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Crystal Structure of a New Form of Copper(II)–Inosine 5′-Monophosphate–2,2′-Dipyridylamine Ternary Complex

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Abstract

Two crystalline forms of the $[Cu(II)(IMP)(DPA)(H_2O)]_2 \cdot nH_2O$ (IMP = inosine 5′-monophosphate, DPA = 2,2′-dipyridylamine) complex were obtained from aqueous solution at pH = 6.2. The crystals of the two forms belong to the monoclinic system, space group $P2_1$. The cell parameters are: $a = 9.445(2)$, $b = 33.902(4)$, $c = 7.802(2)$ Å, $\beta = 90.48(2)°$, $Z = 2$, $D_c = 1.69$ g cm^{-3} and μ(Mo Kα) = 10.49 cm^{-1} (form α, $n = 4$), and $a = 7.828(2)$, $b = 18.552(3)$, $c = 17.378(3)$ Å, $\beta = 91.16(2)°$, $Z = 2$, $D_c = 1.66$ g cm^{-3}, μ(Mo Kα) = 10.40 cm^{-1} (form β, $n = 3.62$). Bau and coworkers reported the preparation of form α by vapor diffusion of CH_3CN into aqueous solution containing $Cu(NO_3)_2$, Na_2IMP and DPA in a 1:1:1 molar ratio and the analysis of the compound by single crystal X-ray diffraction [1].

Intensities for 3412 reflections were collected from a crystal of form β in the present work. Graphite-monochromatized Mo Kα radiation was employed. The structure was refined to final R and R_w values of 0.1000 and 0.1115 respectively. The dimeric units contain two copper ions in square-pyramidal coordination polyhedra. Each polyhedron consists of two nitrogen atoms of DPA, two oxygen atoms from two phosphate groups and a water molecule in the axial position. A statistical disorder was found in a nucleotide moiety of the dimer. Two sets of atomic positions corresponding to the purine system were refined with site occupation factors of 0.62(1) and 0.38(1) respectively. Also the ribose ring shows a disorder with two possible conformations. The puckering mode of the prevailing conformation is C(3′)-endo. In the other nucleotide molecule of the dimer the furanose puckering mode is C(3′)-endo. The rotation around the glycosyl linkages can be described as *'anti'* in the structure of form β. The C(4)–N(9)–C(1′)–O(4′) torsion angle values are −97(2) and −94(3)° for the disordered nucleotide molecule and +91(2)° for the other nucleotide moiety. Strong intermolecular DPA–DPA and purine–purine stacking interactions stabilize the crystal lattice. The differences on the nucleotide conformation between the structure of form α and form β can probably be ascribed to differences in the hydrogen bonds and stacking interactions.

Introduction

The importance of nucleotide–metal species in many biological processes has resulted in considerable efforts to elucidate the nature of donor sites and coordination sphere geometries. Moreover the conformation of the nucleotide moiety in metal complexes can play an important role in enzymatic reactions. Defined structural information on nucleotide–metal compounds is provided by X-ray diffraction studies. In recent decades many studies have been carried out on different model complexes in the solid state [2]. Recently the preparation of a series of ternary complexes involving ATP (ATP = adenosine 5′-triphosphate), DPA and Mg^{2+} or other divalent metal ions appeared [3, 4]. The experimental conditions (like pH, temperature, presence of precipitating agents etc.) are very important to prepare crystalline metal–nucleotide complexes.

With the aim to obtain single crystals containing divalent metal ions and purine nucleotides from almost neutral aqueous solution we investigated the IMP–DPA system. It was possible to prepare two crystalline forms (form α and form β) of a 1:1:1 Cu(II)–IMP–DPA complex from an aqueous solution at pH = 6.2 and room temperature. One of these forms (form α) was previously prepared by Bau and coworkers [1] following a different procedure. Here we report the data relevant to the new form (form β) and a comparison with the structure of form α.

Experimental

Material

Inosine 5′-monophosphoric acid disodium salt was purchased from Sigma and used without any further purification. DPA (Aldrich) was twice recrystallized from ethanol. Copper(II) sulphate was Erba reagent grade product.

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TABLE I. Crystal Data for $[Cu(II)(IMP)(DPA)(H_2O)]_2 \cdot nH_2O$

	Form β, n = 3.62	Form α, n = 4
Formula	$C_{40}H_{51.24}N_{14}O_{21.62}P_2Cu_2$	$C_{40}H_{52}N_{14}O_{22}P_2Cu_2$
a (Å)	7.828(2)	9.445(2)
b (Å)	18.552(3)	33.902(4)
c (Å)	17.378(3)	7.802(2)
β (deg)	91.16(2)	90.48(2)
U (Å^3)	2523(1)	2498(1)
Z	2	2
Space group	$P2_1$	$P2_1$
μ(Mo Kα) (cm^{-1})	10.40	10.49
M	1263.2	1270.0
D_c (g cm^{-3})	1.66	1.69
F(000)	1300.4	
R	0.1000	
R_w	0.1115	
Number of measured reflections	3412	
Number of observed reflections	3055	

The crystalline Cu(II)–IMP–DPA compound was prepared with the following procedure: DPA (1×10^{-3} mol) was dissolved in ethanol (5 ml). The solution was mixed to an aqueous solution (20 ml) of Na_2IMP (1×10^{-3} mol). The resulting mixture was added to a solution (20 ml) of $CuSO_4 \cdot 5H_2O$ (1×10^{-3} mol). The green solution (pH = 6.2) was filtered and allowed to evaporate at room temperature. After a period of about a week, dark green crystals were filtered and washed with water. The examination under the microscope revealed the presence of two different kinds of crystals: tufts of very thin plates and elongated prisms. The crystals were stored in the refrigerator as some efflorescence can occur after six days at room temperature. The two forms gave similar analytical responses. *Anal.* Calc. for $C_{20}H_{26}N_7O_{11}PCu$: C, 37.83; H, 4.13; N, 15.44; Cu, 10.01. Found (form α): C, 38.10; H, 4.25; N, 15.30; Cu, 10.15. Form β: C, 38.20; H, 4.15; N, 15.50; Cu, 9.95%.

