C6	0.9428 (7)	0.4954 (7)	0.1420 (4)	0.057 (4)
O6	0.9719 (6)	0.4469 (6)	0.1550 (4)	0.104 (4)
C11	0.7418 (6)	0.5113 (6)	0.0732 (3)	0.039 (3)
C12	0.6844 (7)	0.5248 (7)	0.0524 (3)	0.051 (3)
C13	0.6495 (8)	0.4649 (9)	0.0373 (3)	0.063 (4)
C14	0.6713 (9)	0.3957 (7)	0.0430 (3)	0.062 (4)
C15	0.7289 (8)	0.3854 (7)	0.0641 (3)	0.060 (4)
C16	0.7630 (6)	0.4424 (6)	0.0790 (3)	0.043 (3)
C21	0.7842 (7)	0.6543 (7)	0.0606 (3)	0.049 (3)
C22	0.7611 (7)	0.7246 (7)	0.0629 (3)	0.051 (3)
C23	0.7745 (8)	0.7729 (8)	0.0377 (4)	0.065 (4)
C24	0.8094 (9)	0.7539 (9)	0.0096 (4)	0.073 (5)
C25	0.8311 (8)	0.6823 (9)	0.0065 (3)	0.068 (4)
C26	0.8195 (8)	0.6334 (7)	0.0320 (3)	0.055 (4)
C31	0.8481 (7)	0.6174 (7)	0.2031 (3)	0.043 (3)
C32	0.8200 (8)	0.6802 (6)	0.2158 (3)	0.050 (3)
C33	0.8530 (9)	0.7141 (8)	0.2423 (3)	0.063 (4)
C34	0.9141 (8)	0.6875 (8)	0.2566 (3)	0.059 (4)
C35	0.9407 (8)	0.6254 (8)	0.2450 (3)	0.064 (4)
C36	0.9074 (7)	0.5897 (7)	0.2181 (3)	0.056 (4)
C41	0.7901 (6)	0.4844 (6)	0.1854 (3)	0.040 (3)
C42	0.7526 (7)	0.4838 (7)	0.2142 (3)	0.047 (3)
C43	0.7287 (8)	0.4225 (8)	0.2298 (4)	0.061 (4)
C44	0.7446 (9)	0.3557 (8)	0.2139 (5)	0.075 (5)
C45	0.7843 (8)	0.3560 (8)	0.1843 (4)	0.067 (4)
C46	0.8041 (7)	0.4197 (6)	0.1698 (4)	0.052 (4)
C51	0.9722 (7)	0.6598 (6)	0.0897 (3)	0.083 (6)
C52	1.0170 (6)	0.6257 (6)	0.1130 (4)	0.075 (5)
C53	0.9944 (6)	0.6457 (6)	0.1451 (3)	0.070 (4)
C54	0.9356 (6)	0.6922 (5)	0.1417 (3)	0.056 (4)
C55	0.9219 (6)	0.7009 (6)	0.1075 (3)	0.071 (5)

Table 2. *Selected geometric parameters* (Å, °)

W1—Cp	2.002 (10)	Mn1—P1	2.384 (4)
W1—P1	2.539 (3)	Mn1—P2	2.390 (4)
W1—P2	2.550 (3)		
C6—W1—C5	81.1 (6)	Cp—W1—C5	116.6 (6)
C6—W1—P1	125.7 (4)	Cp—W1—C6	115.9 (6)
C5—W1—P1	79.7 (4)	P1—Mn1—P2	74.98 (12)
Cp—W1—P1	118.1 (4)	C21—P1—C11	99.8 (6)
C6—W1—P2	82.4 (5)	Mn1—P1—W1	105.47 (12)
C5—W1—P2	126.1 (4)	C41—P2—C31	98.5 (5)
Cp—W1—P2	116.9 (4)	Mn1—P2—W1	104.95 (12)
P1—W1—P2	69.64 (10)		

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 876–879

Effects of Halogen Substitution in Nucleic Acid Components. Structure of Sodium 5-Bromocytidine 5′-Phosphate Hydrate

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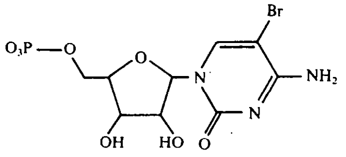
Abstract

The conformation of 5-bromocytidine 5′-monophosphate in the title compound, $Na^+.C_9H_{11}BrN_3O_8P^-.1.25H_2O$, is *anti*, C(3′)-*endo* and *gauche-gauche*, similar to that in analogous non-halogenated nucleosides/nucleotides. The Na ion coordinates directly with phosphate O atoms and base atoms. Br is not involved in any stacking interaction.

