

Crystallographic Studies of Interactions between Nucleotides and Metal Ions.

III. Two Independent Structural Investigations of the Polymeric Complex of Copper(II) with Guanosine 5'-Phosphate*

BY GEORGE R. CLARK AND JOHN D. ORBELL

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

AND KATSUYUKI AOKI

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

(Received 7 July 1977; accepted 2 February 1978)

The results of the two independent X-ray analyses of the complex formed between cupric ions and the nucleotide guanosine 5'-monophosphate are presented and compared. The crystals are polymeric, with a spiralling sequence, $(-\text{Cu}-\text{phosphate}-\text{sugar}-\text{base}-)_{\infty}$, the turns of which are cross-linked by additional bonds between copper and phosphate O atoms and by hydrogen bonding between coordinated water molecules and phosphate O atoms. The purine bases project outwards from the spiral and intercalate between bases of neighbouring chains. This 'base stacking' is associated with significant differences in the sugar ring conformations where two are puckered C(3')-endo and one is C(2')-endo. The square-pyramidal coordination pattern is not the same for the three independent Cu atoms. Each binds to N(7) of the purine, but two bind to three O(H₂O) and one O(phosphate) whereas the other binds to two O(H₂O) and two O(phosphate). Crystal data: orthorhombic, space group $P2_12_12_1$, $Z = 4$ [of the empirical formula $\text{Cu}_3(\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_8\text{P})_3 \cdot (\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$], with $a = 20.758$ (5), $b = 23.370$ (5), $c = 11.345$ (3) Å (Aoki); $a = 20.813$ (4), $b = 23.356$ (3), $c = 11.392$ (1) Å (Clark & Orbell).

Introduction

Never before have we been more aware of the need to fully understand the consequences of subtle conformational changes on the behaviour of biological molecules, especially the nucleic acids. With molecular fine structure of RNA molecules now being revealed by X-ray diffraction (Ladner, Jack, Robertus, Brown, Rhodes, Clark & Klug, 1975; Kim, Suddath, Quigley, McPherson, Sussman, Wang, Seeman & Rich, 1974; Sussman & Kim, 1976) it is possible to visualize with a new confidence the step-by-step processes leading to genetic replication and protein synthesis. Structural investigations of nucleic acid constituents are providing conformational parameters which, in time, will be able to be correlated with those of the free acids.

Metal ions are known to mediate nucleic acid reactions and are even specific components of some DNA and RNA molecules (Izatt, Christensen & Rytting, 1971), and much current research is being directed towards the understanding of the precise role that metal ions play in such systems. Recent crystal structure analyses have shown the complexes nickel-guanosine 5'-phosphate (Ni-GMP) (de Meester, Goodgame, Skapski & Smith, 1974), Mn-GMP (de Meester, Goodgame, Jones & Skapski, 1974a),

Co-GMP (de Meester, Goodgame, Jones & Skapski, 1974b), Cd-GMP (Aoki, 1976a), nickel-adenosine 5'-phosphate (Ni-AMP) (Collins, de Meester, Goodgame & Skapski, 1975), cobalt-inosine 5'-phosphate (Co-IMP) (Aoki, 1975; de Meester, Goodgame, Jones & Skapski, 1974b), and Ni-IMP (Aoki, 1975; Clark & Orbell, 1974) to be monomeric with each metal ion directly bonded to N(7) of the base, and with intramolecular hydrogen bonding between coordinated water molecules and phosphate O atoms. Their sugar rings are puckered C(3')-endo (Jardetsky, 1960), the conformation about the C(4')-C(5') bond is *gauche-gauche* (Shefter & Trueblood, 1965), the orientation of the base and sugar is *anti* (Sundaralingam & Jensen, 1965), and the purine rings assume a 'base-stacking' arrangement. On the other hand, the complexes Zn-IMP (de Meester, Goodgame, Jones & Skapski, 1974c), Cu-IMP (Aoki, 1977), Cd-IMP (Goodgame, Jeeves, Reynolds & Skapski, 1975a), cobalt-cytidine 5'-phosphate (Co-CMP) (Clark & Orbell, 1975), Zn-CMP (Aoki, 1976b), Mn-CMP (Aoki, 1976c), and Cd-CMP (Clark & Orbell, 1975; Goodgame, Jeeves, Reynolds & Skapski, 1975b; Bau, Gellert & Shiba, 1975) exhibit a variety of polymeric structures in which each metal ion is bonded to the base of one nucleotide and to phosphate groups of others, and some complexes assume an alternative C(2')-endo sugar pucker and some adopt base stacking while others do not. In

* Part II: Aoki (1976a).

addition, two platinum–nucleotide complexes, Pt–IMP (Goodgame, Jeeves, Phillips & Skapski, 1975) and Pt–CMP (Louie & Bau, 1977), have been reported; an IMP nucleotide molecule coordinates in a monodentate fashion through the base in the former, and a CMP nucleotide molecule acts as a bridging bidentate ligand *via* the base and a phosphate group, forming a dimeric structure with the C(2')-endo puckered sugars, in the latter. Besides the binary complexes noted above, two ternary complexes have been reported: Cu–uridine 5'-phosphate–2,2'-bipyridylamine complex (Fischer & Bau, 1977) forms a dimeric structure with a metal ion coordinated through the phosphate groups only and sugar rings adopt unusual C(2')-exo and O(1')-endo puckering modes; and Cu–IMP–2,2'-bipyridyl complex (Aoki, 1977) is a monomeric structure with a metal ion coordinated through the base only and the sugar ring has the usual C(3')-endo puckering mode. It is not yet clear which factors are responsible for the observed geometries, and it is therefore important to study as many such complexes as possible.

We have independently investigated the crystal structure of Cu–GMP and in a preliminary report have described its novel polymeric structure as requiring three independent Cu atoms, both C(3')-endo and

C(2')-endo sugar ring conformations, and base stacking (Aoki, Clark & Orbell, 1976). We now jointly present details of the refined structure.

More recently, Sletten & Lie (1976) have reported the crystal structure of the same complex.

X-ray data collection and structure determination

Light-green crystals were obtained by the method of Ogawa & Sakaguchi (1971) from the disodium salt of guanosine 5'-phosphate and copper nitrate trihydrate in an equimolar ratio at pH 4.

Preliminary X-ray photography showed the crystals to belong to the orthorhombic system with systematic absences characteristic of space group $P2_12_12$.

The unit-cell dimensions and intensity data were measured on an automated diffractometer. A listing of experimental quantities associated with data collection is given in Table 1. Lorentz and polarization corrections were made in the normal manner, but no correction was applied for the absorption effect because of the small crystal size and the low linear absorption coefficient.

Table 1. *Crystal data and experimental details*

(a) Crystal data	Aoki	Clark & Orbell
Empirical formula	$\text{Cu}_3(\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_8\text{P})_3(\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$	
System	Orthorhombic	
<i>a</i> (Å)	20.758 (5)	20.813 (4)
<i>b</i> (Å)	23.370 (5)	23.356 (3)
<i>c</i> (Å)	11.345 (3)	11.392 (1)
<i>U</i> (Å ³)	5503.6	5537.7
Space group	$P2_12_12$	
<i>Z</i>	4	
<i>D_m</i> (by flotation) (g cm ⁻³)	1.83	
	(in benzene–methyl iodide)	
<i>D_x</i> (g cm ⁻³)	1.81	
Crystal dimensions (mm)	0.3 × 0.1 × 0.1	0.10 × 0.06 × 0.04
μ (Cu <i>K</i> α) (cm ⁻¹)	31.92	31.92
(b) Measurement of intensity data		
Instrument	Rigaku four-circle diffractometer	Hilger & Watts four-circle diffractometer
Radiation	Cu <i>K</i> α	Cu <i>K</i> α
Reflexions measured	2316 [$>3\sigma(F_o)$]	1705 [$>1.50\sigma(I)$]
2θ limits measured (°)	100	90
Scan type	2θ–ω	2θ–ω
Scan rate	2° min ⁻¹	0.15° min ⁻¹ for θ ≤ 30° 0.3° min ⁻¹ for θ > 30°
Background count time	10 s	40 s for θ ≤ 30° 20 s for θ > 30°
(c) Agreement indices of least-squares refinement		
$R = \sum (F_o - F_c) / \sum F_o $	0.090	0.11
$R_w = \{ \sum w(F_o - F_c)^2 / \sum w(F_o)^2 \}^{1/2}$	0.109	0.09
Weighting scheme	$\sqrt{w} = 0.02$ for $F_o \leq 30.0$ $\sqrt{w} = 1.0$ for $30.0 < F_o \leq 120.0$ $\sqrt{w} = 120.0/F_o$ for $F_o > 120.0$	$\sqrt{w} = 2F_o/\sigma(F_o^2)$
Dispersion-correction atoms	Cu	Cu and P

