Interactions of Hydrated Metal Ions with Nucleotides: the Crystal Structure of Barium Adenosine 5′-Monophosphate Heptahydrate†

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ABSTRACT: The crystal and molecular structure of barium adenosine 5′-monophosphate heptahydrate was determined from x-ray diffraction data. Crystals of barium adenosine 5′-monophosphate heptahydrate are monoclinic, space group $C2$, with $a = 32.559(3)$, $b = 6.969(3)$, $c = 9.597(1)$ Å, and $\beta = 100.31(1)°$. Intensity data were collected with an automated diffractometer. The structure was solved by the heavy-atom method and refined by least-squares to $R = 0.034$. This structure provides an example of an outer-sphere metal–nucleotide complex, in which a completely hydrated metal ion interacts with the nucleotide only through water bridges. The barium ion is coordinated to eight water molecules, which form a slightly distorted square antiprism. Seven of the eight water molecules from the barium hydration shell are hydrogen bonded to phosphate groups; three of these water molecules are also hydrogen bonded to other suitable acceptor sites on the base and ribose moieties. The conformation about the glycosidic bond is anti, with $\chi_{CN} = 69°$, and, as in most nucleotide structures, the conformation about the C(4′)-C(5′) bond is gauche–gauche. However, the ribose displays an unusual conformation (best described as C(4′)-exo) not previously observed in crystal structures of nucleosides or nucleotides, other than 3′,5′-cyclic nucleotides. It is possible that this unusual conformation is a consequence of the metal–water–nucleotide bridging interactions.

Interactions of metal ions with nucleotides and nucleic acids are involved in a number of biological processes. Detailed investigations have been made of these interactions as they occur in aqueous solution, and various aspects of the solution complexes have been reviewed (Phillips, 1966; Izatt et al., 1971; Glassman et al., 1971; Kuntz et al., 1972; Sari and Belaich, 1973; Frey and Stuehr, 1974; Tu and Heller, 1974). Several crystallographic studies of metal complexes with nucleotides have been reported (e.g., Shefter and Trueblood, 1965; DeMeester et al., 1974; Collins et al., 1975). Extensive evidence indicates that adenine nucleotides can interact with metal ions through free hydroxyl groups from the sugar moieties, through their phosphate oxygen atoms, and through nitrogen atoms of the adenine moiety (Izatt et al., 1971; Phillips, 1966). Experimental and theoretical considerations have suggested two basic mechanisms by which metal ions can bind to these ligands (Frey and Stuehr, 1974). One mechanism, generally regarded as the more important, involves direct metal coordination to ligands of the nucleotide. In this mechanism, the nucleotide forms an inner-sphere complex with the metal ion by disrupting the normal hydration shell around the metal ion and substituting appropriate ligands for water molecules in the hydration shell of the metal. An alternate mechanism is based on the assumption that metal ions may retain their hydration shells and indirectly interact, through water molecules, with nucleotides. This type of interaction results in an outer-sphere complex. Proposed mechanisms for the formation of inner-sphere, metal–nucleotide complexes in aqueous media usually include rapid formation of outer-sphere complexes, followed by a much slower step in which bridging water molecules are eliminated and replaced by direct contacts between the metal ion and the ligands of the nucleotide (Frey and Stuehr, 1974).

Results of several physical and chemical studies lend support to the importance of water-mediated interactions between metal ions and nucleotides. However, few data are available concerning the structural properties of outer-sphere complexes. In this paper, we describe the crystal structure of a hydrated barium salt of adenosine 5′-monophosphate, in which the barium ion forms an outer-sphere complex with the nucleotide.