Two well shaped crystals, a prism and a plate were used for the lattice constant determinations on a Philips PW 1100 automated four-circle diffractometer. The parameters were obtained by the least-squares method applied to the setting angle of 25 reflections. The unit cell parameters and other crystal data are reported in Table I.

Collection of X-ray Data

A plate measuring about $0.15 \times 0.15 \times 0.02$ mm was used for data collection. Intensity data were collected with the θ–2θ scan method with a scan speed of 0.05° s^{-1} and a scan width of 1.40° in θ in the range $4 \leqslant 2\theta \leqslant 42°$.

The intensities of three standard reflections were monitored after 120 min during the data collections. They did not show any systematic variation over the duration of the experiments. Total of 3055 reflections with $F \geqslant 4\sigma(F)$ were considered 'observed' and used for the structure refinement. The intensities were corrected for Lorentz and polarization effects; the absorption correction was also applied.

Structure Solution and Refinement

Systematic absences in the 0k0 reflections for $k = 2n + 1$ indicated the presence of a 2_1 screw axes parallel to b. $P2/m$ space group was excluded on the basis of the presence of an optically active ribose in the compound. The structure was solved by the heavy-atom method and completed by a series of three-dimensional Fourier and difference-Fourier maps. The refinement was accomplished by full-matrix least-squares method with anisotropic thermal parameters for Cu and P atoms.

The choice between the two possible enantiomeric structures was made on the basis of the known absolute configuration of D-ribose. Atomic scattering factors of C,N,O,P were taken from SHELX76 [5] those of Cu were taken from ref. 6. During the refinement procedure ten new peaks in the purine region and three new peaks in the ribose region (close to C(2′), O(2′) and O(3′)) of a nucleotide molecule were shown by difference-Fourier maps. This was interpreted as a statistical disorder and two purine systems as well as two C(2′), two O(2′) and two O(3′) positions in a nucleotide moiety were refined. The purine systems were refined as rigid groups. The thermal parameters of the purine atoms were constrained to the same value (refined to 0.0818(36) Å^2). The site occupation factors of the atoms within a set were constrained to the same value. The sum of the occupancies of the two sets was fixed at 1.0. The refined values of the site occupation factors for the two conformations were 0.62(1) and 0.38(1) respectively.

The agreement index $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ was 0.1000 while the index $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ was reduced to 0.1115. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = a/[\sigma^2(F) + bF^2]$ where a and b are variable parameters refined to 0.8717 and 0.0156 respectively. Final atomic coordinates with estimated standard deviations are reported in Table II. The standard deviations relevant to the atomic positions of the nucleoside moieties are somewhat large and prevent a detailed discussion of bond lengths and angles. The conformation of the second ribose ring of the disordered nucleoside moiety is not accurately determined also owing to the large standard deviations. The presence of disorder in a nucleoside moiety and in the molecules of water of crystallization does not allow better results. However we believe that the essential features of the structure are correct.

Description of the Structure

The Coordination Sphere

Figure 1 shows the dimeric molecule found in the structure of form β. Table III and Table IV report the bond distances and selected bond angles.

The two copper ions in the dimer have square-pyramidal coordination polyhedra consisting of two nitrogen atoms from DPA two oxygen atoms from phosphate groups and a water molecule in the axial position. There is no interaction between the metal ions and the purine systems. The deviations of the copper atoms from the basal plane toward the apical water molecule is 0.20(1) and 0.18(1) Å. The two bridging phosphate groups and the two copper ions in each dimer form an eight-membered puckered ring. The Cu–OP bond distances average 1.92(1) Å. The Cu–N bond distances average 2.02(2) Å. A coordination geometry similar to that showed by the copper ions in the structure of form β was found in form α, in $[Cu(II)(AMP)(BIPY)(H_2O)]_2^{2+}$ (AMP = adenosine 5′-monophosphate, BIPY = 2,2′-bipyridyl) [7], in $[Cu(II)(3'\text{-}GMP)(PHEN)(H_2O)]_2$ (3′-GMP = guanosine 3′-monophosphate, PHEN = 1,10-phenanthroline) [8], in $[Cu(II)(UMP)(DPA)(H_2O)]_2$ (UMP = uridine 5′-monophosphate) [9] and in $[Cu(II)(CMP)(DPA)(H_2O)]_2$ (CMP = cytidine 5′-monophosphate) [10].