Table 2. *Final atomic parameters (non-hydrogen atoms $\times 10^4$; hydrogen atoms $\times 10^3$) and their standard deviations*

	Aoki			Clark & Orbell		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Cu(A)	2996 (2)	-1278 (2)	6840 (5)	3006 (2)	-1282 (2)	6823 (4)
P(A)	2312 (4)	-2694 (4)	3145 (8)	2315 (5)	-2700 (4)	3160 (1)
O(W1A)	2266 (11)	-1218 (14)	7951 (22)	2283 (11)	-1221 (10)	7949 (20)
O(W2A)	3384 (12)	-714 (11)	7897 (22)	3368 (9)	-689 (9)	7846 (19)
O(W3A)	2606 (8)	-1989 (9)	6126 (21)	2625 (8)	-2006 (10)	6100 (20)
O(1A)	1781 (8)	-3120 (8)	3497 (19)	1821 (10)	-3132 (10)	3511 (20)
O(2A)	2812 (10)	-2610 (9)	4064 (16)	2800 (9)	-2607 (8)	4080 (18)
O(3A)	2578 (12)	-2848 (10)	2004 (18)	2604 (12)	-2874 (10)	1985 (23)
O(1'A)	1667 (9)	-959 (10)	2339 (20)	1608 (11)	-961 (9)	2373 (20)
O(2'A)	2426 (24)	-422 (14)	275 (29)	2353 (13)	-409 (12)	288 (25)
O(3'A)	2683 (13)	-1550 (12)	129 (24)	2695 (12)	-1519 (11)	188 (23)
O(5'A)	1960 (10)	-2075 (9)	3021 (22)	1979 (11)	-2095 (10)	3031 (20)
O(6A)	2807 (11)	291 (10)	7172 (19)	2826 (10)	296 (9)	7181 (18)
N(1A)	2564 (13)	859 (10)	5674 (26)	2593 (14)	854 (12)	5655 (26)
N(2A)	2339 (14)	1533 (12)	4213 (26)	2291 (13)	1530 (11)	4223 (25)
N(3A)	2303 (15)	546 (11)	3651 (24)	2311 (13)	541 (12)	3722 (25)
N(7A)	2681 (15)	-714 (11)	5400 (26)	2647 (12)	-729 (11)	5284 (23)
N(9A)	2384 (14)	-473 (12)	3480 (31)	2365 (13)	-499 (12)	3513 (25)
C(1'A)	2157 (14)	-541 (14)	2253 (33)	2059 (16)	-514 (15)	2308 (30)
C(2'A)	2613 (16)	-682 (16)	1382 (26)	2604 (21)	-666 (18)	1362 (41)
C(3'A)	2523 (16)	-1336 (15)	1255 (29)	2500 (18)	-1345 (16)	1304 (35)
C(4'A)	1809 (14)	-1396 (16)	1378 (30)	1769 (16)	-1399 (15)	1410 (31)
C(5'A)	1621 (20)	-1958 (13)	1991 (32)	1597 (17)	-2019 (16)	1942 (31)
C(2A)	2395 (18)	975 (14)	4517 (28)	2419 (17)	1000 (15)	4517 (34)
C(4A)	2442 (19)	31 (17)	4161 (33)	2391 (18)	32 (17)	4177 (32)
C(5A)	2558 (12)	-84 (12)	5296 (30)	2584 (18)	-121 (16)	5296 (36)
C(6A)	2693 (21)	319 (18)	6093 (27)	2690 (20)	295 (18)	6103 (37)
C(8A)	2541 (17)	-919 (13)	4343 (39)	2485 (19)	-960 (17)	4190 (36)
Cu(B)	4119 (2)	1734 (2)	6506 (4)	4117 (2)	1741 (2)	6485 (4)
P(B)	4065 (4)	3026 (3)	2858 (8)	4048 (4)	3024 (4)	2843 (9)
O(W1B)	4008 (10)	1117 (8)	7698 (23)	3979 (10)	1105 (9)	7634 (20)
O(W2B)	4309 (11)	2449 (9)	5581 (21)	4278 (10)	2478 (9)	5622 (18)
O(1B)	4773 (10)	2887 (10)	3129 (22)	4762 (11)	2895 (10)	3103 (21)
O(2B)	3672 (9)	2944 (9)	3920 (16)	3626 (10)	2951 (9)	3963 (19)
O(3B)	3953 (10)	3613 (9)	2274 (20)	3945 (9)	3641 (9)	2284 (18)
O(1'B)	4266	1439 (9)	1214 (19)	4264 (11)	1410 (10)	1171 (21)
O(2'B)	2641 (11)	990 (10)	1416 (21)	2617 (11)	977 (10)	1451 (22)
O(3'B)	3113 (9)	1408 (12)	-641 (20)	3077 (12)	1414 (11)	-614 (22)
O(5'B)	3792 (10)	2535 (10)	1980 (23)	3783 (9)	2547 (9)	2012 (19)
O(6B)	4266 (11)	128 (8)	6572 (21)	4267 (9)	143 (9)	6554 (17)
N(1B)	4205 (12)	-395 (11)	4859 (20)	4231 (12)	-393 (11)	4864 (23)
N(2B)	4181 (18)	-1033 (11)	3295 (31)	4174 (14)	-1070 (13)	3235 (27)
N(3B)	4083 (14)	-57 (12)	2946 (23)	4053 (12)	-78 (13)	2936 (22)
N(7B)	4072 (11)	1171 (11)	4856 (27)	4109 (13)	1159 (12)	4807 (24)
N(9B)	3946 (13)	965 (11)	2899 (22)	3905 (14)	953 (15)	2941 (29)
C(1'B)	3807 (16)	1050 (12)	1688 (36)	3741 (16)	1052 (15)	1578 (32)
C(2'B)	3108 (12)	1369 (14)	1493 (30)	3098 (15)	1361 (14)	1546 (29)
C(3'B)	3263 (17)	1706 (17)	395 (27)	3224 (18)	1729 (17)	557 (35)
C(4'B)	3949 (13)	1833 (14)	484 (34)	3964 (17)	1882 (16)	553 (30)
C(5'B)	4092 (14)	2442 (15)	917 (24)	4128 (16)	2474 (15)	919 (30)
C(2B)	4168 (18)	-499 (12)	3772 (27)	4143 (16)	-509 (17)	3639 (32)
C(4B)	4027 (17)	455 (14)	3500 (26)	4039 (16)	431 (17)	3435 (33)
C(5B)	4122 (14)	584 (16)	4661 (25)	4101 (17)	542 (16)	4653 (33)
C(6B)	4212 (12)	113 (14)	5451 (30)	4231 (15)	125 (14)	5489 (29)
C(8B)	3965 (13)	1348 (12)	3793 (23)	3957 (15)	1410 (15)	3751 (32)
Cu(C)	563 (2)	1749 (2)	7421 (4)	562 (2)	1744 (2)	7400 (4)
P(C)	605 (4)	3129 (3)	3861 (7)	606 (5)	3123 (4)	3876 (9)
O(W1C)	1439 (11)	1554 (14)	8282 (33)	1362 (11)	1554 (11)	8252 (23)
O(W2C)	136 (10)	1188 (11)	8475 (19)	101 (10)	1153 (9)	8503 (17)
O(W3C)	999 (6)	2423 (8)	6832 (18)	1016 (10)	2434 (10)	6739 (21)
O(1C)	1166 (9)	3583 (8)	3796 (22)	1106 (11)	3542 (10)	3832 (20)
O(2C)	422 (8)	3002 (9)	5096 (20)	452 (10)	2994 (9)	5102 (18)
O(3C)	53 (12)	3316 (8)	3068 (17)	22 (10)	3337 (9)	3100 (19)

Table 2 (cont.)

