Acta Cryst. (1981). B**37**, 1825–1831

Structure of Disodium Guanosine 5′-Phosphate Heptahydrate

By S. K. Katti, T. P. Seshadri and M. A. Viswamitra

Department of Physics and ICMR Centre on Genetics and Cell Biology, Indian Institute of Science, Bangalore 560 012, *India*

(*Received* 19 *January* 1981; *accepted* 26 *March* 1981)

Abstract

$C_{10}H_{12}N_5O_8P^{2-}.2Na^+.7H_2O$, $M_r = 533{\cdot}3$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 22{\cdot}259\,(4)$, $b = 21{\cdot}356\,(4)$, $c = 9{\cdot}040\,(2)$ Å, $Z = 8$, $U = 4297{\cdot}2$ Å^3, $d_m = 1{\cdot}69$, $d_c = 1{\cdot}65$ Mg m^{-3}, $F(000) = 2292$. Cu *Kα* ($\mu = 2{\cdot}36$ mm^{-1}) intensity data were collected on a diffractometer. The structure was solved by direct methods and electron-density calculations. The final R for 3420 reflections is 0·057. Both molecules in the asymmetric unit have identical conformations. The orientation of the guanine base with respect to the ribose is *anti* ($\chi_{CN} = 56{\cdot}2$ and $57{\cdot}4°$). The conformation of the ribose moiety is C(2′)-*endo* and it has the common *gauche–gauche* conformation about C(4′)—C(5′) ($\psi_{OC} = 56{\cdot}1, 56{\cdot}8°$). Base–base as well as base–ribose interactions occur. A striking feature of the molecular packing is the presence of two non-crystallographic symmetry elements, a pseudo twofold symmetry axis at (0·44, 0·50) parallel to **a**, and a twofold screw axis at (0·0, 0·20) parallel to **c** relating adjacent molecules *A* and *B*.

Introduction

The structure determination of the title compound ($5'$-GMPNa$_2$.7H$_2$O) was undertaken to find out to what extent the geometry of ribonucleotides differs from that of deoxyribonucleotides (Seshadri & Viswamitra, 1974; Viswamitra, Seshadri & Post, 1980; Seshadri, Viswamitra & Kartha, 1980). The structure of 5′-dGMPNa$_2$ has been reported (Young, Tollin & Wilson, 1974; Viswamitra & Seshadri, 1974).

Experimental

Crystals were grown from ethanol/water by liquid diffusion techniques. Crystal data were obtained from rotation and Weissenberg photographs taken with Cu *Kα* radiation. The unit-cell parameters were later refined by least-squares calculations from 25 reflections measured on a CAD-4 diffractometer.

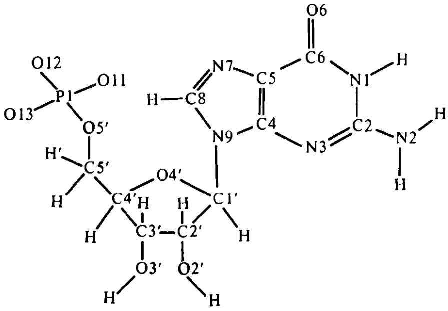

Fig. 1. Numbering of atoms in 5′-GMP.

Density measurements by flotation in acetone/bromoform indicated the presence of two nucleotides and 14 water molecules in the asymmetric unit. Cu *Kα* intensity data up to $\sin\theta/\lambda = 0{\cdot}59$ Å^{-1} were collected from a 0·1 × 0·1 × 1·0 mm crystal on the diffractometer in the ω–2θ scan mode. 3420 out of 3925 reflections were considered observed $[F > 3\sigma(F)]$. Background counts were measured for $\frac{1}{6}$ of the total scan angle on either side of the Bragg peak. The $\overline{12},0,0$ and $0,\overline{10},0$ reflections were monitored during data collection to check crystal and instrument stability. Intensities were corrected for Lorentz and polarization factors. No absorption correction was applied ($\mu r = 0{\cdot}13$). The molecular structure and atomic numbering are shown in Fig. 1.

Structure determination and refinement

The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976). An E map computed for the best set of phases showed the positions of the two phosphate groups and most of the atoms of the guanine bases. The remaining atoms of the nucleotide molecules, Na$^+$ ions and water O atoms were subsequently located from difference Fourier maps. Block-diagonal least-squares refinement with anisotropic temperature factors for all the atoms reduced R to 0·090. All the molecular H atoms and 23 out of 28 water H atoms were located from a difference Fourier map computed at this stage. Further refinement

0567-7408/81/101825-07$01.00

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors of non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = 1/6\pi^2 \textstyle\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i . \mathbf{a}_j.$$

Average e.s.d. in U_{eq} is 0·005 Å^2.