Comment

Although there have been a number of crystallographic studies on halogenated nucleosides, only a few structures of halogenated nucleotides have been reported. We report here the crystal structure of the sodium salt of 5-bromocytidine monophosphate (I); this is the first halogenated pyrimidine mononucleotide to be determined. Cytosine with bulky substituents such as bromine and iodine at the 5 position is found to be a good substrate for human DNA (cytosine-5) methyltransferase (Hardy, Barker, Newman, Sowers, Goodman & Smith, 1987). The presence of monovalent sodium in the present structure is also of interest in view of the fact that earlier



(I)

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structural studies of cytidine 5′-monophosphate (CMP) were carried out on its divalent metal complexes (Co, Cd, Mn, Ba and Zn).

The molecular structure is presented in Fig. 1. The average values of the bond lengths and angles of the base are in agreement with those of unprotonated cytosine bases (Taylor & Kennard, 1982). The ribose assumes a C(3′)-*endo* (^3E) pucker with pseudorotation parameters P and τ_m (Altona & Sundaralingam, 1972) equal to 11.4 and 43.3°, respectively. The conformation of the cytosine base with respect to the ribose ring is *anti* with a glycosyl torsion angle $\chi_{\rm CN}$[C(2)—N(1)—C(1′)—O(4′)] of −161.2 (4)°. The orientation of the phosphate group about the C(4′)—C(5′) bond is *gauche-gauche* (g^+) with the torsion angles $\varphi_{\rm OO}$[O(5′)—C(5′)—C(4′)—O(4′)] and $\varphi_{\rm OC}$[O(5′)—C(5′)—C(4′)—C(3′)] equal to −63.2 (5) and 54.4 (6)°, respectively. The phosphate group is monoionic. The negative charge appears to be associated with O(7) since the P—O(7) bond length of 1.571 (7) Å is appreciably longer than the other two P—O distances. The bond angles at the P atom range from 101.1 (2) to 114.9 (3)° showing a slight distortion of the tetrahedral phosphate.

The Na ion has six neighbours, O(2), O(6), N(3), O(5), O(2)* and O(6)*, at distances ranging from 2.219 to 3.070 Å. The coordination polyhedron can be described as a distorted octahedron. The Na$^+$ bridge between the atoms O(2) and N(3) of the cytosine base is similar to that found in the crystal structures of sodium β-cytidine 2′,3′-cyclic phosphate (Coultar, 1969) and cytidine 5′-diphosphocholine (Viswamitra, Seshadri, Hosur, Post & Kennard, 1975). The present structure shows that Na$^+$ interacts with the phosphate O atoms directly, as opposed to through water molecules as found in some related structures (Pandit, Seshadri & Viswamitra, 1983, 1984). This is a consequence of the smaller degree of hydration in the present crystal.

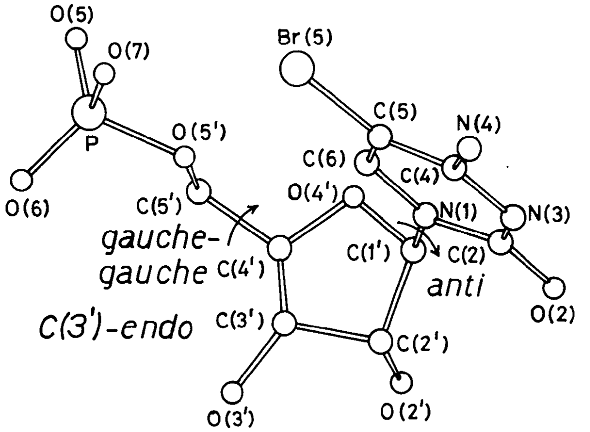

Fig. 1. Molecular structure of the title compound, in which the nucleotide conformation is *anti*, C(3′)-*endo*, *gauche-gauche*.

The crystal structure is stabilized by several intermolecular hydrogen bonds as shown in Table 2. The O(2) and N(3) atoms of the cytosine base are not available for hydrogen bonding as they coordinate to Na$^+$. The H atoms of the disordered water molecule [O*W*(1), O*W*(2), O*W*(3)] have not been located. The crystal packing diagram is shown in Fig. 2.

