ethylenediamines is such that the two amino surfaces, located on opposite ends of the cationic group and with the threefold axis normal to them, are staggered by approximately the same amount, giving additional stability to the observed packing scheme.

References

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature (London)*, **168**, 271–272.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

KORP, J. D. & BERNAL, I. (1980). To be published.

PALMER, R. A. & BERNAL, I. (1980). Unpublished results; to be submitted for publication.

PALMER, R. A. & YANG, M. C.-L. (1975). *Chem. Phys. Lett.* **31**, 492–497.

PALMER, R. A. & YANG, M. C.-L. (1978). *J. Am. Chem. Soc.* **100**, 3780–3784.

REISNER, G. M., BERNAL, I. & DOBSON, G. R. (1978). *J. Organomet. Chem.* **157**, 23–39.

SAITO, Y. (1978). *Top. Stereochem.* **10**, 96–174.

SAITO, Y., NAKATSU, K., SHIRO, M. & KUROYA, H. (1955). *Acta Cryst.* **8**, 729–730.

SWINK, L. N. & ATOJI, M. (1960). *Acta Cryst.* **13**, 639–643.

WERNER, A. (1899). *Z. Anorg. Chem.* **21**, 229.

WERNER, A. & MEGERLE, W. (1899). *Z. Anorg. Chem.* **21**, 213.

Crystal Structure of Hydrated Barium Cytidine 5'-Phosphate, $Ba_2(C_9H_{12}N_3O_8P)_2(8\cdot5H_2O)_2$. Crystal Packing and Conformational Homologies in Alkali-Metal– and Alkaline-Earth-Metal–Ribonucleotide Complexes

BY J. HOGLE* AND M. SUNDARALINGAM†

Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin–Madison, Madison, Wisconsin 53706, USA

AND GEORGE H. Y. LIN

Xerox Corporation, Rochester, New York 14644, USA

Abstract

Hydrated barium cytidine 5'-phosphate [Ba(5'-CMP).8·5H2O] crystallizes in the orthorhombic space group $P2_12_12$ with two independent molecules in the asymmetric unit. The unit-cell dimensions are $a = 20\cdot984$ (5), $b = 23\cdot168$ (8) and $c = 8\cdot940$ (10) Å; $Z = 8$. The structure was solved by the heavy-atom method and refined to an R value of $0\cdot128$ using anisotropic temperature factors for Ba and P and isotropic temperature factors for the other atoms. The two independent nucleotides exhibit very similar overall conformations, *viz* C(2')-*endo*, C(1')-*exo* ($^2T_1$), (χ) *anti*, and (ψ) *gauche*⁺. One of the Ba^{2+} ions is in a general position coordinated to the carbonyl O of a cytosine and seven water oxygens. The other is distributed on two different diad axes and coordinated to the *cis* hydroxyls of the riboses and water molecules.

* Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts, USA.

† To whom correspondence should be addressed.

The two independent molecules are related by a pseudo twofold axis passing roughly through $(\frac{1}{4},0,\frac{1}{4})$ midway between the 2_1 axes running parallel to the *b* axis. The crystal structure is highly hydrated with 18 independent water *sites* in the asymmetric unit, two of which are on diad axes. The crystal packing is dominated by alternating chains of nucleotides and barium–water columns. It is observed that the known alkali-metal– and alkaline-earth-metal–ribonucleotide complexes, crystallizing in either primitive or centered orthorhombic lattices, exhibit a striking similarity in packing scheme, regardless of whether they bear a pyrimidine or a purine base.

Introduction

Cytidine 5'-monophosphate (5'-CMP) is one of the four common ribonucleotides which make up ribonucleic acids (RNA's). The crystal structure of the barium salt of cytidine 5'-monophosphate 8·5 hydrate

reported here completes the list of the common 5'-ribonucleotides which have had their structures elucidated either in the free-acid form or as a salt. The crystals exhibited a significant fall-off of intensities at higher angles and only a limited intensity data set could be collected ($d_{min} = 1$ Å). The atomic parameters obtained from this analysis are therefore not precise by contemporary standards of crystal structure analysis. Nevertheless, we felt that the structure is worth reporting because it has, in the asymmetric unit, two nucleotides, eighteen independent water sites (two on diad axes) and two barium ions distributed over three sites, one in a general position and two on diads. Thus, the structure provides valuable information on the nature of the interaction of alkaline-earth-metal ions with water and nucleotides. [For recent reviews, see Swaminathan & Sundaralingam (1979) and Gellert & Bau (1979).] The structure was reported at the 1973 ACA Summer Meetings in Storrs, Connecticut (Abstract Q7).

