

Crystallographic Studies of Metal–Nucleotide Base Complexes.

I. Triclinic Bis-(6-aminopurine)copper(II) Tetrahydrate

BY EINAR SLETTEN*

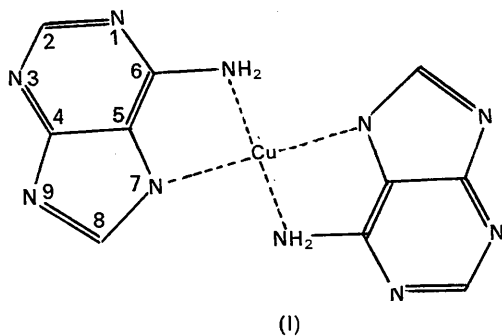
Department of Biological Structure, University of Washington, Seattle, Washington, 98105, U.S.A.

(Received 1 July 1968)

Triclinic bis-(6-aminopurine)copper(II) tetrahydrate crystallizes in space group $P\bar{1}$ with $Z=2$ and $a=9.458$, $b=10.452$, $c=9.410$ Å and $\alpha=102.98$, $\beta=116.58$, $\gamma=79.81^\circ$. The crystal structure has been established by a three-dimensional single crystal X-ray analysis. The atomic parameters were refined by full-matrix least-squares; the final R is 0.053 for 2614 observed reflections measured on a manually operated diffractometer with Mo $K\alpha$ radiation. The complex is a dimer and geometrically resembles copper(II) acetate monohydrate. The four atoms closest to the copper ion are situated in the basal plane of an octahedron; two of these are the N(3) atoms in the pyrimidine rings (mean Cu–N(3) distance 2.032 Å) and the other two, the N(9) atoms in the imidazole rings (mean Cu–N(9) distance 2.007 Å). The copper ion is displaced 0.27 Å out of the equatorial plane toward an apical coordinated water molecule (Cu–O, 2.195 Å). The sixth position in the octahedron is occupied by another copper ion at 2.949 Å. The structure is disordered and for this reason the geometry of the adenine ligands is less well established. The structure of the complex is discussed in relation to the magnetic properties of the compound.

Introduction

In recent years, much effort has been directed toward clarifying the role of purine bases in complexes with bivalent cations. Cheney, Freiser & Fernando (1959) tried to establish the structure of purine derivative complexes of metal ions by titration methods. Earlier, Harker & Freiser (1958) had suggested that the most probable chelating sites in a 2:1 adenine–copper complex were the nitrogen atom N(7) and the amino group substituted on C(6) (I).



Weiss & Venner (1966) have carried out extensive synthetic work on transition metal complexes of purine derivatives. They concluded that the chelating sites of copper adenine complexes are probably the nitrogen atoms N(3) and N(9).

The present structure investigation is the first in a programme of crystallographic studies of metal-

nucleotide base complexes. A preliminary report on the structure has appeared (Sletten, 1967).

Experimental

Bis-(6-aminopurine)copper(II) tetrahydrate was crystallized from a 10% ethanol–water mixture in the form of blue-violet, opaque prisms. The crystals turn into powder when dried over silica gel. The chemical analysis of the dried compound indicates three molecules of water per formula unit (Weiss & Venner, 1963). Weissenberg photographs showed that the crystals belong to a triclinic space group. The density measured by floatation in a mixture of 1,1,2,2-tetrabromoethane and carbon tetrachloride indicates four molecules of water per formula unit.

The compound also crystallizes in a monoclinic form from a 50% *p*-dioxane–water solution. This modification is unstable when exposed to air.

Cell dimensions for each crystal form were determined by least-squares treatment of 2θ settings measured on the diffractometer (Mo $K\alpha$ radiation, $\lambda=0.71069$ Å).

By comparing the dimensions of the monoclinic cell with those of the *C*-centered triclinic cell, it is noticed that the major difference is roughly a doubling of the unit translation along **a**.

Crystal data

Triclinic form
 $(C_5H_4N_5)_2Cu \cdot 4H_2O$
 Space group:

$P\bar{1}$ $C\bar{1}$
 $Z=2$ $Z=4$

Monoclinic form:
 $(C_5H_4N_5)_2Cu \cdot 3\frac{1}{2}H_2O$
 Space group:
 $I2, Im$ or $I2/m$
 $Z=8$

* Permanent address: Department of Chemistry, University of Bergen, Bergen, Norway.

$$\begin{array}{lll}
 a = 9.458(2) & a' = 9.917(2) \text{ \AA} & a = 17.209(3) \text{ \AA} \\
 b = 10.452(2) & b' = 16.052(3) & b = 17.636(4) \\
 c = 9.410(2) & c' = 10.452(2) & c = 11.020(2) \\
 \alpha = 102.98(2)^\circ & \alpha' = 103.65(2)^\circ & \beta = 92.01(1)^\circ \\
 \beta = 116.58(2) & \beta' = 92.55(1) & \\
 \gamma = 79.81(1) & \gamma' = 90.32(3) & \\
 V_{pT} = 807.54 \text{ \AA}^3 & & V = 3342.50 \text{ \AA}^3 \\
 D_x = 1.66 \text{ g.cm}^{-3} & & D_x = 1.57 \text{ g.cm}^{-3} \\
 D_m = 1.68 \text{ g.cm}^{-3} & & D_m = 1.56 \text{ g.cm}^{-3} \\
 \mu = 14.5 \text{ cm}^{-1} & &
 \end{array}$$

Data collection

The crystal used for data collection had dimensions of $0.15 \times 0.20 \times 0.40$ mm and was mounted along the needle axis. Integrated intensities were measured by the moving-crystal moving-counter technique using Nb-filtered Mo $K\alpha$ radiation. The scan ranges were calculated according to the relation $\Delta 2\theta = A + B \tan \theta$ (Alexander & Smith, 1964). The crystal had fairly large mosaic spread and the constant A was assigned a value of 2.4° , derived from measurements of the scan range sufficient for strong, low ordered reflections. The constant B was set equal to 1.0° , a value which has been found to be satisfactory for Mo radiation.