	Aoki			Clark & Orbell		
	x	y	z	x	y	z
O(1'C)	1257 (8)	1467 (8)	2531 (19)	1231 (9)	1448 (9)	2560 (19)
O(2'C)	287 (12)	743 (10)	980 (20)	295 (12)	723 (11)	1004 (23)
O(3'C)	-154 (12)	1810 (10)	872 (22)	-184 (11)	1818 (10)	853 (19)
O(5'C)	894 (10)	2532 (9)	3383 (20)	883 (10)	2512 (10)	3382 (21)
O(6C)	732 (10)	185 (8)	7788 (18)	747 (11)	201 (10)	7776 (19)
N(1C)	907 (11)	-411 (12)	6207 (25)	869 (14)	-441 (13)	6161 (27)
N(2C)	1033 (13)	-1072 (10)	4688 (29)	1021 (11)	-1086 (11)	4677 (22)
N(3C)	871 (16)	-126 (11)	4193 (28)	853 (15)	-100 (15)	4226 (25)
N(7C)	694 (14)	1170 (17)	5928 (22)	689 (12)	1153 (11)	5908 (22)
N(9C)	775 (12)	916 (9)	4021 (19)	756 (13)	921 (13)	4064 (26)
C(1'C)	828 (19)	964 (16)	2749 (29)	890 (16)	975 (14)	2731 (28)
C(2'C)	214 (17)	998 (17)	2057 (26)	237 (17)	1027 (15)	2116 (32)
C(3'C)	205 (16)	1706 (17)	1935 (35)	154 (21)	1698 (19)	1935 (38)
C(4'C)	898 (15)	1847 (10)	1773 (30)	921 (17)	1825 (16)	1894 (31)
C(5'C)	1029 (17)	2481 (13)	2146 (35)	1024 (17)	2449 (16)	2122 (33)
C(2C)	957 (14)	-517 (15)	5039 (29)	924 (16)	-501 (16)	4937 (32)
C(4C)	814 (17)	410 (14)	4658 (36)	816 (19)	412 (20)	4614 (35)
C(5C)	795 (19)	571 (15)	5854 (28)	723 (17)	580 (16)	5842 (31)
C(6C)	792 (14)	154 (11)	6737 (29)	763 (17)	85 (16)	6629 (30)
C(8C)	699 (15)	1342 (19)	4822 (26)	686 (14)	1392 (14)	4869 (26)
O(W4)	6784 (20)	4315 (12)	470 (42)	6754 (13)	4301 (12)	316 (24)
O(W5)	358 (15)	4140 (18)	1502 (43)	352 (12)	4113 (11)	1487 (22)
O(W6)	4152 (15)	4679 (16)	-44 (35)	4132 (13)	4677 (11)	48 (22)
O(W7)	5552 (24)	1247 (30)	669 (47)	5552 (19)	1251 (18)	808 (35)
O(W8)	6224 (36)	2195 (27)	567 (51)	6395 (17)	2271 (15)	461 (33)

	Aoki			Aoki			
	x	y	z	x	y	z	
H(N1A)	257 (11)	127 (10)	595 (20)	H(C3'B)	285 (11)	194 (10)	100 (21)
H(N2A)	206 (11)	164 (10)	372 (20)	H(C4'B)	422 (12)	182 (11)	-25 (24)
H'(N2A)	239 (12)	171 (11)	492 (25)	H(C5'B)	387 (11)	272 (10)	29 (21)
H(C8A)	272 (11)	-127 (10)	407 (21)	H'(C5'B)	455 (12)	233 (10)	86 (22)
H(C1'A)	194 (29)	-27 (25)	264 (55)	H(O2'B)	262 (12)	100 (11)	248 (25)
H(C2'A)	305 (11)	-67 (10)	154 (21)	H(O3'B)*	285	182	-74
H(C3'A)	296 (13)	-157 (12)	193 (25)	H(N1C)	116 (12)	-43 (10)	684 (22)
H(C4'A)	173 (11)	-114 (10)	62 (21)	H(N2C)*	130	-131	531
H(C5'A)	114 (11)	-201 (10)	210 (21)	H'(N2C)*	130	-100	388
H'(C5'A)*	170	-221	119	H(C8C)	39 (11)	181 (9)	503 (20)
H(O2'A)	225 (14)	5 (13)	23 (25)	H(C1'C)*	110	67	244
H(O3'A)*	310	-181	12	H(C2'C)	-11 (15)	100 (13)	272 (26)
H(N1B)	415 (11)	-77 (9)	531 (20)	H(C3'C)	-15 (10)	188 (10)	274 (20)
H(N2B)	388 (11)	-128 (10)	400 (20)	H(C4'C)	88 (11)	188 (9)	95 (20)
H'(N2B)	372 (19)	-114 (17)	258 (37)	H(C5'C)	78 (11)	275 (9)	151 (21)
H(C8B)	369 (11)	163 (10)	369 (21)	H'(C5'C)	141 (11)	257 (10)	215 (21)
H(C1'B)	351 (23)	62 (20)	118 (43)	H(O2'C)*	10	84	11
H(C2'B)	299 (11)	150 (10)	215 (20)	H(O3'C)	-19 (11)	181 (10)	-16 (20)

* These atoms were found on the final difference electron density map and their atomic parameters were not refined.

The structure was solved by conventional Patterson and electron density syntheses. Structure refinement was carried out by the methods of block-diagonal least squares (Aoki) and full-matrix least squares (Clark & Orbell), the function minimized being $\sum w(|F_o| - |F_c|)^2$, yielding final values of $R = 0.090$ and $R_w = 0.109$ (Aoki: 88 non-hydrogen atoms were all given anisotropic thermal parameters and 29 H atoms

isotropic ones), and $R = 0.11$ and $R_w = 0.09$ (Clark & Orbell: six Cu and P atoms were given anisotropic thermal parameters and other non-hydrogen atoms isotropic ones). In both cases, two water molecules [O(W7) and O(W8)] were adjudged to have only 50% occupancy. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) together with corrections for the anomalous scattering

of Cu and P atoms. The final atomic coordinates are listed in Table 2.* Details of the major computer programs employed by one of us (KA) have been mentioned elsewhere (Aoki & Yamamoto, 1976); those used by GRC and JDO were *XRC/HILGOUT*, *XRC/FOURIER*, and *XRC/CUCLS*, written by R. J. Dellaca, University of Canterbury, New Zealand.

Results and discussion

The crystals form by polymerizing individual metal-nucleotide units into helical chains, $(-\text{Cu}-\text{phosphate}-\text{sugar}-\text{base}-)_{\infty}$, whose turns are cross-linked by bridging through O atoms of the phosphate group. The guanine bases project radially from the outside of the spiral and intercalate between bases projecting from adjacent columns. The crystals also contain a number of uncoordinated water molecules of crystallization. The simplest empirical formula is $\text{Cu}_3(\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_8\text{P})_3 \cdot (\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$, but for the purpose of describing this rather complicated structure we have labelled the three crystallographically (and in part chemically) independent metal-nucleotide units *A*, *B*, and *C*. The atomic numbering scheme for one such unit is outlined in Fig. 1, while Fig. 2 gives a schematic representation of the overall structure. For simplicity, individual atoms of the sugar (*S*) and guanine (BASE) are not identified, nor are solvent water molecules. The content of the unit cell is illustrated in the perspective view of Fig. 3. Bond lengths and angles are listed in Tables 3 and 4.

It can be seen that there are two different types of phosphate bridging. The broken lines in Fig. 2 represent hydrogen bonds between phosphate O atoms and copper-coordinated water molecules. In this respect the structure shows a similarity to the majority of other metal-purine nucleotide complexes where intramolecular hydrogen bonds form between two metal-

coordinated water molecules and two phosphate O atoms of the same metal-nucleotide monomer. In the present compound these hydrogen bonds span to O atoms of the second phosphate group (*A* and *B*) along the spiral. The first phosphate group (*C*) is involved in the second type of cross-link, forming normal bonds to two different copper atoms (*A* and *B*). Now there is a similarity to other polymeric metal-purine and metal-pyrimidine structures where the phosphate O atoms act as donors to either two or three different metal atoms.