Experimental

The barium salt of cytidine 5'-monophosphate crystallizes as an 8·5 hydrate ($Ba[C_9H_{12}N_3O_8P].8.5H_2O$) from an aqueous solution of the compound at room temperature. The crystals grew as thin long needles and are orthorhombic, space group $P2_12_12$, with unit-cell dimensions $a = 20.984$ (5), $b = 23.168$ (8), $c = 8.940$ (10) Å, and $D_x = 1.844$, $D_m = 1.845$ Mg m^{-3}.

Intensities of 2266 independent reflections with $2\theta < 100°$ were measured on a Picker FACS-I diffractometer with Ni-filtered Cu radiation using the $\theta/2\theta$-scan technique from a crystal of approximate dimensions $0.05 \times 0.08 \times 0.25$ mm (μ for Cu $K\alpha = 22.5$ mm^{-1}). The crystals showed a rapid fall off in intensities with increasing Bragg angle. Three check reflections monitored every two hours showed an overall decrease of 10% during the data collection. The data were corrected for crystal decay, background and Lorentz and polarization effects. An empirical differential absorption correction was applied by measuring the intensity of the 002 reflection at $\chi = 90°$ as a function of φ (Furnas, 1957). The ratio of the maximum to the minimum values of the intensity of this reflection was 2·0 which compares well with the ratio of the correction calculated using the two smaller dimensions of the crystal and the value of μ given above. A total of 1826 reflections were greater than 3σ and only these were used in the structure analysis.

Structure analysis and refinement

The barium ions were located from a study of the Harker sections. The two barium ions in the asym-

metric unit are distributed among three sites: two in special positions on the two independent diads, and the third in a general position. The structure was solved by the heavy-atom technique. Eighteen independent water sites were found with two of them on the diad axes. The atomic coordinates of the 42 nonhydrogen atoms of the two nucleotides, the three barium sites and the 18 water sites were subjected to six cycles of full-matrix least-squares refinement using isotropic temperature factors for all the atoms. Two final rounds of refinement with anisotropic thermal parameters for the Ba and P atoms resulted in a final R value of 0·128 (1826 reflections, 266 parameters). The weighting scheme used was $w = 1/\sigma^2$, where $\sigma = 12.65$ for $F_o < 110$, $\sigma = 12.65 + (F_o - 110)0.01$ for $F_o \geq 110$. The maximum shift-to-σ ratio for the parameters in the last cycle was 0·24 and the mean value was 0·05. The atomic scattering factors used were from Cromer & Waber (1965). Corrections (f', f'') to the atomic scattering factors due to anomalous dispersion used during the refinement for Ba and P were taken from *International Tables for X-ray Crystallography* (1962). The residual map contained peaks in the range 0·5 to 0·7 e Å^{-3} in the vicinity of the Ba and P sites while the residual peaks in the rest of the map were less than 0·5 e Å^{-3}.

Results

The atomic coordinates are listed in Table 1.* The bond distances and bond angles in both molecules of CMP are given in Tables 2 and 3 and these agree within their combined standard deviations [$\sigma(l) = 0.07$ Å, $\sigma(\theta) = 7°$]. In view of the large errors in the present analysis, no detailed comparison of these values is made with those of similar structures in the literature.

Discussion

Conformation of the nucleotides

Fig. 1 shows similar views of the two nucleotides which have very similar overall conformations, *viz* the sugar puckers are C(2')-*endo*, C(1')-*exo* ($^2T_1$), the glycosyl torsion angles (χ) are *anti*, and the exocyclic C(4')–C(5') bond conformations (ψ) are *gauche*$^+$. This combination is one of the preferred conformations for the 5'-nucleotide building blocks of nucleic acids (Sundaralingam, 1973). These and other pertinent conformational parameters for the two molecules are compared in Table 4.

Barium coordination

The coordination for the three barium ions is shown in Fig. 2. The two barium ions in special positions [Ba(1) and Ba(2)] each have nine nearest neighbors including the *cis* hydroxyls of the ribose moieties and water molecules. The barium ion in the general position [Ba(3)] has eight nearest neighbors including the carbonyl O of one of the cytosine (molecule *A*) and seven water molecules. The carbonyl O of molecule *B* is not directly coordinated to Ba(3), but is bridged by a water molecule to it. The water $W(15)$ bridges Ba(2) and Ba(3). The Ba—O distances range from 2·6–3·1 Å. Ba(1) has five ligands approximately coplanar with it and two ligands on either side of this plane. Ba(3) forms a distorted dodecahedron and is also surrounded by five ligands lying in a plane and with one ligand above and two below this plane. The coordination of Ba(2) can be described as a trigonal prism with three additional ligands extending from each of the three square faces. None of the barium ions is directly coordinated to the negatively charged phosphates; they are linked to the anionic oxygens through water bridges or through ribose hydroxyls, a feature which is quite frequently encountered in alkali-metal and alkaline-earth-metal complexes of nucleotides (Swaminathan & Sundaralingam, 1979).

