Unusual Ribose Conformation in a Ternary Copper(II) 2'Deoxyribonucleotide Complex[†]

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The ternary metal deoxyribonucleotide complex [Cu(bzim)(5'-dGMP)$(H_2O)_3$] (bzim = benzimidazole, 5'-dGMP = 2'-deoxyguanosine 5'-monophosphate) has been prepared and the structure analysed by X-ray diffraction. The compound crystallizes in the space group *P*1 with *a* = 7.069(6), *b* = 13.959(10), *c* = 14.204(12) Å, α = 75.12(6), β = 94.15(6), γ = 97.98(6)° and *Z* = 2. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures on the basis of 2813 observed [$I \geqslant 3\sigma(I)$] reflections to final *R* and *R'* values of 0.050 and 0.052 respectively. There are two independent molecules in the asymmetric unit and both copper(II) centres have square-pyramidal co-ordination geometry. An unusual feature of the structure is the co-ordination of the metal by N(7) of the base, in the presence of a π-aromatic amine, bzim. The structure is stabilized by intermolecular base–bzim stacking. The nucleotides of both the molecules have an *anti* conformation about the glycosyl bond, and a *gauche-gauche* conformation about the C(4')–C(5') bond. A feature of particular interest is the unusual sugar conformation. The base furanose rings of the two nucleotide molecules adopt C(3')-*exo*/C(2')-*endo* pucker and C(3')-*exo* pucker respectively.

The imidazole ring as a histidine moiety and benzimidazole (bzim) as its 5,6-dimethyl derivative function as ligands towards transition-metal ions in a variety of biologically important molecules including haem systems, vitamin B_{12}[1] and its derivatives and several metalloproteins.[2] Metal–nucleotide complexes containing heteroaromatic nitrogen bases are of special interest since they can be considered as models for the substrate-metal ion–aromatic amine centres found in proteins.[3] Solution studies[3,4] on such ternary complexes have shown that, in the presence of the π-aromatic amine, the metal–nucleotide interaction takes place at the phosphate group and not at the base. Crystallographic studies on metal–nucleotide complexes containing diverse π-aromatic amines like bipy, dpa and phen[‡] have provided direct evidence for the existence of such a binding mode of nucleotides in the solid state.[6–10] However, in the structure of [Cu(bzim)$(H_2O)_5$][IMP],[11] we observed for the first time that the nucleotide remains unco-ordinated to the metal. We were, therefore, interested in studying the role of bzim in influencing the co-ordinating ability of the deoxyribonucleotide, dGMP.

Experimental

Copper(II) nitrate (15 mg) dissolved in water (5 cm^3) was added to bzim (8 mg) in hot water (5 cm^3). The pH was lowered to 5.2 using dilute HNO_3 (0.1 mol dm^{-3}). To this solution, Na_2[5'-dGMP] (25 mg) in water (5 cm^3) was added. The reaction mixture was stirred for 0.5 h at room temperature and then kept aside for slow evaporation. Pale blue plate-like crystals appeared after about 2 weeks.

Table 1 Crystal data

Formula	$C_{17}H_{30}CuN_7O_{15}P$
M	651.4
Crystal system	Triclinic
Space group	*P*1
a/Å	7.069(6)
b/Å	13.959(10)
c/Å	14.204(12)
α/°	75.12(6)
β/°	94.15(6)
γ/°	97.98(6)
U/Å^3	1340.52
Z	2
D_m/g cm^{-3}	1.610
D_c/g cm^{-3}	1.613
F(000)	693.97
μ/cm^{-1}	9.72
λ/Å	0.7107
Crystal dimensions (mm)	0.075 × 0.075 × 0.25
2θ range (°)	4.5–40
Scan mode	θ–2θ
Scan speed (° min^{-1})	2.5–15
No. of reflections measured	3704
No. of reflections used [$I \geqslant 3\sigma(I)$]	2813
No. of parameters refined	721
R	0.050
R'	0.052

X-Ray Intensity Data Collection and Reduction.—Details regarding the data collected on an Enraf-Nonius CAD-4 diffractometer are presented in Table 1. The data were corrected for Lorentz and polarization effects. An absorption correction was applied using ψ-scan data.[12] The Niggli parameters were checked for higher symmetry[13] and this possibility was ruled out.