It is worth noting that Cu(II), IMP and BIPY give a crystalline ternary complex whose structure consists of $[Cu(II)(IMP)(BIPY)(H_2O)]^+$ molecules and NO_3^- ions [11]. The metal ion links to IMP just through the N(7) atom without any bonding interaction with the phosphate oxygen atoms. Furthermore the Cu(II)–N(7) only bonding mode was found also in $[Cu(II)(IMP)_2(IM)_{0.8}(H_2O)_{1.2}(H_2O)_2]$ (IM = imidazole) [12], and in $[Cu(II)(IMP)_2(dien)]$ (dien = diethylenetriamine) [13] complexes. Therefore it appears, at least for ternary complexes in the solid state, that Cu(II) ions can interact with the phosphate group of nucleoside monophosphate without any metal–nucleobase interaction. Otherwise copper ions can link just to the nucleobase.

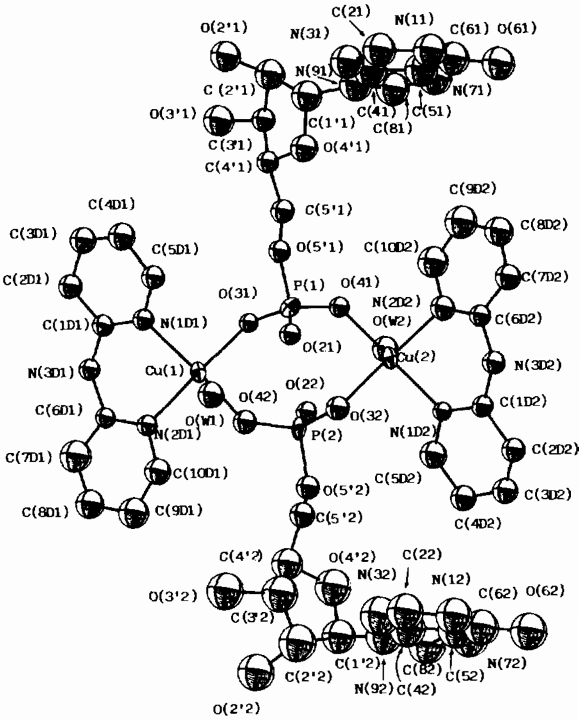

Fig. 1. ORTEP [15] drawing of the $[Cu(II)(IMP)(DPA)(H_2O)]_2$ molecule in form β with the labelling scheme. Ellipsoid enclose 30% probability. (For the disordered nucleotide just the most favourable conformation is reported.)

The Nucleotide Molecule

In spite of the similarities found in the coordination polyhedra of form β and form α, there are many differences in the conformations of the ribose rings and in the rotation around the glycosyl linkage.

One nucleotide molecule of the dimer in form β shows that the ribose puckering mode is mainly C(3′)-endo [14] (62(1)%, see Table V). The ribose ring in the other molecule has a C(3′)-endo conformation. On the other hand the two ribose rings of form α have a C(4′)-exo conformation [1]. The rotation around the glycosyl linkage can be described as *'anti'* in both the nucleotide molecules of form β. It has to be noted that the χ (O(4′)–C(1′)–N(9)–C(4)) torsion angle values are −97(2)° (62(1)%) and −94(3)° (38(1)%) in one nucleotide and +91(2)° in the other one. In the structure of form α both the

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters[a] ($Å^2 \times 10^4$) with Estimated Standard Deviations

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy
Cu(1)	4176(3)	2700(1)	−237(1)	243(12)	218(14)	324(13)	56(11)	33(9)	−40(11)	1
Cu(2)	796(3)	5000	410(1)	212(12)	234(14)	357(14)	31(11)	71(9)	−54(11)	1
P(1)	3981(7)	4065(3)	862(3)	260(29)	282(33)	308(29)	−5(23)	−13(22)	60(22)	1
P(2)	827(6)	3628(3)	−750(3)	148(24)	213(30)	419(31)	56(21)	−28(20)	−48(22)	1

