intermediate[16] have been reported and the "enzymatic oxidation of a quinol phosphate"[17] reported recently may be another example of a concerted oxidative process. The possibility that ethyl sulfate is an intermediate in the formation of ethylene from the reaction of ethyl radicals with cupric sulfate[18,19] is suggested by these results. If this is the case, the reaction with the hypothetical cuprous ethyl sulfate must be a more efficient process.

Acknowledgment. We wish to thank Mr. Paul Bigelow for his enthusiastic help as a National Science Foundation Summer Science Trainee.

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(17) J. Wodak, *ibid.*, **90**, 2991 (1968).

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Stereochemistry of Nucleic Acids and Their Constituents. V. The Crystal and Molecular Structure of a Hydrated Monosodium Inosine 5′-Phosphate. A Commonly Occurring Unusual Nucleotide in the Anticodons of tRNA[1]

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Abstract: The crystal structure of hydrated monosodium inosine 5′-phosphate has been determined from 1420 observed reflections recorded with a Picker four-circle automatic diffractometer using the 2θ scan mode and Ni-filtered Cu radiation. The crystal belongs to the orthorhombic space group $C222_1$ with eight formula units in the unit cell of dimensions $a = 8.682 \pm 0.003$, $b = 23.216 \pm 0.009$, and $c = 21.917 \pm 0.007$ Å. The structure was determined by three-dimensional Patterson and Fourier methods, and was refined by anisotropic full-matrix least-squares to an R value of 0.10. The occupancy parameters of the water molecules were varied during the isotropic refinement, but were held fixed during the anisotropic refinement. The nucleotide assumes the preferred *anti* conformation about the glycosidic linkage with the ribose ring showing the C(2′)-*endo* pucker. The torsion angle around the C(5′)–O(5′) bond is 176°. The sugar phosphate assumes the extended conformation. The sodium ion is not directly coordinated to the phosphate oxygens but is coordinated to both the ribose hydroxyls and to four water molecules. There are close contacts between O(1′) of the ribose and the base of a symmetry-related molecule as found in other similar structures. The waters are distributed over nine sites, four of which are disordered. A plausible hydrogen-bonding scheme is suggested.

The triplet anticodon of tRNA (transfer ribonucleic acid) is often found to contain one unusual nucleotide besides the common ribotides. Inosine is present in four of the tRNAs, alanine tRNA, serine tRNA 1, serine tRNA 2, and valine tRNA, whereas 2′-O-methylguanosine and pseudouridine are present in tyrosine tRNA and phenylalanine tRNA, respectively. We are currently investigating the detailed crystal structures of several unusual nucleic acid constituents occurring in the anticodon loops of tRNAs in order to gain information concerning their function. The detailed stereochemical and hydrogen-bonding properties of inosine 5′-phosphate are presented here. A brief account of the structure has already been published.[3] The occurrence of a large number of waters of crystallization and a sodium ion provides also some indication of the manner in which water and alkali metal ions interact with nucleic acids.

Experimental Section

The monosodium salt of inosine 5′-phosphate (IMP), which was obtained from Sigma Biochemical Co., St. Louis, Mo., gave well-formed needles on recrystallization from water. Oscillation and Weissenberg photographs established the crystal system to be orthorhombic with the systematic absences hkl, $h + k = 2n + 1$, and $00l$, $l = 2n + 1$, thus indicating that the space group is $C222_1$. The cell constants were determined from medium- and high-angle reflections measured on a Picker automatic diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and were found to be $a = 8.682 \pm 0.003$, $b = 23.216 \pm 0.009$, and $c = 21.917 \pm 0.007$ Å. The density of the crystal, 1.576 g cm^{-3}, obtained by the method of flotation using a mixture of chloroform and bromoform, is in agreement with the calculated density of 1.580 g cm^{-3} assuming eight formula units of $C_{10}N_4O_8H_{12}P\cdot Na\cdot 8H_2O$ in the unit cell. However, it will be seen that the structure determination can account for only about six water molecules. Presumably the remaining crystal waters slowly effloresced before and during the recording of the data. The crystal used in the experimental work was not enclosed in a capillary. The chemical formula of IMP and the atom numbering scheme are shown below.

Complete three-dimensional intensity data up to $2\theta = 134°$ were collected on the Picker automatic diffractometer with Ni-filtered Cu radiation employing the 2θ scan technique. About 2200 independent reflections were thus recorded. On the basis of the counting statistics derived from the systematically absent reflections, a reflection was considered observed if $I > 1.5\sigma(I)$ where

$$\sigma(I) = [I_{\text{scan}} + I_{\text{bkg}}]^{1/2}$$

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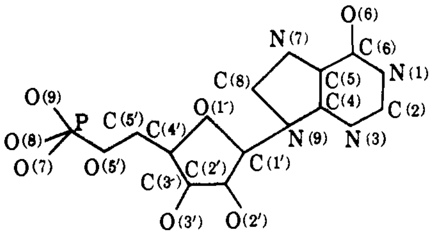
(1) For parts III and IV see M. Sundaralingam, *Acta Crystallogr.*, **21**, 495 (1966), and M. Sundaralingam, *Biopolymers*, in press, respectively.

(2) Research supported by the National Institutes of Health Grant GM14828, and a U. S. Public Health Service Research Center Development Award GM42412 to M. S.

(3) S. T. Rao and M. Sundaralingam, *Chem. Commun.*, 995 (1968).



There were 1420 reflections above background. The structure analysis was carried out using these reflections only. The data were corrected both for anisotropy of absorption by measuring the intensity of a reflection at $\chi = 90°$ as a function of ϕ and for the Lorentz-polarization factors.