Structure solution and refinement. The structure was solved by conventional Patterson and Fourier techniques and refined by a full-matrix least-squares procedure. All the 80 non-hydrogen

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

[‡] Abbreviations used as in accord with the recommendations of the IUPAC–IUB Commission on Biochemical Nomenclature (ref. 5): bipy = 2,2'-bipyridine, dpa = bis(2-pyridyl)amine, phen = 1,10-phenanthroline, en = ethane-1,2-diamine, Him = imidazole, terpy = 2,2':6',2''-terpyridine, AMP, IMP, UMP, CMP, GMP = the 5'-monophosphates(2−) of adenosine, inosine, uridine, cytidine and guanosine, 3'-GMP = guanosine 3'-monophosphate(2−), ATP = adenosine 5'-triphosphate(2−), AMPH = adenosine 5'-monophosphate(1−), dCMP = 2'-deoxycytosine 5'-monophosphate(2−), dUMP = 2'-deoxyuridine 5'-monophosphate(2−).

Table 2 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule A							
Cu	10 000(0)	0(0)	10 000(0)	O(3′)	9 600(13)	6 033(5)	8 146(5)
N(1)	12 323(16)	1 652(7)	12 661(7)	P(1)	5 287(6)	2 040(3)	8 546(2)
C(2)	12 797(19)	2 680(8)	12 374(8)	O(5′)	6 482(13)	3 138(6)	8 445(6)
N(2)	13 608(16)	3 140(7)	13 056(7)	O(7)	6 561(16)	1 552(6)	8 051(7)
N(3)	12 381(17)	3 241(7)	11 455(7)	O(8)	5 237(15)	1 528(7)	9 623(7)
C(4)	11 591(18)	2 666(8)	10 872(9)	O(9)	3 282(13)	2 161(6)	8 096(6)
C(5)	11 224(17)	1 634(8)	11 105(8)	N(11)	9 664(16)	−1 417(7)	9 971(7)
C(6)	11 560(18)	1 080(9)	12 024(8)	C(11)	9 976(19)	−2 224(8)	10 741(8)
O(6)	11 080(12)	157(6)	12 355(6)	N(12)	9 329(17)	−2 795(8)	9 466(8)
N(7)	10 346(14)	1 356(6)	10 270(6)	C(12)	9 702(19)	−3 097(9)	10 482(8)
C(8)	10 160(18)	2 183(9)	9 613(9)	C(13)	9 322(21)	−1 791(9)	9 217(8)
N(9)	10 861(15)	3 022(6)	9 937(7)	C(14)	10 366(18)	−2 231(9)	11 774(10)
C(1′)	10 494(20)	4 052(8)	9 518(9)	C(15)	10 527(21)	−3 142(9)	12 420(10)
C(2′)	10 377(18)	4 337(8)	8 393(8)	C(16)	10 286(22)	−4 016(13)	12 072(12)
C(3′)	8 826(18)	5 027(8)	8 148(8)	C(17)	9 840(21)	−4 034(9)	11 105(12)
C(4′)	7 459(22)	4 610(9)	9 002(9)	O(W1)	12 788(14)	−72(6)	10 039(7)
C(5′)	5 811(21)	3 873(10)	8 825(10)	O(W2)	7 211(12)	−61(6)	9 789(6)
O(1′)	8 686(14)	4 149(6)	9 846(6)	O(W3)	10 105(16)	639(7)	8 394(6)
Molecule B							
Cu	5 979(2)	8 868(1)	3 653(1)	O(3′)	2 294(16)	2 906(6)	6 275(6)
N(1)	5 212(16)	6 967(7)	1 335(7)	P(2)	1 085(5)	7 058(2)	5 693(2)
C(2)	4 855(20)	5 933(9)	1 672(8)	O(5′)	1 636(14)	5 953(6)	5 700(7)
N(2)	4 554(19)	5 421(8)	937(7)	O(7′)	2 908(14)	7 498(6)	6 141(6)
N(3)	4 824(16)	5 447(7)	2 559(7)	O(8′)	−601(14)	6 921(7)	6 320(5)
C(4)	5 153(18)	6 048(8)	3 180(8)	O(9′)	735(14)	7 572(6)	4 617(6)
C(5)	5 601(20)	7 070(8)	2 952(8)	N(11)	6 193(15)	286(6)	2 891(6)
C(6)	5 591(19)	7 581(9)	1 979(9)	C(11)	7 141(17)	1 178(8)	3 124(10)
O(6)	5 953(15)	8 520(6)	1 650(6)	N(12)	6 209(15)	1 537(7)	1 555(7)
N(7)	5 766(15)	7 376(7)	3 812(6)	C(12)	7 135(17)	1 947(9)	2 289(8)
C(8)	5 415(21)	6 591(9)	4 540(10)	C(13)	5 643(8)	546(8)	1 942(8)
N(9)	5 050(16)	5 723(6)	4 201(7)	C(14)	7 994(19)	1 267(10)	3 974(1)
C(1′)	4 265(21)	4 732(8)	4 703(8)	C(15)	8 936(23)	2 294(11)	3 977(11)
C(2′)	4 390(20)	4 497(9)	5 812(8)	C(16)	8 822(25)	3 062(8)	3 115(11)
C(3′)	2 433(20)	3 974(8)	6 129(8)	C(17)	7 926(23)	2 918(9)	2 270(10)
C(4′)	1 139(21)	4 392(10)	5 279(9)	C(18)	8 760(12)	9 019(6)	3 913(6)
C(5′)	192(21)	5 292(10)	5 350(9)	C(19)	3 194(13)	8 706(6)	3 388(6)
O(1′)	2 284(14)	4 615(6)	4 450(6)	C(20)	5 427(16)	8 967(6)	5 150(6)
Water of crystallization							
O(W4)	3 010(20)	595(8)	4 615(7)	O(W8)	7 995(21)	2 339(15)	6 288(9)
O(W5)	5 517(22)	6 410(10)	7 153(11)	O(W9)	8 271(28)	8 841(18)	6 602(13)
O(W6)	4 210(18)	8 373(9)	9 443(7)	O(W10)	5 466(39)	9 684(19)	7 652(19)
O(W7)	4 672(19)	2 285(7)	5 130(7)	O(W11)	3 728(22)	6 292(10)	8 869(9)