Table 1. *Positional parameters* $(\times 10^4)$ *and isotropic thermal parameters for the nonhydrogen atoms*

Standard deviations refer to the least significant digits.

	x	y	z	B (Å²)
P*A*	4386 (7)	1543 (6)	8443 (15)	2·0*
OP(1)*A*	4320 (16)	1363 (14)	10085 (39)	3·1
OP(2)*A*	3906 (18)	1223 (17)	7362 (44)	4·3
OP(3)*A*	5072 (20)	1424 (15)	7901 (40)	4·3
O(5')*A*	4276 (14)	2165 (13)	8343 (34)	2·0
C(5')*A*	4234 (25)	2458 (22)	6862 (60)	2·8
C(4')*A*	4053 (22)	3076 (19)	6955 (52)	1·7
O(4')*A*	3402 (18)	3133 (16)	7562 (44)	4·1
C(3')*A*	4442 (26)	3437 (24)	8032 (62)	3·2
O(3')*A*	4609 (18)	3967 (16)	7397 (42)	3·8
C(2')*A*	4015 (25)	3506 (23)	9385 (62)	3·3
O(2')*A*	4133 (18)	4066 (16)	10160 (47)	4·4
C(1')*A*	3336 (30)	3549 (28)	8602 (74)	5·0
N(1)*A*	2761 (21)	3347 (17)	9557 (50)	3·5
C(2)*A*	2318 (25)	3738 (21)	9876 (61)	3·3
O(2)*A*	2399 (19)	4291 (17)	9693 (50)	5·2
N(3)*A*	1799 (18)	3562 (16)	10733 (42)	2·1
C(4)*A*	1737 (19)	3028 (16)	10922 (46)	0·7
N(4)*A*	1166 (20)	2813 (18)	11663 (49)	3·1
C(5)*A*	2202 (26)	2628 (21)	10724 (58)	3·0
C(6)*A*	2753 (25)	2793 (20)	9855 (61)	3·1
P*B*	195 (6)	1435 (6)	6609 (16)	2·4*
OP(1)*B*	289 (23)	1291 (22)	4994 (57)	3·3
OP(2)*B*	672 (15)	1134 (14)	7668 (39)	6·9
OP(3)*B*	−477 (21)	1336 (19)	7248 (52)	5·6
O(5')*B*	279 (15)	2073 (14)	6687 (38)	2·9
C(5')*B*	310 (28)	2389 (26)	8095 (71)	4·2
C(4')*B*	468 (29)	2992 (26)	8027 (71)	4·2

Table 1 (cont.)

	x	y	z	B (Å²)
O(4')*B*	1178 (17)	3043 (16)	7503 (42)	3·9
C(3')*B*	131 (26)	3372 (22)	6842 (59)	3·2
O(3')*B*	−18 (21)	3921 (15)	7381 (40)	4·3
C(2')*B*	601 (27)	3439 (24)	5567 (67)	3·9
O(2')*B*	508 (16)	3956 (14)	4737 (41)	3·2
C(1')*B*	1235 (21)	3472 (19)	6480 (51)	1·7
N(1)*B*	1841 (19)	3349 (16)	5599 (45)	2·5
C(2)*B*	2228 (25)	3782 (20)	5453 (58)	2·8
O(2)*B*	2173 (19)	4275 (15)	5798 (43)	4·3
N(3)*B*	2794 (20)	3630 (16)	4437 (47)	3·2
C(4)*B*	2872 (23)	3100 (19)	4077 (54)	2·1
N(4)*B*	3419 (25)	2949 (24)	3182 (62)	5·4
C(5)*B*	2447 (30)	2607 (27)	4274 (73)	5·0
C(6)*B*	1896 (26)	2797 (23)	5266 (68)	3·8
Ba(1)	0 (0)	5000 (0)	5935 (5)	2·6*
Ba(2)	5000 (0)	5000 (0)	8777 (6)	2·8*
Ba(3)	2229 (2)	329 (2)	9673 (4)	3·2*
$W(1)$	0 (0)	5000 (0)	9009 (48)	2·4
$W(2)$	0 (0)	0 (0)	8172 (99)	9·7
$W(3)$	3570 (16)	393 (16)	385 (42)	3·8
$W(4)$	2393 (19)	1194 (17)	1795 (46)	4·8
$W(5)$	2660 (22)	1343 (19)	8353 (52)	6·2
$W(6)$	3697 (17)	97 (16)	3188 (39)	4·0
$W(7)$	851 (19)	4390 (17)	1026 (48)	4·8
$W(8)$	2984 (19)	5022 (22)	7327 (45)	5·6
$W(9)$	3489 (21)	1155 (19)	4598 (54)	6·2
$W(10)$	3805 (18)	4458 (16)	4289 (44)	4·5
$W(11)$	1094 (19)	1623 (17)	2807 (47)	4·7
$W(12)$	4234 (22)	174 (20)	6503 (55)	6·7
$W(13)$	766 (18)	248 (16)	3786 (44)	4·5
$W(14)$	3545 (19)	1827 (17)	2055 (45)	4·4
$W(15)$	948 (17)	829 (15)	535 (44)	3·8
$W(16)$	2127 (26)	1179 (23)	5017 (66)	9·0
$W(17)$	1545 (25)	422 (24)	7012 (60)	7·6
$W(18)$	2155 (29)	4878 (27)	2838 (68)	10·0

* These values are equal to $(B_1 B_2 B_3)^{1/3}$ where B_1, B_2 and B_3 are the principal values of the anisotropic thermal-vibration tensor.