Experimental Procedures

Clear platelike crystals of $BaAMP \cdot 7H_2O$ were obtained by slowly cooling an aqueous solution that contained a 2:1 molar ratio of adenylic acid (AMP[1]) and barium hydroxide ($Ba(OH)_2$). Oscillation and Weissenberg photographs showed the optically active crystals to be monoclinic, and space group $C2$ was indicated by the systematic absence of reflections hkl with $h + k$ odd. A crystal with approximate dimensions of 0.25 × 0.1 × 0.05 mm was mounted on a Picker FACS-1 diffractometer with its b axis slightly inclined to the ϕ axis of the diffractometer. Approximate cell parameters for use in collection of intensity data were calculated by a least-squares analysis of the angular settings for eight medium-angle reflections (Cu $K\bar{\alpha}$, $\lambda = 1.5418$ Å). Intensity data were collected with the diffractometer by use of a scintillation counter, nickel-filtered copper radiation, and a θ–2θ scanning technique. The scanning speed was 1°/min, and the background was counted for 20 s at each terminus of the scans. Measurements were made for each of the 1943 independent reflections with $2\theta < 128°$. Three reference reflections, which were monitored

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[1] Abbreviations used are: ATP, AMP, adenosine tri- and monophosphates; NMR, nuclear magnetic resonance.

TABLE I: Crystal Data Cu $K\alpha_1$ = 1.5405 Å.[a]

Stoichiometry	$C_{10}H_{12}PN_5O_7Ba \cdot 7H_2O$
Z	4
Space Group	$C2$
a	32.559(3) Å
b	6.969(3)
c	9.597(1)
β	100.31 (1)°
ρ (calculated)	1.886 g cm^{-3}
ρ (observed)	1.91 g cm^{-3}
μ (Cu K$\bar{\alpha}$)	159.8 cm^{-1}

[a] The density was measured by flotation in a mixture of carbon tetrachloride and dibromoethane.

periodically, showed no significant intensity fluctuations during the collection of intensity data. More accurate values for the unit cell parameters were determined immediately after data collection by a least-squares analysis of 2θ values for 10 high-angle reflections (Cu $K\alpha_1$, λ = 1.54051 Å). These cell parameters were not significantly different from those obtained prior to collecting intensity data. Crystal data are listed in Table I.

Sixteen reflections that had scan counts below background level were assigned intensity values of 0.0 and were retained in all subsequent calculations. This manner of handling "unobserved" reflections introduces a bias in our refinement on F^2 but probably has a negligible effect on the final results. The intensities were assigned variances, $\sigma^2(I)$, according to the statistics of the scan and background counts plus a correctional term $(0.03S)^2$, S being the scan count. Intensities and their variances were corrected for Lorentz and polarization factors, and absorption corrections were applied by using the computer program ORABS (Wehe et al., 1962). The data were scaled by means of a Wilson (1942) plot.

The barium ion was located in a three-dimensional Patterson map. A three-dimensional Fourier synthesis calculated with the phases from the barium ion revealed the positions of the phosphorus atom and its four covalently linked oxygen atoms. A Fourier map phased with the barium ion and the phosphate moiety revealed the atoms of the ribose ring and its substituents. An electron density map then revealed all the atoms of the purine ring as well as the oxygen atoms of eight water molecules, two of which were found to lie on diad axes.

The trial structure was refined by use of a modified version of the full-matrix least-squares program ORFLS (Busing et al., 1962; Busing, 1971). The quantity minimized was $\Sigma w(F_o^2 - F_c^2/k^2)^2$, where k is a scale factor and the weight w is equal to $1/\sigma^2(F_o^2)$. Scattering factors for Ba^{2+} were from Thomas and Umeda (1957), those for the other nonhydrogen atoms were from *International Tables for X-ray Crystallography* (1962), and real and imaginary dispersion corrections for these atoms were from Cromer and Liberman (1970). The hydrogen atoms of the nucleotide were located in difference Fourier maps during the latter stages of refinement. The hydrogen atoms of the water molecules could not be located with certainty; therefore, their positions were deduced from the apparent hydrogen-bonding scheme and confirmed in the final difference Fourier map. Scattering factors for the hydrogen atoms were from Stewart et al. (1965). Final cycles of refinement included the scale factor, k, the positional and anisotropic temperature parameters of the nonhydrogen atoms, and Zachariasen's (1963) isotropic extinction parameter g (as formulated by Coppens and Hamilton (1970)). Hydrogen atom parameters were not refined, but those of the nucleotide were included in the structure factor calculations with arbitrary isotropic temperature factors of U = 0.038 Å^2 (B = 3.0 Å^2). Since limited core storage prevented simultaneous variation of all parameters, they were refined in alternate cycles with about half the parameters included in each cycle. The final R index $\{\Sigma(|F_o| - |F_c|)/\Sigma F_o|\}$ is 0.034 and the goodness-of-fit $([\Sigma w(F_o^2 - F_c^2)^2/(m-s)]^{1/2}$, where m is the number of reflections used and s is the number of parameters refined) is 2.03. During the last cycle of refinement, no parameter shifted more than one-third of its estimated standard deviation, and the average parameter shift was about one-tenth of the estimated standard deviation. At the conclusion of refinement, a three-dimensional electron-density difference map was calculated with only the heavy atom contributions included in the values for the calculated structure factor. This map showed regions of electron density between 0.46 and 0.97 eÅ^{-3} at all hydrogen atom positions. A final difference Fourier that included all atoms showed several peaks and troughs of magnitudes below 0.5 eÅ^{-3} and one peak of 0.84 eÅ^{-3} within 3.0 Å of the barium ion. (A list of structure factors is available (see paragraph at end of paper regarding supplementary material).)