There is no Br–base stacking of the sort which is often observed in halogenated nucleosides/nucleotides. Molecules related by a translation along the *a* axis (shortest axis) are positioned such that exocyclic N(4) and sugar O(4′) atoms are stacked over cytosine bases at distances of 3.4 and 3.1 Å, respectively. There is no direct overlap of the bases. O(4′)–base overlap is similar to that found in the orthorhombic form of Cd.5′-CMP (Clark & Orbell, 1978). The stacking of N(4) over the base is as found in most of the unmodified 5′-CMP structures (Shiba & Bau, 1978; Clark & Orbell, 1978; Aoki, 1976).

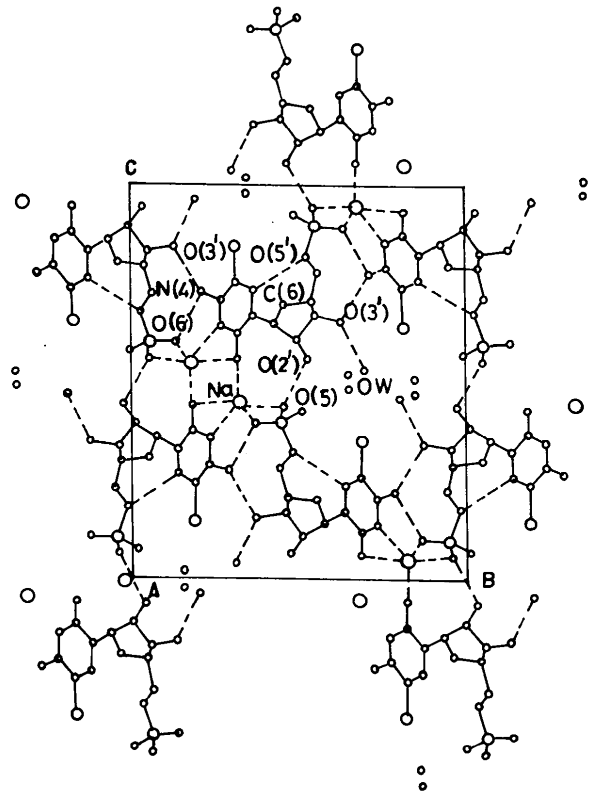

Fig. 2. Crystal packing of the title compound. Molecules related by translation along the shortest axis are positioned so that the exocyclic N(4) and ribose O(4′) atoms stack over the cytosine bases.

Experimental

Crystals of the title compound (Sigma Chemical Co.) were grown by the liquid-diffusion technique.

Crystal data

$Na^+.C_9H_{11}BrN_3O_8P^-.$-
$1.25H_2O$
$M_r = 445.6$
Orthorhombic
$P2_12_12_1$
$a = 4.733$ (1) Å
$b = 17.305$ (1) Å
$c = 19.243$ (1) Å
$V = 1576.09$ Å^3
$Z = 4$
$D_x = 1.88$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 15$–$40°$
$\mu = 5.35$ mm^{-1}
$T = 293$ K
Needle
0.01 × 0.08 × 0.02 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1858 measured reflections
1858 independent reflections
1800 observed reflections $[F_o \geq 3\sigma(F_o)]$

$\theta_{max} = 72°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 23$
2 standard reflections monitored every 100 reflections
intensity variation: <4%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.049$
$S = 0.62$
1800 reflections
279 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.28$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
N(1)	−0.0775 (8)	0.3679 (2)	0.6690 (2)	1.80 (6)
C(2)	−0.1927 (10)	0.3170 (3)	0.6210 (2)	1.98 (7)
O(2)	−0.1138 (9)	0.3192 (3)	0.5598 (2)	2.90 (7)
N(3)	−0.3956 (9)	0.2669 (3)	0.6421 (2)	2.09 (7)
C(4)	−0.4775 (10)	0.2652 (3)	0.7083 (2)	1.82 (7)
N(4)	−0.6882 (10)	0.2159 (3)	0.7250 (3)	2.29 (7)
C(5)	−0.3536 (10)	0.3146 (3)	0.7584 (2)	1.93 (7)
Br(5)	−0.4765 (2)	0.31336 (4)	0.85130 (3)	4.00 (1)
C(6)	−0.1530 (10)	0.3654 (3)	0.7372 (2)	1.90 (8)
C(1′)	0.1302 (9)	0.4254 (3)	0.6416 (3)	1.78 (7)
C(2′)	−0.0177 (10)	0.4944 (3)	0.6076 (2)	1.80 (7)
O(2′)	0.1701 (9)	0.5309 (2)	0.5604 (2)	2.51 (6)
C(3′)	−0.0485 (9)	0.5481 (3)	0.6699 (2)	1.66 (7)
O(3′)	−0.1103 (8)	0.6262 (2)	0.6555 (2)	2.71 (7)
C(4′)	0.2370 (9)	0.5375 (3)	0.7045 (2)	1.62 (7)
O(4′)	0.2923 (7)	0.4551 (2)	0.6969 (2)	1.95 (5)
C(5′)	0.2613 (10)	0.5600 (3)	0.7801 (3)	2.22 (8)
O(5′)	0.0508 (7)	0.5211 (2)	0.8209 (2)	2.19 (6)
P	0.0073 (2)	0.55243 (6)	0.89838 (5)	1.57 (2)
O(5)	0.2838 (7)	0.5469 (3)	0.9369 (2)	2.47 (7)
O(6)	−0.1180 (8)	0.6312 (2)	0.8958 (2)	2.73 (7)
O(7)	−0.2045 (7)	0.4909 (2)	0.9281 (2)	2.32 (6)
Na	0.5309 (5)	0.1761 (1)	0.5498 (1)	2.78 (4)
O*W*(1)	0.016 (4)	0.6959 (7)	0.5348 (7)	6.3 (3)
O*W*(2)	0.506 (5)	0.1500 (9)	0.0129 (8)	6.0 (3)
O*W*(3)	0.388 (3)	0.1474 (8)	0.9796 (8)	4.5 (3)