atoms were refined with anisotropic thermal parameters. The shifts in parameters in the last cycle were less than 0.1σ. The weighting scheme employed was of the form $w = [\sigma^2|F_o| + 0.0001|F_o|^2]^{-1}$. Final *R* and *R′* values were 0.050 and 0.052 respectively. The final difference electron density map revealed no peak higher than 0.2 e Å^{-3}.

The neutral scattering factors for Cu were taken from ref. 14 and for the rest of the atoms were used as available in the SHELX 76 program.[15] Anomalous dispersion corrections were applied to the scattering factors of all non-hydrogen atoms.[16] Diagrams were drawn using the programs ORTEP II[17] and PLUTO 78.[18] Final atomic coordinates for non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results

The molecular structure and atom labelling scheme are shown in Fig. 1. Selected bond lengths and angles are given in Tables 3 and 4 respectively. Torsion angles are listed in Table 5.

Metal Co-ordination.—The copper(II) ions of both the molecules have square-pyramidal geometry. The purine base atom N(7), bzim ring nitrogen, N(11) and two water molecules constitute the square base [Cu–N(7) 2.01(1), 2.02(1) Å; Cu–N(11) 1.97(1), 1.99(1) Å, Cu–O (mean) 1.97(1) Å]. (The two values are for molecules A and B respectively.) The axial position is occupied by another water molecule O(W3) at a longer distance [Cu–O(W3) 2.228(8), 2.231(10) Å]. The *cis* bond angles around the metal range between 85.2 and 96.9° in molecule A and between 88.5 and 103.0° in molecule B. The *trans* bond angles are 170.1 and 170.5° in A and 154.4 and 179.5° in B. The copper(II) ion shows a deviation from the square plane of 0.164 Å in A and 0.183 Å in B.