Within the sphere of reflection, limited at $\sin \theta/\lambda = 0.6$, 2839 unique reflections were measured. Of these, 225 were less than the threshold value of σ_c , $\sigma_c = (N_{B1} + N_{pk} + N_{B2})^{1/2}$ where N_{B1} and N_{B2} are the background counts on each side of the peak and N_{pk} is the counts in a scan. The estimated error in the net intensity of each reflection is $\sigma_I = [\sigma_c^2 + (0.01\sigma_c^2)^2]^{1/2}$. The data were corrected for Lorentz and polarization effects and coincidence loss (Sletten, Sletten & Jensen, 1969). Absorption correction was not made. As a result, the structure factors suffer from absorption effects; the minimum reduction, occurring at low 2θ , is 11% and the maximum reduction, at a 2θ of 50° , is somewhat less than 18%. The standard deviation in the structure factors was taken as $\sigma_F = [F^2 + \sigma_I(Lp)^{-1}]^{1/2} - F$.

Structure determination

The copper ion was located by a three-dimensional Patterson synthesis, and a Fourier synthesis based on the phases determined by the heavy atom, revealed the position of the two adenine ligands and the water molecule O(1) coordinated to copper.

The noncoordinating water molecules could not be located unambiguously in the first electron density map. Five peaks with appreciably lower electron density than the coordinated water molecule O(1) were found. A succeeding Fourier synthesis based on the phases determined by the heavy atom, the atoms in the adenine ligands and O(1) showed essentially the same features. One peak close to a center of symmetry and two other peaks only 1 Å apart indicated the presence of disordered water molecules. Oxygen atoms with multiplicities 0.5 were assigned to these sites, while

oxygen atoms of unit multiplicities were initially assigned to the remaining two sites. Structure factor calculations were based on the following scattering curves: copper(II) ion, Watson & Freeman (1961); oxygen, nitrogen, carbon, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); hydrogen, Stewart, Davidson & Simpson (1965). All calculations were carried out on an IBM 7094 computer with programs from *X-ray 63* (Stewart, 1964).

The structure with isotropic thermal parameters was refined in four cycles of full-matrix least-squares to an R of 0.16 [$R = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|$]. The function minimized was $\Sigma w[|F_o| - (1/k)F_c]^2$ where $w = 1/\sigma_F^2$. In the last two isotropic cycles the multiplicities of the disordered water molecules were allowed to vary while the thermal parameters were kept constant. The multiplicities arrived at are listed in Table 2(a). Owing to limited data ($\sin \theta/\lambda < 0.6$) the multiplicities and the thermal parameters could not be refined simultaneously. Thus only a rough estimate of the occupancies of the different oxygen sites can be obtained. At this stage, a difference map gave the positions of the hydrogen atoms attached to the adenine ligands and the coordinated oxygen O(1). However, one hydrogen atom in each of the amino groups had suspiciously large electron density ($0.8 \text{ e.}\text{\AA}^{-3}$) while the other amino hydrogen barely showed up ($0.25 \text{ e.}\text{\AA}^{-3}$).

Two cycles of refinement with anisotropic thermal parameters assigned to the non-hydrogen atoms brought the R to 0.075. The hydrogen atoms were included in the structure factor calculation but not refined. In the following cycle only the atoms which carry hydrogens were included in the refinement together with the attached hydrogen atoms. The R decreased to 0.065 and the hydrogen atoms attached to the rings and to the oxygen O(1) refined to reasonable positions and B values. The four hydrogen atoms in the amino groups, however, behaved differently. The two atoms which appeared with unusually large electron densities in the difference map [H(612), H(622)] had B values of only $1.2\text{--}1.5 \text{ \AA}^2$ and refined to positions which did not comply with the geometry of sp^2 hybridized nitrogen atoms. The two other hydrogen atoms [H(611) and H(621)] showed high thermal motion and refined to positions which were not physically meaningful.

A calculation of bond lengths and angles at this stage gave some peculiar values for one of the adenine ligands. The carbon-carbon bonds C(41)–C(51) and C(51)–C(61) were calculated at 1.55 \AA and 1.21 \AA , respectively, values deviating appreciably from the expected value of 1.4 \AA . Furthermore, the bond C(61)–N(61) expected to be $1.35 \pm 0.05 \text{ \AA}$ was calculated to be 1.52 \AA . The other dimensions in ligand (1) were within the expected range and agreed well with those calculated for ligand (2). A three-dimensional difference map showed alternate positive and negative regions of approximately $0.9 \text{ e.}\text{\AA}^{-3}$ in the vicinity of atoms C(51) and C(61), a pattern indicating that each of the two atoms tried to match two discrete peaks of electron

density. In the corresponding region in ligand (2) two 'satellite' peaks, $0.4 \text{ e.}\text{\AA}^{-3}$ in height, were found; however, in this case, the peaks were clearly resolved from the adjacent carbon atoms C(52) and C(62), thus explaining why the geometry of this ligand was not noticeably distorted.