Table 2. *Bond lengths* (Å) *and standard deviations*

	Molecule *A*	Molecule *B*
P—OP(1)	1·53 (4)	1·50 (5)
P—OP(2)	1·58 (4)	1·54 (4)
P—OP(3)	1·54 (4)	1·54 (5)
P—O(5')	1·46 (3)	1·49 (3)
O(5')—C(5')	1·49 (6)	1·46 (7)
C(5')—C(4')	1·48 (7)	1·44 (9)
C(4')—O(4')	1·48 (6)	1·57 (7)
C(4')—C(3')	1·51 (7)	1·55 (8)
O(4')—C(1')	1·35 (8)	1·36 (6)
C(1')—C(2')	1·59 (8)	1·56 (7)
C(2')—C(3')	1·51 (8)	1·52 (8)
C(2')—O(2')	1·49 (7)	1·42 (7)
C(3')—O(3')	1·40 (7)	1·40 (6)
C(1')—N(1)	1·55 (8)	1·52 (6)
N(1)—C(2)	1·33 (7)	1·30 (6)
N(1)—C(6)	1·31 (6)	1·32 (7)
C(2)—N(3)	1·41 (7)	1·54 (7)
C(2)—O(2)	1·30 (6)	1·19 (6)
N(3)—C(4)	1·25 (5)	1·28 (6)
C(4)—C(5)	1·36 (7)	1·46 (8)
C(4)—N(4)	1·46 (6)	1·44 (7)
C(5)—C(6)	1·44 (8)	1·52 (9)

Table 3. *Bond angles (°) and standard deviations*

	Molecule *A*	Molecule *B*
OP(1)–P–OP(2)	114 (3)	114 (3)
OP(1)–P–OP(3)	110 (3)	117 (4)
OP(1)–P–O(5')	108 (3)	105 (3)
OP(2)–P–OP(3)	109 (3)	107 (3)
OP(3)–P–O(5')	109 (3)	110 (3)
OP(3)–P–O(5')	108 (3)	103 (3)
P–O(5')–C(5')	121 (4)	123 (4)
O(5')–C(5')–C(4')	114 (5)	118 (6)
C(5')–C(4')–O(4')	110 (5)	108 (6)
C(5')–C(4')–C(3')	116 (5)	118 (6)
O(4')–C(4')–C(3')	102 (5)	101 (5)
C(4')–O(4')–C(1')	114 (5)	110 (5)
O(4')–C(1')–C(2')	100 (6)	104 (5)
C(1')–C(2')–C(3')	101 (6)	100 (6)
C(1')–C(2')–O(2')	107 (5)	110 (5)
O(2')–C(2')–C(3')	111 (5)	113 (5)
C(2')–C(3')–C(4')	104 (5)	106 (6)
C(2')–C(3')–O(3')	112 (5)	108 (5)
C(4')–C(3')–O(3')	111 (5)	113 (5)
N(1)–C(1')–O(4')	104 (6)	107 (4)
N(1)–C(1')–C(2')	116 (6)	116 (5)
C(1')–N(1)–C(2)	117 (5)	115 (5)
C(1')–N(1)–C(6)	115 (5)	112 (5)
C(2)–N(1)–C(6)	128 (6)	132 (6)
N(1)–C(2)–N(3)	118 (5)	111 (5)
N(1)–C(2)–O(2)	124 (6)	131 (6)
O(2)–C(2)–N(3)	117 (5)	117 (5)
C(2)–N(3)–C(4)	115 (5)	118 (5)
N(3)–C(4)–C(5)	126 (5)	130 (6)
N(3)–C(4)–N(4)	118 (5)	118 (5)
N(4)–C(4)–C(5)	115 (5)	111 (6)
C(4)–C(5)–C(6)	118 (5)	108 (6)
C(5)–C(6)–N(1)	112 (5)	119 (6)

Molecular packing and hydrogen bonding

The contents of the unit cell projected down the *c* axis of the crystal are shown in Fig. 3. A notable feature of the packing is the alternating columns of the stacked nucleotides and the coordinated barium ions. The nucleotide layers are extensively linked through the barium–water layer. The bases of the two independent molecules are stacked; the closest contact of 3·41 (4) Å is between the carbonyl O atoms O(2) of molecule *A* and molecule *B*. The base planes make a dihedral angle

Table 4. *Conformational angles (°) in hydrated barium cytidine 5'-phosphate*

Torsion-angle notations are after Sundaralingam (1969) and pseudorotation parameters are after Altona & Sundaralingam (1972). Standard deviations in the torsion angles range from 5 to 7°.