Structure Analysis and Refinement

A. Structure Determination. The coordinates of the phosphorus atom were found from an analysis of a gradient-sharpened three-dimensional Patterson function.[4] From the three-dimensional electron density map computed with the phosphorus phases, six atoms belonging to the base were clearly identified. A second electron density map with these six atoms included as carbons in the phasing revealed the positions of the phosphate oxygens, the remaining atoms of the base and the sodium ion. A further iteration of calculation of the electron density using all these atoms in the phasing revealed all the atoms of the nucleotide as well as a number of possible sites for the water molecules. The scattering factors used throughout the analysis were those of Hoerni and Ibers[5] for C, N, and O, that of Boys[6] for Na^+ and that of Freeman and Watson[7] for P, as given in the International Tables for X-ray Crystallography.

B. Determination of the Positions of the Water Molecules and Refinement of the Structure. Four cycles of isotropic full-matrix least-squares refinement with all the atoms found so far reduced the R value, defined by

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

from 0.35 to 0.20. A Hughes[8] type of weighting scheme, which was used in the initial stages of the refinement, was replaced by the Cruickshank[9] weighting scheme in the final stages of the refinement. For the latter weighting scheme, the weight, w, is expressed

$$w = \frac{1}{\sigma^2(F)} = \frac{1}{4.5 + |F| + 0.007|F|^2}$$

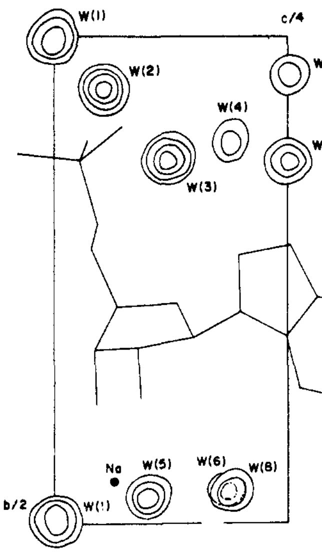


Figure 1. A perspective view of the electron density at the sites of the water molecules. The nucleotide and the sodium ion were used in the phasing calculations. The contours are at intervals of 1 $e/\text{Å}^3$ beginning from 0.5 $e/\text{Å}^3$.

A difference electron density map computed at this stage, including only the atoms of the nucleotide and the sodium ion in the phasing, is shown in Figure 1. This map clearly indicates not only the water molecules already noted in the earlier electron density maps, but also shows a few other sites for waters which vary in electron density between 1.5 and 3 $e/\text{Å}^3$. All of these sites satisfy a plausible hydrogen-bonding scheme with the remaining part of the structure. In addition, a few distances between these sites, especially those of low density, are as short as 2.0 Å. A total of nine sites were found for the water molecules, three of which lie in special positions: one on the twofold axis parallel to the a axis and two on the twofold axis parallel to the b axis.

A further four cycles of least-squares refinement varying the positional and isotropic thermal parameters of all the atoms in addition to the occupancy parameters of all the water molecules reduced the R value to 0.14. A difference electron density map showed no sites with electron densities greater than 0.7 $e/\text{Å}^3$. Of the nine sites that were found occupied by water molecules, the three sites in general positions have occupancy parameters less than 1.0 and the one on the diad (parallel to the b axis) has a value less than 0.5. Thus, four of these sites are disordered. The occupancy parameters determined for the water molecules were therefore assigned to them for anisotropic least-squares refinement.

Three cycles of refinement were performed using the block-diagonal approximation to the normal equations on the IBM 7040 computer at the Roswell Park Memorial Institute, Buffalo, N. Y. This calculation reduced the R value to 0.11. Four further rounds of least-squares calculations were made on the UNIVAC 1108 using the full-matrix least-squares program of Busing, Martin, and Levy.[10] Due to the limitation of the memory size, only 180 parameters could be varied at a time. Therefore, the atoms were divided into two groups of 18 atoms each with the phosphorus and so-

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(4) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 598 (1961).

(5) J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

(6) S. F. Boys, unpublished work, 1958.

(7) A. J. Freeman and R. E. Watson, unpublished work, 1961.

(8) E. Hughes, *J. Amer. Chem. Soc.*, **63**, 1737 (1941).

(9) D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-ray Crystal Structure Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961, pp 32-78.

(10) W. R. Busing, K. O. Martin, and H. A. Levy, "Fortran Crystallographic Least Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

Table I. Occupancy and Positional Parameters of the Atoms[a]

Atom	α	$x/a \times 10^4$	$y/b \times 10^4$	$z/c \times 10^4$
P	1.00	1116 (4)	1232 (2)	0287 (2)
N(1)	1.00	3593 (15)	3333 (7)	3525 (8)
C(2)	1.00	2876 (28)	3729 (10)	3149 (9)
N(3)	1.00	2301 (21)	3597 (7)	2637 (7)
C(4)	1.00	2405 (17)	3055 (7)	2500 (8)
C(5)	1.00	3148 (18)	2652 (8)	2815 (8)
C(6)	1.00	3749 (18)	2759 (9)	3416 (7)
O(6)	1.00	4329 (15)	2442 (6)	3794 (6)
N(7)	1.00	3000 (23)	2111 (6)	2538 (9)
C(8)	1.00	2231 (21)	2237 (9)	1975 (9)
N(9)	1.00	1893 (18)	2794 (6)	1969 (7)
C(1′)	1.00	1026 (18)	3093 (6)	1494 (7)
O(1′)	1.00	−0226 (11)	2722 (5)	1323 (5)
C(2′)	1.00	1927 (17)	3177 (7)	0899 (7)
C(3′)	1.00	0640 (18)	3205 (7)	0429 (7)
C(4′)	1.00	−0508 (15)	2742 (6)	0675 (7)
O(2′)	1.00	2788 (12)	3691 (5)	0920 (5)
O(3′)	1.00	0003 (18)	3763 (5)	0468 (6)
C(5′)	1.00	−0500 (17)	2160 (7)	0402 (8)
O(5′)	1.00	1011 (12)	1907 (5)	0478 (5)
O(7)	1.00	0549 (14)	1185 (6)	−0370 (6)
O(8)	1.00	2821 (14)	1082 (5)	0363 (6)
O(9)	1.00	0098 (14)	0897 (5)	0723 (5)
Na	1.00	1447 (11)	4594 (4)	0628 (5)
W(1)	0.50	−0849 (40)	5000	0000
W(2)	1.00	7108 (16)	0572 (7)	0515 (8)
W(3)	1.00	5020 (21)	1290 (8)	1218 (8)
W(4)	0.59	8893 (46)	1101 (11)	1847 (9)
W(5)	1.00	5517 (52)	4801 (7)	1011 (14)
W(6)	0.40	1086 (97)	4682 (23)	1935 (31)
W(7)	0.33	0	0405 (16)	2500
W(8)	0.59	3368 (81)	4719 (18)	1946 (17)
W(9)	0.50	5000	1282 (18)	2500