Results

The heavy-atom coordinates and their estimated standard deviations are listed in Table II. Tables of thermal parameters and hydrogen-atom parameters are available (see paragraph at end of paper regarding supplementary material). The estimated errors in positional coordinates are about 0.0004 Å for Ba^{2+}; 0.002 Å for P; and 0.008 Å for C, N, and O atoms. The conformation of the nucleotide, together with bond lengths and angles involving only nonhydrogen atoms, is shown in Figure 1.

The ribose is in an unusual conformation. The best four-atom plane through the pentose ring is defined by atoms C(1′), C(2′), C(3′), and O(1′), none of which deviates by more than 0.07 Å from the plane. Atom C(4′) is displaced by 0.60 Å from this plane, in the opposite direction from atom N(9). Atoms C(3′) and C(4′) are displaced by 0.29 and 0.38 Å, respectively, in opposite directions from the plane defined by atoms O(1′), C(1′), and C(2′). The torsion angles τ_0, τ_1, τ_2, τ_3, and τ_4 (Sundaralingam, 1971; Sundaralingam and Abola, 1972) assume values of −16.3, −11.1, 32.3, −42.4, and 37.4°, respectively. According to the notation of pseudorotation, this corresponds to a phase angle, P, of 41° with an amplitude of pucker, τ_m, equal to 42° (Altona and Sundaralingam, 1972). Thus, the conformation of the ribose is best described as C(4′)-exo (or C(4′)-exo, C(3′)-endo). This conformation has not previously been observed in crystal structures of nucleosides or normal nucleotides, although it is commonly found in the 3′,5′-cyclic nucleotides (Chwang and Sundaralingam, 1974a).

In agreement with the observations from most other crystal structures of nucleotides (Donohue and Trueblood, 1960; Sundaralingam, 1969; Saenger, 1973), the conformation about the glycosidic bond is anti; the torsion angle χ_{CN}[O(1′)-C(1′)-N(9)-C(8)] is 69°. The conformation about the C(4′)-C(5′) bond is gauche-gauche, with the torsion angles ϕ_{oo}(O(5′)-C(5′)-C(4′)-O(1′)) = −61° and ϕ_{oc}-(O(5′)-C(5′)-C(4′)-C(3′)) = 59°. The torsion angle P-O(5′)-C(5′)-C(4′) is −143° (+217°) and lies within the range of 149–230° covered by other nucleotides (Sundaralingam, 1969). The purine ring is essentially planar with atom N(1) showing the largest deviation (0.022 Å) from the plane through the nine atoms of the purine ring. The substituents N(6) and

TABLE II: Nonhydrogen Atom Coordinates and their Estimated Standard Deviations.[a]