	x	y	z	U_{eq} (Å^2)
Molecule *A*				
P	8758 (1)	2344 (1)	6433 (2)	0·015
O(11)	8450 (2)	2863 (2)	5587 (6)	0·032
O(12)	8630 (2)	2364 (2)	8101 (5)	0·032
O(13)	8635 (2)	1706 (2)	5777 (6)	0·029
O(5')	9479 (2)	2459 (2)	6317 (6)	0·027
C(5')	9749 (3)	2335 (3)	4904 (8)	0·025
C(4')	10402 (3)	2547 (3)	4884 (8)	0·021
O(4')	10448 (2)	3217 (2)	5029 (6)	0·027
C(3')	10813 (3)	2270 (3)	6090 (8)	0·023
O(3')	11409 (2)	2193 (2)	5555 (6)	0·031
C(2')	10811 (3)	2790 (3)	7244 (8)	0·023
O(2')	11331 (2)	2819 (2)	8169 (6)	0·032
C(1')	10783 (3)	3384 (3)	6294 (8)	0·021
N(9)	10473 (3)	3897 (3)	7023 (7)	0·025
C(8)	9888 (3)	3889 (3)	7498 (10)	0·031
N(7)	9722 (3)	4415 (3)	8122 (8)	0·037
C(6)	10314 (3)	5418 (3)	8471 (9)	0·028
O(6)	9953 (3)	5786 (3)	9097 (8)	0·051
C(5)	10227 (3)	4795 (3)	8027 (9)	0·027
C(4)	10693 (3)	4484 (3)	7344 (8)	0·021
N(3)	11251 (3)	4700 (3)	7050 (7)	0·030
C(2)	11318 (3)	5278 (3)	7474 (9)	0·029
N(2)	11839 (3)	5591 (3)	7251 (9)	0·045
N(1)	10888 (3)	5631 (3)	8203 (7)	0·029
Molecule *B*				
P	6328 (1)	3444 (1)	8589 (2)	0·016
O(11)	6622 (2)	3953 (2)	9494 (6)	0·030
O(12)	6463 (2)	3498 (2)	6924 (5)	0·027
O(13)	6452 (2)	2802 (2)	9208 (6)	0·024
O(5')	5610 (2)	3550 (2)	8695 (6)	0·028
C(5')	5336 (3)	3441 (4)	10121 (9)	0·030
C(4')	4699 (3)	3673 (3)	10118 (9)	0·026
O(4')	4678 (2)	4338 (2)	9934 (6)	0·026
C(3')	4283 (3)	3397 (3)	8925 (9)	0·027
O(3')	3692 (2)	3334 (3)	9451 (6)	0·042
C(2')	4297 (3)	3900 (3)	7749 (8)	0·022
O(2')	3767 (2)	3913 (3)	6852 (6)	0·037
C(1')	4322 (3)	4495 (3)	8665 (8)	0·021
N(9)	4607 (3)	5015 (3)	7901 (7)	0·025
C(8)	5188 (3)	5032 (3)	7347 (10)	0·019
N(7)	5317 (3)	5576 (3)	6751 (8)	0·035
C(6)	4659 (3)	6546 (3)	6415 (10)	0·031
O(6)	4982 (3)	6924 (2)	5756 (8)	0·046
C(5)	4800 (3)	5922 (3)	6884 (8)	0·024
C(4)	4355 (3)	5584 (3)	7630 (8)	0·022
N(3)	3799 (3)	5768 (3)	8004 (7)	0·026
C(2)	3683 (4)	6347 (3)	7612 (9)	0·030
N(2)	3151 (3)	6609 (3)	7951 (9)	0·042
N(1)	4072 (3)	6714 (3)	6789 (7)	0·026
Na(1)	8850 (1)	4422 (1)	9719 (3)	0·032
Na(2)	3002 (1)	1741 (2)	8378 (4)	0·040
Na(3)	2132 (2)	494 (2)	6001 (4)	0·036
Na(4)	2862 (2)	3420 (2)	7925 (6)	0·072
W(1)	6176 (2)	4452 (3)	5066 (7)	0·039
W(2)	1997 (2)	1340 (2)	7680 (6)	0·036
W(3)	7583 (2)	3825 (3)	5926 (7)	0·038
W(4)	7620 (2)	2499 (3)	9902 (7)	0·044
W(5)	2691 (3)	2515 (3)	6549 (6)	0·043
W(6)	2826 (3)	557 (3)	9514 (7)	0·050

Table 1 (*cont.*)

	x	y	z	U_{eq} (Å^2)
W(7)	8846 (2)	3320 (2)	9985 (6)	0·037
W(8)	9135 (5)	5046 (5)	5366 (12)	0·108
W(9)	8299 (3)	4721 (3)	7421 (7)	0·050
W(10)	2039 (4)	3843 (5)	9024 (14)	0·121
W(11)	3686 (3)	1299 (3)	6590 (7)	0·050
W(12)	3081 (3)	124 (3)	6693 (7)	0·048
W(13)	2054 (4)	4870 (4)	821 (10)	0·079
W(14)	2438 (5)	3956 (5)	5538 (11)	0·133

Table 2. *Fractional coordinates* ($\times 10^3$) *and isotropic temperature factors of* H *atoms*

Average e.s.d. in U is 0·038 Å^2.

	x	y	z	U (Å^2)
Molecule *A*				
H(N1)	1113 (5)	613 (6)	845 (15)	0·122
H(N2)	1188 (3)	604 (3)	734 (8)	0·027
H'(N2)	1225 (6)	525 (6)	675 (16)	0·153
H(C8)	968 (3)	350 (4)	733 (9)	0·030
H(C1')	1122 (3)	355 (3)	598 (8)	0·012
H(C2')	1046 (3)	278 (3)	792 (7)	0·007
H(O2')	1162 (6)	270 (6)	782 (17)	0·139
H(C3')	1064 (2)	188 (3)	651 (7)	0·008
H(O3')	1146 (5)	194 (5)	465 (14)	0·122
H(C4')	1055 (3)	243 (3)	376 (9)	0·027
H(C5')	949 (4)	264 (4)	407 (9)	0·045
H'(C5')	977 (3)	185 (3)	472 (7)	0·013
Molecule *B*				
H(N1)	393 (3)	714 (3)	667 (8)	0·019
H(N2)	306 (5)	695 (5)	778 (12)	0·072
H'(N2)	289 (5)	632 (5)	844 (14)	0·095
H(C8)	549 (3)	463 (3)	737 (8)	0·019
H(C1')	389 (3)	462 (3)	903 (7)	0·007
H(C2')	466 (3)	384 (3)	711 (9)	0·019
H(O2')	381 (4)	381 (5)	638 (12)	0·068
H(C3')	443 (4)	294 (4)	874 (10)	0·046
H(O3')	369 (5)	319 (5)	1023 (14)	0·122
H(C4')	456 (5)	358 (5)	1111 (13)	0·087
H(C5')	558 (3)	376 (3)	1089 (8)	0·018
H'(C5')	529 (3)	294 (3)	1028 (7)	0·006
H1(*W*1)	576 (4)	418 (4)	504 (11)	0·098
H1(*W*2)	174 (5)	165 (6)	727 (12)	0·120
H2(*W*2)	186 (4)	106 (5)	864 (11)	0·118
H1(*W*3)	719 (6)	387 (4)	648 (10)	0·116
H2(*W*3)	773 (5)	340 (9)	591 (11)	0·094
H1(*W*4)	727 (4)	284 (8)	955 (10)	0·115
H2(*W*4)	787 (4)	236 (7)	932 (12)	0·110
H1(*W*5)	226 (5)	250 (8)	657 (11)	0·085
H2(*W*5)	295 (6)	226 (9)	568 (12)	0·103
H1(*W*6)	244 (5)	62 (8)	978 (10)	0·112
H1(*W*7)	864 (4)	311 (6)	932 (11)	0·086
H2(*W*7)	925 (5)	307 (4)	1022 (10)	0·109
H1(*W*8)	880 (7)	541 (5)	495 (11)	0·133
H2(*W*8)	955 (5)	528 (4)	568 (10)	0·125
H1(*W*9)	818 (4)	435 (6)	767 (11)	0·128
H1(*W*10)	182 (5)	340 (7)	852 (11)	0·086
H2(*W*10)	243 (4)	387 (8)	932 (12)	0·094
H1(*W*11)	409 (7)	104 (4)	682 (9)	0·120
H2(*W*11)	364 (6)	160 (5)	591 (10)	0·122
H1(*W*13)	197 (5)	434 (4)	34 (11)	0·118
H2(*W*13)	247 (6)	518 (7)	34 (12)	0·135
H1(*W*14)	788 (5)	283 (7)	92 (11)	0·063
H2(*W*14)	197 (4)	387 (5)	500 (10)	0·063