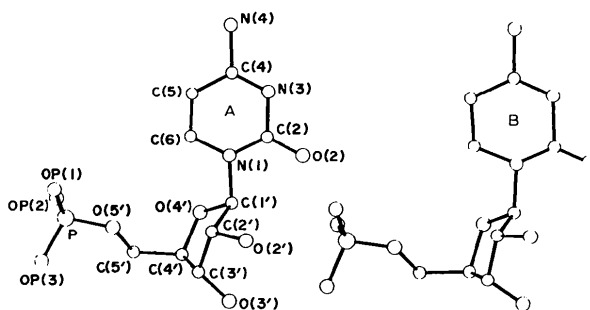|		Molecule *A*	Molecule *B*
		41 (*anti*)	42 (*anti*)
Glycosyl torsion	χ		
Ribose pucker		$^2T_1$	$^2T_1$
Endocyclic torsion angles	τ_0	−34	−36
	τ_1	42	45
	τ_2	−36	−36
	τ_3	17	17
	τ_4	12	12
Pseudorotation parameters			
Amplitude of puckering	τ_m	43 (5)	45 (5)
Phase angle of pseudorotation	P	147 (8)	146 (8)
Backbone torsions	φ	176	172
	ψ	54	49
	ψ'	136	142

Fig. 1. The two independent molecules of CMP showing their conformational similarity.

of 20·8 (8)°. The stacking interaction between the bases of adjacent unit cells is even shorter, being 3·14 (4) Å between the C(5) atoms of molecule *A* and a translation-related molecule *B*.

The atoms involved in possible hydrogen bonds and the hydrogen-bonding distances are listed in Table 5. It can be seen that both nucleotides are engaged in extensive hydrogen bonding with the waters of crystallization. The two nucleotides are linked to each other
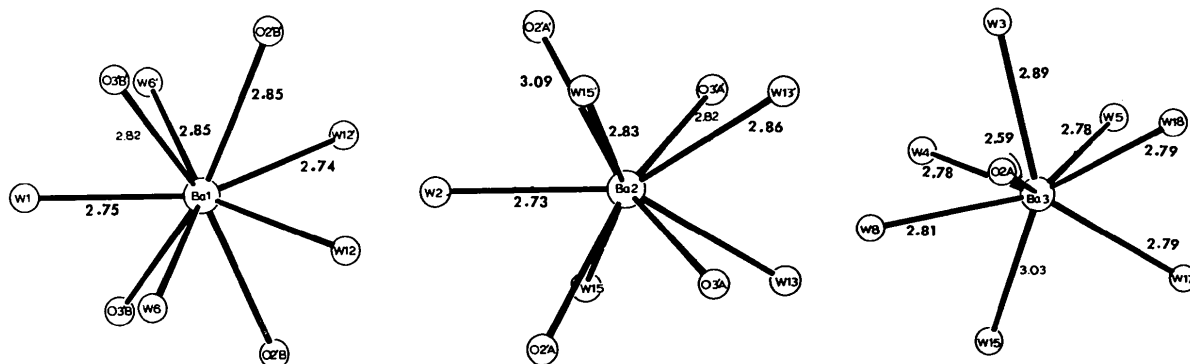

Fig. 2. The coordination of the barium ions in Ba(5'-CMP).8·5H₂O. Ba(1) and Ba(2) lie on the diad axes while Ba(3) is in a general position. The Ba···O distances (Å) are shown. The standard error on these distances is in the range 0·03–0·06 Å (mean = of 0·04 Å).
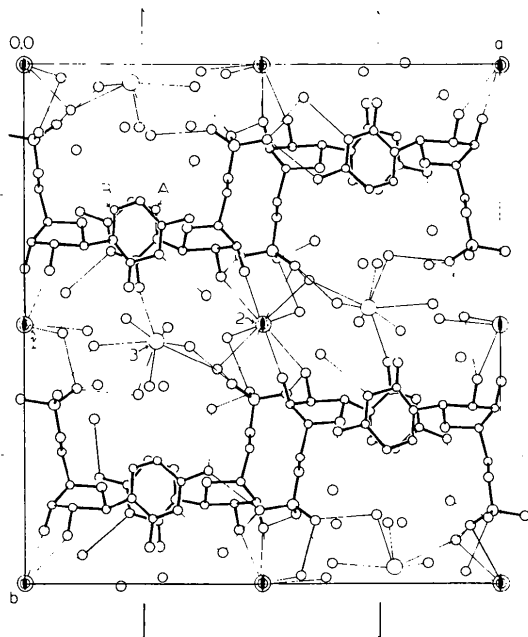
Fig. 3. A projection down the c axis of the structure of Ba(5'-CMP).8·5H$_2$O showing the molecular packing. The large numbered circles represent the barium ions, the smaller non-nucleotide circles represent water oxygens, and the fine lines indicate possible hydrogen or coordinate bonds. A and B refer to the two independent molecules of CMP.