Molecular Structure.—The purine base and the bzim ring in both molecules are planar. The pyrimidine and benzimidazole rings of the purine framework are inclined to each other about the C(4)–C(5) bond by 5.6° in A and 5.1° in B. The dihedral angle between the purine plane and the best sugar plane in 88.1° in A and 77.5° in B. The orientation of the sugar with respect to the purine ring is *anti*, $\chi_{CN} = -81.9°$ (A), $-66.1°$ (B).[19] The conformation about the C(4′)–C(5′) bond is *gauche-gauche*, the angles ψ_{OO} and ψ_{OC} being −71 and −76° in A and 48 and 44° in B respectively.

Although there is similarity in the sugar–base linkage, there is a major difference in the sugar conformation between the two

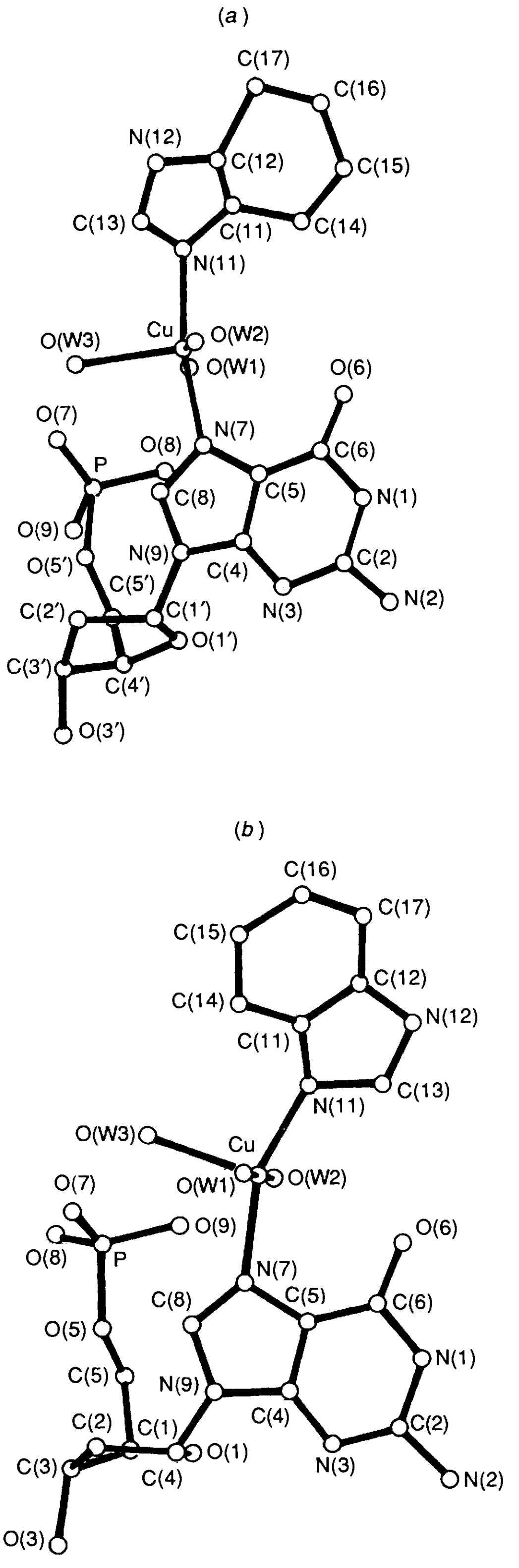

Fig. 1 An ORTEP plot of the two molecules A(*a*) and B(*b*) in the asymmetric unit of [Cu(bzim)(5′-dGMP)$(H_2O)_3$]·$2H_2O$ with the numbering scheme