Atom	x/a	y/b	z/c	U	Occupancy	Atom	x/a	y/b	z/c	U	Occupancy
O(21)	5143(18)	4477(8)	315(8)	331(32)	1	0(22)	−611(17)	3291(8)	−344(8)	307(33)	1
O(31)	3668(16)	3291(7)	629(7)	263(29)	1	O(32)	1275(20)	4378(9)	−461(9)	411(38)	1
O(41)	2400(16)	4459(8)	1048(7)	299(30)	1	O(42)	2339(19)	3112(9)	−820(9)	407(37)	1
O(2'1)	7750(37)	3337(18)	4458(18)	678(86)	0.62(1)	O(2'2)	715(47)	3520(24)	−4653(21)	1548(139)	1
O(2'11)	5298(55)	3905(25)	5105(23)	489(111)	0.38(1)						
O(3'1)	5162(39)	2634(15)	3689(18)	690(83)	0.62(1)	O(3'2)	3621(49)	3610(22)	−3663(22)	1544(135)	1
O(3'11)	6613(43)	2986(20)	4011(21)	378(97)	0.38(1)						
O(4'1)	6098(22)	4476(9)	3186(9)	563(43)	1	O(4'2)	−1009(35)	4118(14)	−3091(15)	984(78)	1
O(5'1)	5125(18)	4044(9)	1637(8)	357(35)	1	O(5'2)	93(19)	3731(9)	−1613(8)	405(38)	1
O(W1)	6138(21)	3557(10)	−792(10)	495(43)	1	O(W2)	−1357(22)	4262(9)	763(9)	494(43)	1
O(61)	5433(33)	7443(9)	4679(17)	818(36)	0.62(1)	O(62)	−1454(40)	7529(19)	−3669(19)	1342(106)	1
O(611)	3475(50)	7428(15)	4445(26)	818(36)	0.38(1)						
N(11)	8203(33)	7025(9)	4569(17)	818(36)	0.62(1)	N(12)	1192(42)	6960(18)	−3722(19)	966(91)	1
N(111)	6451(50)	7253(15)	4461(26)	818(36)	0.38(1)						
N(31)	8794(33)	5784(9)	4307(17)	818(36)	0.62(1)	N(32)	1433(43)	5734(19)	−3777(19)	1101(95)	1
N(311)	7574(50)	6061(15)	4312(26)	818(36)	0.38(1)						
N(71)	4203(33)	6023(9)	4545(17)	818(36)	0.62(1)	N(72)	−3015(48)	6048(22)	−3661(21)	1263(114)	1
N(711)	3038(50)	5906(15)	4268(26)	818(36)	0.38(1)						
N(91)	5908(33)	5116(9)	4252(17)	818(36)	0.62(1)	N(92)	−1217(40)	5082(18)	−3833(18)	926(82)	1
N(911)	5296(50)	5179(15)	4183(26)	818(36)	0.38(1)						
C(21)	9310(33)	6469(9)	4452(17)	818(36)	0.62(1)	C(22)	2064(51)	6339(25)	−3770(24)	990(117)	1
C(211)	7777(50)	6780(15)	4418(26)	818(36)	0.38(1)						
C(41)	7058(33)	5699(9)	4362(17)	818(36)	0.62(1)	C(42)	−305(47)	5720(21)	−3791(21)	924(103)	1
C(411)	5891(50)	5870(15)	4217(26)	818(36)	0.38(1)						
C(51)	5886(33)	6246(9)	4504(17)	818(36)	0.62(1)	C(52)	−1385(54)	6247(23)	−3677(24)	934(113)	1
C(511)	4490(50)	6328(15)	4255(26)	818(36)	0.38(1)						
C(61)	6479(33)	6941(9)	4634(17)	818(36)	0.62(1)	C(62)	−552(48)	6956(22)	−3717(22)	913(104)	1
C(611)	4778(50)	7061(15)	4348(26)	818(36)	0.38(1)						
C(81)	4309(33)	5345(9)	4346(17)	818(36)	0.62(1)	C(82)	−2861(60)	5361(28)	−3799(27)	1254(138)	1
C(811)	3596(50)	5267(15)	4106(26)	818(36)	0.38(1)						
C(1'1)	6452(35)	4492(13)	3989(14)	693(78)	1	C(1'2)	−1025(47)	4351(21)	−3869(21)	829(98)	1
C(2'1)	6314(47)	3741(18)	4333(23)	677(127)	0.62(1)	C(2'2)	840(56)	4191(24)	−4180(26)	1048(126)	1
C(2'11)	5039(68)	4003(24)	4311(22)	550(175)	0.38(1)						
C(3'1)	5090(27)	3396(11)	3727(11)	401(51)	1	C(3'2)	1859(50)	4058(22)	−3506(23)	952(111)	1

C(4'1)	5736(25)	3777(11)	2984(11)	360(50)	1	C(4'2)	695(41)	3753(19)	−2907(19)	731(84)	1
C(5'1)	4342(27)	3761(13)	2351(12)	405(52)	1	C(5'2)	1216(31)	4034(13)	−2166(14)	474(58)	1
N(1D1)	5648(21)	2028(11)	437(10)	321(44)	1	N(1D2)	−493(21)	5690(10)	−293(9)	261(40)	1
N(2D1)	4404(21)	2022(10)	−1123(10)	306(39)	1	N(2D2)	659(25)	5748(12)	1239(11)	440(49)	1
N(3D1)	4824(24)	985(10)	−305(10)	338(41)	1	N(3D2)	459(23)	6733(11)	402(10)	387(44)	1
C(1D1)	5620(27)	1328(13)	329(12)	345(52)	1	C(1D2)	−397(27)	6405(13)	−213(12)	332(48)	1
C(2D1)	6259(31)	835(15)	880(13)	420(57)	1	C(2D2)	−1152(30)	6843(14)	−809(13)	418(56)	1
C(3D1)	7034(34)	1152(15)	1541(15)	499(63)	1	C(3D2)	−1985(31)	6572(15)	−1377(14)	477(61)	1
C(4D1)	7116(33)	1845(16)	1612(15)	537(67)	1	C(4D2)	−2137(32)	5815(15)	−1496(15)	485(63)	1
C(5D1)	6411(30)	2298(13)	1038(13)	401(54)	1	C(5D2)	−1329(35)	5407(16)	−899(15)	542(67)	1
C(6D1)	4439(25)	1285(12)	−1020(11)	289(45)	1	C(6D2)	718(27)	6437(13)	1128(12)	345(50)	1
C(7D1)	4229(40)	803(19)	−1622(18)	735(84)	1	C(7D2)	1002(32)	6898(15)	1725(15)	497(62)	1
C(8D1)	4087(38)	1141(16)	−2373(17)	610(74)	1	C(8D2)	1369(36)	6718(17)	2406(17)	616(73)	1
C(9D1)	3957(38)	1893(18)	−2478(17)	677(78)	1	C(9D2)	1172(43)	5974(20)	2561(20)	784(94)	1
C(10D1)	4148(35)	2258(15)	−1826(16)	518(66)	1	C(10D2)	775(42)	5478(19)	1955(18)	694(84)	1
O(WD1)	3971(37)	−999(17)	2357(17)	1140(92)	1	O(WD2)	88(44)	−1491(19)	7991(20)	1421(113)	1
O(WD3)	578(44)	4021(19)	3426(20)	1315(106)	1	O(WD4)	12074(52)	7564(23)	4276(24)	955(118)	0.62(1)

[a] Anisotropic Thermal Parameters are of the form: $\exp(-2\pi^2(\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}h_ih_ja_i^*a_j^*U_{ij}))$.