Table 5. Potential hydrogen bonds with distances less than 3·1 Å

The standard deviations in the distances are in the range 0·04 to 0·08 Å.

		Symmetry code*				Symmetry code*	
OP(1)A	W(3)	1,001	2·74 Å	W(1)	W(7)	1,001	2·90 Å
OP(1)A	W(14)	1,001	2·62	W(3)	W(6)	1,000	2·60
OP(1)A	O(3')B	3,002	2·75	W(3)	W(7)	4,010	2·92
OP(2)A	W(5)	1,000	2·77	W(4)	W(8)	4,011	2·89
OP(2)A	W(9)	1,000	2·62	W(4)	W(11)	1,000	3·04
OP(2)A	W(12)	1,000	2·63	W(4)	W(14)	1,000	2·89
OP(3)A	O(2')B	3,001	2·69	W(4)	W(16)	1,000	2·97
OP(3)A	W(7)	3,001	2·68	W(6)	W(9)	1,000	2·79
OP(3)	N(4)A	3,002	2·93	W(7)	W(12)	4,001	2·83
O(2)A	W(18)	1,001	3·15	W(8)	W(13)	4,001	2·89
N(3)A	W(17)	1,001	2·80	W(9)	W(14)	1,000	2·74
N(4)A	W(11)	1,001	2·95	W(9)	W(16)	1,000	2·86
				W(10)	W(13)	4,001	2·68
OP(1)B	W(2)	1,000	2·99	W(10)	W(17)	4,001	2·61
OP(1)B	W(17)	1,000	2·54	W(11)	W(15)	1,000	2·74
OP(1)B	W(15)	1,001	2·72	W(12)	W(18)	4,001	3·03
OP(2)B	W(11)	1,000	2·72				
OP(2)B	W(13)	1,000	2·81				
OP(2)B	O(3')A	3,101	2·62				
OP(3)B	W(10)	3,101	2·74				
OP(3)B	N(4)B	3,101	2·86				
OP(3)B	O(2')A	3,102	2·65				
O(3')B	W(1)	2,010	2·89				
O(2')B	W(12)	4,001	3·09				
O(2)B	W(6)	4,001	2·79				

* The first number denotes the symmetry element and the next three numbers denote the subsequent translations along the cell edges. (1) x,y,z; (2) $\bar{x},\bar{y},z$; (3) $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$; (4) $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$.
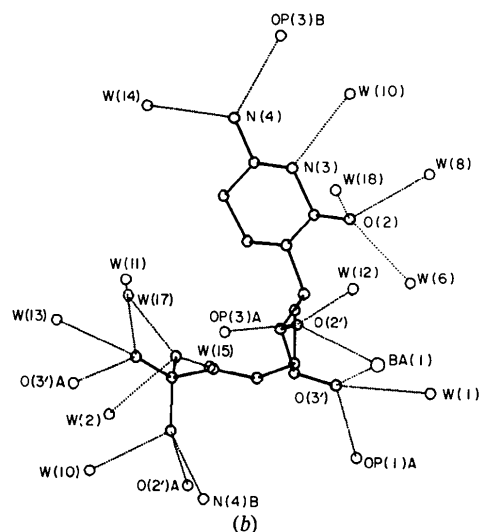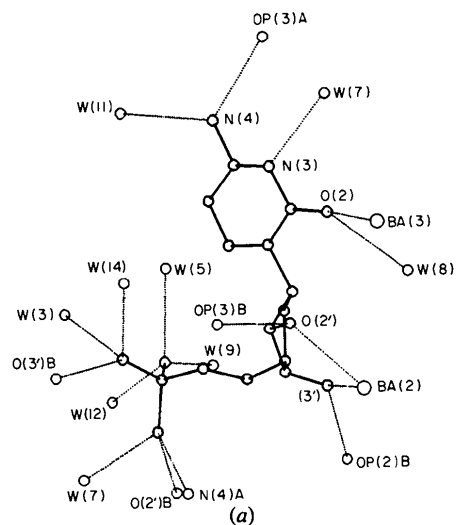

Fig. 4. The environs of the two independent nucleotide molecules showing the water of hydration and barium coordination sites. (a) Molecule A, (b) molecule B.

by direct hydrogen bonds involving the ribose hydroxyls of one molecule and the anionic phosphate O atoms of the other, and by hydrogen bonds through the waters 8, 11, 12, and 14. Each molecule of CMP is also linked to a symmetry-equivalent molecule from a neighboring unit cell by a hydrogen bond between the base amino group and a phosphate O, and by coordination bridges involving the barium ions (Fig. 3). All of the potential hydrogen-bond donors and acceptors (including the lone-pair electrons) in the two nucleotide units are engaged in their full complement of hydrogen bonds except the hydroxyl oxygens O(2'), O(3') of the ribose and the carbonyl O(2) of the base of molecule A which are involved in a hydrogen bond and metal coordination, leaving a lone pair available for hydrogen bonding. An interesting feature of the

hydrogen bonding is that each of the six anionic phosphate O atoms accepts three hydrogen bonds.