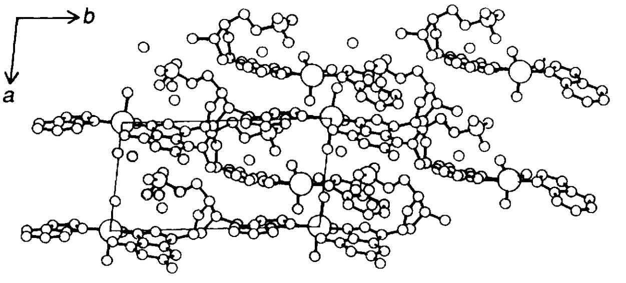

Fig. 2 The packing of the molecules of [Cu(bzim)(5′-dGMP)$(H_2O)_3$]·$2H_2O$ in the unit cell viewed down the *c* axis

molecules in the asymmetric unit. The sugar ring of molecule A shows a C(2′)-*endo*/C(3′)-*exo* twist pucker. On the other hand, the deoxyribose ring of molecule B displays C(3′)-*exo* pucker. Thus, the sugar moieties show two diverse puckering modes, one with a twist form and the other in the envelope form. Both these sugar geometries are unusual and there are no reports of these sugar puckering modes so far. Other unusual puckering modes found previously are C(2′)-*exo* and O(1′)-*endo* in [{Cu(5′-UMP)(dpa)(H_2O)}$_2$],[7] C(1′)-*exo* and C(4′)-*endo* in [{Cu(5′-CMP)(dpa)(H_2O)}$_2$],[8] C(4′)-*exo* in [{Cu(5′-IMP)(dpa)(H_2O)}$_2$],[9] C(3′)-*endo*-C(4′)-*exo* in [Cd_2(5′-dCMP)$_2$$(H_2O)_2$],[20] C(3′)-*endo*/C(2′)-*exo* in [Cd(5′-UMP)$(H_2O)_2$][21] and C(1′)-*endo* and C(4′)-*exo* in [Cd_2(5′-dUMP)$_2$$(H_2O)_6$].[21] A C(3′)-*exo* pucker ring is very uncommon while C(3′)-*exo*/C(2′)-*endo* pucker was observed for the deoxyribose of thymidine,[22] deoxyadenosine[23] and Na_2[5′-dCMP][24] and C(3′)-*exo*/C(2′)-*exo* pucker in the free acid of 5′-dCMP.[25] This observation suggests that the 3′-*exo* conformation may be energetically more favoured for deoxyribose groups.

The conformation about C(5′)–O(5′) bond as defined by the torsion angle φ is 156.9° for A and 171.3° for B.

Packing and Hydrogen-bonding Interactions.—In the case of molecules containing planar π-aromatic rings, there is a general tendency for parallel stacking between the planar groups with a separation of *ca.* 3.5 Å. In the present structure, there is stacking between intercomplex base–bzim at an average distance of 3.5 Å (Fig. 2). These interactions are necessarily of the AB-type cross stacking which also occur in [{Cu(3′-GMP)(phen)(H_2O)}$_2$],[26] [{Cu(5′-AMPH)(bipy)(H_2O)}$_2$][10] and in [Cu(bzim)(H_2O)]-[5′-IMP].[11] A general observation among all these complexes with AB cross stacking is that the aromatic ring and the nucleotide base are in a parallel arrangement. The crystal packing is further stabilized through intermolecular hydrogen bonding and hydrogen bonds involving lattice water molecules.

Discussion

The present study is the first example of a ternary metal complex involving a deoxynucleotide and a π-aromatic amine. It is interesting that in this complex the nucleotide co-ordination is through the N(7) of the base in contrast to the expected phosphate co-ordination, which has been proposed from the results of solution studies of Sigel and co-workers,[3,4,6] and also confirmed in the solid state for the complexes, [Cu(3′-GMP)(phen)(H_2O)],[26] [{Cu(AMPH)(bipy)(H_2O)}$_2$],[10] [Cu(IMP)(dpa)(H_2O)][9] and [{Cu(5′-UMP)(dpa)$(H_2O)_2$}$_n$].[7] Ternary metal complexes containing ATP namely, [Cu(ATP)(phen)][27] and [Zn(ATP)(bipy)][28] also showed a 'phosphate-only' binding mode. The present structure represents only the second example of metal binding to N(7) following the earlier report on Na_2[Cu(5′-IMP)$_2$(Him)$_{0.8}$$(H_2O)_{3.2}$][29] where the novel metal interaction was attributed to the less π-accepting property of the imidazole. In the present case, bzim although having more π-accepting character than Him, is not as strong a π-acceptor as bipy or dpa to impart discriminating qualities to the metal ion. Hence the metal prefers to bind to the nitrogen donors of the base.