Copper ion coordination

The coordination about each Cu ion is distorted $(4 + 1)$ square pyramidal. The apical coordination sites are occupied by N(7) of the guanine base in each case, but for Cu(*A*) and Cu(*C*) the four planar donors are

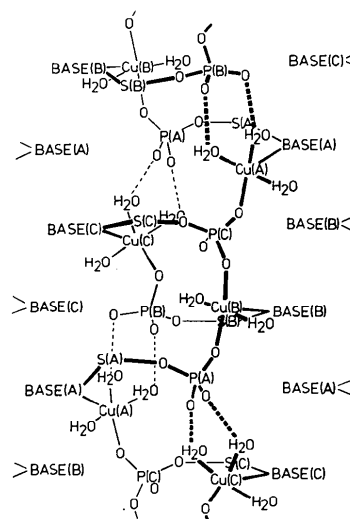


Fig. 2. Schematic representation of the polymeric structure. Broken lines indicate hydrogen bonds.

* Lists of structure factors and thermal parameters for both determinations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33430 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

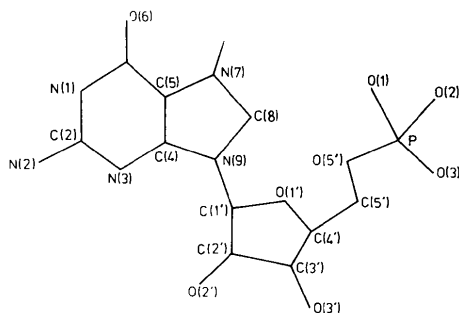


Fig. 1. The atomic numbering scheme for one nucleotide.

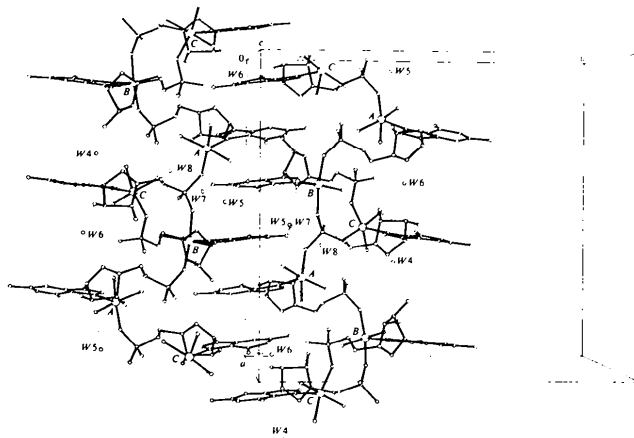


Fig. 3. Molecular packing viewed along the *c* axis. Large circles represent copper ions and broken lines hydrogen bonds.

Table 3. Bond lengths (Å) with their estimated standard deviations

	Molecule A		Molecule B		Molecule C	
	Aoki	Clark & Orbell	Aoki	Clark & Orbell	Aoki	Clark & Orbell
N(1)—C(2)	1.38 (4)	1.39 (4)	1.26 (4)	1.43 (5)	1.35 (4)	1.41 (5)
C(2)—N(2)	1.35 (4)	1.31 (4)	1.36 (4)	1.40 (4)	1.37 (4)	1.41 (5)
C(2)—N(3)	1.42 (4)	1.42 (4)	1.41 (4)	1.30 (5)	1.34 (4)	1.25 (5)
N(3)—C(4)	1.37 (4)	1.31 (5)	1.36 (4)	1.32 (5)	1.36 (4)	1.28 (5)
C(4)—C(5)	1.34 (5)	1.38 (6)	1.36 (4)	1.42 (6)	1.41 (5)	1.47 (6)
C(5)—C(6)	1.33 (5)	1.36 (6)	1.43 (5)	1.39 (5)	1.40 (4)	1.47 (6)
C(6)—N(1)	1.37 (5)	1.42 (5)	1.36 (4)	1.40 (4)	1.47 (4)	1.36 (5)
C(6)—O(6)	1.25 (4)	1.26 (5)	1.28 (4)	1.22 (3)	1.20 (4)	1.34 (5)
C(5)—N(7)	1.50 (4)	1.43 (5)	1.39 (5)	1.45 (5)	1.42 (4)	1.34 (5)
N(7)—C(8)	1.32 (5)	1.40 (5)	1.29 (4)	1.38 (4)	1.32 (4)	1.31 (4)
C(8)—N(9)	1.47 (5)	1.39 (5)	1.35 (4)	1.42 (4)	1.36 (4)	1.44 (4)
N(9)—C(4)	1.41 (5)	1.45 (5)	1.38 (4)	1.37 (5)	1.39 (4)	1.35 (5)
N(9)—C(1')	1.48 (5)	1.51 (4)	1.42 (5)	1.61 (4)	1.45 (4)	1.55 (4)
C(1')—C(2')	1.41 (5)	1.60 (6)	1.65 (4)	1.52 (5)	1.50 (5)	1.53 (5)
C(2')—C(3')	1.55 (5)	1.60 (6)	1.51 (5)	1.44 (5)	1.66 (6)	1.59 (6)
C(3')—C(4')	1.49 (4)	1.53 (6)	1.46 (4)	1.58 (6)	1.49 (5)	1.62 (6)
C(4')—O(1')	1.52 (4)	1.54 (5)	1.40 (4)	1.45 (5)	1.44 (4)	1.33 (5)
O(1')—C(1')	1.41 (4)	1.41 (4)	1.42 (4)	1.45 (4)	1.50 (4)	1.33 (4)
C(2')—O(2')	1.45 (5)	1.46 (5)	1.32 (4)	1.35 (4)	1.37 (4)	1.46 (5)
C(3')—O(3')	1.41 (4)	1.40 (5)	1.40 (4)	1.55 (5)	1.44 (5)	1.45 (5)
C(4')—C(5')	1.54 (5)	1.61 (6)	1.54 (5)	1.48 (6)	1.56 (4)	1.50 (6)
C(5')—O(5')	1.39 (4)	1.48 (5)	1.37 (4)	1.45 (5)	1.43 (5)	1.47 (5)
P—O(5')	1.63 (2)	1.58 (3)	1.62 (3)	1.56 (2)	1.61 (2)	1.64 (2)
P—O(1)	1.54 (2)	1.50 (2)	1.54 (2)	1.55 (2)	1.58 (2)	1.43 (2)
P—O(2)	1.48 (2)	1.47 (2)	1.47 (2)	1.56 (2)	1.48 (2)	1.46 (2)
P—O(3)	1.45 (3)	1.52 (3)	1.54 (2)	1.59 (2)	1.52 (2)	1.58 (2)