TABLE III. Bond Distances (Å) with their Estimated Standard Deviations in Parenthesis

Cu(1)–O(31)	1.91(1)	Cu(2)–O(32)	1.94(2)
Cu(1)–O(42)	1.90(1)	Cu(2)–O(41)	1.94(1)
Cu(1)–N(1D1)	2.05(2)	Cu(2)–N(1D2)	2.02(2)
Cu(1)–N(2D1)	2.00(2)	Cu(2)–N(2D2)	2.01(2)
Cu(1)–O(W1)	2.42(2)	Cu(2)–O(W2)	2.27(2)
P(1)–O(21)	1.53(1)	P(2)–O(22)	1.48(1)
P(1)–O(31)	1.51(1)	P(2)–O(32)	1.52(2)
P(1)–O(41)	1.48(1)	P(2)–O(42)	1.53(2)
P(1)–O(5'1)	1.60(1)	P(2)–O(5'2)	1.61(1)
C(1'1)–N(91)	1.32(4)	C(1'2)–N(92)	1.37(4)
C(1'1)–O(4'1)	1.42(3)	C(1'2)–O(4'2)	1.42(4)
C(1'1)–C(2'1)	1.52(3)	C(1'2)–C(2'2)	1.59(5)
C(2'1)–O(2'1)	1.37(3)	C(2'2)–O(2'2)	1.49(5)
C(2'1)–C(3'1)	1.55(3)	C(2'2)–C(3'2)	1.43(5)
C(3'1)–O(3'1)	1.42(3)	C(3'2)–O(3'2)	1.64(5)
C(3'1)–C(4'1)	1.56(2)	C(3'2)–C(4'2)	1.51(5)
C(4'1)–O(4'1)	1.37(2)	C(4'2)–O(4'2)	1.52(4)
C(4'1)–C(5'1)	1.54(2)	C(4'2)–C(5'2)	1.44(4)
C(5'1)–O(5'1)	1.49(3)	C(5'2)–O(5'2)	1.43(3)
C(1'1)–N(911)	1.60(4)		
C(1'1)–C(2'11)	1.54(4)		
C(2'11)–C(3'1)	1.52(3)		
C(2'11)–O(2'11)	1.40(4)		
C(3'1)–O(3'11)	1.49(3)		
N(11)–C(21)	1.37	N(12)–C(22)	1.34(5)
C(21)–N(31)	1.36	C(22)–N(32)	1.23(5)
N(31)–C(41)	1.37	N(32)–C(42)	1.36(5)
C(41)–C(51)	1.39	C(42)–C(52)	1.31(5)
C(51)–C(61)	1.39	C(52)–C(62)	1.47(5)
C(61)–O(61)	1.24	C(62)–O(62)	1.28(4)
C(61)–N(11)	1.37	C(62)–N(12)	1.37(4)
C(51)–N(71)	1.38	C(52)–N(72)	1.33(5)
N(71)–C(81)	1.31	N(72)–C(82)	1.30(5)
C(81)–N(91)	1.34	C(82)–N(92)	1.39(5)
N(91)–C(41)	1.42	N(92)–C(42)	1.38(5)
N(111)–C(211)	1.36		
C(211)–N(311)	1.35		
N(311)–C(411)	1.37		
C(411)–C(511)	1.39		
C(511)–C(611)	1.39		
C(611)–O(611)	1.24		
C(611)–N(111)	1.37		
C(511)–N(711)	1.38		
N(711)–C(811)	1.30		
C(811)–N(911)	1.35		
N(911)–C(411)	1.37		
N(1D1)–C(1D1)	1.31(3)	N(1D2)–C(1D2)	1.34(3)
C(1D1)–C(2D1)	1.41(3)	C(1D2)–C(2D2)	1.43(3)
C(2D1)–C(3D1)	1.42(4)	C(2D2)–C(3D2)	1.28(3)
C(3D1)–C(4D1)	1.29(4)	C(3D2)–C(4D2)	1.43(4)
C(4D1)–C(5D1)	1.41(4)	C(4D2)–C(5D2)	1.42(4)
C(5D1)–N(1D1)	1.29(3)	C(5D2)–N(1D2)	1.34(3)
C(1D1)–N(3D1)	1.41(3)	C(1D2)–N(3D2)	1.39(3)
N(3D1)–C(6D1)	1.39(3)	N(3D2)–C(6D2)	1.39(3)
C(6D1)–C(7D1)	1.38(4)	C(6D2)–C(7D2)	1.36(3)
C(7D1)–C(8D1)	1.45(4)	C(7D2)–C(8D2)	1.26(4)

(continued)

TABLE III. *(continued)*

C(8D1)–C(9D1)	1.41(4)	C(8D2)–C(9D2)	1.41(4)
C(9D1)–C(10D1)	1.33(4)	C(9D2)–C(10D2)	1.43(5)
C(10D1)–N(2D1)	1.31(3)	C(10D2)–N(2D2)	1.34(4)
N(2D1)–C(6D1)	1.38(3)	N(2D2)–C(6D2)	1.29(3)

nucleotide molecules have an unusual *'syn'* conformation around the glycosyl bond [1].