Atom	X	Y	Z	Atom	X	Y	Z
Ba	5142(1)	0(0)	37602(4)	C(5′)	3609(2)	1242(13)	215(7)
N(1)	1792(2)	4492(13)	4837(8)	O(2′)	2902(2)	6617(12)	−342(8)
C(2)	1736(3)	4304(17)	3432(10)	O(3′)	3726(2)	5775(9)	−173(5)
N(3)	2019(2)	4261(12)	2584(7)	O(5′)	3837(2)	807(9)	1599(5)
C(4)	2413(2)	4380(12)	3357(8)	P	4313(0)	73(6)	1713(1)
C(5)	2517(3)	4483(11)	4803(8)	O(1)	4449(2)	−101(16)	3304(5)
C(6)	2183(3)	4566(12)	5554(8)	O(2)	4317(2)	−1800(9)	935(6)
N(6)	2252(3)	4715(14)	7004(7)	O(3)	4547(2)	1654(11)	1096(6)
N(7)	2945(2)	4558(11)	5211(7)	W(1)	4621(2)	5040(19)	2691(7)
C(8)	3092(3)	4495(13)	4007(9)	W(2)	3735(2)	4564(12)	7145(6)
N(9)	2784(2)	4366(11)	2850(7)	W(3)	4629(2)	2099(15)	8296(8)
C(1′)	2836(2)	4318(13)	1376(8)	W(4)	3977(2)	2147(14)	4836(8)
C(2′)	3112(2)	5914(14)	973(9)	W(5)	1084(2)	2267(13)	5641(8)
C(3′)	3511(2)	4830(19)	781(7)	W(6)	532(5)	2915(24)	1926(19)
C(4′)	3331(2)	2908(13)	238(7)	W(7)	5000(0)	2357(18)	5000(0)
O(1′)	3028(2)	2547(9)	1129(6)	W(8)	0(0)	2546(16)	5000(0)

[a] Values for the barium ion were multiplied by 10^5 and all others by 10^4; the Y coordinate for Ba and the X and Z coordinates of W(7) and W(8) were not refined.

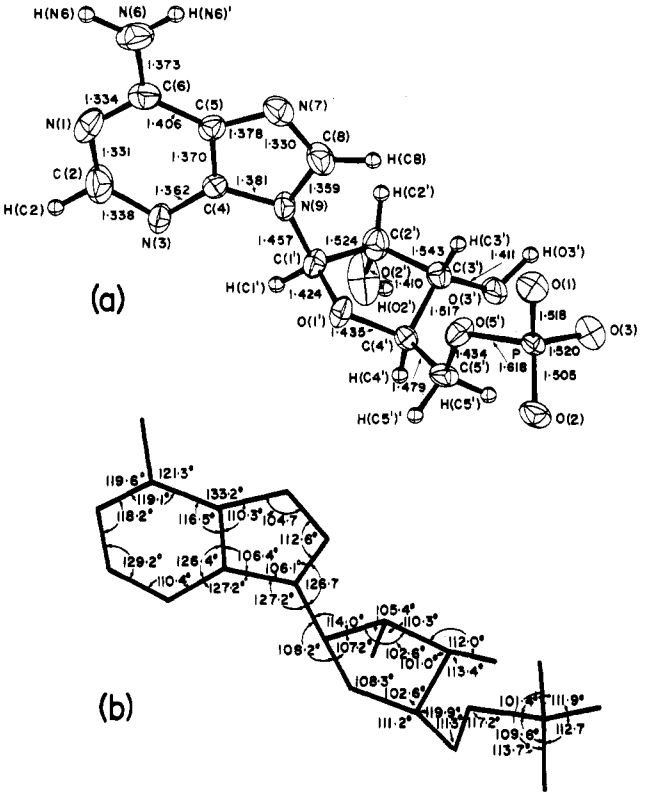

FIGURE 1: Conformation of barium adenosine 5′-monophosphate heptahydrate. Nonhydrogen atoms are represented by thermal ellipsoids defined by the principal axes of thermal vibration and scaled to include 50% probability. Hydrogen atoms are represented by spheres of 0.1 Å radius. Estimated standard deviations are about 0.01 Å (0.008 Å involving P) and 0.5° for (a) bond lengths and (b) bond angles, respectively. (This drawing and those in Figures 2–7 were prepared by using the computer program ORTEP (Johnson, 1965).)

C(1′) deviate from this plane by 0.015 and 0.068 Å, respectively.

