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Structure of the Monopotassium Salt of Adenosine 5'-Diphosphate Dihydrate, KADP.$2H_2O$*

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Abstract

Crystals of the title compound, $K^+.C_{10}H_{14}N_5O_{10}P_2^-.2H_2O$, were grown at pH 4 from a water/ethanol mixture. They have space group $P2_12_12$ with $a = 28.502$ (5), $b = 10.461$ (2), $c = 6.321$ (2) Å, $Z = 4$, $D_c = 1.76$ Mg m^{-3}. The structure was solved from 1726 three-dimensional X-ray diffraction data and refined to $R_w = 9.3\%$. The ribose adopts the C(2')-*endo* conformation, the orientation about the C(4')—C(5') bond is *gauche,gauche* and the heterocycle is *anti* with respect to the ribose. The pyrophosphate O(5')—P(1)—O(6')—P(2) chain is in a staggered conformation, with P—O—P angle 130° and P(1)—O(6') 1.65, P(2)—O(6') 1.60 Å. K^+ is coordinated to pyrophosphate oxygens, to ribose O(2'), to heterocycle N(3) and to water. The two other negative charges of ADP are compensated by protons at N(1) and at O(23) of the pyrophosphate. This crystal structure is isomorphous with RbADP.H_2O [Viswamitra, Hosur, Shakked & Kennard (1976). *Nature* (*London*), **262**, 234–236].

Introduction

Adenosine mono-, di- and triphosphates, AMP, ADP and ATP, are key substances controlling energy transfer in living organisms. This transfer is associated with the hydrolysis of pyrophosphate to release inorganic phosphate P_i and a nucleotide with lower phosphorylation: ATP $\rightleftharpoons$ ADP + P_i $\rightleftharpoons$ AMP + P_i $\rightleftharpoons$ Ade + P_i. The free energy of hydrolysis ($\Delta G'$) is around 35 kJ mol^{-1} at pH 7 for the release of P_i from ATP and from ADP but only 9.6 kJ mol^{-1} for AMP (Metzler, 1977; Lehninger, 1975). Therefore the pyrophosphate group in ATP and in ADP is called 'energy rich' and has attracted considerable interest from different disciplines in natural sciences.

In this paper, we concentrate on structural aspects of ADP in the crystalline salt KADP.$2H_2O$. The results will be correlated with those obtained for different salts of ADP, ATP, CDP, and derivatives such as NAD$^+$ and CDP choline.

Experimental

The potassium salt of ADP was crystallized from aqueous solution containing about 40% ethanol and adjusted with HCl to pH 4. A crystal of dimensions 0.025 × 0.03 × 0.4 mm was sealed in a quartz capillary to avoid decomposition and used for all X-ray experiments. 1726 intensity data up to $2\theta = 120°$ were collected on a four-circle diffractometer operated in the $2\theta/\omega$ scan mode with Ni-filtered Cu $K\alpha$ radiation and corrected for geometrical factors but not for absorption. Standard deviations were assigned according to counting statistics.

The crystal structure was solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1970) and refined by full-matrix least-squares methods (Busing, Martin & Levy, 1962) using scattering factors given in *International Tables for X-ray Crystallography* (1974). C, N, and O atoms were refined isotropically while the phosphate groups and the potassium ion were treated anisotropically. One of the two water molecules, O(*W*1), is twofold disordered (50/50). The final R index $\sum||F_o| - |F_c||/\sum|F_o|$ for all reflections is 12.4%, with the weighted R index R_w 9.3%. The relatively high R factor is due to the weak reflections obtained from the small crystal specimens.†

Results and discussion

In Tables 1 to 5 are listed final atomic coordinates, intramolecular bond angles, distances and torsion

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35449 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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angles. Fig. 1 describes the atom numbering scheme, Fig. 2 gives a stereoplot of the unit cell viewed along **c** and in Fig. 3 the protonation scheme is presented.

Table 1. *Fractional atomic coordinates* (×10^4) *and isotropic temperature factors*

E.s.d.'s are given in parentheses. *B*'s marked with an asterisk have been converted from anisotropic temperature factors. Occupancy factors of O(*W*1) and O(*W*12) are 0·50/0·50.