The DPA Molecule

The pyridine rings in the DPA molecules are essentially planar. The two rings are tilted in each

TABLE IV. Bond Angles (deg) with the Estimated Standard Deviations in Parenthesis Relevant to the Coordination Polyhedra

O(31)–Cu(1)–O(42)	91(1)	O(32)–Cu(2)–O(41)	90(1)
O(31)–Cu(1)–N(1D1)	91(1)	O(32)–Cu(2)–N(1D2)	90(1)
O(31)–Cu(1)–N(2D1)	172(1)	O(32)–Cu(2)–N(2D2)	170(1)
O(31)–Cu(1)–O(W1)	95(1)	O(32)–Cu(2)–O(W2)	90(1)
O(42)–Cu(1)–N(1D1)	164(1)	O(41)–Cu(2)–N(1D2)	169(1)
O(42)–Cu(1)–N(2D1)	86(1)	O(41)–Cu(2)–N(2D2)	90(1)
O(42)–Cu(1)–O(W1)	90(1)	O(41)–Cu(2)–O(W2)	90(1)
N(1D1)–Cu(1)–N(2D1)	90(1)	N(1D2)–Cu(2)–N(2D2)	88(1)
N(1D1)–Cu(1)–O(W1)	106(1)	N(1D2)–Cu(2)–O(W2)	100(1)
N(2D1)–Cu(1)–O(W1)	92(1)	N(2D2)–Cu(2)–O(W2)	100(1)

TABLE V. Selected Least-squares Planes with Deviations of the Atoms (Å)

Plane	Atom	Deviations	Direction Cosines			Plane	Atom	Deviations	Direction Cosines		
1	N(1D1)	−0.026	0.8868	0.0155	−0.4797	2	C(6D1)	0.004	0.9935	0.0131	−0.1333
	C(1D1)	0.024					C(7D1)	−0.032			
	C(2D1)	−0.006					C(8D1)	0.040			
	C(3D1)	−0.010					C(9D1)	−0.019			
	C(4D1)	0.008					C(10D1)	−0.012			
	C(5D1)	0.010					N(2D1)	0.018			
	Cu(1)[a]	−0.467					Cu(1)[a]	−0.347			
	N(3D1)[a]	−0.010					N(3D1)[a]	0.130			
3	N(1D2)	−0.004	−0.8592	0.0071	0.5289	4	C(6D2)	0.001	−0.9826	0.0987	0.1775
	C(1D2)	0.014					C(7D2)	0.052			
	C(2D2)	−0.020					C(8D2)	−0.054			
	C(3D2)	0.014					C(9D2)	0.009			
	C(4D2)	−0.003					C(10D2)	0.037			
	C(5D2)	−0.002					N(2D2)	−0.045			
	Cu(2)[a]	−0.234					Cu(2)[a]	−0.543			
	N(3D2)[a]	0.008					N(3D2)[a]	0.031			
5	N(1D1)	−0.071	0.7399	0.5981	−0.3229	6	N(1D2)	0.004	0.8162	0.5034	−0.2999
	N(2D1)	0.076					N(2D2)	−0.004			
	O(31)	0.075					O(32)	−0.004			
	O(42)	−0.080					O(41)	0.004			
	Cu(1)[a]	0.200					Cu(2)[a]	−0.183			
	O(W1)[a]	2.599					O(W2)[a]	−2.432			
7	C(1′1)	−0.001	0.9722	−0.1587	−0.1916	8	C(1′2)	−0.030	0.3329	0.8828	0.3245
	C(2′1)	0.001					C(2′2)	0.018			
	O(4′1)	0.001					O(4′2)	0.031			
	C(4′1)	−0.001					C(4′2)	−0.019			
	C(3′1)[a]	−0.627					C(3′2)[a]	0.447			
	C(5′1)[a]	−0.846					C(5′2)[a]	0.995			

[a] Not defining the plane.