It is well known that the sugar in a deoxyribonucleotide has greater flexibility and hence shows a broad range of puckering compared to a ribonucleotide. Swaminathan and Sundaralingam[30] have pointed out that the fundamental conform-

Table 3 Bond distances involving non-hydrogen atoms with e.s.d.s in parentheses

	Molecule A	Molecule B		Molecule A	Molecule B
Cu–N(7)	2.01(1)	2.02(1)	C(2′)–C(3′)	1.52(2)	1.51(2)
Cu–N(11)	1.97(1)	1.99(1)	C(3′)–C(4′)	1.55(2)	1.50(2)
Cu–O(W1)	1.98(1)	1.97(1)	C(3′)–O(3′)	1.43(1)	1.44(1)
Cu–O(W2)	1.97(1)	1.97(1)	C(4′)–C(5′)	1.50(2)	1.53(2)
Cu–O(W3)	2.23(1)	2.23(1)	C(4′)–O(1′)	1.49(2)	1.42(2)
N(1)–C(2)	1.39(2)	1.39(2)	C(5′)–O(5′)	1.42(2)	1.43(2)
N(1)–C(6)	1.39(2)	1.40(2)	P(1)–O(5′)	1.62(1)	1.64(1)
C(2)–N(2)	1.35(2)	1.40(2)	P(1)–O(7)	1.51(1)	1.52(1)
C(2)–N(3)	1.37(1)	1.27(1)	P(1)–O(8)	1.51(1)	1.50(1)
N(3)–C(4)	1.34(2)	1.35(1)	P(1)–O(9)	1.52(1)	1.53(1)
C(4)–C(5)	1.38(2)	1.38(2)	N(11)–C(11)	1.38(1)	1.43(1)
C(4)–N(9)	1.38(2)	1.41(1)	N(11)–C(13)	1.30(2)	1.35(1)
C(5)–C(6)	1.36(2)	1.38(2)	C(11)–C(12)	1.35(2)	1.38(2)
C(5)–N(7)	1.42(1)	1.39(1)	C(11)–C(14)	1.47(2)	1.34(1)
C(6)–O(6)	1.26(2)	1.27(2)	N(12)–C(12)	1.41(2)	1.39(2)
N(7)–C(8)	1.30(2)	1.31(2)	N(12)–C(13)	1.35(2)	1.37(2)
C(8)–N(9)	1.38(2)	1.40(2)	C(12)–C(17)	1.39(2)	1.39(2)
N(9)–C(1′)	1.46(1)	1.44(1)	C(14)–C(15)	1.38(2)	1.49(2)
C(1′)–C(2′)	1.54(2)	1.52(2)	C(15)–C(16)	1.41(2)	1.41(2)
C(1′)–O(1′)	1.43(2)	1.42(2)	C(16)–C(17)	1.39(2)	1.36(2)