To account for the features described above, some kind of disorder was assumed to be present in the crystal. Accordingly, fractions of carbon atoms were assigned to the four 'satellite' peaks and refined isotropically together with the adjacent atoms. Tentatively, multiplicities of 0.2 were used for C(51') and C(61') in ligand (1) and 0.1 for C(52') and C(62') in ligand (2). After two cycles of refinement, the geometry of ligand (1) became quite reasonable, while no significant changes occurred in ligand (2).

The disorder may be explained as shown in Fig. 1. With N(3) and N(9) as donor atoms, each of the adenine ligands in the dimer may chelate to the copper

ions in two different orientations relative to the other ligands. The Figure shows that the adenine molecules in the two orientations overlap almost completely; the only atoms which do not coincide are C(5), C(6) and N(6). If the assumption is made that the oversized hydrogen atom in each of the amino groups is actually the non-coinciding nitrogen atom N(6'), the disorder is explained by the occurrence of differently oriented ligand pairs in the crystal.

To determine the approximate amount of each configuration, the multiplicities of the non-coinciding atoms in each ligand were allowed to vary during two cycles of refinement. As a starting point, the atoms C(51), C(61), N(61) were given multiplicities 0.8, while the components of the anisotropic thermal motion were reduced by 20%. The corresponding atoms in ligand (2) were assigned multiplicities 0.9 and the *B* values were reduced by 10%. The thermal parameters were kept constant during the refinement of the multi-

Table 1. Fractional atomic coordinates

	C-centered cell			Primitive cell		
	x'/a'	y'/b'	z'/c'	x/a	y/b	z/c
Cu ²⁺	0.24150 (6)	0.15797 (3)	0.43442 (5)	0.0834?	0.43442	0.39947
N(11)	0.65916 (46)	0.38523 (27)	0.45774 (42)	0.2739	0.4577	1.0444
C(21)	0.54178 (57)	0.39440 (31)	0.51607 (49)	0.1474	0.5161	0.9362
N(31)	0.45009 (39)	0.33135 (24)	0.50255 (35)	0.1187	0.5025	0.7814
C(41)	0.49443 (44)	0.25787 (30)	0.42670 (40)	0.2366	0.4267	0.7523
C(51)	0.61750 (71)	0.24083 (51)	0.36496 (65)	0.3767	0.3650	0.8583
C(61)	0.70548 (82)	0.30685 (54)	0.37869 (75)	0.3986	0.3787	1.0123
N(61)	0.82583 (61)	0.29749 (55)	0.31776 (76)	0.5283	0.3178	1.1233
N(71)	0.63317 (48)	0.15511 (27)	0.29123 (38)	0.4781	0.2912	0.7883
C(81)	0.51319 (55)	0.12601 (32)	0.31700 (45)	0.3872	0.3170	0.6392
N(91)	0.43067 (39)	0.18150 (23)	0.39261 (34)	0.2492	0.3926	0.6122
N(12)	0.10089 (56)	0.17914 (30)	0.04923 (43)	0.0782	0.9508	0.7200
C(22)	0.14332 (67)	0.15167 (32)	0.15392 (48)	0.0083	0.8461	0.7050
N(32)	0.17832 (40)	0.19890 (23)	0.27250 (33)	0.0206	0.7275	0.6228
C(42)	0.16675 (44)	0.28327 (28)	0.27760 (39)	0.1165	0.7224	0.5500
C(52)	0.12141 (65)	0.31820 (56)	0.17377 (60)	0.1968	0.8262	0.5604
C(62)	0.08838 (62)	0.26141 (41)	0.05331 (59)	0.1730	0.9467	0.6502
N(62)	0.04240 (65)	0.28674 (43)	-0.05543 (49)	0.2443	1.0554	0.6709
N(72)	0.11976 (58)	0.40817 (29)	-0.21413 (43)	0.2884	0.7859	0.4721
C(82)	0.16364 (71)	0.41982 (34)	0.33837 (52)	0.2562	0.6616	0.4165
N(92)	0.19399 (39)	0.34954 (23)	0.38319 (33)	0.1555	0.6168	0.4565
O(1)	0.24075 (62)	0.01956 (40)	0.34641 (51)	0.2212	0.3464	0.2603
O(2)	0.4804 (25)	0.0227 (9)	-0.0079 (17)	0.4577	0.9921	0.5030
O(31)	0.7834 (34)	0.0348 (11)	0.1077 (20)	0.7485	0.1077	0.8182
O(32)	0.8474 (12)	0.0953 (11)	0.1529 (12)	0.7522	0.1529	0.9427
O(41)	0.7633 (19)	0.4325 (8)	0.0992 (11)	0.3308	0.0992	0.1958
O(42)	0.4754 (10)	0.4415 (6)	0.1847 (8)	0.0339	0.1847	0.9168
C(51')	0.6173 (23)	0.3040 (14)	0.4074 (19)	0.3133	0.4073	0.9214
C(61')	0.6993 (20)	0.2373 (12)	0.3194 (17)	0.4620	0.3194	0.9366
N(61')	0.8265 (25)	0.2466 (14)	0.2731 (22)	0.5798	0.2731	1.0731
C(52')	0.1112 (55)	0.2755 (31)	0.1471 (61)	0.1643	0.8529	0.6133
C(62')	0.0968 (41)	0.3543 (26)	0.1221 (41)	0.2574	0.8779	0.5489
N(62')	0.0471 (33)	0.3583 (21)	-0.0053 (30)	0.3112	1.0052	0.5945
H(21)	0.5324 (47)	0.4473 (31)	0.5709 (45)	0.0852	0.5709	0.9797
H(81)	0.4915 (55)	0.0656 (36)	0.2756 (52)	0.4259	0.2756	0.5571
H(611)	0.889	0.355	0.323	0.5340	0.3230	1.2440
H(22)	0.1483 (49)	0.0914 (33)	0.1404 (44)	-0.0568	0.8594	0.7603
H(82)	0.1557 (56)	0.4705 (36)	0.3979 (53)	0.3148	0.6021	0.3739
H(621)	0.018	0.236	-0.129	0.218	1.129	0.746
H(011)	0.7070 (82)	0.4807 (53)	0.3671 (76)	-0.2263	0.6329	0.8124
H(012)	0.7461 (69)	0.4923 (42)	0.2792 (69)	-0.2539	0.7208	0.7616