[a] Standard deviation in parentheses in the same units.

dium atoms being included in both groups and all of the water molecules contained in one group. This procedure dropped R to its final value of 0.10. The refinement was terminated at this stage as the shifts in the parameters were all less than one-third their estimated standard deviations. The distribution of $\Sigma w(\Delta F)^2$ was calculated as a function of both F and $\sin\theta$ and was found to be uniform to about 7%.

The significant differences between the positions of the water molecules as found in the block-diagonal and the full-matrix least-squares refinements could be directly traced to the approximations made to the normal equations in the former method of calculation. In view of the disorder in the structure, no attempt has been made to locate the hydrogen atoms in the structure. A list of the observed and calculated structure factors can be obtained from the authors. The final positional and occupational parameters of the atoms are shown in Table I, and the anisotropic thermal parameters are shown in Table II.

Results and Discussion

A. Molecular Structure and Conformation. A perspective view of the conformation of the nucleotide is shown in Figure 2. Bond lengths and bond angles calculated from the coordinates listed in Table I are shown in Table III. The average standard deviations in the different bond lengths are: σ(P–O) = 0.013 Å; σ(C–O) = σ(C–N) = σ(C–C) = 0.02 Å. The average standard deviation in the bond angle is about 1.3°. The standard deviations in the parameters were estimated from the diagonal terms of the inverse matrix.

Table II. Anisotropic Thermal Parameters of the Atoms[a]

Atom	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$
P	481	133	166	−6	63	17
N(1)	769	207	261	−105	7	7
C(2)	1,852	247	239	−101	−58	64
N(3)	1,837	193	173	−66	−139	−28
C(4)	532	230	94	−40	−27	0
C(5)	632	255	134	176	90	8
C(6)	678	283	103	−161	−43	−4
O(6)	1,734	321	239	271	−161	−37
N(7)	2,043	195	212	257	−74	−44
C(8)	1,190	230	207	250	61	−31
N(9)	1,075	189	162	−41	−110	2
C(1′)	800	149	165	−38	4	−50
O(1′)	575	238	172	−36	16	23
C(2′)	696	194	173	4	69	23
C(3′)	1,040	183	134	−51	58	13
C(4′)	577	137	150	56	−55	−54
O(2′)	852	228	232	−167	22	−18
O(3′)	1,767	161	333	−50	−254	26
C(5′)	815	177	252	85	−86	−10
O(5′)	706	191	193	22	−42	−24
O(7)	1,187	214	196	47	59	6
O(8)	1,066	173	253	24	7	30
O(9)	1,030	191	158	−87	77	28
Na	1,972	245	487	−106	−89	12
W(1)	2,654	371	417	0	0	−43
W(2)	1,493	297	458	−176	−122	6
W(3)	2,069	417	418	126	−357	−61
W(4)	5,171	361	155	686	32	−247
W(5)	10,300	130	909	609	599	−80
W(6)	5,438	342	627	−592	15	−70
W(7)	1,797	251	282	0	−38	0
W(8)	8,753	530	378	157	726	273
W(9)	3,350	469	526	0	24	0

[a] The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$. The range of standard deviations in the parameters for the atoms in the nucleotide and water molecules are given below in the same units.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
nucleotide	38–258	7–48	8–51	17–130	18–119	7–43
water	292–1010	38–188	42–200	93–450	99–500	31–170

It is reasonable to assume that the disorder involving some water sites accounts for the high standard deviations. There are no significant departures in the bond lengths and bond angles from normal values within the experimental error. The orientation of the sugar and the base, defined by ϕ_{CN},[11] is +41°. Hence the nucleotide displays the preferred *anti* conformation.[12] The conformation about the C(4′)–C(5′) bond is denoted by the angles ϕ_{OO} and ϕ_{OC}, which are −63 and 59°, respectively. This conformation is the one most commonly observed.[15–17] The torsion angle, ϕ_{OP},

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[11] J. Donohue and K. N. Trueblood, *J. Mol. Biol.*, **2**, 363 (1960).

[12] The sign of ϕ_{CN} as used here is opposite to the earlier definition of Donohue and Trueblood,[11] modified by Sundaralingam and Jensen.[13] Both the earlier definitions employ a left-hand convention for this angle, whereas we have maintained the right-hand convention throughout the definition of the rotation angles.[14]

[13] M. Sundaralingam and L. H. Jensen, *J. Mol. Biol.*, **13**, 930 (1965).

[14] M. Sundaralingam, presented at the Summer Meeting of the American Crystallographic Association, Buffalo, N. Y., August 1968, Abstract L1.

[15] E. Shefter and K. N. Trueblood, *Acta Crystallogr.*, **18**, 1067 (1965).

[16] M. Sundaralingam, *J. Amer. Chem. Soc.*, **87**, 599 (1965).

[17] It should be noted that the angles ϕ_{OO} and ϕ_{OC} as used here are with the signs based on the right-hand convention for rotation angles. In the Shefter-Trueblood[14] definition, only the magnitudes of the angles were considered and the conformation observed here would be termed *gauche-gauche*.