Table 4 Bond angles involving non-hydrogen atoms with e.s.d.s in parentheses

	Molecule A	Molecule B		Molecule A	Molecule B
N(7)–Cu–N(11)	170.5(4)	154.4(4)	C(2′)–C(1′)–O(1′)	107.6(10)	105.3(10)
N(7)–Cu–O(W1)	93.5(4)	94.2(4)	C(1′)–C(2′)–C(3′)	103.3(9)	105.0(10)
N(7)–Cu–O(W2)	94.8(4)	85.3(4)	C(2′)–C(3′)–C(4′)	103.3(10)	103.1(10)
N(7)–Cu–O(W3)	92.6(4)	102.2(4)	C(2′)–C(3′)–O(3′)	111.0(9)	112.5(10)
N(11)–Cu–O(W1)	86.4(4)	89.3(4)	C(4′)–C(3′)–O(3′)	109.1(10)	109.2(10)
N(11)–Cu–O(W2)	86.3(4)	91.0(4)	C(3′)–C(4′)–C(5′)	105.3(11)	116.0(11)
N(11)–Cu–O(W3)	96.9(4)	103.0(4)	C(3′)–C(4′)–O(1′)	105.2(10)	105.1(10)
O(W1)–Cu–O(W2)	170.1(4)	179.5(4)	C(5′)–C(4′)–O(1′)	110.7(11)	112.1(11)
O(W1)–Cu–O(W3)	88.9(4)	91.9(4)	C(4′)–C(5′)–O(5′)	109.5(11)	106.8(11)
O(W2)–Cu–O(W3)	85.2(4)	88.5(4)	C(1′)–O(1′)–C(4′)	109.9(9)	112.2(10)
C(2)–N(1)–C(6)	123.3(10)	121.3(11)	O(5′)–P(1)–O(7)	101.6(5)	100.8(5)
N(1)–C(2)–N(2)	117.3(11)	114.4(11)	O(5′)–P(1)–O(8)	107.0(5)	108.5(2)
N(1)–C(2)–N(3)	123.1(11)	125.8(12)	O(5′)–P(1)–O(9)	108.8(5)	105.2(5)
N(2)–C(2)–N(3)	119.5(11)	119.7(12)	O(7)–P(1)–O(8)	109.8(10)	112.5(5)
C(2)–N(3)–C(4)	111.6(10)	112.6(11)	O(7)–P(1)–O(9)	117.0(6)	113.5(5)
N(3)–C(4)–C(5)	127.3(11)	127.7(11)	O(8)–P(1)–O(9)	111.6(6)	114.9(5)
N(3)–C(4)–N(9)	124.7(11)	125.0(11)	C(5′)–O(5′)–P(1)	121.7(8)	116.9(8)
C(5)–C(4)–N(9)	107.9(10)	107.2(10)	Cu(1)–N(11)–C(11)	126.7(8)	130.9(8)
C(4)–C(5)–C(6)	121.2(11)	118.3(11)	Cu(1)–N(11)–C(13)	128.1(9)	121.9(8)
C(4)–C(5)–N(7)	107.4(10)	108.1(10)	C(11)–N(11)–C(13)	104.8(10)	106.5(9)
C(6)–C(5)–N(7)	131.2(11)	133.1(11)	N(11)–C(11)–C(12)	112.7(11)	107.9(10)
N(1)–C(6)–C(5)	113.2(11)	114.1(11)	N(11)–C(11)–C(14)	127.9(11)	127.5(11)
N(1)–C(6)–O(6)	119.2(11)	119.8(11)	C(12)–C(11)–C(14)	119.1(11)	124.5(12)
C(5)–C(6)–O(6)	127.1(11)	126.0(12)	C(12)–N(12)–C(13)	107.9(11)	108.7(10)
Cu(1)–N(7)–C(5)	127.8(7)	115.4(8)	C(11)–C(12)–N(12)	102.7(11)	106.7(10)
Cu(1)–N(7)–C(8)	124.3(8)	134.6(9)	C(11)–C(12)–C(17)	125.7(12)	122.5(12)
C(5)–N(7)–C(8)	106.5(10)	108.7(10)	N(12)–C(12)–C(17)	131.5(12)	130.9(12)
N(7)–C(8)–N(9)	112.7(11)	110.4(11)	N(11)–C(13)–N(12)	111.6(11)	110.2(10)
C(4)–N(9)–C(8)	105.5(10)	105.5(10)	C(11)–C(14)–C(15)	117.2(12)	114.8(11)
C(4)–N(9)–C(1′)	124.7(10)	123.4(10)	C(14)–C(15)–C(16)	119.4(13)	118.4(13)
C(8)–N(9)–C(1′)	128.1(10)	129.4(10)	C(15)–C(16)–C(17)	124.4(15)	123.6(14)
N(9)–C(1′)–C(2′)	113.3(10)	115.9(10)	C(12)–C(17)–C(16)	113.9(13)	116.0(13)
N(9)–C(1′)–O(1′)	107.1(10)	107.7(10)			

ational preferences of the sugar moieties in nucleosides and nucleotides is less affected by the 5′-phosphate group than by the 2′-hydroxy group. Also, they suggested that metal binding by itself does not affect the preferred nucleotide conformation. The deoxyribose sugar in many structures reported earlier with general formula [M(nucleotide)$(H_2O)_5$] is in the C(3′)-*endo* puckering mode as found for corresponding ribonucleotide complexes. Hence, C(3′)-*endo* pucker is preferred despite the presence of the 2′-hydroxyl group.