Table 2. *Selected geometric parameters* (Å, °)

P—O(7)	1.571 (4)	N(3)—C(2)	1.355 (6)
P—O(6)	1.487 (4)	C(2)—O(2)	1.236 (7)
P—O(5)	1.507 (3)	C(2)—N(1)	1.388 (6)
P—O(5′)	1.600 (3)	N(1)—C(1′)	1.495 (7)
O(5′)—C(5′)	1.437 (7)	C(1′)—C(2′)	1.531 (6)
C(5′)—C(4′)	1.510 (4)	C(2′)—O(2′)	1.419 (6)
N(1)—C(6)	1.360 (7)	C(2′)—C(3′)	1.524 (6)
C(6)—C(5)	1.358 (7)	C(3′)—O(3′)	1.411 (6)
C(5)—Br(5)	1.881 (4)	C(3′)—C(4′)	1.517 (6)
C(4)—C(5)	1.415 (6)	C(4′)—O(4′)	1.459 (6)
C(4)—N(4)	1.351 (7)	O(4′)—C(1′)	1.408 (6)
C(4)—N(3)	1.333 (6)		
O(5′)—P—O(7)	101.1 (3)	N(4)—C(4)—N(3)	117.2 (4)
O(7)—P—O(6)	112.2 (2)	C(4)—N(3)—C(2)	120.4 (4)
O(6)—P—O(5)	114.9 (2)	N(3)—C(2)—O(2)	121.2 (5)
O(5)—P—O(5′)	109.0 (2)	N(3)—C(2)—N(1)	119.1 (4)
O(5′)—P—O(6)	109.3 (2)	C(6)—N(1)—C(2)	121.3 (5)
O(5)—P—O(7)	109.4 (2)	O(2)—C(2)—N(1)	119.7 (5)
P—O(5′)—C(5′)	116.1 (3)	C(2)—N(1)—C(1′)	116.5 (4)
O(5′)—C(5′)—C(4′)	110.7 (4)	N(1)—C(1′)—O(4′)	109.5 (4)
C(5′)—C(4′)—O(4′)	109.6 (4)	N(1)—C(1′)—C(2′)	111.7 (4)
C(5′)—C(4′)—C(3′)	117.4 (4)	C(1′)—C(2′)—O(2′)	109.5 (4)
C(1′)—N(1)—C(6)	122.3 (4)	C(1′)—C(2′)—C(3′)	100.6 (3)
N(1)—C(6)—C(5)	119.7 (4)	O(2′)—C(2′)—C(3′)	107.0 (4)
C(6)—C(5)—Br(5)	120.6 (4)	C(2′)—C(3′)—O(3′)	116.7 (4)
C(6)—C(5)—C(4)	118.5 (5)	C(2′)—C(3′)—C(4′)	100.8 (4)
Br(5)—C(5)—C(4)	120.8 (4)	O(3′)—C(3′)—C(4′)	112.7 (4)
C(5)—C(4)—N(4)	121.7 (4)	C(3′)—C(4′)—O(4′)	103.5 (3)
C(5)—C(4)—N(3)	121.1 (4)	C(4′)—O(4′)—C(1′)	109.5 (3)

The crystals were characterized by rotation and Weissenberg photographs. The structure was solved by interpretation of Patterson and difference Fourier maps. A difference Fourier map computed at this stage showed three peaks corresponding to disordered water. These peaks were refined with one third occupancies which led to $R = 0.072$. Full-matrix least-squares refinement using anisotropic displacement parameters for all atoms except water O atoms (isotropic) converged to $R = 0.053$. The occupancies of the water O atoms refined to 0.51, 0.36 and 0.42, suggesting the presence of 1.25 water molecules per nucleotide molecule, *i.e.* five water molecules disordered over four unit cells. H atoms, except for those of the water molecules, were located from difference Fourier maps and refined isotropically along with anisotropic refinement of the non-H atoms. All calculations were performed with Enraf–Nonius (1985) *SDP* on a PDP 11/44 computer.