Table 3. *Bond lengths* (Å) *involving non*-H *atoms*

	A	*B*		*A*	*B*		*A*	*B*
P–O(11)	1·512 (5)	1·510 (5)	C(3′)–O(3′)	1·422 (8)	1·405 (9)	C(6)–O(6)	1·258 (10)	1·234 (10)
P–O(12)	1·534 (5)	1·539 (5)	C(2′)–C(1′)	1·533 (10)	1·516 (10)	C(6)–C(5)	1·403 (10)	1·435 (10)
P–O(13)	1·511 (5)	1·506 (5)	C(2′)–O(2′)	1·429 (9)	1·432 (9)	C(5)–C(4)	1·377 (10)	1·399 (10)
P–O(5′)	1·626 (5)	1·617 (5)	C(1′)–O(4′)	1·412 (9)	1·434 (9)	C(4)–N(3)	1·353 (9)	1·342 (9)
O(5′)–C(5′)	1·436 (9)	1·445 (9)	C(1′)–N(9)	1·454 (9)	1·454 (9)	N(3)–C(2)	1·300 (9)	1·312 (9)
C(5′)–C(4′)	1·523 (10)	1·502 (10)	N(9)–C(8)	1·370 (10)	1·388 (10)	C(2)–N(2)	1·352 (10)	1·346 (10)
C(4′)–O(4′)	1·439 (8)	1·431 (8)	N(9)–C(4)	1·376 (9)	1·359 (9)	C(2)–N(1)	1·387 (10)	1·386 (10)
C(4′)–C(3′)	1·542 (10)	1·539 (10)	C(8)–N(7)	1·310 (10)	1·312 (10)	N(1)–C(6)	1·377 (9)	1·395 (9)
C(3′)–C(2′)	1·524 (10)	1·513 (10)	N(7)–C(5)	1·389 (10)	1·372 (9)			

Table 4. *Bond angles* (°) *involving non*-H *atoms*

	A	*B*		*A*	*B*		*A*	*B*
O(11)–P–O(12)	113·08 (29)	113·05 (28)	O(3′)–C(3′)–C(2′)	108·62 (55)	108·87 (58)	O(6)–C(6)–N(1)	117·66 (67)	119·64 (69)
O(11)–P–O(13)	112·33 (29)	112·07 (28)	C(3′)–C(2′)–O(2′)	115·50 (56)	113·30 (57)	C(5)–C(6)–N(1)	113·00 (64)	111·82 (63)
O(11)–P–O(5′)	107·68 (28)	107·20 (28)	C(3′)–C(2′)–C(1′)	102·65 (54)	102·27 (55)	N(7)–C(5)–C(6)	130·32 (68)	131·12 (66)
O(12)–P–O(13)	112·13 (29)	113·28 (27)	O(2′)–C(2′)–C(1′)	108·99 (54)	108·95 (55)	N(7)–C(5)–C(4)	110·77 (63)	111·02 (61)
O(12)–P–O(5′)	104·05 (27)	103·88 (27)	O(4′)–C(1′)–C(2′)	105·46 (53)	105·22 (53)	C(6)–C(5)–C(4)	118·89 (66)	117·86 (64)
O(13)–P–O(5′)	106·92 (27)	106·62 (27)	O(4′)–C(1′)–N(9)	107·88 (53)	108·47 (53)	N(9)–C(4)–C(5)	105·47 (59)	104·80 (59)
P–O(5′)–C(5′)	116·24 (43)	116·59 (44)	C(2′)–C(1′)–N(9)	112·92 (55)	113·40 (56)	N(9)–C(4)–N(3)	126·65 (62)	126·62 (62)
O(5′)–C(5′)–C(4′)	110·80 (56)	110·09 (59)	C(1′)–N(9)–C(8)	125·73 (60)	126·69 (60)	C(5)–C(4)–N(3)	127·88 (65)	128·58 (64)
C(5′)–C(4′)–O(4′)	111·29 (55)	111·03 (58)	C(1′)–N(9)–C(4)	127·82 (57)	126·04 (58)	C(4)–N(3)–C(2)	111·83 (62)	112·92 (61)
C(5′)–C(4′)–C(3′)	116·30 (58)	116·23 (61)	C(8)–N(9)–C(4)	106·44 (58)	107·25 (58)	N(3)–C(2)–N(2)	121·52 (71)	120·31 (69)
O(4′)–C(4′)–C(3′)	105·94 (53)	106·22 (56)	N(9)–C(8)–N(7)	113·10 (68)	111·96 (66)	N(3)–C(2)–N(1)	125·28 (68)	123·70 (67)
C(4′)–O(4′)–C(1′)	111·27 (50)	110·02 (51)	C(8)–N(7)–C(5)	104·21 (64)	104·93 (62)	N(2)–C(2)–N(1)	113·19 (66)	115·93 (67)
C(4′)–C(3′)–O(3′)	110·96 (55)	111·22 (59)	O(6)–C(6)–C(5)	129·31 (71)	128·54 (72)	C(6)–N(1)–C(2)	122·97 (62)	124·79 (62)
C(4′)–C(3′)–C(2′)	101·74 (54)	102·02 (57)						

converged with $R = 0{\cdot}057$. The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/(a + b|F_o| + c|F_o|^2)$, and $a = 1{\cdot}06$, $b = 0{\cdot}0024$, $c = 0{\cdot}0001$ (Cruickshank, 1961). The scattering factors for C, N, O, P and Na were computed from the function of Cromer & Waber (1965) and for H atoms those of Stewart, Davidson & Simpson (1965) were used.

Results and discussion

The final parameters of the non-H and H atoms are listed in Tables 1 and 2.* Bond distances and angles involving heavy atoms are given in Tables 3 and 4. Average e.s.d.'s in bond distances are P–O, 0·005, and C–N,O,C, 0·009 Å; those in bond angles vary from 0·3 to 0·6°.

(*A*) *Molecular geometry and conformation*

Glycosidic bond

Both molecules in the asymmetric unit have identical conformational features. The orientation of the guanine base with respect to the ribose is *anti* as in other guanine mononucleotides (Aoki, Clark & Orbell, 1976; Aoki, 1976; Sletten & Lie, 1976; DeMeester, Goodgame, Jones & Skapski, 1974; DeMeester, Goodgame, Skapski & Smith, 1974; Murayama, Nagashima & Shimizu, 1969). The glycosidic torsion angle [O(4′)–C(1′)–N(9)–C(8)] is 56·2 and 57·4° for molecules *A* and *B* respectively, close to that (52·3°) observed for 5′-dGMPNa$_2$ (Young *et al.*, 1974; Viswamitra & Seshadri, 1974). It is significantly different from that (−12·3°) found in 5′-GMP (Murayama, Nagashima & Shimizu, 1969) and 5′-GMPCd (13·0°) (Aoki, 1976). Potential-energy calculations show that guanine-containing nucleotides prefer the *syn* over the *anti* conformation about the glycosidic bond (Yathindra & Sundaralingam, 1973). In the recently reported hexanucleotide d(CpGpCpGpCpG) (Wang, Quigley, Kolpak, Crawford, van Boom, van der Marel & Rich, 1979) the dG residues have the *syn* conformation.