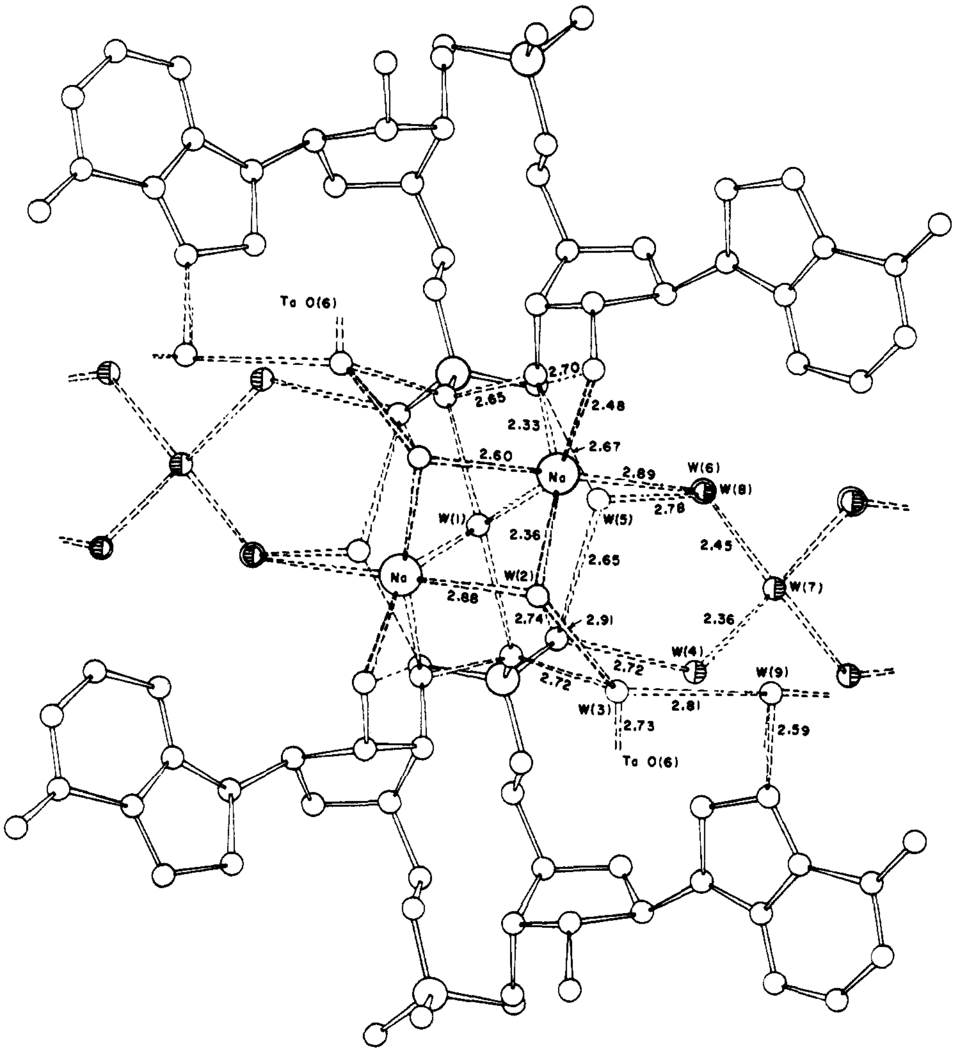

Figure 2. A perspective view of the surroundings of the phosphate group and the sodium ion. The possible scheme of hydrogen bonds involving the water molecules and the nucleotide is also shown. The disordered water molecules are shown as shaded circles.

defined by the clockwise rotation of the C(4′)–C(5′) bond with respect to the O(5′)–P bond when looking down the C(5′)–O(5′) bond is 176°. Hence, the sugar phosphate assumes the usual extended conformation.

The least-squares plane through the nine atoms of the base, excluding the substituent atom O(6), was calculated. The deviations of the various atoms from this plane are given in Table IV. The root-mean-square displacement of the atoms fitted to this plane is 0.024 Å. C(5) is the only atom that appears to be significantly out of plane. Its deviation from the least-squares plane is 0.06 Å. The substituent atoms O(6) and C(1′) are displaced on the same side of the base by −0.09 and −0.07 Å, respectively.

The five possible four-atom planes through the five atoms of the furanose ring were also calculated. The best plane was through atoms other than C(2′). The deviation of this atom from the plane is 0.61 Å. The rms displacement of the remaining four atoms from this plane is 0.016 Å. The deviations of the atoms from this plane are also given in Table IV. The torsion angles about the different bonds in the ribose moiety are given in Table V together with other torsion angles in the nucleotide. Thus, the ribose ring shows the C(2′)-*endo* pucker.[16] The dihedral angle between the plane of the base and the sugar is 59°, which is similar to the values observed in other nucleosides and nucleotides.

B. Coordination of the Sodium Ion. The sodium ion has six nearest neighbors at distances between 2.33 and 2.89 Å. Two of the nearest neighbors are the hydroxyl groups of the sugar and the remaining four are water molecules. The distances of the atoms from the sodium ion, together with the angles at the central sodium ion, are given in Figure 3. Thus the coordination number of sodium is 6 and the coordination polyhedron is a distorted octahedron. It should be noted, however, that one of the water molecules in the coordination sphere is disordered. The hydroxyl groups form two of the shortest $Na^+\cdots O$ contacts, with the 2′-hydroxyl more tightly bound to the Na^+ than the 3′-hydroxyl. One water molecule is 2.36 Å away from the Na^+ and two others are at distances of 2.60 Å, whereas the longest $Na^+\cdots H_2O$ interaction of 2.89 Å involves a disordered water. The distance between the two sodium ions related by the diad axis parallel to

Table III. Bond Lengths and Bond Angles in the Molecule[a]