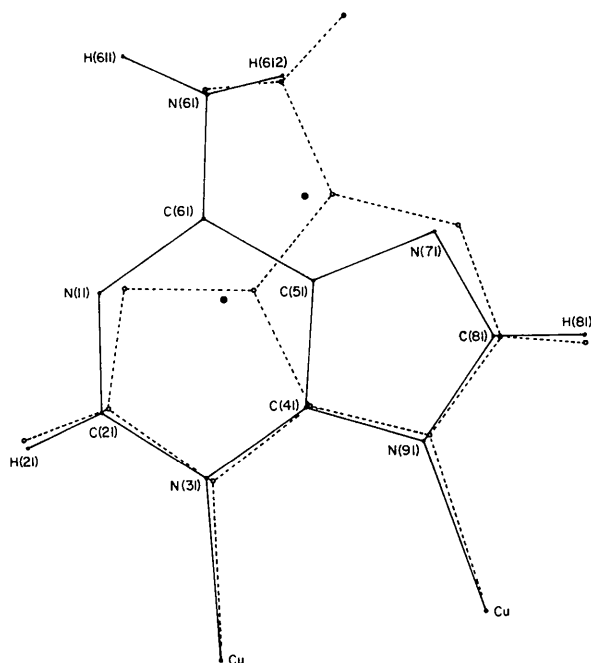


Fig. 1. The molecule drawn in full line is ligand (1) connected to the copper ions, as viewed along the c axis in the C -centered cell. The molecule in dashed lines is arrived at by rotating ligand (1) 180° around a line lying in the plane of the ligand and going through the center of symmetry, normal to the Cu-Cu 'bond'. The circles with crosses in them are the refined positions of the disordered atoms C(51') and C(61').

plicities, but were allowed to adjust during a final least-squares cycle.

Before the final least-squares cycle, a difference synthesis was calculated in an attempt to locate the hydrogen atoms attached to the disordered water molecules. Some of these could be located with reasonable certainty, although there were other equally prominent peaks in the regions close to the oxygen atoms, which could not be accounted for. The occurrence of additional peaks may imply that the scheme of disorder of the water molecules is more complex than the model used in the least-squares refinement. Accordingly, the hydrogen atoms on the non-coordinated water molecules were not included in the structure factor calculation.

In the next least-squares cycle all shifts in parameters for the atoms in the complex unit were less than one standard deviation, and the refinement was terminated at an R of 0.053, even though some of the non-coordinated water molecules had shifts in coordinates of nearly 2σ and shifts in thermal parameters of close to 4σ . The final goodness of fit of 1.97 is higher than the value expected for this type of compound, and may reflect the difficulty in assigning a proper model to the disordered structure.

The final coordinates are given in Table 1. The anisotropic and isotropic thermal parameters together with the refined multiplicities are given in Tables 2(a) and 2(b). The observed and calculated structure factors are listed in Table 3.

Table 2(a). Anisotropic thermal parameters referred to the C -centered cell, and multiplicities of disordered atoms