On the other hand, for $[Co(en)_2(H_2O)][Co(GMP)_2(H_2O)_4]$,[31] its IMP analogue, $[Ni(en)_2(H_2O)_2][Ni(GMP)_2(H_2O)_4]$ and its dGMP analogue,[32] and in $Na_2[Cu(5'\text{-}IMP)_2(Him)_{0.8}(H_2O)_{3.2}]$,[29] where the *cis* positions of the metal co-ordination are occupied by nucleotides, the sugar takes up the C(2′)-*endo* puckering mode irrespective of the presence of the 2′-hydroxyl group. When the sugar is in the *endo* conformation the phosphate group is in a favourable position to form two strong metal–water–phosphate bridging interactions resulting in a loose six-membered chelate. These interactions apparently require the ribose ring to adopt a particular puckering mode so as effectively to bring the phosphate group in the proximity of the metal ion. In the case of self base-stacked complexes where nucleotides are in *cis* positions, the phosphate is not in a position to form such a type

Table 5 Torsional angles (°) involving the sugar ring and the phosphate group with e.s.d.s in parentheses

	Molecule A	Molecule B
C(4)–N(9)–C(1′)–O(1′)	−82(1)	−66(1)
C(4)–N(9)–C(1′)–C(2′)	159(1)	176(1)
C(8)–N(9)–C(1′)–O(1′)	81(1)	97(1)
C(8)–N(9)–C(1′)–C(2′)	−38(2)	−20(2)
N(9)–C(1′)–C(2′)–C(3′)	144(1)	−134(1)
N(9)–C(1′)–O(1′)–C(4′)	−129(1)	−121(1)
C(2′)–C(1′)–O(1′)–C(4′)	−7(1)	3(1)
O(1′)–C(1′)–C(2′)–C(3′)	25(1)	16(1)
C(1′)–C(2′)–C(3′)–C(4′)	−32(1)	−28(1)
C(2′)–C(3′)–C(4′)–O(1′)	28(1)	30(1)
C(1′)–O(1′)–C(4′)–C(3′)	−13(1)	−21(1)
C(1′)–C(2′)–C(3′)–O(3′)	84(1)	90(1)
O(1′)–C(4′)–C(3′)–O(3′)	−89(1)	−90(1)
C(1′)–O(1′)–C(4′)–C(5′)	112(1)	105(1)
C(2′)–C(3′)–C(4′)–C(5′)	−94(1)	−94(1)
O(3′)–C(3′)–C(4′)–C(5′)	148(1)	146(1)
O(1′)–C(4′)–C(5′)–O(5′)	−71(1)	−76(1)
C(3′)–C(4′)–C(5′)–O(5′)	48(1)	44(1)
C(4′)–C(5′)–O(5′)–P	157(1)	171(1)
O(7)–P–O(5′)–C(5′)	−180(1)	178(1)
O(8)–P–O(5′)–C(5′)	−64(1)	91(1)
O(9)–P–O(5′)–C(5′)	56(1)	−64(1)

of hydrogen-bonded co-ordination and forms only hydrogen bonding interactions with the metal. Thus the sugar appears to be stabilized in the C(2′)-*endo* puckering mode.

It was suggested[30] that in ternary complexes involving bulkier ligands like bipy or terpy the effect of cocrystallization seems more pronounced and the nucleotides may adopt less preferred ribose puckering. It is also possible that the competition between packing forces and the tendency to maximize metal–phosphate and/or base interactions, as well as base–base or base–ligand stacking hinders the adoption of the usual nucleotide conformations. In the present structure the ternary ligand, bzim, is not very bulky and it is likely that metal–base binding and the nucleobase–bzim stacking have influenced the unusual conformation of the flexible deoxyribose ring.

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