The water molecules over the 18 sites involved in hydrogen bonds or close contacts within a distance of 3·1 Å are listed in Table 6. It can be seen that for each water site the number of close contacts ranges from four to one and that there are no more than two interactions with the atoms of the nucleotide. Four waters are involved in a total of six interactions, five waters in three interactions and six waters in two interactions and $W(5)$ is involved in only one interaction.

Table 6. *The number of potential hydrogen bonds involving the water sites within a distance of* 3·1 Å

	Number of interactions				Number of interactions		
	with other waters	with nucleotides	Total		with other waters	with nucleotides	Total
$W(1)$*	2	2	4	$W(10)$	2	1	3
$W(2)$*	–	2	2	$W(11)$	2	2	4
$W(3)$	2	1	3	$W(12)$	2	2	4
$W(4)$	4	–	4	$W(13)$	2	1	3
$W(5)$	–	1	1	$W(14)$	2	1	3
$W(6)$	1	1	2	$W(15)$	1	1	2
$W(7)$	3	1	4	$W(16)$	2	–	2
$W(8)$	2	–	2	$W(17)$	1	2	3
$W(9)$	3	1	4	$W(18)$	1	1	2

* On the twofold axis.

The two molecules in the asymmetric unit are related by a pseudo twofold axis parallel to the **b** direction passing roughly through $(\frac{1}{4},0,\frac{1}{4})$ (see Fig. 3). [The r.m.s. deviation for 21 atoms = 0·18 Å, corresponding to a rotation of 178° about a line passing through $(0\cdot248, 0, 0\cdot251)$ and having direction cosines of $-0\cdot03$, 1·00, 0·01.] The pseudosymmetry also extends to the hydration and cation shell around the two nucleotides, as shown in Fig. 4. The basic differences between the two lie in the surroundings of the atoms O(2), O(2') and O(3').

It is observed that all but one (see below) of the alkali (Na^+) or alkaline-earth (Ba^{2+}) metal complexes of purine and pyrimidine 5'-nucleotides crystallize in a highly hydrated state in the primitive or C-centered orthorhombic lattice with very similar cell constants and $Z = 8$ (Table 7). These structures exhibit strikingly similar crystal-packing schemes with alternate layers of stacked nucleotides and water channels in which the metal ions are embedded. In all these cases, a metal ion is directly coordinated to both the ribose hydroxyl O atoms. In cases with a second metal-ion site (*e.g.* BaCMP, BaIMP), the metal ion is coordinated to the carbonyl O(2) of pyrimidine bases or the ring N(7) of purine bases. In the latter situation the metal can be replaced by a water molecule or even a *cis*-Pt(NH$_3$)$_2$

Table 7. *Crystal data and pertinent conformational parameters for complexes between alkali/alkaline-earth metals and 5'-ribonucleotides*

Reference	(1)	(2)	(2)*	(3)	(4)	(5)*	(6)*
Compound	NaIMP	Na$_2$IMP	BaIMP (A,B)	Na$_2$UMP	BaUMP	Na$_2$CMP	BaCMP (A,B)
Crystal data							
Space group	$C2_12$	$C2_12$	$P2_12_12_1$	$C2_12$	$C2_12$	$P2_12$	$P2_12_1$
Unit-cell constants							
a (Å)	21·717	21·92	21·45	19·53	20·98	20·804	20·984
b (Å)	8·682	8·64	8·85	8·967	9·06	8·846	8·940
c (Å)	23·215	23·06	21·75	23·03	21·11	23·25	23·168
Z	8	8	8	8	8	8	8
D_m (Mg m^{-3})	1·576	1·62	1·935	1·64	2·05	1·582	1·845
D_x (Mg m^{-3})	1·580	1·616	1·928	1·628	1·99	1·587	1·844
Number of solvent molecules per unit cell	64	60	48	56	64	64	64
Metal ions in general positions and nucleotide ligands†	1(A)	2(A,B)	2(A,B)	2(A,C)	–	–	1(C)
Metal ions in special positions and nucleotide ligands†	–	–	–	–	2(A,C)	2(A,C)	2(A,A)
Conformational parameters							
P (°)	167	163	159,152	^2E	170		152,14
τ_m (°)	40	41	30,40		34		42,46
χ (°)	41	43	46,34	45	43		41,42
ψ (°)	59	56	49,51	75	70		54,49
φ (°)	176	172	170,160		176		176,17