Table 4. Bond angles (°) with their estimated standard deviations

	Molecule A		Molecule B		Molecule C	
	Aoki	Clark & Orbell	Aoki	Clark & Orbell	Aoki	Clark & Orbell
N(1)—C(2)—N(3)	124(3)	117(3)	122(3)	118(3)	125(3)	124(4)
N(1)—C(2)—N(2)	117(3)	122(3)	124(3)	120(3)	118(3)	108(3)
N(3)—C(2)—N(2)	120(3)	121(3)	114(3)	122(3)	117(3)	127(4)
C(2)—N(3)—C(4)	108(3)	114(3)	111(3)	116(3)	111(3)	119(4)
N(3)—C(4)—C(5)	129(3)	130(4)	129(3)	126(4)	128(3)	126(4)
C(4)—C(5)—C(6)	123(3)	119(4)	117(3)	124(4)	120(3)	111(4)
C(5)—C(6)—N(1)	112(3)	113(4)	111(3)	105(3)	110(3)	119(4)
C(6)—N(1)—C(2)	124(3)	127(3)	131(3)	131(3)	125(3)	120(3)
C(5)—C(6)—O(6)	132(4)	134(4)	128(3)	132(3)	132(3)	116(3)
H(1)—C(6)—O(6)	115(3)	112(4)	121(3)	99(2)	119(3)	97(2)
C(4)—C(5)—N(7)	108(3)	106(4)	111(3)	108(3)	109(3)	109(3)
C(5)—N(7)—C(8)	104(3)	112(3)	100(3)	108(3)	104(3)	112(3)
N(7)—C(8)—N(9)	113(3)	104(3)	119(3)	106(3)	115(3)	105(2)
C(8)—N(9)—C(4)	102(3)	112(3)	101(2)	113(3)	106(3)	113(3)
N(9)—C(4)—C(5)	112(3)	106(3)	108(3)	105(3)	106(3)	101(3)
N(3)—C(4)—N(9)	119(3)	124(3)	123(3)	129(4)	126(3)	132(4)
C(6)—C(5)—N(7)	127(3)	135(4)	132(3)	128(3)	130(3)	139(4)
C(8)—N(9)—C(1')	129(3)	125(3)	130(3)	123(3)	128(3)	126(3)
C(4)—N(9)—C(1')	129(3)	121(3)	129(3)	125(3)	125(3)	121(3)
O(1')—C(1')—C(2')	112(3)	110(3)	105(3)	112(3)	112(3)	110(3)
C(1')—C(2')—C(3')	102(3)	99(3)	99(3)	98(3)	96(3)	104(3)
C(2')—C(3')—C(4')	102(3)	102(3)	105(3)	108(3)	103(3)	94(3)
C(3')—C(4')—O(1')	101(3)	103(3)	112(3)	104(3)	107(3)	110(3)
C(4')—O(1')—C(1')	106(2)	108(3)	109(2)	106(3)	106(2)	112(3)
N(9)—C(1')—O(1')	104(3)	105(3)	109(3)	104(2)	106(3)	108(3)
N(9)—C(1')—C(2')	118(3)	109(3)	112(3)	106(3)	117(3)	107(3)
C(1')—C(2')—O(2')	109(3)	103(3)	111(3)	110(3)	111(3)	107(3)
O(2')—C(2')—C(3')	108(3)	109(3)	117(3)	118(3)	111(3)	112(3)
C(2')—C(3')—O(3')	114(3)	107(3)	113(3)	111(3)	104(3)	111(3)
O(3')—C(3')—C(4')	107(3)	110(3)	112(3)	107(3)	111(3)	115(3)
C(3')—C(4')—C(5')	112(3)	109(3)	114(3)	116(3)	110(3)	108(3)
C(5')—C(4')—O(1')	102(3)	106(3)	109(3)	118(3)	109(2)	119(3)
C(4')—C(5')—O(5')	115(3)	108(3)	110(3)	104(3)	108(3)	104(3)
C(5')—O(5')—P	118(2)	115(2)	119(2)	116(2)	118(2)	120(2)
C(5')—P—O(1)	106(1)	109(1)	108(1)	109(1)	107(1)	109(1)
O(5')—P—O(2)	105(1)	104(1)	103(1)	103(1)	104(1)	103(1)
O(5')—P—O(3)	108(1)	109(1)	108(1)	111(1)	109(1)	111(1)
O(1)—P—O(2)	114(1)	112(1)	110(1)	111(1)	112(1)	110(1)
O(1)—P—O(3)	110(1)	109(1)	115(1)	113(1)	110(1)	109(1)
O(2)—P—O(3)	113(1)	113(1)	113(1)	111(1)	115(1)	115(1)

one O from a phosphate group and three water molecules, whereas for Cu(B) they comprise two phosphate O atoms and two water molecules. Thus there exist two chemically distinct as well as three crystallographically independent Cu atoms in the crystal.

Bond lengths and angles within the metal coordination spheres are listed in Table 5. The O donors are at an average distance of 1.98 Å (range 1.90–2.10 Å). The apical Cu—N(7) bonds average 2.22 Å for A and C, and 2.32 Å for B, and are thus generally shorter than those quoted by Hathaway (1973) in a selection of other square-pyramidal Cu complexes where the average distance is 2.38 Å. The shortest bonds are found in units A and C, where the nucleotide adopts the more common C(3')-endo sugar ring conformation; the longest Cu—N bond occurs in unit B where the sugar ring assumes the C(2')-endo pucker and where the overall strain is likely to be the greatest.

As is usually found for square-pyramidal Cu complexes, the Cu atom is displaced from the plane of O donors towards the apical N atom. The average distances from the best plane are 0.26, 0.22, and 0.26 Å for units A, B, and C respectively. These rather large displacements of the Cu atoms are also reflected in the N—Cu—O angles which are all substantially greater than 90° (range 93.4–101.8°).

The ribose rings

The bond lengths and angles of the ribose rings have normal values within experimental errors. Sugar rings A

Table 5. Bond lengths (Å) and angles (°), with their estimated standard deviations, within the metal coordination spheres

Bond	Of molecule	Aoki	Clark & Orbell		Aoki	Clark & Orbell
Cu(A)—N(7A)	I(000)	2.198 (29)	2.302 (23)	O(W1A)—Cu(A)—O(W3A)	90.4 (10)	91.5 (9)
Cu(A)—O(W1A)	I(000)	1.973 (24)	1.982 (23)	O(W1A)—Cu(A)—O(1C)	162.0 (11)	160.2 (9)
Cu(A)—O(W2A)	I(000)	1.956 (26)	1.961 (22)	O(W2A)—Cu(A)—O(W3A)	165.1 (10)	167.0 (9)
Cu(A)—O(W3A)	I(000)	2.015 (21)	2.041 (21)	O(W2A)—Cu(A)—O(1C)	88.3 (10)	90.7 (9)
Cu(A)—O(1C)	IV(010)	1.910 (20)	2.035 (23)	O(W3A)—Cu(A)—O(1C)	94.3 (9)	92.2 (9)
				Cu(A)—N(7A)—C(5A)	134.3 (21)	125.5 (22)
N(7A)—Cu(A)—O(W1A)	101.7 (11)	101.9 (9)		Cu(A)—N(7A)—C(8A)	121.4 (24)	122.7 (23)
N(7A)—Cu(A)—O(W2A)	100.0 (11)	100.4 (9)		Cu(A)—O(1C)—P(C)	143.5 (14)	144.3 (15)
N(7A)—Cu(A)—O(W3A)	94.4 (10)	91.8 (8)				
N(7A)—Cu(A)—O(1C)	95.3 (10)	97.4 (9)				
O(W1A)—Cu(A)—O(W2A)	82.9 (11)	81.7 (9)				
Bond	Of molecule	Aoki	Clark & Orbell		Aoki	Clark & Orbell
Cu(B)—N(7B)	I(000)	2.289 (29)	2.346 (23)	O(W1B)—Cu(B)—O(1A)	91.0 (9)	88.2 (9)
Cu(B)—O(W1B)	I(000)	1.988 (22)	2.001 (22)	O(W1B)—Cu(B)—O(3C)	84.6 (9)	84.9 (9)
Cu(B)—O(W2B)	I(000)	2.011 (22)	2.010 (21)	O(W2B)—Cu(B)—O(1A)	92.4 (9)	92.1 (9)
Cu(B)—O(1A)	IV(001)	1.898 (18)	1.975 (22)	O(W2B)—Cu(B)—O(3C)	89.2 (9)	92.2 (9)
Cu(B)—O(3C)	III(000)	2.000 (25)	1.951 (22)	O(1A)—Cu(B)—O(3C)	164.6 (9)	165.5 (9)
				Cu(B)—N(7B)—C(5B)	133.8 (21)	132.4 (21)
N(7B)—Cu(B)—O(W1B)	97.7 (9)	95.9 (8)		Cu(B)—N(7B)—C(8B)	125.8 (20)	117.9 (19)
N(7B)—Cu(B)—O(W2B)	93.4 (9)	95.7 (8)		Cu(B)—O(1A)—P(A)	145.2 (13)	141.4 (14)
N(7B)—Cu(B)—O(1A)	93.4 (9)	94.7 (9)		Cu(B)—O(3C)—P(C)	124.8 (13)	125.2 (13)
N(7B)—Cu(B)—O(3C)	101.8 (9)	98.6 (9)				
O(W1B)—Cu(B)—O(W2B)	168.2 (9)	168.4 (9)				
Bond	Of molecule	Aoki	Clark & Orbell		Aoki	Clark & Orbell
Cu(C)—N(7C)	I(000)	2.184 (26)	2.205 (23)	O(W1C)—Cu(C)—O(W3C)	88.3 (11)	88.2 (9)
Cu(C)—O(W1C)	I(000)	1.954 (27)	1.978 (23)	O(W1C)—Cu(C)—O(1B)	164.4 (12)	163.5 (10)
Cu(C)—O(W2C)	I(000)	1.982 (23)	2.099 (22)	O(W2C)—Cu(C)—O(W3C)	162.7 (9)	164.7 (9)
Cu(C)—O(W3C)	I(000)	1.935 (19)	2.014 (23)	O(W2C)—Cu(C)—O(1B)	96.1 (10)	94.0 (9)
Cu(C)—O(1B)	III(100)	1.948 (22)	1.952 (23)	O(W3C)—Cu(C)—O(1B)	85.9 (9)	86.8 (9)
				Cu(C)—N(7C)—C(5C)	132.5 (22)	132.3 (23)
N(7C)—Cu(C)—O(W1C)	98.0 (12)	97.9 (9)		Cu(C)—N(7C)—C(8C)	123.4 (23)	115.4 (18)
N(7C)—Cu(C)—O(W2C)	96.5 (10)	96.0 (9)		Cu(C)—O(1B)—P(B)	130.4 (14)	132.8 (14)
N(7C)—Cu(C)—O(W3C)	100.3 (9)	99.0 (9)				
N(7C)—Cu(C)—O(1B)	97.3 (10)	98.4 (9)				
O(W1C)—Cu(C)—O(W2C)	85.3 (11)	86.8 (9)				