The crystal-packing and hydrogen-bonding schemes are depicted in Figure 2. Since it was difficult to locate the hydrogen atoms from water molecules, certain features of the proposed hydrogen-bonding schemes are somewhat tentative; distances and angles for proposed hydrogen-bonded contacts are available (see paragraph at end of paper regarding supplementary material). The two hydrogen atoms of the N(6) amino group form relatively long intermolecular contacts with O(1′) and O(2′), and these could represent weak hydrogen bonds. Atom O(1′) of ribose and deoxyribose moieties does not usually participate in hydrogen bonding, although this atom has, in some instances, been observed to form weak hydrogen-bonded contacts (Chwang and Sundaralingam, 1974b; Sprang and Sundaralingam, 1973; Sundaralingam and Arora, 1972). Atoms O(2′) and O(3′) form hydrogen bonds to symmetry-related nucleotides. Possible hydrogen-bonded contacts can be proposed for all 16 hydrogen atoms from the water molecules. As stated earlier, the water-hydrogen atoms were first deduced and only then located in the difference Fourier map. Nevertheless, the proposed hydrogen-bonding contacts involving water molecules are reasonable, since all postulated donor–acceptor distances (except one) lie between 2.66 and 3.00 Å, and the acceptor(1)–donor–acceptor(2) angles lie between 85 and 118°.

The overall crystal packing scheme consists of columns of hydrated barium ions running parallel to [011] and of continuous columns of approximately parallel adenine moieties that are stacked in the b direction. Adjacent nucleotides are joined by direct hydrogen bonds, by bridging hydrogen bonds involving water molecules from the barium hydration shell, and by base-stacking interactions. Figure 3 shows that the closest stacking contacts involve adenine moieties that are related by the crystallographic twofold axis. The planes are inclined about 8° relative to each other and are 3.2–3.4 Å apart. The amino group is positioned over the imidazole ring of the adjacent base, resulting in a stacking pattern similar to those found in several other crystal structures of adenine derivatives (Bugg et al., 1971).

The environment of the barium ion can be seen in Figure 4. The ion is surrounded by a coordination polyhedron composed of the oxygen atoms from eight water molecules, two of which bridge symmetry-related barium ions. The eight oxygen atoms of the barium hydration shell form a slightly distorted square antiprism with barium–oxygen distances ranging from 2.70 to 2.91 Å. Within the hydration shell, the nearest-neighbor oxygen–oxygen distances range from 3.31 to 3.76 Å. Seven of the eight water molecules from the barium hydration shell are hydrogen bonded to phosphate groups. Three of the seven

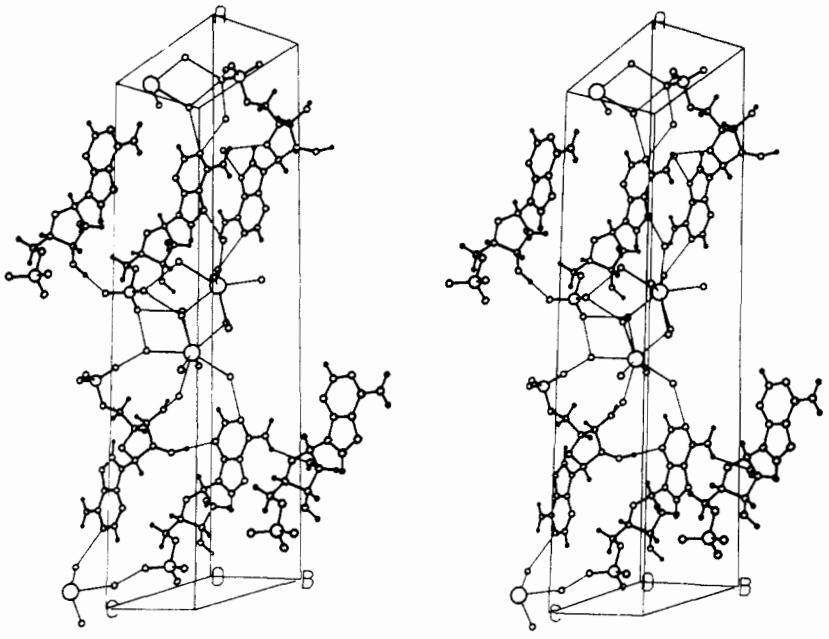

FIGURE 2: Stereo drawing in which the crystal packing is viewed approximately down the c axis. Large circles represent barium ions, heavy lines—the covalent bond, and light lines—the hydrogen bonds and water-barium contacts.