$$T_i = \exp \left[-\frac{1}{4}(B_{11}h^2a^*{}^2 + B_{22}k^2b^*{}^2 + B_{33}l^2c^*{}^2 + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*) \right].$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	M
Cu ²⁺	3.63 (3)	2.86 (2)	2.73 (2)	0.11 (2)	0.04 (2)	1.04 (2)	
N(11)	4.64 (13)	4.58 (20)	5.21 (21)	-1.05 (18)	-0.97 (17)	2.04 (17)	
C(21)	4.82 (28)	4.41 (22)	4.92 (24)	-1.04 (21)	-0.64 (21)	2.09 (19)	
N(31)	3.86 (19)	3.89 (17)	4.06 (17)	-0.87 (15)	-0.70 (14)	2.04 (14)	
C(41)	2.90 (19)	5.31 (22)	3.06 (17)	0.72 (17)	0.60 (14)	2.24 (16)	
C(51)	3.57 (33)	6.38 (44)	4.03 (28)	0.64 (29)	0.02 (24)	2.40 (29)	0.79
C(61)	3.80 (39)	7.56 (49)	5.57 (36)	-0.13 (33)	-0.51 (30)	3.27 (35)	0.76
N(61)	2.79 (27)	9.66 (49)	7.77 (43)	-0.03 (31)	1.72 (26)	4.35 (40)	0.78
N(71)	5.59 (26)	5.12 (20)	3.64 (17)	2.00 (19)	-0.06 (16)	0.75 (15)	
C(81)	4.60 (27)	5.14 (24)	3.86 (21)	1.60 (21)	0.51 (18)	1.00 (18)	
N(91)	3.92 (19)	3.85 (17)	3.38 (16)	0.98 (15)	0.23 (14)	1.21 (13)	
N(12)	7.90 (33)	5.44 (24)	4.37 (21)	-0.61 (22)	-1.41 (20)	1.68 (17)	
C(22)	8.80 (40)	4.26 (22)	3.84 (23)	-0.24 (24)	-1.37 (23)	1.01 (18)	
N(32)	4.53 (20)	3.75 (16)	3.04 (15)	-0.01 (15)	-0.04 (13)	1.05 (12)	
C(42)	2.81 (19)	4.40 (19)	2.86 (16)	0.05 (16)	0.49 (14)	1.49 (14)	
C(52)	4.15 (31)	5.17 (37)	3.63 (27)	0.00 (28)	-0.06 (21)	1.89 (28)	0.88
C(62)	4.56 (31)	6.10 (33)	3.30 (25)	-0.10 (25)	-0.13 (20)	1.85 (22)	0.90
N(62)	7.47 (38)	9.22 (39)	3.79 (22)	0.44 (30)	-1.11 (22)	2.91 (24)	0.87
N(72)	9.29 (36)	4.92 (22)	4.22 (21)	1.33 (22)	-0.75 (21)	1.84 (17)	
C(82)	9.26 (44)	4.08 (23)	3.88 (23)	1.12 (25)	-0.54 (24)	1.35 (19)	
N(92)	4.43 (19)	3.93 (16)	3.00 (15)	0.29 (14)	0.06 (13)	1.52 (13)	
O(1)	11.08 (45)	2.95 (20)	4.87 (26)	-0.35 (23)	1.66 (26)	0.51 (19)	
O(2)	18.8 (14)	8.4 (10)	7.2 (5)	0.9 (9)	-2.2 (6)	2.8 (6)	0.56
O(31)	26.4 (22)	7.2 (8)	12.7 (10)	0.2 (10)	12.4 (13)	0.0 (7)	0.48
O(32)	7.1 (6)	14.8 (10)	10.0 (6)	0.5 (6)	4.0 (5)	2.4 (6)	0.61
O(41)	33.8 (20)	7.7 (7)	3.0 (4)	9.3 (9)	-0.4 (7)	-0.9 (4)	0.51
O(42)	13.7 (9)	15.3 (7)	8.8 (6)	2.5 (6)	-3.9 (6)	-3.9 (5)	0.74

Table 2(b). Isotropic thermal parameters and multiplicities

	<i>B</i>	<i>M</i>
C(51')	2.8 (4)	0.28
C(61')	3.6 (3)	0.30
N(61')	5.1 (5)	0.23
C(52')	2.8 (7)	0.13
C(62')	4.8 (7)	0.13
N(62')	5.1 (6)	0.14
H(21)	3.1 (7)	
H(81)	4.5 (8)	
H(611)	15	
H(22)	5.2 (6)	
H(82)	6.9 (9)	
H(621)	15	
H(011)	7.2 (9)	
H(012)	4.5 (9)	

In Fig. 2 the electron density through the plane of ligand (1) and the electron density of the water molecules are shown projected along the c' axis. The electron density in the plane of ligand (2) is shown pro-

jected along the a' axis. The corresponding difference maps, based on F_c values excluding hydrogen atoms and the fractional atoms C(5'), C(6') and N(6'), are shown in Fig. 3.

Tests to distinguish between a centric and an acentric space group

If a center of symmetry is imposed in a non-centrosymmetric unit cell, the structure may appear to be disordered. Consequently, the possibility of having an ordered, non-centric adenine-copper structure could not be ruled out on the basis of the refinement in $P\bar{1}$.

A survey of reflection statistics was carried out at this stage (Tables 4 and 5).

The results given in Tables 4 and 5 together with an $N(z)$ plot for the $hk0$ zone gave the impression that the structure may, indeed, be noncentric. However, these

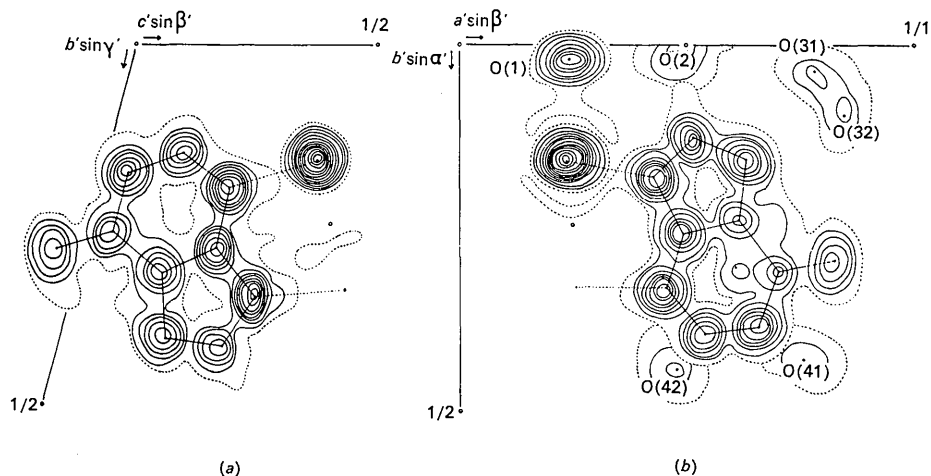


Fig. 2. (a) Electron density of the copper ion and ligand (2) projected along the a axis in the C -centered cell, (b) electron density of copper ion, water molecules and ligand (1) projected along the c axis in the C -centered cell. Contours are at intervals of $4 \text{ e.}\text{\AA}^{-3}$ for the copper ion and of $1 \text{ e.}\text{\AA}^{-3}$ for the oxygen, nitrogen and carbon atoms, starting at $1 \text{ e.}\text{\AA}^{-3}$ (dashed).