	Bond lengths, Å		Bond angles, deg
N(1)–C(2)	1.38	N(1)–C(2)–N(3)	123
C(2)–N(3)	1.27	C(2)–N(3)–C(4)	114
N(3)–C(4)	1.30	N(3)–C(4)–C(5)	127
C(4)–C(5)	1.33	C(4)–C(5)–C(6)	122
C(5)–C(6)	1.44	C(5)–C(6)–N(1)	107
C(6)–O(6)	1.22	C(6)–N(1)–C(2)	126
C(6)–N(1)	1.36	C(4)–C(5)–N(7)	111
C(5)-N(7)	1.40	C(5)–N(7)–C(8)	103
N(7)–C(8)	1.43	N(7)–C(8)–N(9)	108
C(8)–N(9)	1.33	C(8)–N(9)–C(4)	110
N(9)–C(4)	1.39	N(9)–C(4)–C(5)	107
N(9)–C(1′)	1.46	N(3)–C(4)–N(9)	127
		C(5)–C(6)–O(6)	132
		N(1)–C(6)–O(6)	121
		C(6)–C(5)–N(7)	126
		C(8)–N(9)–C(1′)	126
		C(4)–N(9)–C(1′)	124
O(1′)–C(1′)	1.43	O(1′)–C(1′)–C(2′)	104
C(1′)–C(2′)	1.54	C(1′)–C(2′)–C(3′)	102
C(2′)–C(3′)	1.52	C(2′)–C(3′)–C(4′)	102
C(3′)–C(4′)	1.56	C(3′)–C(4′)–O(1′)	105
C(4′)–O(1′)	1.44	C(4′)–O(1′)-C(1′)	111
C(2′)–O(2′)	1.41	N(9)–C(1′)–O(1′)	107
C(3′)–O(3′)	1.41	N(9)–C(1′)–C(2′)	114
C(4′)–C(5′)	1.48	C(1′)–C(2′)–O(2′)	111
C(5′)-O(5′)	1.45	O(2′)–C(2′)–C(3′)	112
		C(2′)–C(3′)–O(3′)	107
		O(3′)–C(3′)–C(4′)	111
		C(3′)–C(4′)–C(5′)	119
		C(5′)-C(4′)–O(1′)	112
		C(4′)–C(5′)–O(5′)	109
P–O(5′)	1.62	C(5′)–O(5′)–P	114
P–O(7)	1.53	O(5′)–P–O(7)	107
P–O(8)	1.53	O(5′)–P–O(8)	104
P–O(9)	1.52	O(5′)–P–O(9)	107
		O(7)–P–O(8)	113
		O(7)–P–O(9)	112
		O(8)–P–O(9)	112

[a] Estimated standard deviations in the bond lengths are P–O = 0.013 Å, C–O = C–N = 0.02 Å, and in bond angles about 1.3°.

Table IV. Least-Squares Planes through the Base and Sugar[a,b]

Atom	Dev from plane I, Å	Dev from plane II, Å
N(1)	0.002*	0.357
C(2)	−0.002*	−0.590
N(3)	0.004*	−0.514
C(4)	−0.020*	0.512
C(5)	0.060*	1.508
C(6)	−0.024*	1.456
O(6)	−0.091	2.190
N(7)	−0.018*	2.436
C(8)	0.003*	1.983
N(9)	−0.005	0.849
C(1′)	−0.072	0.012*
O(1′)	−0.105	−0.020*
C(2′)	1.234	0.610
C(3′)	0.728	−0.011*
C(4′)	−0.587	0.018*
O(2′)	2.093	0.232
O(3′)	0.450	−1.334
C(5′)	−0.569	1.105
O(5′)	0.394	2.378

[a] The equation to the plane is $lx + my + nz = d$ where l, m, n are the direction cosines of the normal to the plane and d is the distance of the plane from the origin in ångströms. x, y, z are coordinates in ångström units. [b] Asterisks denote atoms used in calculating the plane. Plane I: $0.875x + 0.188y - 0.446z = 0.741$. Plane II: $0.666x - 0.728y - 0.166z = -5.188$.

Table V. Torsion Angles in the Nucleotide

Atoms	Angle, deg
ϕ_{CN}C(8)–N(9)–C(1′)–O(1′)	41
C(4′)–O(1′)–C(1′)–N(9)	−142
C(4′)–O(1′)–C(1′)–C(2′)	−21
O(1′)–C(1′)–C(2′)–C(3′)	37
C(1′)–C(2′)–C(3′)–C(4′)	−39
C(2′)–C(3′)–C(4′)–O(1′)	27
C(3′)–C(4′)–O(1′)–C(1′)	−4
N(9)–C(1′)–C(2′)–C(3′)	153
O(1′)–C(1′)–C(2′)–O(2′)	157
N(9)–C(1′)–C(2′)–O(2′)	−88
O(2′)–C(2′)–C(3′)–O(3′)	−40
O(2′)–C(2′)–C(3′)–C(4′)	−157
O(3′)–C(3′)–C(4′)–O(1′)	−87
C(5′)–C(4′)–O(1′)–C(1′)	127
ϕ_{OO}O(1′)–C(4′)–C(5′)–O(5′)	−63
ϕ_{OC}C(3′)–C(4′)–C(5′)–O(5′)	59
ϕ_{OP}C(4′)–C(5′)–O(5′)–P	172
C(5′)–O(5′)–P–O(7)	55
C(5′)–O(5′)–P–O(8)	176
C(5′)–O(5′)–P–O(9)	−65

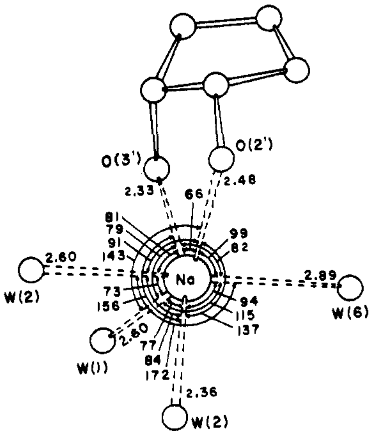

Figure 3. The coordination around the sodium ion. The distances to the six nearest atoms and the angles at the sodium ion made by these interactions are shown.

the *a* axis is 3.34 Å. A notable feature of the sodium ion coordination is that the ion is not directly attached to the phosphate oxygen atoms but is connected through water bridges, as is found for barium in the crystal structures of barium uridine 5′-phosphate[15] and barium 5′-ribose phosphate.[18] It may be noted that in the structure of calcium thymidylate,[19] in which the 2-hydroxyl group is absent, the calcium ion coordinates directly with the phosphate oxygens.