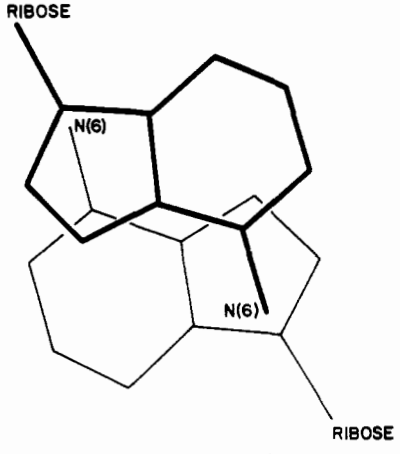

FIGURE 3: Base stacking pattern as viewed perpendicular to the plane of the base that is represented by the bold lines. The base planes intersect with an angle of about 8°, and are separated by 3.2–3.4 Å.

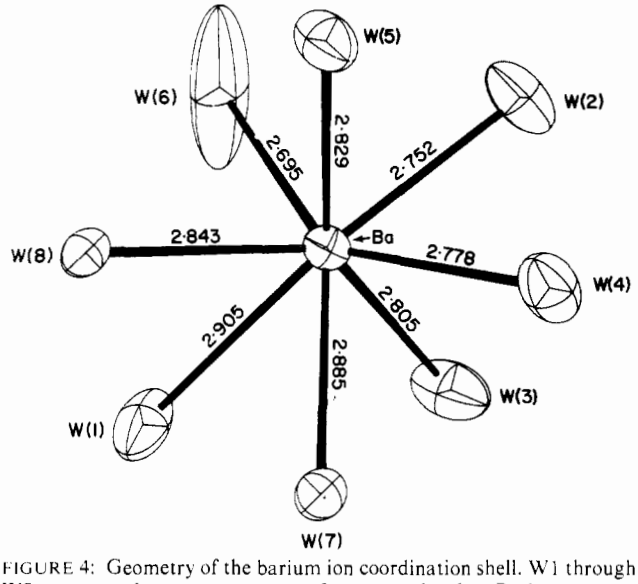

FIGURE 4: Geometry of the barium ion coordination shell. W1 through W8 correspond to oxygen atoms of water molecules. Barium-oxygen distances are shown.

water molecules are simultaneously hydrogen bonded to other suitable acceptor sites as follows: one to the O(3′) hydroxyl group, one to atom N(1), and one to atom N(7). Thus, the barium–nucleotide interactions are of the outer-sphere type, with contacts mediated through water molecules (Frey and Stuehr, 1974). The sites at which barium ions interact through water bridges are depicted in more detail in Figure 5.

Discussion

Other crystal structures of metal–nucleotide salts and complexes also display water-mediated binding of the metal ions to various ligands on the nucleotides. However, in all of these other crystal structures the indirect metal–water–ligand interactions at one site occur in combination with direct metal–ligand contacts at other sites. For example, in the crystal structure of barium 5′-uridylate (Shefter and Trueblood, 1965), the barium ion is chelated to the O(2′)–O(3′) pair of hydroxyl groups and is brided to the phosphate group through water molecules. Similarly, in the crystal structures of hydrated nickel complexes of guanosine 5′-monophosphate (DeMeester et al., 1974) and of adenosine 5′-monophosphate (Collins et al., 1975), the nickel ion is coordinated directly to N(7) of the purine moieties and the coordination polyhedron around the nickel ion is then completed by five water molecules, two of which are hydrogen bonded to the phosphate moiety. To our knowledge, the crystal structure of barium 5′-AMP provides the first reported example of a completely hydrated metal ion complexed with a nucleotide.

Solution studies have also supported the possible importance of water-mediated metal interactions with nucleotides (Brintzinger, 1961; Frey and Stuehr, 1974). NMR studies of metal binding to adenine nucleotides have provided direct evidence of water-mediated contacts; these investigations indicate that the metal ion is probably in direct contact with the phosphate moieties, but is bridged to atom N(7) of the purine