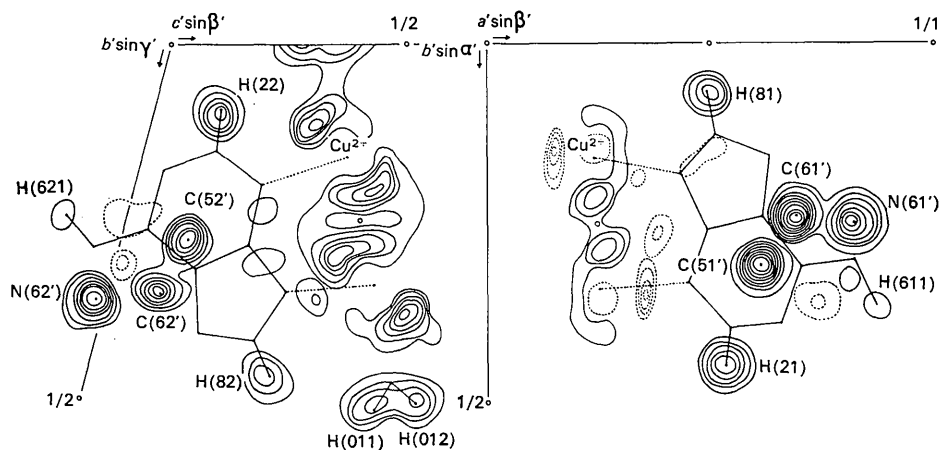


Fig. 3. Difference maps based on F_c values excluding hydrogen atoms and the fractional atoms, C(5'), C(6') and N(6'). Contours are at intervals of $0.2 \text{ e.}\text{\AA}^{-3}$ for C(51'), C(61') and N(61'), and at intervals of $0.1 \text{ e.}\text{\AA}^{-3}$ for the other atoms, starting at $0.2 \text{ e.}\text{\AA}^{-3}$.

and copper(II) succinate dihydrate (O'Connor & Maslen, 1966). In both compounds the four bridging groups are aliphatic carboxylate ions and the Cu-Cu distance is essentially the same (2.64 Å–2.61 Å). The geometry of the ligands does not seem to be significantly affected by the coordination to the copper ions. The displacement of the copper ion out of the equatorial plane observed in the copper adenine complex is also found in the carboxy dimers.

Until the last few years, the Cu(II) ion has usually been associated with a preferred six-coordination, the resulting octahedral geometry being distorted as a result of the Jahn-Teller effect. More recently, however, several papers have been published describing square-pyramidal coordination, *e.g.* Freeman & Szymanski (1967) and Ueki, Ashida, Sasada & Kakudo (1967). A survey of recent literature seems to indicate that the [4+1] coordination is more common than usually realized, and that in the solid state truly six-coordinated copper complexes only appear as special cases caused by crystallographic symmetry requirements. When the copper ion is in a general position, it forms four short bonds in the equatorial plane and is displaced out of this plane toward an apical ligand at a somewhat longer

distance. Very often there is a sixth 'ligand' apparently at a nonbonding distance completing the octahedron. In the monomers the distance to the apical water molecule is appreciably longer than the corresponding distance in the dimers. The same trend is also observed when there is a close apical ligand other than water, *e.g.* pyridine.

Direct interaction between the copper ions in the bridged dimers does not produce a coordination scheme substantially different from that found in monomers. The copper-copper separation in the dimers seems to be determined by the width of the 'bite' of the ligand, though there is an indication of a slight shortening of the Cu-Cu distance in the copper-adenine complex. This can be seen by constructing a model where the coordinating orbitals on N(3) and N(9) have directions halving the angles C(2)-N(3)-C(4) and C(4)-N(9)-C(8), respectively, resulting in a Cu-Cu separation of approximately 3.07 Å which is 0.12 Å longer than the observed distance. The out-of-plane displacement in the model is 0.35 Å. It is difficult to say if the apparent shortening reflects a direct metal-metal interaction, a tendency toward an out-of-plane displacement characteristic of [4+1] coordination, or if it is simply brought about by packing forces in the crystal. It should be mentioned that off-center displacement is a phenomenon which is observed not only in five coordinated copper complexes. Recently, Megaw (1968) has proposed a theory which relates such displacement in octahedral complexes to relief of tension caused by repulsion between ligands. Orgel (1958) describes the effect as loosening of the central ion as the stereochemistry changes from octahedral to tetrahedral symmetry, when the metal ion becomes 'smaller'.

A common feature of the copper(II) carboxylate dimers is the observed subnormal magnetic moment, which indicates an anti-paramagnetic spin-pairing of the odd electrons on the copper ions. Two mechanisms are possible for this spin-pairing, either a direct interaction through overlapping copper orbitals or an electron migration through the bridging groups, so-called superexchange. Several theoretical approaches have

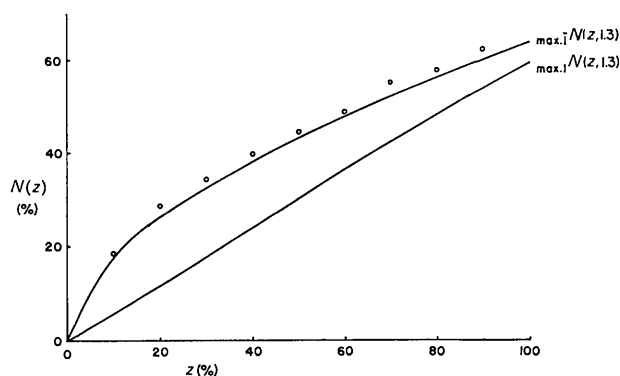


Fig. 4. The experimental distribution $N(Z)$ for bis(6-amino-purine)copper(II) tetrahydrate (marked with circles), together with the theoretical distribution $\max_{z,1} N(z, 1.30)$ and $\max_{z,1} N(z, 1.30)$ for centric and noncentric cells respectively.