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Lists of structure factors, anisotropic displacement parameters, Na-ion geometry, hydrogen-bond geometry, H-atom coordinates, least-squares-planes data and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71612 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1008]

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$[Ir(dppm)_2(O_2)](C_4N_3)$

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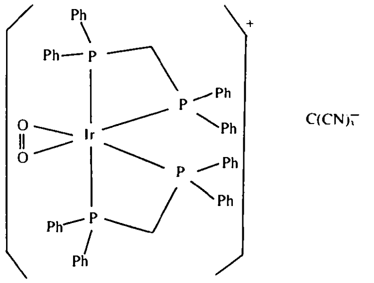
Abstract

The compound bis[bis(diphenylphosphino)methane]-peroxoiridium(I) tricyanomethanide crystallized in the triclinic system. There are two independent molecules per asymmetic unit. The geometry of the uncoordinated tricyanomethanide (TCM) is planar. The average C—C distance is 1.38 (4) Å and the average C—N distance is 1.16 (5) Å in the TCM group. The coordination about the Ir centre is distorted trigonal bipyramidal (TBP). The Ir—P distances range from 2.307 (4) to 2.343 (5) Å and the Ir—O distances range from 2.00 (1) to 2.07 (1) Å. The O—O distances are 1.39 (2) and 1.43 (1) Å.

Comment

The tricyanomethanide anion [$C(CN)_3^-$, TCM] displays various bonding modes with transition-metal ions. It can form a polymeric structure (Konnert & Britton, 1966; Biondi, Bonamico, Torelli & Vaciage, 1965; Chow & Britton, 1975; Summerville, Cohen, Hatano & Scheidt, 1978; Britton & Chow, 1983), coordinate to transition metals through its N atom (Wang, Shih, Chen, Wang, Fronczek & Watkins, 1993), form weak interactions with metal ions (Wang & Wang, 1993) or can serve as an uncoordinated counter ion (Baukova *et al.*, 1989). The title compound, $Ir(dppm)_2(O)_2(TCM)$ (I), is the second example of the counter-ion type TCM–transition metal complex.



(I)

There are two independent molecules per asymmetric unit with almost identical molecular geometry. The geometry of uncoordinated TCM is, as expected, planar. The largest deviation from the least-squares plane formed by the four C atoms and three N atoms in TCM is 0.07 Å. The coordination

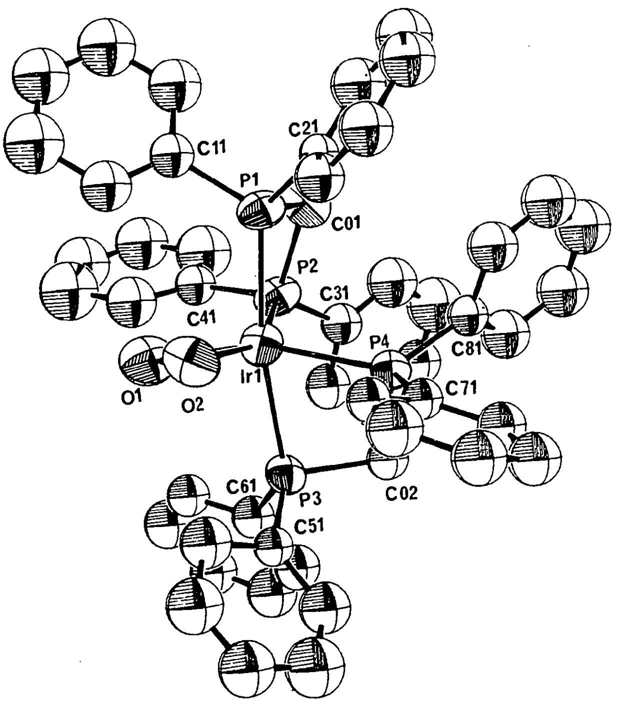


Fig. 1. *ORTEP* drawing of the title compound with 50% probability ellipsoids for non-H atoms.

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