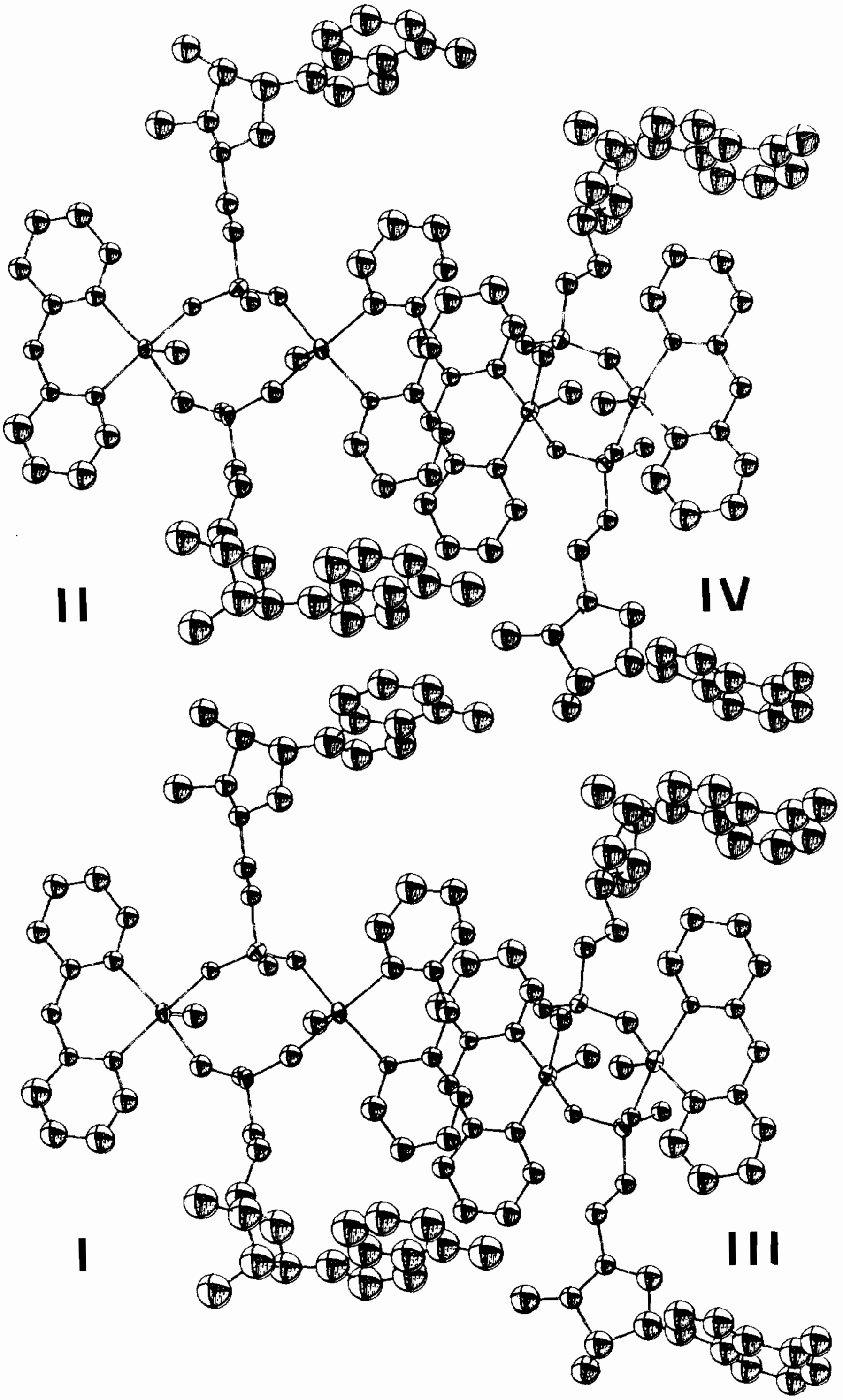

Fig. 2. Diagram of four $[Cu(II)(IMP)(DPA)(H_2O)]_2$ dimeric units in form β. The molecules are in the following positions: I (x, y, z), II $(x + 1, y, z + 1)$, III $(-x, \frac{1}{2} + y, -z)$, IV $(-x + 1, \frac{1}{2} + y, -z + 1)$. Water molecules have been omitted for clarity. There are two types of intermolecular stacking: DPA–DPA and purine–purine interactions (see Figs. 3 and 4).

ligand molecule. The dihedral angles average 21(2)°. A similar tilted configuration was found in the structure of $[Cu(II)(UMP)(DPA)(H_2O)]_2$ [9]. The metal ions have deviations between 0.23(1) and 0.54(1) Å from the pyridine planes in the present structure.

TABLE VI. Significant Stacking Distances (Å) for $[Cu(II)(IMP)(DPA)(H_2O)]_2 \cdot 3.62H_2O$

DPA–DPA			Purine–Purine		
C(1D1) ... C(3D2)	3.44	$(\bar{x}, y + \frac{1}{2}, \bar{z})$	N(11) ... C(52)	3.38	$(x - 1, y, z - 1)$
C(1D1) ... C(4D2)	3.56		N(11) ... C(62)	3.12	
C(2D1) ... C(4D2)	3.42		N(11) ... O(62)	3.21	
N(1D1) ... C(3D2)	3.44		C(21) ... N(12)	3.59	
			C(21) ... C(42)	3.36	
C(1D1) ... N(3D2)	3.43	$(\bar{x} + 1, y + \frac{1}{2}, \bar{z})$	C(21) ... C(52)	3.33	
C(2D1) ... N(1D2)	3.50		C(21) ... C(62)	3.31	
C(4D1) ... C(2D2)	3.48		N(31) ... C(42)	3.37	
N(1D1) ... N(3D2)	3.45		N(31) ... N(92)	3.48	
			C(41) ... N(72)	3.50	
			C(41) ... C(82)	3.26	
			C(41) ... N(92)	3.58	
			C(51) ... N(72)	3.31	
			C(51) ... C(82)	3.50	
			C(61) ... O(62)	3.51	
			C(61) ... C(52)	3.59	
			C(61) ... N(72)	3.41	
			N(311) ... C(52)	3.59	
			N(311) ... N(72)	3.56	
			N(311) ... C(82)	3.55	
			C(211) ... C(52)	3.50	
			C(211) ... C(62)	3.49	

Hydrogen Bonds

The crystal lattice is stabilized by an extensive network of hydrogen bonds. Intramolecular hydrogen bonds involve the coordinated water molecules and the non-coordinated phosphate oxygen atoms. Similar interactions were found in the structure of $[Cu(II)(UMP)(DPA)(H_2O)]_2$ [9]. Moreover intermolecular hydrogen bonds also occur between the coordinated water molecules and phosphate oxygen atoms belonging to adjacent complex molecules. Furthermore the non-coordinated phosphate oxygen atoms interact with the bridging nitrogen atoms of DPA molecules (namely N(3D1) and N(3D2)). Significant hydrogen bonding interactions occur between the N(1) nitrogen atom from the purine systems and O(2′) or O(3′) oxygen atoms from the ribose rings. The O(6) oxygen atoms from the purine systems interact with O(2′) or O(3′) ribose oxygen atoms. The O(4′) oxygen atoms interact with free water molecules.