Table 6. Deviations of the atoms from different least squares planes

x , y and z in the equations of the planes are in fractions of unit cell edges. σ is the standard deviations of the atoms from the plane.

Deviations from plane (Å)												
(I)	N(91)	N(32) (ii)	N(31) (ii)	N(92)	Cu							
	-0.002	+0.002	-0.002	+0.002	+0.268							
(II)	N(11)	C(21)	N(31)	C(41)	C(51)	C(61)	N(61)	N(71)	C(81)	N(91)	Cu	Cu (ii)
	+0.004	-0.016	+0.007	+0.008	-0.018	-0.008	-0.023	-0.015	-0.011	+0.018	+0.189	+0.241
(III)	N(12)	C(22)	N(32)	C(42)	C(52)	C(62)	N(62)	N(72)	C(82)	N(92)	Cu	Cu (ii)
	-0.004	+0.006	+0.008	-0.007	+0.002	-0.010	+0.004	+0.006	+0.004	+0.008	+0.043	+0.029

(I) Square of ligand atoms, N(91), N(32) (ii), N(31) (ii), N(92), $\sigma=0.003$

Equation: $0.0661x + 14.562y + 2.024z = 3.463$

(II) Ligand (1), $\sigma=0.015$. Equation: $3.809x - 7.127y + 9.137z = 3.952$

(III) Ligand (2), $\sigma=0.007$. Equation: $9.476x + 1.688y - 3.490z = 1.083$

ligand (2) is situated relative to a center of symmetry leads to an alternating hydrogen bonding to the water oxygen O(2). In addition to the hydrogen bonds involving the adenine ligands, there exists bonding between the water molecules as shown in Fig. 8.

An explanation of the occurrence of different configurations of the complex in the unit cells may be found by considering the resulting packing energies in the crystal. By rotating the ligand pairs, hydrogen bond acceptors N(1) and N(7) are interchanged while the donor nitrogens N(6) are moved approximately 1 Å from their previous positions. The arrangement of hydrogen bonds in this case is shown in Fig. 9. The major change from configuration (a) is the involvement of the disordered water molecule O(31) instead of O(32) in the hydrogen bonding scheme [O(31)...O(32), 1.14 Å]. Except for the very weak hydrogen bond N(61)-H...O(32)=3.31 Å which is disrupted, the number of hydrogen bonds remains the same. Accordingly, the rather drastic rearrangement of ligands in the crystal does not seem to produce sufficient change in the packing energy to prevent the compound from crystallizing as a mixture of 'rotamers'. A similar type of disorder is reported for diindenyl iron (Trotter, 1958) where two different orientations of the indenyl ligand occur at random throughout the crystal.

Thermal motion

The thermal parameters for all the atoms are listed in Table 2(a) and (b). The water molecules which are coordinated to copper display large thermal motion and have multiplicities less than unity. Since thermal vibration and multiplicity are closely correlated, it is difficult to decide when a B value is no longer physically meaningful but rather reflects partial occupancy. The two water oxygen atoms O(41) and O(42) have average

B values of 15.0 Å² and 12.6 Å² and multiplicities 0.50 and 0.75, respectively. While O(41) is obviously in a partially occupied site, O(42) is probably in a fully occupied site.

The effect of disorder on the thermal parameters of the adenine molecules can be seen in Fig. 10 where the thermal ellipsoids at 50% probability are plotted in the plane of the ligands. The larger fraction of disorder in

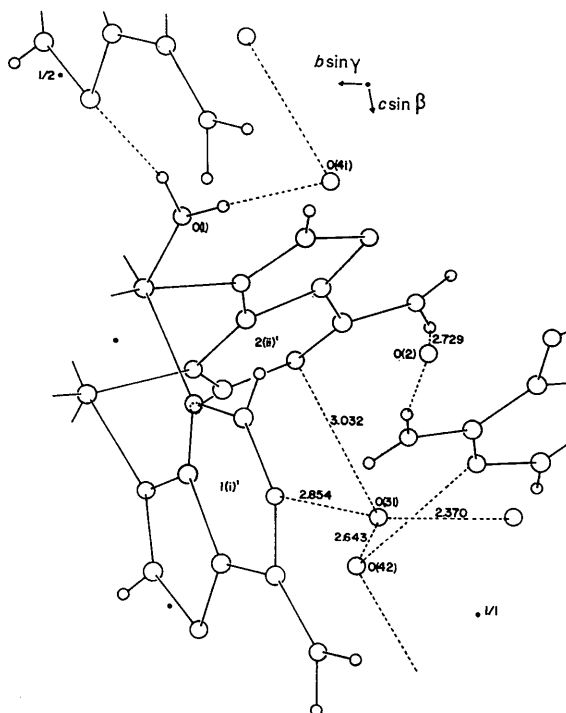


Fig. 9. Ligand pairs (1) and (2) displayed in their alternative orientations relative to the structure in Fig. 8.