and C are puckered in the commonly observed C(3')-endo conformation, with atom C(3') being displaced by 0.64 and 0.58 Å from the planes of the best fit to the other ring atoms [C(1'),O(1'),C(2'),C(4')] (Table 6). These values are very similar to the other reported values in metal-nucleotide complexes of 0.56 Å in Co-IMP (Aoki, 1975; de Meester, Goodgame, Jones & Skapski, 1974b), 0.57 Å in Ni-IMP (Aoki, 1975; Clark & Orbell, 1974), 0.55 Å in Cd-GMP (Aoki, 1976a), 0.56 Å in Cd-CMP (Clark & Orbell, 1975; Goodgame, Jeeves, Reynolds & Skapski, 1975b; Bau, Gellert & Shiba, 1975), and 0.61 Å in Mn-CMP (Aoki, 1976c). On the other hand, sugar ring B is puckered C(2')-endo, with C(2') being displaced by 0.51 Å from the best plane [C(1'),O(1'),C(3'),C(4')] (Table 6). This value can be compared with those observed in C(2')-endo nucleotide-metal complexes of 0.48 Å in Co-CMP (Clark & Orbell, 1975) and 0.41 Å in Zn-CMP (Aoki, 1976b).

The orientation of the ribose rings relative to the guanine bases is given by torsion angle χ_{CN} about the glycosidic bond for the sequence of atoms C(8)—N(9)—C(1')—O(1') (Sundaralingam & Jensen, 1965). From Table 7, the average χ_{CN} angles for nucleotides A, B, and C are 40.8, 60.2, and 36.2° respectively. Each nucleotide is therefore in the preferred *anti* conformation. The difference between the values for nucleotides A (or C) and B shows that the nucleotides can twist to accommodate the best overall packing requirements. The average dihedral angles between the base and ribose planes (Table 6) are 71.7, 100.7, and 109.3°.

Hydrogen bonding and base stacking

The crystal packing is dominated by a large number of hydrogen bonds and extensive base stacking along the helical chain.

Table 6. Deviations (Å) of atoms from least-squares planes through the base and sugar

	Molecule A		Molecule B		Molecule C	
	Aoki	Clark & Orbell	Aoki	Clark & Orbell	Aoki	Clark & Orbell
(1) Plane through the guanine ring						
N(1)	-0.004*	0.007	-0.039*	-0.013	0.017*	0.020
C(2)	0.007*	0.027	0.010*	0.009	0.047*	0.056
N(3)	-0.012*	-0.010	0.042*	0.038	-0.057*	-0.033
C(4)	0.027*	-0.059	-0.038*	0.018	-0.014*	0.032
C(5)	-0.082*	-0.036	-0.026*	-0.057	0.038*	-0.057
C(6)	0.037*	-0.013	0.004*	-0.025	-0.047*	-0.051
N(7)	0.108*	0.010	0.023*	0.053	-0.008*	0.011
C(8)	-0.001*	-0.011	-0.015*	-0.016	0.007*	0.008
N(9)	0.010*	0.067	-0.014*	-0.064	0.017*	0.000
N(2)	0.084	-0.067	-0.013	0.036	0.040	0.105
O(6)	-0.044	-0.071	-0.035	-0.143	-0.121	0.002
C(1')	-0.111	-0.227	-0.116	-0.130	0.089	0.221
A	0.9652	0.9615	0.9886	0.9834	0.9928	0.9938
B	0.0792	0.0590	0.0916	0.0840	0.1151	0.1012
C	-0.2492	-0.2685	-0.1194	-0.1607	0.0344	0.0453
D	3.6918	3.5706	7.9200	7.7047	1.9820	1.9911
(2) Plane through the ribose ring						
C(1')	-0.017*	-0.037	0.008*	0.018	0.024*	0.007
O(1')	0.016*	0.015	-0.014*	-0.012	-0.024*	-0.003
C(2')	0.011*	0.037	0.532	0.483	0.015*	-0.005
C(3')	0.618	0.660	-0.008*	-0.24	0.622	0.54
C(4')	-0.010*	0.032	0.014*	0.038	0.015*	-0.006
O(2')	-1.346	-1.371	0.087	-2.811	-1.306	-1.374
O(3')	0.215	0.228	-1.290	-1.515	0.100	-0.077
C(5')	0.931	0.897	1.212	1.102	0.894	0.717
	C(3')-endo		C(2')-endo		C(3')-endo	
A	0.5360	0.5490	-0.1666	-0.0813	-0.4258	-0.3963
B	-0.5258	-0.4957	0.6090	0.5360	0.4469	0.4081
C	0.6605	0.6730	0.7755	0.8403	0.7867	0.8224
D	4.7667	4.7541	1.6533	2.1760	2.7024	2.7606
(3) The dihedral angle (°) between planes (1) and (2)						
	71.9	71.5	101.6	99.8	110.1	108.4

* Atoms included in the calculations of the least-squares planes. The equation of the least-squares plane is defined by $AX + BY + CZ = D$, where X , Y and Z are the orthogonal coordinates in Å along the crystallographic a , b and c axes, respectively.

The hydrogen-bonding network is shown in Fig. 3 and listed in Table 8. Besides intra-helical-chain hydrogen bonds between phosphate O atoms and copper-coordinated water molecules as noted earlier, each nucleotide base forms a strong intramolecular hydrogen bond between carbonyl O(6) and the copper-coordinated water molecule, which stabilizes the molecular structure, as is the common case in the highly hydrated metal-purine nucleotide complexes such as Co-GMP, Ni-GMP, Mn-GMP, Cd-GMP, Co-IMP, Ni-IMP, and Ni-AMP. Helical chains are held together by hydrogen bonds, mainly between N(1) and N(2) atoms of the guanine bases and phosphate groups of the adjacent columns and between N(2) atoms of the bases A and C and O(1') atoms of the sugars C and A respectively. These base-backbone hydrogen bonds may be important interstrand inter-

actions that stabilize tertiary structures of ribonucleic acids. In fact, this guanine N(2)···O(1') sugar hydrogen bonding plays an important role in yeast phenylalanine tRNA, between G₅₇ N(2) and sugar₁₉ O(1'), that is, it stabilizes interaction of D and TψC loops by augmenting the stacking interaction (Ladner *et al.*, 1975).