Conformation of the ribose moiety

The best four-atom plane for the ribose moiety contains C(1′), C(3′), O(4′) and C(4′). Table 5 shows the deviations of the atoms from this plane. C(2′) is displaced by 0·54 (in *A*) and 0·56 Å (in *B*) on the same side as C(5′). The conformation of the ribose is therefore C(2′)-*endo* in contrast to O(4′)-*endo* for the 5′-dGMPNa$_2$ and C(3′)-*endo* reported for all other guanine mononucleotides.

---

* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36121 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Conformation about C(4')–C(5')

The nucleotide has the common *gauche–gauche* conformation about C(4')–C(5'). The torsion angle O(5')–C(5')–C(4')–C(3') (ψ) is 56·1 and 56·8° for *A* and *B* respectively. This differs from 5'-dGMPNa$_2$ which shows the unusual *gauche–trans* (*gt*) conformation in the crystal structure. The differences between their geometries can be seen clearly in Fig. 2.

Table 5. *Least-squares planes and deviations of atoms* (Å) *from them*

Average e.s.d. in the atom deviation is 0·007 Å.

	Molecule *A*	Molecule *B*
C(1')	−0·029	−0·017
C(2')	−0·539*	0·563*
C(3')	0·027	−0·017
C(4')	−0·045	0·029
O(4')	0·024	−0·014
C(5')	−1·250*	1·194*

Equations of the planes

Molecule *A* $0{\cdot}8080X + 0{\cdot}0446Y - 0{\cdot}5874Z = -16{\cdot}4027$

Molecule *B* $0{\cdot}7968X - 0{\cdot}0748Y - 0{\cdot}5996Z = -2{\cdot}2336$

	Molecule *A*	Molecule *B*
N(1)	−0·020	0·030
C(2)	0·019	−0·046
N(3)	−0·002	−0·007
C(4)	−0·003	0·003
C(5)	−0·009	0·003
C(6)	0·014	0·004
N(7)	−0·002	−0·031
C(8)	0·013	0·006
N(9)	−0·009	0·025
N(2)	0·057*	−0·105*
O(6)	0·021*	−0·007*

Equations of the planes

Molecule *A* $-0{\cdot}3126X + 0{\cdot}3308Y - 0{\cdot}8904Z = 10{\cdot}1800$

Molecule *B* $-0{\cdot}3419X - 0{\cdot}3524Y - 0{\cdot}8712Z = 13{\cdot}5276$

* Atoms not included in the calculation of the plane.

Phosphate group

The phosphate group exists in a staggered conformation as seen from the torsion angles (Table 6). The P–O distances are close to those observed in other nucleotide structures.

Guanine base

The guanine base is essentially planar (Table 5). There is extensive overlap of bases of the molecules *A* and *B* at a separation of 3·3 Å. The overlap is such that the N(7)–C(5) bonds of the two molecules form a letter 'V' with an angle of 68° between them. The stacking pattern observed in the present structure is significantly different from that found in 5'-dGMPNa$_2$ which has hardly any overlap of bases (Fig. 3). It is close to the stacking pattern reported for 9-methyladenine (Bugg, Thomas, Sundaralingam & Rao, 1971). In the present structure there is a strong interaction between the ribose O(4') and the purine ring. O(4')*A* and O(4')*B* are situated in the voids just above the purine rings of molecules *B* and *A*, respectively. [N(1)*A*–O(4')*B* = 3·13 and N(1)*B*–O(4')*A* = 3·14 Å]. The nature of this interaction is somewhat

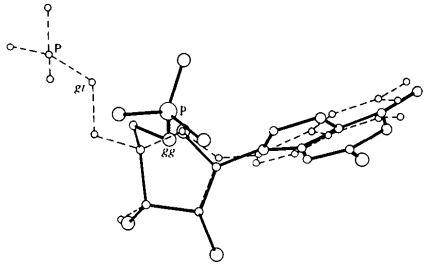

Fig. 2. Superposition of 5'-GMPNa$_2$ (dark lines) on 5'-dGMP-Na$_2$ (dotted lines) viewed perpendicular to the plane of atoms C(2'), C(3') and C(4'), showing the *gg* and *gt* conformational differences.

Table 6. *Torsion angles* (°) *involving non*-H *atoms*

Average e.s.d. is 0·6°.

	A	*B*		*A*	*B*
O(11)–P–O(5')–C(5')	−72·4	−68·3	C(4')–O(4')–C(1')–N(9)	−136·7	−140·9
O(12)–P–O(5')–C(5')	167·4	171·8	C(4')–C(3')–C(2')–O(2')	−153·4	−153·4
O(13)–P–O(5')–C(5')	48·6	51·9	O(3')–C(3')–C(2')–O(2')	−36·3	−35·7
P–O(5')–C(5')–C(4')	172·0	169·3	C(4')–C(3')–C(2')–C(1')	−34·9	−36·3
O(5')–C(5')–C(4')–O(4')	−65·3	−64·7	O(3')–C(3')–C(2')–C(1')	82·2	81·4
O(5')–C(5')–C(4')–C(3')	56·1	56·8	C(3')–C(2')–C(1')–O(4')	32·1	35·0
C(5')–C(4')–O(4')–C(1')	120·3	123·0	O(2')–C(2')–C(1')–O(4')	155·1	155·1
C(3')–C(4')–O(4')–C(1')	−7·0	−4·3	C(3')–C(2')–C(1')–N(9)	149·7	153·3
C(5')–C(4')–C(3')–O(3')	147·0	145·8	O(2')–C(2')–C(1')–N(9)	−87·4	−86·5
O(4')–C(4')–C(3')–O(3')	−88·8	−90·8	O(4')–C(1')–N(9)–C(8)	56·2	57·4
C(5')–C(4')–C(3')–C(2')	−97·7	−98·3	C(2')–C(1')–N(9)–C(8)	−60·0	−59·1
O(4')–C(4')–C(3')–C(2')	26·6	25·8	O(4')–C(1')–N(9)–C(4)	−122·3	−121·0
C(4')–O(4')–C(1')–C(2')	−15·7	−19·3	C(2')–C(1')–N(9)–C(4)	121·6	122·6

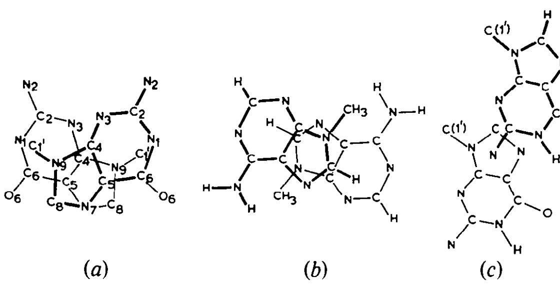

Fig. 3. Base-stacking patterns in (*a*) 5′-GMPNa$_2$, (*b*) 9-methyladenine and (*c*) 5′-dGMPNa$_2$.