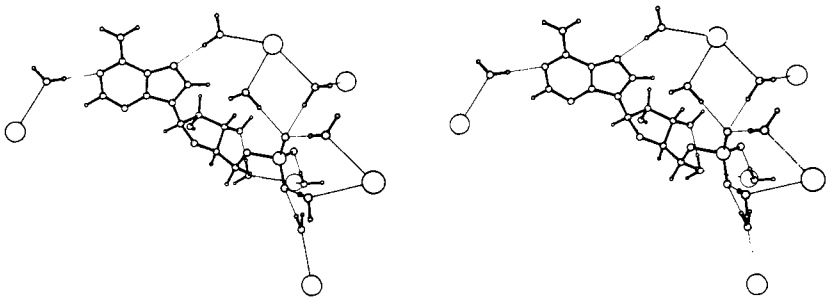

FIGURE 5: Stereo drawing showing the six sites at which barium ions interact with the nucleotide through water bridges. Large circles represent barium ions, heavy lines—the covalent bonds, thin single lines—hydrogen bonds, and thin double lines—water to barium contacts.

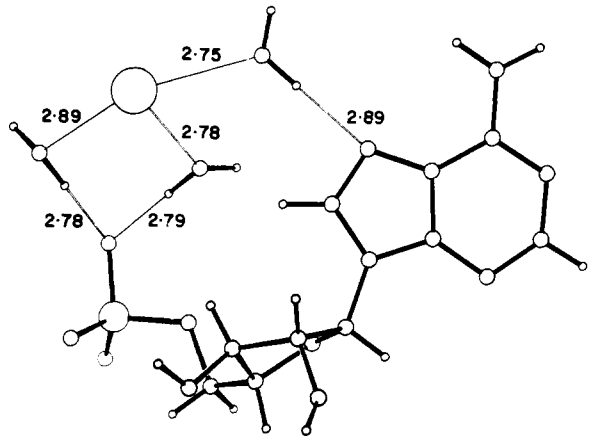

FIGURE 6: Interaction of the hydrated barium ion at the site that involves the formation of water bridges to the phosphate moiety and to atom N(7) of the base. The barium–oxygen and donor–acceptor distances (Å) are given.

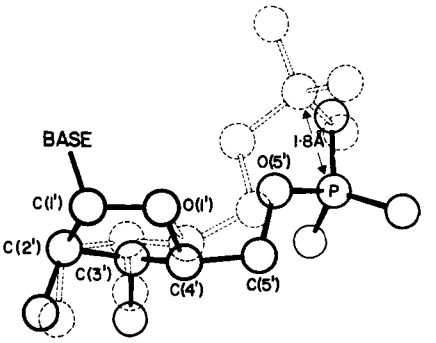

FIGURE 7: Comparison of the ribose conformation in barium 5′-AMP (heavy lines) with that found for 11-fold RNA (broken lines). The ribose conformation shown for RNA is typical of that found in most other crystal structures of 5′-ribonucleotides, and is similar to that proposed in most other models of ribonucleic acids. The comparison was arbitrarily selected so that the C(1′)–C(2′), C(1′)–O(1′), and glycosidic bonds are superposed.

moiety through a water molecule that is coordinated to the metal and hydrogen bonded to the purine (Glassman et al., 1971). Microcalorimetric studies further support the possibility of metal–water–N(7) interactions in metal complexes of the 5′-ribonucleotides of guanine and hypoxanthine (Sari and Belaich, 1973).

Nucleotides possess several sites that might be involved in water-mediated metal interactions. As shown in Figure 5, barium ions interact (through water bridges) with a hydroxyl group of the ribose, with all phosphate–oxygen atoms except the one involved in the C(5′) linkage, and with atoms N(7) and N(1) of the adenine moiety. However, solution and crystallographic studies clearly indicate that the most important sites for metal-binding to adenine nucleotides are provided by the phosphate moieties and atom N(7) of the adenine base. Of these, the phosphate moiety makes the major contribution to the stability of the complexes, since the association constants for metal complexes usually decrease in the order 5′-ATP > 5′-ADP > 5′-AMP ≫ adenosine (Tu and Heller, 1974). One of the principal metal-binding sites in the barium 5′-AMP structure is provided by the phosphate group acting in concert with atom N(7). As depicted in Figure 5 and in greater detail in Figure 6, the hydrated barium ion forms a phosphate–metal–N(7) linkage that is mediated through three water molecules: one that is hydrogen bonded to N(7), and two that are hydrogen bonded to an oxygen atom of the phosphate moiety. One might reasonably expect that similar water-mediated interactions could also occur between other hydrated metal ions and 5′-AMP. It is also conceivable that metal ions could form related complexes with 5′-ADP and 5′-ATP, in which case interactions involving the additional phosphate groups could further stabilize the complex. Examination of space-filling molecular models of 5′-ATP suggests that hydrated barium ions could, through interactions like those shown in Figure 6, bind to N(7) and to the α-phosphate group of the triphosphate while forming additional barium–water–phosphate bridges to the β- and γ-phosphate groups.