Fig. 4 shows the six types of base-stacked pairs (see also Fig. 3), where θ is the angle between the base planes and d is the average distance apart of the atoms of the bases. There is a very noticeable regularity in the angles, namely, right-hand members of the three pairs shown in Fig. 4 adopt smaller θ values (average 6.5°) than those of the left-hand ones (average 17.1°) and they appear alternately in Fig. 3 when one proceeds up the base-stacked sequence. The AB'(BA') pair is dimerized *via* a copper-coordinated water [$W(2A)$],

Table 7. Torsion angles ($^{\circ}$) around the ribose and phosphate groups

	Molecule A		Molecule B		Molecule C		χ_{CN}
	Clark & Orbell	Aoki	Clark & Orbell	Aoki	Clark & Orbell	Aoki	
C(8)-N(9)-C(1')-O(1')	46.2	35.3	60.2	60.1	41.8	30.6	
C(8)-N(9)-C(1')-C(2')	-78.2	-82.1	-54.6	-78.4	-84.1	-87.8	
C(4')-O(1')-C(1')-C(2')	-3.2	-6.1	-17.4	-16.4	4.5	1.2	
O(1')-C(1')-C(2')-C(3')	-21.5	-19.5	29.9	31.0	-25.5	-19.7	
C(1')-C(2')-C(3')-C(4')	37.9	37.2	-30.9	-32.3	37.5	27.3	
C(2')-C(3')-C(4')-O(1')	-39.0	-42.3	23.6	25.2	-38.3	-30.8	
C(3')-C(4')-O(1')-C(1')	27.3	30.8	-2.7	-4.6	22.4	21.8	
N(9)-C(1')-C(2')-C(3')	98.9	94.2	147.4	143.4	97.1	97.4	
N(9)-C(1')-C(2')-O(2')	-147.3	-154.0	-89.1	-87.1	-147.5	-144.3	
O(2')-C(2')-C(3')-O(3')	37.1	45.7	-27.5	-32.7	38.7	31.4	
O(2')-C(2')-C(3')-C(4')	-77.1	-69.5	-149.9	-150.0	-77.3	-87.1	
C(2')-C(3')-C(4')-C(5')	-146.5	-154.1	-100.3	-106.4	-157.0	-161.6	
O(3')-C(3')-C(4')-C(5')	93.8	92.3	137.0	134.0	92.1	96.8	
C(5')-C(4')-O(1')-C(1')	142.8	145.2	123.5	125.5	141.7	146.0	
O(1')-C(4')-C(5')-O(5')	-59.1	-57.9	-69.3	-74.6	-53.6	-53.6	
C(3')-C(4')-C(5')-O(5')	48.2	52.0	55.8	50.0	63.5	72.3	
C(4')-C(5')-O(5')-P	-127.5	-135.0	156.9	158.1	-146.6	-151.1	
C(5')-O(5')-P-O(1)	-79.9	-76.5	-57.7	-56.6	-71.1	-70.7	
C(5')-O(5')-P-O(2)	159.3	163.6	-173.6	-174.5	170.6	173.0	
C(5')-O(5')-P-O(3)	38.2	42.5	67.0	67.4	47.4	49.1	

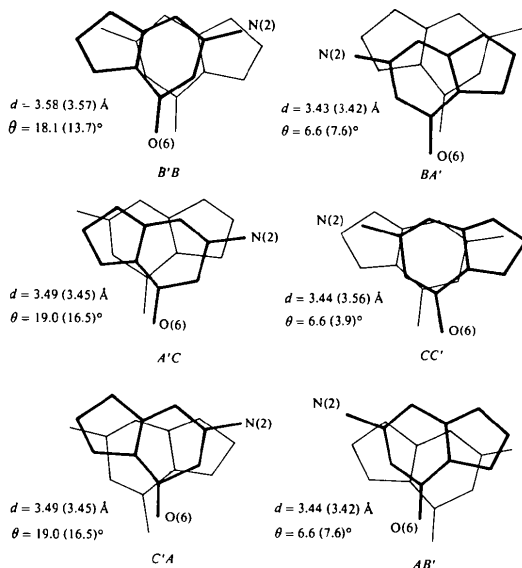


Fig. 4. The six different kinds of base-stacked pairs. Values out of and in the brackets are calculated from Clark & Orbell's and Aoki's atomic parameters, respectively.

which bridges between each carbonyl O(6) of each AB'(BA') pair. This may cause the rather smaller stacking spacing and θ angle in the AB'(BA') pair.

References

- AOKI, K. (1975). *Bull. Chem. Soc. Jpn.* **48**, 1260–1271.
 AOKI, K. (1976a). *Acta Cryst.* **B32**, 1454–1459.
 AOKI, K. (1976b). *Biochim. Biophys. Acta*, **447**, 379–381.
 AOKI, K. (1976c). *J. Chem. Soc. Chem. Commun.* pp. 748–749.

Table 8. Presumed hydrogen bonds

Hydrogen bond from	To	Of molecule†	Distance (Å)		Angle ($^{\circ}$) subtended at the donor atom		
			Code	Aoki	Clark & Orbell	Aoki	Clark & Orbell
N(1A)	O(1A)	IV(000)	1	2.90(3)	2.83(3)	C(2A)-N(1A)...105(2)	103(2)
						C(6A)-N(1A)...123(2)	126(2)
N(2A)	O(1'C)	I(000)	2	2.95(4)	2.91(3)	C(2A)-N(2A)...100(2)	105(2)
N(2A)	O(2A)	IV(000)	3	2.81(4)	2.80(3)	C(2A)-N(2A)...121(2)	121(2)
						2...N(2A)...114(1)	116(1)
O(2'A)	O(W4)	III(100)	4	3.03(5)	2.95(3)	C(2'A)-O(2'A)...136(3)	135(2)
O(3'A)	O(W8)	II(000)	5	2.77(8)	2.60(4)	C(3'A)-O(3'A)...103(2)	107(2)
N(1B)	O(1C)	IV(000)	6	2.94(3)	2.98(3)	C(2B)-N(1B)...110(2)	107(2)
						C(6B)-N(1B)...117(2)	118(2)
N(2B)	O(W7)	II(000)	7	3.07(3)	2.86(5)	C(2B)-N(2B)...123(3)	118(2)
N(2B)	O(2C)	IV(010)	8	3.01(4)	3.00(3)	C(2B)-N(2B)...117(2)	119(2)
						7...N(2B)...115(2)	117(1)
O(2'B)	N(3A)	I(000)	9	2.83(4)	2.85(4)	C(2'B)-O(2'B)...112(2)	109(2)
O(3'B)	O(3A)	IV(001)	10	2.73(3)	2.69(3)	C(3'B)-O(3'B)...106(2)	108(2)
N(1C)	O(3B)	IV(010)	11	2.87(4)	2.81(3)	C(2C)-N(1C)...116(2)	123(2)
						C(6C)-N(1C)...119(2)	118(2)
N(2C)	O(1'A)	I(000)	12	2.98(4)	2.91(3)	C(2C)-N(2C)...103(2)	99(2)
N(2C)	O(2B)	IV(010)	13	2.86(3)	2.83(3)	C(2C)-N(2C)...129(2)	134(2)
						12...N(2C)...118(1)	118(1)
O(2'C)	O(W2C)	I(001)	14	3.04(3)	3.05(3)	C(2'C)-O(2'C)...132(2)	130(2)
O(3'C)	O(W2C)	I(001)	14	3.14(3)	3.15(3)	C(3'C)-O(3'C)...123(2)	123(2)
O(W1A)	O(3B)	IV(010)	11	2.57(3)	2.59(3)	Cu(A)-O(W1A)...133(1)	132(1)
O(W1A)	O(3'A)	I(001)	15	2.73(4)	2.78(3)	Cu(A)-O(W1A)...108(1)	110(1)
						11...O(W1A)...111(1)	112(1)
O(W2A)	O(6A)	I(000)	16	2.76(3)	2.67(3)	Cu(A)-O(W2A)...102(1)	106(1)
O(W2A)	O(6B)	I(000)	17	3.01(3)	3.07(3)	Cu(A)-O(W2A)...112(1)	113(1)
						16...O(W2A)...165(1)	65(1)
O(W3A)	O(2A)	I(000)	18	2.79(3)	2.72(3)	Cu(A)-O(W3A)...135(1)	136(1)
O(W3A)	O(2B)	IV(010)	13	2.66(3)	2.61(3)	Cu(A)-O(W3A)...117(1)	116(1)
						16...O(W3A)...133(1)	95(1)
O(W1B)	O(3'B)	I(001)	19	2.73(3)	2.83(3)	Cu(B)-O(W1B)...112(1)	112(1)
O(W1B)	O(6B)	I(000)	17	2.69(3)	2.63(3)	Cu(B)-O(W1B)...106(1)	107(1)
						19...O(W1B)...133(1)	134(1)
O(W2B)	O(2B)	I(000)	20	2.57(3)	2.58(3)	Cu(B)-O(W2B)...131(1)	140(1)
O(W2B)	O(2C)	III(000)	21	2.65(3)	2.81(3)	Cu(B)-O(W2B)...90(1)	87(1)
						20...O(W2B)...114(1)	114(1)
O(W1C)	O(3A)	IV(000)	22	2.65(4)	2.55(3)	Cu(C)-O(W1C)...121(2)	123(1)
O(W1C)	O(W4)	III(100)	23	2.63(5)	2.71(3)	Cu(C)-O(W1C)...137(2)	136(1)
						22...O(W1C)...101(2)	101(1)
O(W2C)	O(6C)	I(000)	24	2.76(3)	2.73(3)	Cu(C)-O(W2C)...101(1)	97(1)
O(W2C)	O(3B)	III(100)	25	2.64(3)	2.61(3)	Cu(C)-O(W2C)...96(1)	95(1)
						24...O(W2C)...118(1)	120(1)
O(W3C)	O(2A)	IV(000)	3	2.67(3)	2.64(3)	Cu(C)-O(W3C)...123(1)	123(1)
O(W3C)	O(2C)	I(000)	26	2.67(3)	2.56(3)	Cu(C)-O(W3C)...117(1)	118(1)
						3...O(W3C)...226	99(1)
						27...O(W4)...116(2)	120(1)
O(W4)	O(2'B)	III(001)	27	2.87(5)	2.78(3)		
O(W4)	O(W6)	II(101)	28	3.10(5)	3.03(3)		
O(W5)	O(W2A)	IV(000)	29	2.72(4)	2.81(3)	29...O(W5)...30	148(2)
O(W5)*	O(W1B)	III(100)	30	3.01(4)	3.07(3)	29...O(W5)...31	99(2)
O(3C)	I(000)		31	2.69(5)	2.67(3)	30...O(W5)...31	56(1)
O(W6)	O(6C)	IV(000)	32	2.83(4)	2.78(3)	32...O(W6)...33	115(1)
O(W6)*	O(2'C)	III(001)	33	2.76(4)	2.86(3)	32...O(W6)...34	87(1)
	O(2'C)	IV(001)	34	2.94(4)	2.97(3)	33...O(W6)...34	80(1)
O(W7)	O(1'B)	I(000)	35	2.78(5)	2.74(5)	35...O(W7)...36	97(2)
O(W7)	O(W5)	III(001)	36	2.65(7)	2.78(5)		
O(W8)	O(W3C)	III(000)	37	3.12(6)	3.36(4)	37...O(W8)...38	97(2)
O(W8)	O(W7)	I(000)	38	2.62(9)	2.99(6)		