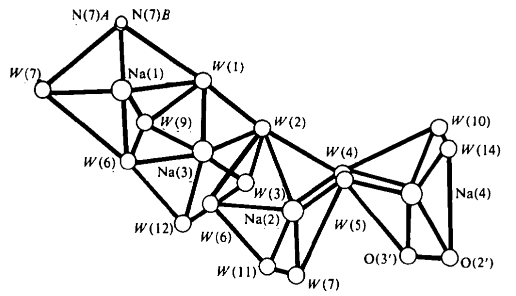

Fig. 4. Sodium coordination polyhedra viewed along **c**.

similar to that observed in 3′-*O*-acetyladenosine (Bugg *et al.*, 1971). Thus, base–base as well as base–ribose interactions occur.

Sodium-ion coordination

There are four crystallographically independent Na$^+$ ions in the structure. Na(1) has *W*(1), *W*(6), *W*(7), *W*(9), N(7)*A* and N(7)*B* as neighbours at distances ranging from 2·36 to 2·61 Å. N(7) taking part in metal coordination has been reported for 5′-ATPNa$_2$ (Kennard *et al.*, 1971), 5′-GMPCu (Aoki *et al.*, 1976; Sletten & Lie, 1976), 5′-GMPCd (Aoki, 1976). Na(2) and Na(3) are completely surrounded by water O atoms at distances ranging from 2·34 to 2·76 Å. Na$^+$ ions coordinating only with water molecules are also present in 3′-UMPNa$_2$ (Viswamitra, Reddy, James & Williams, 1972), 5′-dAMPNa (Reddy & Viswamitra, 1975) and 5′-dUMPNa$_2$ (Viswamitra *et al.*, 1980). Na(4) coordinates with *W*(4), *W*(5), *W*(10), *W*(14), O(2′)*B* and O(3′)*B* in the range 2·31 to 2·83 Å. Phosphate O atoms and O(6) of the guanine base are not involved in the Na coordination unlike the crystal structure of 5′-dGMPNa$_2$. Each Na$^+$ ion has six neighbours in contrast to 5′-dGMPNa$_2$ where one of the Na$^+$ ions is five coordinated. Details of the Na$^+$ octahedra are given in Table 7 and Fig. 4.

The nature of Na coordination found in various nucleotide structures is summarized in Table 8. Na—O(P) distances are in the range 2·32 to 2·52 Å whereas Na—O(*W*) distances have a wider range, 2·20 to 2·90 Å. In all these hydrated crystal structures the Na$^+$ ions are either partly or completely surrounded by water O atoms. This shows the strong affinity of Na$^+$ ions for water O atoms and also that the role of Na$^+$ is much more than simply neutralizing the charges on the phosphate group. The hydroxyl oxygens O(2′) and O(3′) of the ribose always seem to be involved in the Na coordination. There is also one case (5′-ATPNa$_2$) where O(4′) is involved in the Na binding. Sequence-specific binding of Na has been reported in the ApU structure (Seeman, Rosenberg, Suddath, Kim & Rich, 1976).

Table 7. *Sodium coordination polyhedra* (Å *and* deg)

E.s.d.'s in distances and angles are 0·007 Å and 0·5°.

Na(1)–*W*(7)	2·365	Na(1)–*W*(1$^{\text{i}}$)	2·426
Na(1)–*W*(9)	2·495	Na(1)–N(7)*B*$^{\text{i}}$	2·611
Na(1)–N(7)*A*	2·419	Na(1)–*W*(6$^{\text{ii}}$)	2·384
W(1)–Na(1)–*W*(6)	85·36	*W*(6)–Na(1)–N(7)*B*	133·71
W(1)–Na(1)–*W*(7)	166·60	*W*(7)–Na(1)–*W*(9)	109·73
W(1)–Na(1)–*W*(9)	80·94	*W*(7)–Na(1)–N(7)*A*	93·36
W(1)–Na(1)–N(7)*A*	94·04	*W*(7)–Na(1)–N(7)*B*	87·14
W(1)–Na(1)–N(7)*B*	68·35	*W*(9)–Na(1)–N(7)*A*	84·27
W(6)–Na(1)–*W*(7)	89·26	*W*(9)–Na(1)–N(7)*B*	146·79
W(6)–Na(1)–*W*(9)	76·47	N(7)*A*–Na(1)–N(7)*B*	66·00
W(6)–Na(1)–N(7)*A*	160·26		
Na(2)–*W*(2)	2·477	Na(2)–*W*(11)	2·414
Na(2)–*W*(5)	2·439	Na(2)–*W*(4$^{\text{iii}}$)	2·403
Na(2)–*W*(6)	2·758	Na(2)–*W*(7$^{\text{iii}}$)	2·396
W(2)–Na(2)–*W*(4)	94·54	*W*(5) Na(2) *W*(11)	89·42
W(2)–Na(2)–*W*(5)	78·77	*W*(6)–Na(2)–*W*(4)	109·17
W(2)–Na(2)–*W*(6)	69·47	*W*(6)–Na(2)–*W*(7)	80·27
W(2)–Na(2)–*W*(7)	147·88	*W*(6)–Na(2)–*W*(11)	88·89
W(2)–Na(2)–*W*(11)	105·32	*W*(7)–Na(2)–*W*(4)	85·18
W(5)–Na(2)–*W*(4)	83·13	*W*(7)–Na(2)–*W*(11)	84·03
W(5)–Na(2)–*W*(6)	146·49	*W*(4)–Na(2)–*W*(11)	157·03
W(5)–Na(2)–*W*(7)	132·75		
Na(3)–*W*(2)	2·379	Na(3)–*W*(3$^{\text{iv}}$)	2·482
Na(3)–*W*(12)	2·341	Na(3)–*W*(6$^{\text{v}}$)	2·618
Na(3)–*W*(1$^{\text{iv}}$)	2·338	Na(3)–*W*(9$^{\text{vi}}$)	2·384
W(1)–Na(3)–*W*(2)	96·42	*W*(12)–Na(3)–*W*(9)	88·12
W(1)–Na(3)–*W*(3)	92·90	*W*(6)–Na(3)–*W*(2)	169·60
W(1)–Na(3)–*W*(6)	82·22	*W*(6)–Na(3)–*W*(3)	97·34
W(1)–Na(3)–*W*(9)	85·22	*W*(6)–Na(3)–*W*(9)	74·22
W(1)–Na(3)–*W*(12)	161·43	*W*(9)–Na(3)–*W*(2)	95·38
W(12)–Na(3)–*W*(2)	101·46	*W*(9)–Na(3)–*W*(3)	171·52
W(12)–Na(3)–*W*(3)	91·14	*W*(2)–Na(3)–*W*(3)	93·05
W(12)–Na(3)–*W*(6)	79·30		
Na(4)–*W*(5)	2·329	Na(4)–*W*(4$^{\text{iii}}$)	2·828
Na(4)–*W*(10)	2·271	Na(4)–O(2′)*B*	2·471
Na(4)–*W*(14)	2·619	Na(4)–O(3′)*B*	2·314
W(5)–Na(9)–*W*(10)	115·49	O(3′)*B*–Na(4)–*W*(14)	144·42
W(5)–Na(4)–*W*(14)	82·17	*W*(10)–Na(4)–*W*(14)	84·00
W(5)–Na(4)–O(2′)*B*	106·14	*W*(4)–Na(4)–*W*(5)	76·44
W(5)–Na(4)–O(3′)*B*	113·09	*W*(4)–Na(4)–O(3′)*B*	71·57
O(2′)*B*–Na(4)–O(3′)*B*	67·44	*W*(4)–Na(4)–O(2′)*B*	136·46
O(2′)*B*–Na(4)–*W*(14)	77·50	*W*(4)–Na(4)–*W*(10)	79·48
O(2′)*B*–Na(4)–*W*(10)	131·12	*W*(4)–Na(4)–*W*(14)	143·76
O(3′)*B*–Na(4)–*W*(10)	114·50		