References: (1) Rao & Sundaralingam (1969); (2) Nagashima & Iitaka (1968); Nagashima (1974); (3) Gupta, Sequeira, Seshadri & Viswamitra (1975); (4) Shefter & Trueblood (1965); (5) Lin (unpublished results); (6) This work.
* Two independent molecules in the asymmetric unit.
† Code for nucleotide ligands: A = O(2'), O(3'); B = N(7); C = O(2).

group (Goodgame, Jeeves, Phillips & Skapski, 1975; see also Swaminathan & Sundaralingam, 1979).

Besides the crystal-packing similarities, the conformations of the ribonucleotides in these structures are remarkably similar with only small fluctuations in their preferred domains (Table 7). The glycosyl torsion angle χ is *anti*; the ribose pucker is C(2')-*endo*; the exocyclic C(4')—C(5') conformation ψ is *gauche*$^+$ and the C(5')—O(5') conformation φ is *trans*. The crystal structure of the disodium salt of cytidine 5'-phosphate (Table 7) has not yet been solved, but the similarity between its cell constants and the related structures suggests that it, too, would be expected to be homologous with the others. The only exception to the above structures is barium adenosine 5'-monophosphate heptahydrate which is monoclinic, space group C2 ($Z = 4$) (Sternglanz, Subramanian, Lacey & Bugg, 1976). The main difference between this structure and the others (Table 7) is in the sugar pucker and the barium coordination which is exclusively by water molecules. The nucleotide sugar conformation is C(4')-*exo*, C(3')-*endo*, $P = 41$ (2)°, $\tau_m = 42$ (1)°; χ is *anti* [69 (1)°], ψ is *gauche*$^+$ [58 (1)°] and φ is *trans* [217 (1)°].

It might be mentioned that in contrast to ribonucleotides, deoxyribonucleotides generally tend to show greater conformational variability, stemming from the fact that the deoxyribofuranoid ring is inherently more flexible than the ribofuranoid ring (Sundaralingam, 1975, and references therein).

References

ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

FURNAS, T. C. (1957). *Single-Crystal Orienter Instruction Manual.* General Electric Co., Milwaukee.

GELLERT, R. W. & BAU, R. (1979). *Metal Ions in Biological Systems.* Vol. 8, edited by H. SIEGEL. New York: Marcel Dekker. In the press.

GOODGAME, D. M. L., JEEVES, I., PHILLIPS, F. L. & SKAPSKI, A. C. (1975). *Biochim. Biophys. Acta,* **378**, 153–157.

GUPTA, S. C., SEQUEIRA, A., SESHADRI, T. P. & VISWAMITRA, M. A. (1975). *Acta Cryst.* A**31**, S42.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

NAGASHIMA, N. (1974). Private communication.

NAGASHIMA, N. & IITAKA, Y. (1968). *Acta Cryst.* B**24**, 1136–1138.

RAO, S. T. & SUNDARALINGAM, M. (1969). *J. Am. Chem. Soc.* **91**, 1210–1217.

SHEFTER, E. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 1067–1077.

STERNGLANZ, H., SUBRAMANIAN, E., LACEY, J. C. JR & BUGG, C. E. (1976). *Biochemistry,* **15**, 4797–4802.

SUNDARALINGAM, M. (1969). *Biopolymers,* **7**, 821–860.

SUNDARALINGAM, M. (1973). *Jerusalem Symp. Quantum Chem. Biochem.* **5**, 417–456.

SUNDARALINGAM, M. (1975). *Structure and Conformation of Nucleic Acids and Protein–Nucleic Acid Interactions,* edited by M. SUNDARALINGAM & S. T. RAO, pp. 487–524. Baltimore: Univ. Park Press.

SWAMINATHAN, V. & SUNDARALINGAM, M. (1979). *CRC Crit. Rev. Biochem.* **6**, 245–336.

Neutron Profile Refinement of Potassium and Rubidium Oxalate Monoperhydrates

BY J. M. ADAMS AND VIJAYALAKSHMI RAMDAS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, Wales

AND A. W. HEWAT

Institut Laue–Langevin, 156X, Grenoble 38042 CEDEX, France

Abstract

Neutron powder data collected at 300 K with 1·9 Å radiation have been refined to give the D atom positions in the isotypic perhydrates $K_2[C_2O_4].D_2O_2$ and $Rb_2[C_2O_4].D_2O_2$. The atomic parameters for the Rb compound have been improved considerably (except for Rb) over the previous single-crystal X-ray results, whereas the values for the K compound are comparable with the X-ray work. The dihedral angles