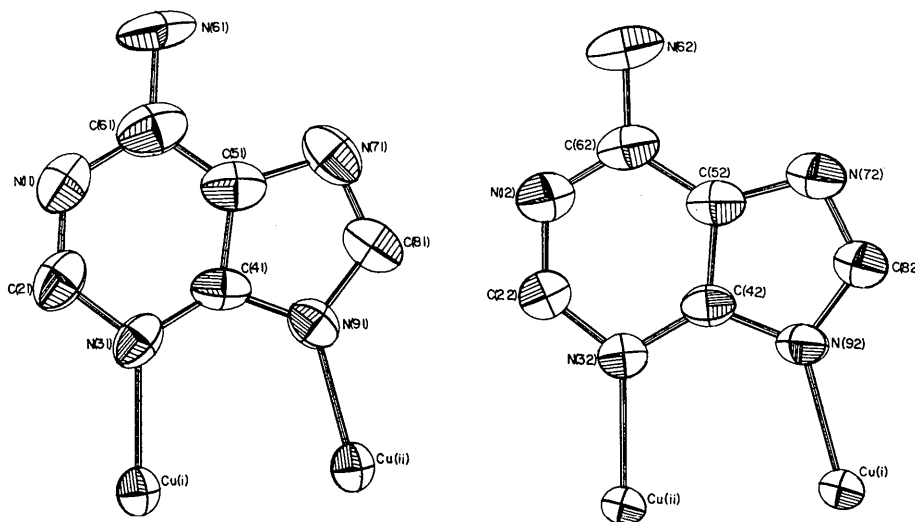


Fig. 10. Thermal ellipsoids as viewed normal to the plane of the ligands.

ligand (1) has been compensated for by an apparently larger thermal vibration in the plane of the ligand.

The author thanks Dr Roland Weiss for a sample of the compound, Dr Ken Emerson for carrying out the magnetic measurements, and cand. real. Jorunn Sletten and Dr Lyle H. Jensen for helpful discussions. He also acknowledges a fellowship from the Royal Norwegian Council for Scientific and Industrial Research and financial support under Grant AM 3288 from the National Institutes of Health.

References

- ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BOUDREAU, E. A. (1963). *Trans. Faraday Soc.* **59**, 1055.
- CHENEY, G. E., FREISER, H. & FERNANDO, Q. (1959). *J. Amer. Chem. Soc.* **81**, 2611.
- DUBICKI, L. & MARTIN, R. L. (1966). *Inorg. Chem.* **5**, 2203.
- EMERSON, K. (1968). Private communication.
- FIGGIS, B. N. & MARTIN, R. L. (1956). *J. Chem. Soc.* p. 3837.
- FIGGIS, B. N. & MARTIN, D. J. (1966). *Inorg. Chem.* **5**, 100.
- FREEMAN, H. C. & SZYMANSKI, J. T. (1967). *Acta Cryst.* **22**, 406.
- HANSEN, A. E. & BALLHAUSEN, C. J. (1965). *Trans. Faraday Soc.* **61**, 631.
- HARKER, T. R. & FREISER, H. (1958). *J. Amer. Chem. Soc.* **80**, 1132.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
- MEGAW, H. D. (1968). *Acta Cryst.* **B24**, 149.
- NIKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* **6**, 227.
- O'CONNOR, B. H. & MASLEN, E. N. (1966). *Acta Cryst.* **20**, 824.
- ORGEL, L. E. (1958). *Disc. Faraday Soc.* **26**, 138.
- SIM, G. A. (1958). *Acta Cryst.* **11**, 123.
- SLETTEN, E. (1967). *Chem. Comm.* p. 1119.
- SLETTEN, E., SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* To be published.
- STEWART, J. M. (1964). *Crystal Structure Calculations System*, Computer Science Center, Univ. of Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- TROTTER, J. (1958). *Acta Cryst.* **11**, 355.
- UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1967). *Acta Cryst.* **22**, 870.
- WATSON, R. E. & FREEMAN, A. J. (1961). *Acta Cryst.* **14**, 123.
- WEISS, R. & VENNER, H. (1963). *Hoppe-Seyle. Z.* **333**, 169.
- WEISS, R. & VENNER, H. (1966). *Hoppe-Seyle. Z.* **345**, 122.

Acta Cryst. (1969). **B25**, 1491

Determination of the Crystal Structure and the Absolute Configuration of (+)-2,2'-Dihydroxy-1,1'-Binaphthalene-3,3'-Dicarboxylic Acid Dimethyl Ester Bromobenzene Solvate

BY HIROSHI AKIMOTO AND YOICHI IITAKA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

(Received 27 July 1968)

In order to establish the absolute configuration of binaphthyl derivatives, an X-ray diffraction study on the crystal structure of (+)-2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid dimethyl ester bromobenzene solvate has been carried out. The crystals are monoclinic, space group $P2_1$ and the lattice constants are: $a=15.78 \text{ \AA}$, $b=9.22$, $c=9.12$, $\beta=97.0^\circ$. The unit cell contains two molecules together with two molecules of bromobenzene. The structure was solved by the heavy atom method using the bromine atoms of the solvate molecules. Refinement was carried out by the block-matrix least-squares method for 1213 observed reflexions including anisotropic temperature factors. The final R value was 0.101.

It was found that the two naphthyl groups are twisted from the exact *cis*-conformation by an angle of $76^\circ 38'$. The absolute configuration was determined by utilizing the anomalous dispersion effect of the bromine atom for $\text{Cu K}\alpha$ radiation, showing that the molecule has the (*R*)-configuration.

Introduction

It has been shown that the restricted rotation about the single bond joining the two benzene rings in biphenyl derivatives produces a pair of optical enantiomers, where the molecule cannot readily exist in a planar form because of the steric interference of the

substituents. The term atropisomerism is often used to denote such kinds of stereoisomerism (Eliel, 1962). In many cases the resolution of the optically active forms is possible provided that the rate of interconversion of the enantiomers is sufficiently slow. The determination of the absolute configuration of this type of compound is very interesting because the optical rotation