The conformation of the ribose moiety in this structure is noteworthy because it is unlike that found in any previous crystal structures of nucleosides or nucleotides, other than 3′,5′-cyclic nucleotides. Like almost all other 5′-nucleotides, the conformation about the glycosidic linkage is anti, and the conformation about the C(4′)–C(5′) bond is gauche–gauche. Whereas ribose moieties of most simple nucleotides are either in the C(2′)- or the C(3′)-endo conformation, the ribose group of Ba 5′-AMP assumes a C(4′)-exo conformation. This unusual mode of pucker influences the overall conformation of the sugar–phosphate moiety. Figure 7, which compares the Ba 5′-AMP conformation with that of the sugar–phosphate group from 11-fold RNA (Arnott et al., 1969) illustrates this effect. In RNA, the ribose is in the C(3′)-endo conformation that is found in most crystal structures of ribonucleotides. Although the altered conformation in the Ba 5′-AMP structure corresponds to rather small shifts in the atoms of the ribose rings, these shifts are greatly amplified when propagated to atom C(5′), and finally to the phosphate group. The end result is that, relative to RNA, the phosphorus atom has moved by about 1.8 Å. Similar comparisons with the conformations of the acid form of 5′-adenylic acid (Kraut and Jensen, 1963), of tenfold RNA (Arnott et al., 1969) and of sodium inosine 5′-monophosphate (Rao and Sundaralingam, 1969) show that the phosphorus atoms have undergone even larger displacements (2.2, 1.9, and 2.0 Å, respectively).

Although the ribose conformation in this barium complex is unlike that usually found for 5′-nucleotides, it is remarkably similar to the conformations observed in crystal structures of 3′,5′-cyclic nucleotides (Chwang and Sundaralingam, 1974a). In all of the cyclic nucleotides that have been examined, the ribose moieties assume C(4′)-exo conformations, which are characterized by pseudorotation phase angles, *P*, ranging from about 40 to 50°. In the case of cyclic nucleotides this unusual ribose conformation can be rationalized as arising from strain induced by the phosphate group, which bridges the C(3′) and C(5′) positions. In the ribose rings of cyclic nucleotides, the lengths of the C(1′)-O(1′) and C(4′)-O(1′) bonds are generally equal within experimental error, as contrasted to other nucleotides which exhibit C(1′)-O(1′) bond lengths that are considerably shorter than the C(4′)-O(1′) distances (Chwang and Sundaralingam, 1974a). In the barium AMP structure the C(1′)-O(1′) and C(4′)-O(1′) bond lengths are also equal within experimental error and are about the same as in cyclic nucleotides.

It is not clear whether the unusul ribose conformation in the barium AMP structure is directly attributable to influences of the barium ion, but it appears that this may be the case. The bridging contact, seen in Figure 6, which might contribute to this conformation, involves the hydrated barium ion, atom N(7) of the adenine moiety, and the phosphate group. All these interactions lead to normal contacts, including the coordination bonds between barium and water and the hydrogen bonds between the water molecules and the nucleotide. To assume a more normal ribose conformation the phosphate group would have to move about 2 Å toward the barium ion; this would effectively disrupt the bridging interactions. Therefore, it is possible that the ribose conformation is largely a consequence of the favorable interactions of the hydrated metal ion with the phosphate group and atom N(7) of the base.

Acknowledgments

We thank Dr. Gunther Eichhorn for a valuable discussion of metal-nucleotide complexes, Professor Robert Langridge for his interest and support, and Miss Mary Ann Comer and Miss Catherine Sims for assistance in the preparation of the manuscript.

Supplementary Material Available.

A listing of heavy-atom parameters, hydrogen-atom parameters, hydrogen-bond distances and angles, and of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal (15 pages). Ordering information is given on any current masthead page.

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