Symmetry code: (i) $\frac{3}{2}-x, 1+\bar{y}, \frac{1}{2}+z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 2+\bar{z}$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, 2+\bar{z}$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, 1+\bar{z}$; (v) $\frac{1}{2}-x, \bar{y}, -\frac{1}{2}+z$; (vi) $1+\bar{x}, -\frac{1}{2}+y, \frac{3}{2}+z$.

Table 8. *Nature of sodium coordination in nucleotide structures* (Å)

Compound		Phosphate	Sugar	Base	Water
I	Na(1)	—	—	—	2·365 to 2·620
	Na(2)	—	O(2′) 2·336 O(3′) 2·697 O(5′) 2·350	—	2·402 to 2·790
II	Na(1)		O(3′) 2·354	O(6) 2·559	2·352 to 2·527
	Na(2)	O(1) 2·383 O(2) 2·322		O(6) 2·355	2·397 to 2·510
III	Na(1)	—	O(3′) 2·348	O(6) 2·553	2·356 to 2·507
	Na(2)	O(II) 2·318 O(III) 2·368	—	O(6) 2·367	2·367 to 2·527
IV	Na	—	—	—	2·370 to 2·453
V	Na(1)	—	—	N(7)*A* 2·419 N(7)*B* 2·611	2·365 to 2·495
	Na(2)	—	—	—	2·396 to 2·758
	Na(3)	—	—	—	2·338 to 2·618
	Na(4)	—	O(2′)*B* 2·471 O(3′)*B* 2·314		2·329 to 2·828
VI	Na	—	O(2′) 2·48 O(3′) 2·33	—	2·36 to 2·89
VII	Na	O(2) 2·39 O(2) 2·30	—	—	2·34 to 2·49
VIII	Na(1)	—	—	O(2)U1 2·37 O(2)U2 2·34	2·35 to 2·90
	Na(2)	O(1) 2·37 O(1) 2·32	O(3′)*A*1 2·50 O(3′)*A*2 2·58		2·32 to 2·45
IX	Na	O 2·46	—	O(2) 2·42 O(2) 2·54	2·36 to 2·45
X	Na(1)	O(1)*B* 2·59 O(22)*B* 2·42 O(33)*B* 2·65 O(333)*B* 2·53 O(333)*A* 2·47	—	N(7)*A* 2·90	—
	Na(2)	O(1)*A* 2·45 O(22)*A* 2·48 O(33)*A* 2·54 O(333)*A* 2·32 O(333)*B* 2·32	—	N(7)*B* 2·69	—
	Na(3)	O(2)*A* 2·32 O(2)*B* 2·32	—	—	2·32 to 2·82
	Na(4)	O(11)*B* 2·72	O(4′)*A* 2·80 O(2′)*B* 2·84 O(2′)*A* 2·80 O(3′)*B* 2·69		—

Compounds: (I) 3′-UMPNa$_2$ (Viswamitra *et al.*, 1972), (II) 5′-dGMPNa$_2$ (Young *et al.*, 1974), (III) 5′-dGMPNa$_2$ (Viswamitra & Seshadri, 1974), (IV) 5′-dAMPNa (Reddy & Viswamitra, 1975), (V) 5′-GMPNa$_2$ (present work), (VI) 5′-IMPNa (Rao & Sundaralingam, 1969), (VII) GpCNa (Rosenberg, Seeman, Day & Rich, 1976), (VIII) ApUNa (Seeman *et al.*, 1976), (IX) pTpTNa (Camerman & Fawcett, 1976), (X) 5′-ATPNa$_2$ (Kennard *et al.*, 1971).

(*B*) *Molecular packing and hydrogen bonding*

A striking feature of the molecular packing in the extended structure is the presence of two non-crystallographic symmetry elements. A pseudo twofold symmetry axis at (0·44, 0·50) parallel to **a** and a pseudo twofold screw axis at (0·0, 0·20) parallel to **c** relate adjacent molecules *A* and *B* as shown in Figs. 5 and 6. The symmetry elements are nearly perfect, the r.m.s. deviations between observed and symmetry-generated positions for all the molecular atoms being only 0·013 Å for the twofold axis and 0·010 Å for the 2_1 screw axis.

There are 56 water molecules in the unit cell. These and the Na$^+$ ions form columns parallel to **b** between

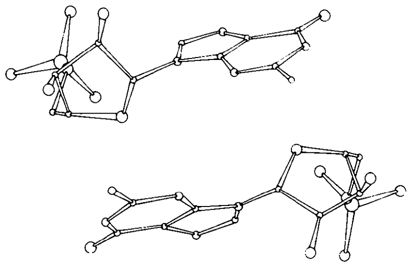

Fig. 5. Pseudo twofold axis parallel to **a**.

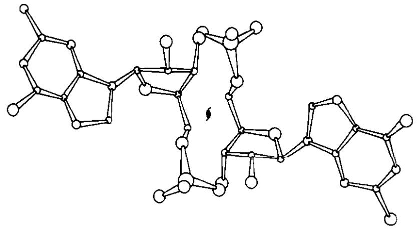

Fig. 6. Pseudo 2_1 axis parallel to **c**.