C. Hydrogen Bonding. Some features of the hydrogen bonding remain uncertain, since hydrogen atoms were not located. The most probable hydrogen bonds are listed in Table VI together with the relevant angles. The packing diagram viewed down the *a* axis is shown in Figure 4. The base, sugar, and phosphate moieties are all hydrogen bonded to different degrees with the water molecules. As expected, the highest concentrations of water molecules are around the anionic phosphate group of the nucleotide and around the sodium ion. Perspective views of the surroundings of the sodium ion and the phosphate group are shown in Figure 2.

[18] S. Furburg and A. Mostad, *Acta Chem. Scand.*, **16**, 1627 (1962).

[19] K. N. Trueblood, P. Horn, and V. Luzzati, *Acta Cryst.*, **14**, 965 (1961).

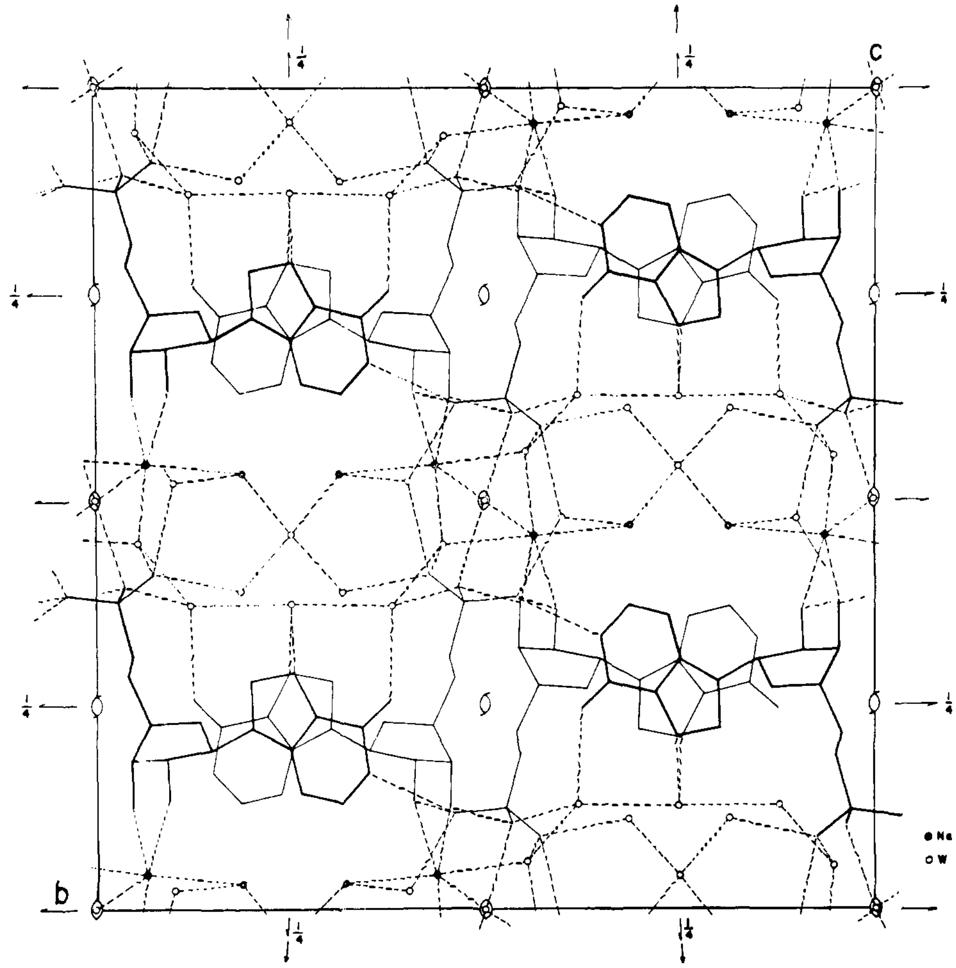

Figure 4. The contents of one unit cell as viewed down the *a* axis. Possible hydrogen bonds are shown in dashed lines.

Atom N(1) acts as a donor in the hydrogen bonding with phosphate oxygen O(7). These atoms are 2.77 Å apart. Atom O(6) accepts a proton from W(3). These atoms are separated by a distance of 2.71 Å. The water molecule W(9) on the twofold axis parallel to the *b* axis donates both of its hydrogen atoms to the N(7) atoms of the adjacent molecules which are related by the twofold axis. These hydrogen bonding distances are each 2.60 Å (Figure 4). This kind of hydrogen bonding by water to O(6) and N(7) of inosine is possible in the native state of the nucleic acids.

The hydroxyl groups of the sugar form hydrogen bonds with two different phosphate groups: O(2′) bonded to O(7) and O(3′) to O(8). These hydrogen bonds have the lengths of 2.69 and 2.65 Å, respectively. The ribose ring oxygen is not involved in hydrogen bonding as it is in all other known β-linked nucleosides and nucleotides.[20] However, characteristically, O(1′) has quite close contacts with the atoms of the adjacent base related by a two fold axis (Figure 5). These contacts are: O(1′)···N(1), 3.29; O(1′)···C(6), 3.13; O(1′)···C(2), 3.46; O(1′)···C(4), 3.31; and O(1′)···C(5), 3.18 Å. Similar close contacts have been observed in barium uridine 5′-phosphate,[15] adenosine 3′-phosphate dihydrate,[21] and adenylyl 2′-phosphate

Table VI. Possible Hydrogen Bonds and Angles[a]

Atom A	Atom B	Code	Distance, Å	Bond	Angle, deg
N(1)	O(7)	VII	2.77	C(2)–N(1)··O(7) C(6)–N(1)··O(7)	112 122
N(7)	W(9)	VIII	2.59	N(7)··W(9)··N(7)	84
O(2′)	O(7)	V	2.70	C(2′)–O(2′)··O(7)	123
O(3′)	O(8)	VI	2.65	C(3′)–O(3′)··O(8)	111
O(7)	W(5)	VIVI	2.69	P–O(7)··W(5)	124
O(8)	W(3)	I	2.72	P–O(8)··W(3)	136
O(8)	W(1)	III	2.88	P–O(8)··W(1)	124
O(9)	W(2)	II	2.74	P–O(9)··W(2)	126
O(9)	W(4)	II	2.72	P–O(9)··W(4)	135
O(9)	W(5)	IV	2.65	P–O(9)··W(5)	124
W(2)	W(3)	I	2.91		
W(3)	W(9)	I	2.81		
W(5)	W(8)	I	2.78		
W(7)	W(8)	IV	2.45		

[a] Atom A belongs to the basic set listed in Table I and atom B is related to this set by the symmetry operations of the space group and/or translations. The code used is as follows.

