at distances 3·22—3·34 Å. These three chlorine atoms, O(1), and N(1) are approximately coplanar, so clearly not all the chlorine atoms can be taking part in hydrogen bonding, although it may well be that some of these three do. In both this structure and that of $[Cu_2(ade)_4Cl_2]Cl_2,6H_2O$ [4] the same two nitrogen atoms, N(1) and N(7), are involved in the strongest and the second strongest hydrogen bonds respectively; thus in the former N(1)–H ··· O(1) is 2·67 and N(7)–H ··· O(2) 2·71 Å, while in the latter N(1) ··· H–O(1) is 2·71 and N(7)–H ··· O(1) is 2·80 Å.

TABLE 5

Potential hydrogen bonding distances (Å)

N(1)–H(1) ··· O(1)	2·667(13)
O(1) ··· Cl(1^{II})	3·217(7)
O(1) ··· Cl(1^{III})	3·267(9)
O(1) ··· Cl(4^{III})	3·343(7)
N(7)–H(7) ··· O(2)	2·712(9)
N(10)–H(101) ··· O(2)	2·930(14)
O(2) ··· Cl(2^{IV})	3·259(9)
O(2) ··· Cl(2^{V})	3·240(8)
N(10)–H(102) ··· Cl(3^{III})	3·156(10)

Superscripts refer to atoms in the following positions:

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

A least-squares calculation performed to test the planarity of the adeninium ligand, showed that the amino-group nitrogen, N(10), was not strictly in the plane of the ligand. When only the atoms of the pyrimidine and imidazole rings were used to define the plane the result was much more satisfactory, with all atoms within 2σ of the plane. The results are summarised in Table 6. The deviation of N(10) from this plane, *ca.* 0·1 Å, is slight but statistically significant, as is also that of the two copper atoms bonded to N(3) and N(9).

TABLE 6

Planarity of the adeninium ligand. The equation of the plane is: $-0{\cdot}549x + 12{\cdot}10y - 2{\cdot}51z = 0{\cdot}176$ and the atoms defining it are N(1), N(3), N(7), N(9), C(2), C(4)–(6), and C(8)

Deviations (Å) of atoms from the plane: *

N(1) −0·013, C(2) −0·014, N(3) 0·023, C(4) 0·000, C(5) −0·009, C(6) 0·020, N(7) 0·004, C(8) −0·006, N(9) −0·004, N(10) 0·097, Cu(1) 0·126, Cu(2) 0·176

* $\sigma\Delta = 0{\cdot}013$ Å.

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