Table 9. *Hydrogen-bond distances and angles*

E.s.d.'s in hydrogen-bond distances and angles are 0·008 Å and 9°.

A–H···*B*	*A*···*B*	H···*B*	*A* Ĥ *B*	Symmetry of *B*
W(1)–H1(*W*1)···O(6)*A*	2·710 Å	1·84 Å	137·0°	$\frac{3}{2}-x, 1+\bar{y}, -\frac{1}{2}+z$
W(1) ···O(12)*B*	2·716			
W(2)–H1(*W*2)···O(3′)*A*	2·953	2·07	153·7	$-1+x, y, z$
W(2)–H2(*W*2)···O(11)*B*	2·760	1·77	147·8	$-\frac{1}{2}+x, \frac{1}{2}-y, 2+\bar{z}$
W(3)–H1(*W*3)···O(12)*B*	2·742	1·84	145·3	
W(3)–H2(*W*3)···O(11)*A*	2·835	2·01	144·6	
W(4)–H1(*W*4)···O(13)*B*	2·752	1·85	135·0	
W(4)–H2(*W*4)···O(12)*A*	2·972	2·01	156·5	
W(5)–H1(*W*5)···O(3′)*A*	3·069	2·23	149·8	$-1+x, y, z$
W(5)–H2(*W*5)···O(11)*A*	2·691	1·62	159·9	$-\frac{1}{2}+x, \frac{1}{2}-y, 1+\bar{z}$
W(6) ···*W*(12)	2·772			
W(6) ···*W*(2)	2·992			
W(7)–H1(*W*7)···O(12)*A*	2·703	1·94	144·2	
W(7)–H2(*W*7)···O(6)*B*	2·750	1·80	149·8	$\frac{3}{2}-x, 1+\bar{y}, \frac{1}{2}+z$
W(8)–H1(*W*8)···O(11)*B*	2·834	1·73	143·3	$\frac{3}{2}-x, 1+\bar{y}, -\frac{1}{2}+z$
W(8)–H2(*W*8)···O(4′)*B*	2·976	2·04	145·6	$\frac{1}{2}+x, 1+\bar{y}, \frac{3}{2}-z$
W(9) ···*W*(8)	2·720			
W(9) ···*W*(3)	2·833			
W(10)–H1(*W*10)···O(2′)*A*	2·802	1·69	161·8	$-1+x, y, z$
W(11)–H1(*W*11)···N(7)*B*	3·092	2·10	152·9	$-1+x, -\frac{1}{2}+y, \frac{3}{2}-z$
W(11)–H2(*W*11)···O(11)*A*	2·710	1·82	171·0	$-\frac{1}{2}+x, \frac{1}{2}-y, 1+\bar{z}$
W(12) ···*W*(11)	2·852			
W(12) ···O(11)*B*	2·799			$1+\bar{x}, -\frac{1}{2}+y, \frac{3}{2}-z$
W(13)–H1(*W*13)···*W*(10)	2·730	1·60	149·3	$x, y, -1+z$
W(13)–H2(*W*13)···*W*(14)	2·763	1·96	143·3	$\frac{1}{2}-x, 1+\bar{y}, -\frac{1}{2}+z$
N(1)*A*–H(N1)*A*···O(13)*A*	2·692	1·53	163·5	$2+\bar{x}, \frac{1}{2}+y, \frac{3}{2}-z$
N(2)*A*–H′(N2)*A*···*W*(13)	2·952	1·60	153·0	$\frac{3}{2}-x, 1+\bar{y}, \frac{1}{2}+z$
O(2′)*A*–H(O2′)*A*···O(13)*B*	2·731	1·92	138·1	$\frac{1}{2}+x, \frac{1}{2}-y, 2+\bar{z}$
O(3′)*A*–H(O3′)*A*···O(12)*B*	2·686	1·70	173·3	$\frac{1}{2}+x, \frac{1}{2}-y, 1+\bar{z}$
N(1)*B*–H(N1)*B*···O(13)*B*	2·752	1·84	157·6	$1+\bar{x}, \frac{1}{2}+y, \frac{3}{2}-z$
N(2)*B*–H′(N2)*B*···*W*(14)	2·940	2·12	143·3	$\frac{1}{2}-x, 1+\bar{y}, \frac{1}{2}+z$
O(2′)*B*–H(O2′)*B*···O(13)*A*	2·736	1·98	153·8	$-\frac{1}{2}+x, \frac{1}{2}-y, 1+\bar{z}$
O(3′)*B*–H(O3′)*B*···O(12)*A*	2·672	1·92	165·2	$-\frac{1}{2}+x, \frac{1}{2}-y, 2+\bar{z}$

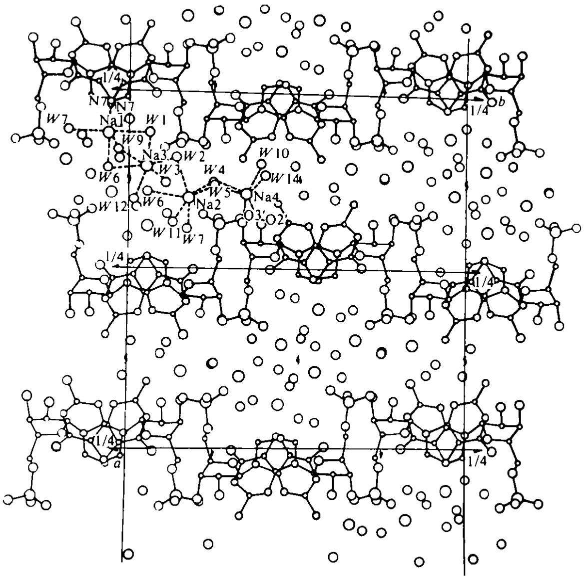

Fig. 7. Packing of 5'-GMPNa$_2$.7H$_2$O in the unit cell viewed along **c**.

the nucleotide chains as shown in Fig. 7. The various H bonds are summarized in Table 9.

We thank the DST and DAE for financial support. TPS thanks the Indian Institute of Science for the award of a Senior Research Fellowship. SKK thanks the CSIR for financial support. Finally we thank Dr Larry Falvello for discussions and diagrams.

References

AOKI, K. (1976). *Acta Cryst.* B**32**, 1454–1459.

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

BUGG, C. E., THOMAS, J. M., SUNDARALINGAM, M. & RAO, S. T. (1971). *Biopolymers*, **10**, 175–219.

CAMERMAN, N. & FAWCETT, J. K. (1976). *J. Mol. Biol.* **107**, 601–621.

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

CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.

DEMEESTER, P., GOODGAME, D. M. L., JONES, T. J. & SKAPSKI, A. C. (1974). *Biochem. J.* **139**, 791–792.