I	x	y	z
II	$-1+x$	y	z
III	$1/2+x$	$-1/2+y$	z
IV	$-1/2+x$	$-1/2+y$	z
V	$1/2+x$	$1/2-y$	$-z$
VI	$-1/2+x$	$1/2-y$	$-z$
VII	$1/2-x$	$1/2-y$	z
VIII	$1-x$	y	$1/2-z$

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(20) M. Sundaralingam, *Biopolymers*, **6**, 189 (1968).
(21) M. Sundaralingam, *Acta Crystallogr.*, **21**, 495 (1966).

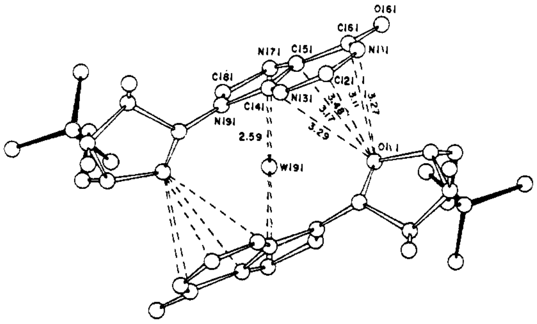

Figure 5. View down the b axis showing the two nucleotides related by the twofold axis parallel to the b axis. The close contacts between the atom O(1′) and the atoms in the base are also shown.

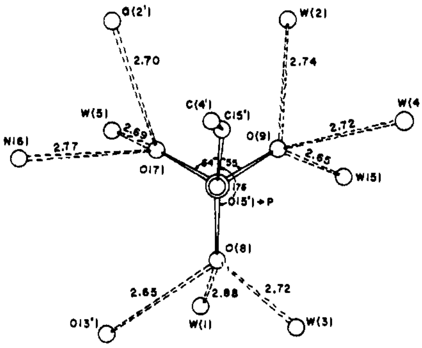

Figure 6. The hydrogen-bonded atoms around the three phosphate oxygen atoms are viewed along the ester bond O(5′)–P. The distribution around each P–O bond is roughly tetrahedral.

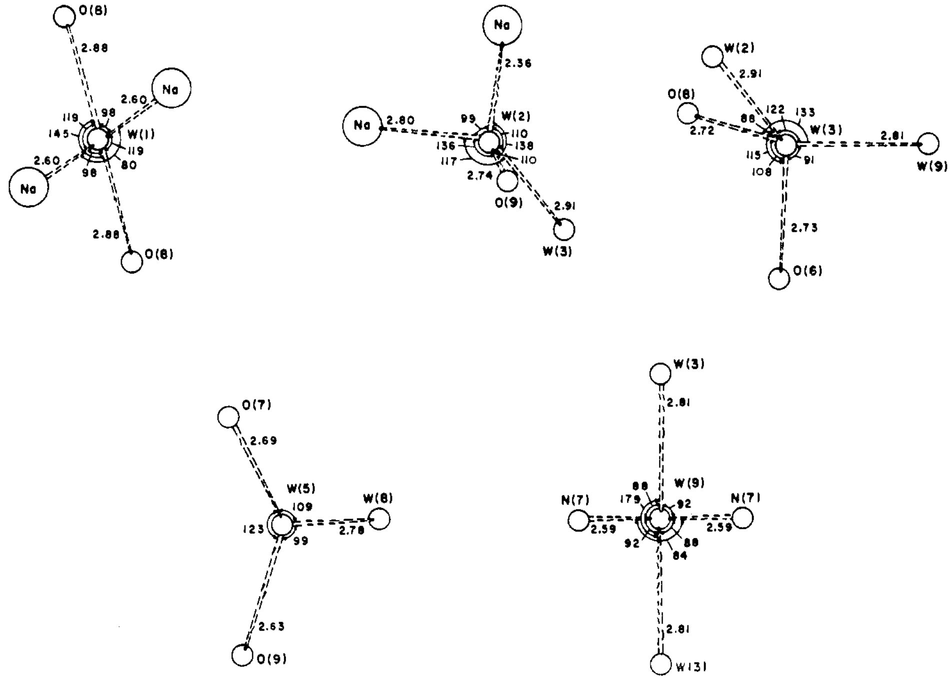

Figure 7. The coordination around the five water molecules which are not disordered.

5′-uridine tetrahydrate.[22]

The hydrogen bonding around the phosphate group is shown in Figure 6. There are three hydrogen bonds involving each of the three phosphate oxygen atoms. The disposition of these hydrogen bonds around the P–O bonds is roughly tetrahedral. Since the hydrogen atoms were not located, the acidic hydrogen in the phosphate can not be directly established. However, from a study of the environment of the phosphate and the hydrogen bonding involving the water molecules, it is possible to deduce the phosphate oxygen atom to which the proton is attached. The water W(9) donates both its protons to the N(7) atoms of the bases of two different molecules, and is also at a distance of 2.81 Å from W(3). Thus W(3) donates one of its protons to the hydrogen bond formation with W(9). The water W(3) donates its second proton to form a hydrogen bond of length 2.73 Å with the carbonyl oxygen atom of the base. The O(8) atom of the phosphate group is hydrogen bonded to W(3), separated by a distance of 2.72 Å. Therefore, atom O(8) should be the protonated oxygen atom. Interestingly, the P–O(8) bond is the longest of the P–O bonds, excepting the ester bond, although the differences among all the P–O bond lengths are not statistically significant. A search of the final difference electron density map showed a density of 0.2 e/Å^3 at the place where this proton is expected to occur, thus providing additional circumstantial evidence that the phosphate proton residues on O(8).