Stacking Interactions

There are two types of intermolecular stacking interactions (Fig. 2 and Table VI). In one case the DPA molecules from adjacent dimeric units are involved (Fig. 3). The dihedral angles between the stacked aromatic rings are about 5(2)°.

The second type interaction involves the purine systems. It is evident from Fig. 4 that stacking interactions with an extensive overlapping region exist between the purine moieties.

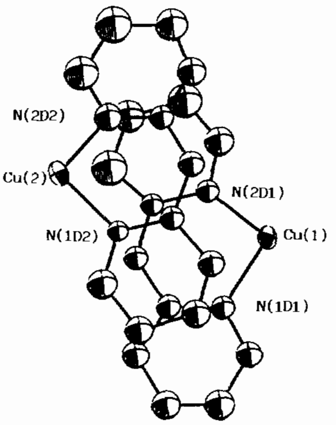

Fig. 3. Perspective view of the intermolecular stacking interaction involving coordinated DPA molecules. The metal ions are also drawn.

Conclusion

The structures of $[Cu(II)(IMP)(DPA)(H_2O)]_2$ (form α and form β) show that the metal ion prefers to link to the phosphate oxygen atoms of the nucleotide molecule. The differences in lattice forces between the structures of form α and form β are not able to change the coordination sphere. Probably some other factors as the presence of Cu(II)–DPA bonding interactions and the negatively charged phosphate oxygen atoms (at pH = 6.2) make the metal–phosphate only binding mode possible.

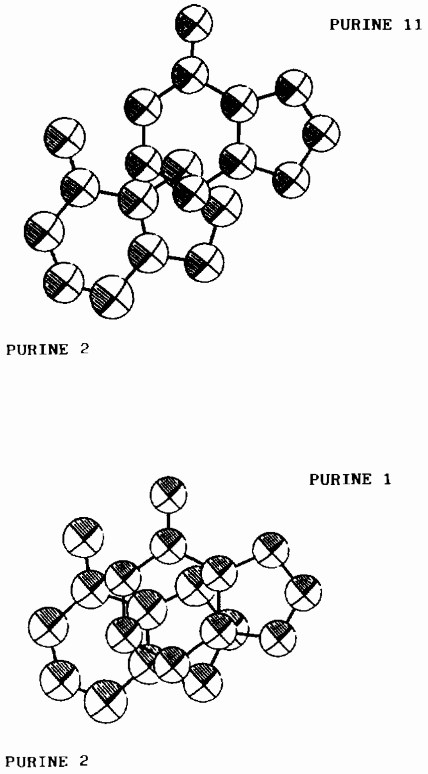

Fig. 4. Perspective view of the intermolecular stacking interactions involving the purine systems.

On the other hand some differences in the hydrogen bonds and stacking interactions have a large influence on the conformation of the nucleotide molecules in the solid state.

This means that we must be careful to draw some general conclusion on nucleotide conformation from solid state studies.

Supplementary Material

Tables of bond angles, and observed and calculated structure factors are available from the authors on request.

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References

1. R. W. Gellert, B. E. Fischer and R. Bau, *Biochem. Biophys. Res. Commun., 88,* 1443 (1979).
2. L. G. Marzilli, T. J. Kistenmacher and G. L. Eichhorn, in T. G. Spiro (ed.), 'Nucleic Acid–Metal Ion Interactions', Wiley, New York, 1980, chap. 5.
3. R. Cini, M. C. Burla, A. Nunzi, G. P. Polidori and P. F. Zanazzi, *J. Chem. Soc., Dalton Trans.,* 2467 (1984).
4. M. Sabat, R. Cini, T. Haromy and M. Sundaralingam, *Biochemistry, 24,* 7827 (1985).
5. G. M. Sheldrick, 'SHELX76', program for crystal structure determination, Cambridge University, 1976.
6. 'International Tables for X-ray Crystallography', Vol. 4, Kynoch Press, Birmingham, 1974.
7. K. Aoki, *J. Am. Chem. Soc., 100,* 7106 (1978).
8. C. Y. Wei, B. E. Fischer and R. Bau, *Chem. Commun.,* 1053 (1978).
9. B. E. Fischer and R. Bau, *Inorg. Chem., 17,* 27 (1978).
10. K. Aoki, *Chem. Commun.,* 589 (1979).
11. K. Aoki, *Chem. Commun.,* 600 (1977).
12. M. Damodara Poojary and H. Manohar, *Inorg. Chem., 24,* 1065 (1985).
13. C. C. Chiang, T. Sorrel, T. J. Kistenmacher and L. G. Marzilli, *J. Am. Chem. Soc., 100,* 5102 (1978).
14. IUPAC–IUB Joint Commission on Biochemical Nomenclature (JCBN), *Eur. J. Biochem., 131,* 9 (1983).
15. C. K. Johnson, 'ORTEP', *Report ORNL-3794 (revised),* Oak Ridge National Laboratory, Tennessee, 1971.