* Hydrogen atoms attached to these atoms probably form bifurcated hydrogen bonds.

† The positions of the molecules are denoted as follows: I(000) x, y, z ; II(000) $1-x, -y, z$; III(000) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; IV(000) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$, with the x, y and z coordinates as given in Table 2.

‡ Some of the atoms are designated by the code number.

AOKI, K. (1977). *J. Chem. Soc. Chem. Commun.* pp. 600–602.

AOKI, K., CLARK, G. R. & ORBELL, J. D. (1976). *Biochim. Biophys. Acta*, **425**, 369–371.

AOKI, K. & YAMAMOTO, Y. (1976). *Inorg. Chem.* **15**, 48–52.
 BAU, R., GELLERT, R. W. & SHIBA, J. K. (1975). Abstracts of the Seventh International Conference on Organometallic Chemistry, Venice, Italy, p. 238.

- CLARK, G. R. & ORBELL, J. D. (1974). *J. Chem. Soc. Chem. Commun.* pp. 139–140.
- CLARK, G. R. & ORBELL, J. D. (1975). *J. Chem. Soc. Chem. Commun.* pp. 697–698.
- COLLINS, A. D., DE MEESTER, P., GOODGAME, D. M. L. & SKAPSKI, A. C. (1975). *Biochim. Biophys. Acta*, **402**, 1–6.
- FISCHER, B. E. & BAU, R. (1977). *J. Chem. Soc. Chem. Commun.* pp. 272–273.
- GOODGAME, D. M. L., JEEVES, I., PHILLIPS, F. L. & SKAPSKI, A. C. (1975). *Biochim. Biophys. Acta*, **378**, 153–157.
- GOODGAME, D. M. L., JEEVES, I., REYNOLDS, C. D. & SKAPSKI, A. C. (1975a). *Nucleic Acid Res.* **2**, 1375–1379.
- GOODGAME, D. M. L., JEEVES, I., REYNOLDS, C. D. & SKAPSKI, A. C. (1975b). *Biochem. J.* **151**, 467–468.
- HATHAWAY, B. J. (1973). *Struct. Bonding (Berlin)*, **14**, 49–67.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- IZATT, R. M., CHRISTENSEN, J. J. & RYTTING, J. H. (1971). *Chem. Rev.* **71**, 439–481.
- JARDETSKY, C. D. (1960). *J. Am. Chem. Soc.* **82**, 229–233.
- KIM, S. H., SUDDATH, F. L., QUIGLEY, G. J., MCPHERSON, A., SUSSMAN, J. L., WANG, A. H. J., SEEMAN, N. C. & RICH, A. (1974). *Science*, **185**, 435–440.
- LADNER, J. E., JACK, A., ROBERTUS, J. D., BROWN, R. S., RHODES, D., CLARK, B. F. C. & KLUG, A. (1975). *Nucleic Acid Res.* **2**, 1629–1637; *Proc. Natl Acad. Sci. USA*, **72**, 4414–4418.
- LOUIE, S. & BAU, R. (1977). *J. Am. Chem. Soc.* **99**, 3874–3876.
- MEESTER, P. DE, GOODGAME, D. M. L., JONES, T. J. & SKAPSKI, A. C. (1974a). *Biochem. J.* **139**, 791–792.
- MEESTER, P. DE, GOODGAME, D. M. L., JONES, T. J. & SKAPSKI, A. C. (1974b). *C. R. Acad. Sci. Sér. C*, **279**, 667–669.
- MEESTER, P. DE, GOODGAME, D. M. L., JONES, T. J. & SKAPSKI, A. C. (1974c). *Biochim. Biophys. Acta*, **353**, 392–394.
- MEESTER, P. DE, GOODGAME, D. M. L., SKAPSKI, A. C. & SMITH, B. T. (1974). *Biochim. Biophys. Acta*, **340**, 113–115.
- OGAWA, M. & SAKAGUCHI, T. (1971). *Yakugaku Zasshi*, **91**, 750–754.
- SHEFTER, E. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 1067–1077.
- SLETTEN, E. & LIE, B. (1976). *Acta Cryst.* **B32**, 3301–3304.
- SUNDARALINGAM, M. & JENSEN, L. H. (1965). *J. Mol. Biol.* **13**, 914–929.
- SUSSMAN, J. L. & KIM, S. H. (1976). *Biochem. Biophys. Res. Commun.* **68**, 89–96.

Acta Cryst. (1978). **B34**, 2128–2133

The Crystal Structures of Two Modifications of Isocyanato(2-dipropylaminoethanolato)copper(II)

BY L. MERZ AND W. HAASE

Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, Federal Republic of Germany

(Received 12 December 1977; accepted 21 February 1978)

The structures of two modifications of isocyanato(2-dipropylaminoethanolato)copper(II) [$C_{18}H_{36}N_4O_4Cu_2$ (*A*), $C_{36}H_{72}N_8O_8Cu_4$ (*B*)] have been determined by single-crystal X-ray diffraction methods from 1793 (*A*) and 1390 (*B*) independent reflections. (*A*) crystallizes as monoclinic crystals of space group $P2_1/n$ [$a = 10.469$ (7), $b = 12.742$ (8), $c = 8.695$ (6) Å, $\beta = 95.92$ (1)°, $Z = 2$]; (*B*) crystallizes as orthorhombic crystals of space group $Pnna$ [$a = 12.83$ (1), $b = 19.03$ (2), $c = 19.28$ (2) Å, $Z = 4$]. Both structures were solved from three-dimensional Patterson and electron density maps and refined by least-squares methods to a final R of 0.035 (*A*) and 0.077 (*B*). The monoclinic modification is built up from discrete centrosymmetric oxygen-bridged dimeric molecules with an intramolecular Cu–Cu separation of 3.010 (1) Å and Cu–O separations of 1.891 (2) and 1.924 (2) Å. The orthorhombic modification consists of oxygen-bridged cubane-type tetramers with Cu–Cu separations (mean values) of 3.168 (2×) and 3.202 Å (4×) and Cu–O separations (mean values) of 1.923 (4×), 2.230 (4×) and 2.154 Å (4×). The different structural features are responsible for the different magnetic properties. Whereas the dimeric compound shows strong antiferromagnetic interaction, the tetrameric compound has a normal magnetic moment at room temperature.