There is an intricate system of hydrogen bonds involving the water molecules themselves. The plausible hydrogen bonds and the relevant angles are found in Table VI. The surroundings of the five water molecules which are not disordered are shown in Figure 7. With the exception of W(5), the other four water molecules have four nearest neighbors, thus exhibiting maximum coordination. There are short contacts between W(6) and W(8) (1.98 Å), W(4) and W(7) (2.36 Å), and W(7) and W(8) (2.45 Å). In all of these cases the water sites are only partially occupied and hence dis-

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[22] E. Shefter, M. Barlow, R. Sparks, and K. N. Trueblood, *J. Amer. Chem. Soc.*, **86**, 1872 (1964).

ordered. It is noted that the sum of the two occupancies at the sites of W(6) and (W(8) is nearly 1.00, suggesting that one water molecule is perhaps trapped in a canal and is occupying the two positions statistically. When the water occupies the site W(6), it is coordinated to the sodium ion, and when it is at site W(8), it is hydrogen bonded to W(5) and perhaps also to W(7). It is also interesting that the sum of the occupancies of the water molecules W(7) on the twofold axis and W(4) and W′(4) related by this twofold axis is approximately 2.0. This indicates that two water molecules occupy these three sites.

A striking feature of the crystal packing is that there are alternating layers of nucleotides and water channels in which the sodium ions are embedded. Interestingly, the atomic groups that are capable of taking part in hydrogen-bond formation are all either pointing toward the water layer or are coordinated to the sodium ion. The crystal density indicates the presence of eight water molecules in the asymmetric unit, while only a total of about six have been located. In the final difference electron density map, there is a diffuse region of density 0.6 e/Å^3 in the region centered on (0.20, 0.05, 0.20). This position occurs in the "hole" in the structure in the region surrounded by the hydrogen bonds forming a pentagon. It is the region of the disordered water molecules (Figure 2). Therefore, it appears likely that the "volatile" water molecules that have escaped were loosely bound in this "hole" region of the lattice.

Many of the programs used in this work were written by S. T. R. for use with the UNIVAC 1107 and 1108 computers on the Case Western Reserve University campus. The full-matrix least-squares program of Busing, Martin, and Levy[10] was adapted for the UNIVAC computers.

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Communications to the Editor

Structural Interconversions and Ligand-Exchange Reactions of Phosphine Adducts to Platinum(II) Complexes

Sir:

Recently several five-coordinate platinum(II) complexes have been reported.[1-4] While these compounds might be expected to undergo stereochemical rearrangements[5] with relative ease, the ligand structure permitting, no conclusive evidence has been reported for such behavior. Eaton[6] observed that the inability to find the tin nuclear magnetic resonance in $Pt(SnCl_3)_5{}^{3-}$ might be attributed "to the effects of a rapid exchange reaction." In this communication we report *direct evidence for both ligand exchange and molecular rearrangement* by studies of the temperature-dependent proton magnetic resonance (pmr) spectra of methyldiphenylphosphine adducts of platinum(II) dithiolates.

Earlier[4] we reported the isolation of crystalline methyldiphenylphosphinebis(*p*-dithiocumato)platinum (II) (Ia, X = H; Y = *i*-C_3H_7). In addition, methyldiphenylphosphinebis(3,4,5-trimethoxydithiobenzoato)platinum(II) (Ib, X = Y = OCH_3) has been prepared. The pmr spectra of these complexes were observed in $CHCl_3$. With increasing temperature, the ^{195}Pt coupling ($J_{Pt-P-CH_3}$ = 39 cps) on the methyldiphenylphosphine is relaxed (Figure 1), but J_{P-CH_3} remains at −10.8 cps. Since the J_{P-CH_3} coupling constant in uncoordinated methyldiphenylphosphine[7] is +3.4 cps, more than 95% of the phosphine must be present as the coordinated species.

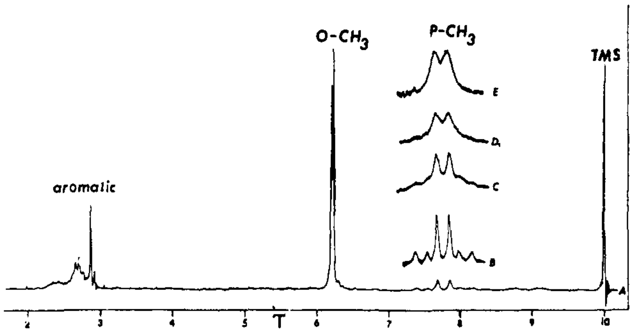

Figure 1. Nmr spectrum of bis(3,4,5-trimethoxydithiobenzoato)platinum(π)methyldiphenylphosphine (Ib) in $CDCl_3$: A, complete spectrum at 33°; B, increased spectrum amplitude of trace A; C, 46°; D, 54°; E, 61°.

The temperature-dependent lifetime, τ, for the phosphine complex was calculated[8] from a computer output line-shape analysis (Figure 2) based on the adiabatic approximation.[9] Plots of log $1/\tau$ *vs.* $1/T$ yielded activation energies (E_a) of 4.2 and 19.7 kcal/mole for Ia and Ib, respectively. Values of τ at a given temperature decrease when (1) triphenylphosphine is added, (2) the concentration of complex is increased, or (3) the complex is dissolved in CS_2 instead of $CHCl_3$.

The pmr studies of Ia and Ib show that phosphine

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(4) J. P. Fackler, Jr., W. C. Seidel, and J. A. Fetchin, *ibid.*, **90**, 2707 (1968).

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966, p 132.

(6) D. R. Eaton, *J. Am. Chem. Soc.*, **90**, 4272 (1968).

(7) J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *ibid.*, in press.

(8) Dr. M. J. Weeks is acknowledged for this contribution.

(9) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 36 (1965).