DEMEESTER, P., GOODGAME, D. M. L., SKAPSKI, A. C. & SMITH, B. J. (1974). *Biochem. Biophys. Acta*, **340**, 113–115.

KENNARD, O., ISAACS, N. W., MOTHERWELL, W. D. S., COPPOLA, J. C., WAMPLER, D. L., LARSON, A. C. & WATSON, D. G. (1971). *Proc. R. Soc. London Ser. A*, **325**, 401–436.

MURAYAMA, W., NAGASHIMA, N. & SHIMIZU, Y. (1969). *Acta Cryst.* B**25**, 2236–2245.

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

REDDY, B. S. & VISWAMITRA, M. A. (1975). *Acta Cryst.* B**31**, 19–26.

ROSENBERG, J. M., SEEMAN, N. C., DAY, R. & RICH, A. (1976). *J. Mol. Biol.* **104**, 145–159.

SEEMAN, N. C., ROSENBERG, J. M. SUDDATH, F. L., KIM, J. J. P. & RICH, A. (1976). *J. Mol. Biol.* **104**, 109–144.

SESHADRI, T. P. & VISWAMITRA, M. A. (1974). *Curr. Sci.* **43**, 111–112.

SESHADRI, T. P., VISWAMITRA, M. A. & KARTHA, G. (1980). *Acta Cryst.* B**36**, 925–927.

SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

SLETTEN, E. & LIE, B. (1976). *Acta Cryst.* B**32**, 3301–3304.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VISWAMITRA, M. A., REDDY, B. S., JAMES, M. N. G. & WILLIAMS, G. J. B. (1972). *Acta Cryst.* B**28**, 1108–1116.

VISWAMITRA, M. A. & SESHADRI, T. P. (1974). *Nature (London)*, **252**, 176–177.

VISWAMITRA, M. A., SESHADRI, T. P. & POST, M. L. (1980). *Acta Cryst.* B**36**, 2019–2024.

WANG, A. H. J., QUIGLEY, G. J., KOLPAK, F. J., CRAWFORD, J. L., VAN BOOM, J. H., VAN DER MAREL, G. & RICH, A. (1979). *Nature (London)*, **282**, 680–686.

YATHINDRA, N. & SUNDARALINGAM, M. (1973). *Biopolymers*, **12**, 2075–2082.

YOUNG, D. W., TOLLIN, P. & WILSON, H. R. (1974). *Nature (London)*, **248**, 513–515.

Acta Cryst. (1981). B**37**, 1832–1835

A Complex of 2,11-Diaza-5,8,14,17-tetraoxa[$8^{2,11}$][12](4,4″)*o*-terphenylophane, Sodium Thiocyanate and Methanol (1 : 1 : 1)

By Gabriela Weber

Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, *D*-3400 *Göttingen, Federal Republic of Germany*

(*Received* 26 *January* 1981; *accepted* 18 *March* 1981)

Abstract

$C_{32}H_{40}N_2O_4.NaSCN.CH_3OH$, M_r = 629·80, is triclinic, space group $P\bar{1}$; a = 11·965 (4), b = 12·148 (5), c = 14·116 (6) Å, α = 90·33 (2), β = 113·16 (3), γ = 114·57 (3)°, Z = 2, D_c = 1·245 Mg m^{-3}, μ = 0·146 mm^{-1}, R = 0·058, R_w = 0·056 for 3262 independent reflexions. The 'boat' configuration of the crown-analogous section of the ligand enables all six hetero atoms to coordinate to the cation in a bi-apical square-pyramidal arrangement, whilst the terphenyl residue folds away. There is no direct contact between Na^+ and SCN^-; the anion is hydrogen bonded to a methanol molecule.

Introduction

According to the size of their inner cavities, macrobicyclic ligands display considerable selectivity in ligating spherical electron acceptors (Lehn & Sauvage, 1975). In complexes thus formed, 'fitting' cations are well shielded from their environments (Mathieu, Metz, Moras & Weiss, 1978; Moras, Metz & Weiss, 1973). Substitution of one coordinating chain by a large and rigid organic residue reduces the complexing ability of the ligand to that of the respective crown analogue. On the other hand it might provide an intramolecular cavity sufficiently large to accommodate a cation–anion pair (Rossa & Vögtle, 1981).

Experimental

Colourless irregular blocks of the title complex were grown from a mixture of methanol and ethyl acetate (Rossa & Vögtle, 1981). A crystal of approximate size 0·3 × 0·2 × 0·2 mm was used for collecting 4697 diffractometer data (6° < 2θ < 46°) in a profile-fitting procedure (Clegg, 1981) with monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). Corrections for Lp and crystal delay (*ca* 7%) were applied. Averaging equivalents gave 3270 unique reflexions with $F > 4\sigma(F)$. Cell dimensions were obtained from a least-squares analysis of angle measurements of 24 strong reflexions between 2θ = 20 and 25°.

The structure was solved by direct methods. Anisotropic refinement of all non-H atoms, followed by difference syntheses, showed the positions of all H atoms (except that of the hydroxyl group), which were idealized (distances 0·96 Å, angles 109·5°, aromatic H on external bisector). H atoms were assigned fixed isotropic thermal parameters 1·2 times the U values of attached C atoms; in further refinement a riding model was employed. Omission of eight poorly agreeing low-angle reflexions (probably caused by machine error) and application of an empirical extinction correction [$F_c^* = F_c(1 - xF_c^2/\sin\theta)$, x = 3·9 (5) × 10^{-7}] led to a final R = 0·058 and R_w = 0·056, where $R = \sum \Delta/\sum F_o$, $R_w = \sum w^{1/2}\Delta/\sum w^{1/2}F_o$, $\Delta = ||F_o| - |F_c||$ and $w^{-1} = \sigma^2(F_o) + 0{\cdot}00025\,F_o^2$.

Coordinates and thermal parameters of non-H atoms are given in Table 1, with derived bond lengths and angles in Tables 2 and 3.† Views of the complex are shown in Fig. 1; the numbering scheme is arbitrary.

Results and discussion

The title ligand is reported to form stable crystalline complexes with $Ba(SCN)_2$ and NaSCN (Rossa & Vögtle, 1981). In general, the diameter of the inner cavity of an 18-membered annular oligoether is such that Ba^{2+} and similar sized cations fit well (Dunitz, Dobler, Seiler & Phizackerley, 1974; Hughes, Mortimer & Truter, 1978; Moras, Metz, Herceg & Weiss, 1972). With smaller cations like Na^+, however, such a ligand has to adapt its original conformation to the ionic radius of the guest (Dobler, Dunitz & Seiler, 1974). This also holds for the present structure.

---

† Lists of structure factors, anisotropic thermal parameters, H atom parameters and a complete list of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36102 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/81/101832-04$01.00