	x	*y*	*z*	B_{eq}/B_{iso} (Å^2)
K	1047 (2)	5123 (5)	291 (12)	11·6 (1)*
P(2)	3168 (1)	1976 (4)	2975 (7)	1·8 (1)*
O(21)	2710 (3)	2594 (9)	3653 (17)	2·6 (2)*
O(22)	3245 (3)	664 (8)	3534 (15)	2·5 (2)*
O(23)	3225 (4)	2091 (12)	506 (16)	4·0 (2)*
O(6′)	3562 (3)	2920 (11)	3869 (18)	3·5 (2)*
P(1)	4131 (1)	2718 (4)	4154 (8)	2·5 (1)*
O(11)	4317 (3)	2005 (12)	2222 (1)	3·7 (2)*
O(13)	4228 (4)	2176 (14)	6313 (21)	5·0 (3)*
O(5′)	4271 (3)	4184 (9)	4176 (17)	2·4 (2)*
O(1′)	3646 (3)	6309 (10)	3988 (17)	2·4 (2)*
O(2′)	4324 (3)	7822 (10)	8016 (16)	2·8 (2)*
O(3′)	4431 (4)	8328 (10)	3758 (20)	3·9 (2)*
C(1′)	3695 (5)	6983 (14)	5873 (25)	2·5 (3)
C(2′)	4211 (5)	6860 (13)	6570 (23)	1·9 (3)
C(3′)	4443 (5)	7019 (14)	4269 (27)	2·1 (3)
C(4′)	4105 (5)	6336 (14)	2887 (25)	2·3 (3)
C(5′)	4216 (5)	4997 (17)	2347 (28)	3·3 (4)
N(1)	2683 (3)	7221 (11)	12581 (18)	1·6 (2)
C(2)	2916 (4)	8140 (13)	11544 (22)	2·0 (3)
N(3)	3183 (4)	7962 (11)	9754 (18)	1·8 (2)
C(4)	3169 (5)	6757 (12)	9256 (23)	1·6 (2)
C(5)	2965 (5)	5750 (14)	10192 (22)	1·8 (3)
C(6)	2694 (5)	5983 (14)	12019 (26)	2·0 (3)
N(6)	2450 (4)	5113 (12)	13098 (21)	2·6 (3)
N(7)	3057 (4)	4583 (12)	9204 (23)	3·1 (3)
C(8)	3326 (5)	4933 (15)	7475 (24)	2·2 (3)
N(9)	3389 (4)	6248 (11)	7499 (19)	1·8 (2)
O(*W*1)	87 (9)	5005 (39)	9367 (31)	4·8 (6)
O(*W*12)	5095 (7)	9769 (21)	6002 (30)	3·5 (5)
O(*W*2)	5146 (3)	6963 (11)	9244 (18)	4·4 (2)

Table 2. *Intramolecular bond distances* (Å)

E.s.d.'s are 0·01 Å for the bond distances around phosphates and 0·02 Å for the other bonds.

N(1)–C(2)	1·34	C(2′)–C(3′)	1·61
N(1)–C(6)	1·34	C(3′)–O(3′)	1·41
C(2)–N(3)	1·38	C(3′)–C(4′)	1·48
N(3)–C(4)	1·23	C(4′)–O(1′)	1·48
C(4)–C(5)	1·34	C(4′)–C(5′)	1·48
C(4)–N(9)	1·38	C(5′)–O(5′)	1·44
C(5)–C(6)	1·41	O(5′)–P(1)	1·59
C(5)–N(7)	1·40	P(1)–O(11)	1·53
C(6)–N(6)	1·33	P(1)–O(13)	1·50
N(7)–C(8)	1·38	P(1)–O(6′)	1·65
C(8)–N(9)	1·40	O(6′)–P(2)	1·60
N(9)–C(1′)	1·55	P(2)–O(21)	1·52
C(1′)–O(1′)	1·39	P(2)–O(22)	1·43
C(1′)–C(2′)	1·54	P(2)–O(23)	1·57
C(2′)–O(2′)	1·40		

Fully ionized ADP contains three negative charges located on the pyrophosphate moiety. Under crystallization conditions around pH 4, it is expected that N(1) of the adenine ring (p*K* = 3·93) and the pyrophosphate (p*K* = 6·83) are protonated (Metzler, 1977). From geometrical data described later we deduce that protons are attached to N(1) and to O(23) (Fig. 3), the third negative charge being compensated by the K$^+$ cation. This KADP salt crystallizes as the dihydrate while the

Table 3. *Bond angles* (°)

E.s.d.'s are 0·6° for the bond angles around the P atoms and 1·2° for the other angles.

C(2)–N(1)–C(6)	123	O(2′)–C(2′)–C(3′)	115
N(1)–C(2)–N(3)	125	C(1′)–C(2′)–C(3′)	97
C(2)–N(3)–C(4)	108	O(3′)–C(3′)–C(2′)	107
N(3)–C(4)–C(5)	132	O(3′)–C(3′)–C(4′)	109
N(3)–C(4)–N(9)	124	C(2′)–C(3′)–C(4′)	103
C(5)–C(4)–N(9)	104	O(1′)–C(4′)–C(3′)	108
C(4)–C(5)–C(6)	118	O(1′)–C(4′)–C(5′)	106
C(4)–C(5)–N(7)	114	C(3′)–C(4′)–C(5′)	117
C(6)–C(5)–N(7)	128	O(5′)–C(5′)–C(4′)	113
N(1)–C(6)–C(5)	113	O(11)–P(1)–O(13)	118·6
N(1)–C(6)–N(6)	121	O(11)–P(1)–O(5′)	113·1
C(5)–C(6)–N(6)	126	O(13)–P(1)–O(5′)	108·1
C(5)–N(7)–C(8)	103	O(6′)–P(1)–O(11)	108·5
N(7)–C(8)–N(9)	109	O(6′)–P(1)–O(13)	109·1
C(4)–N(9)–C(8)	109	O(6′)–P(1)–O(5′)	97·2
C(1′)–N(9)–C(4)	127	P(1)–O(6′)–P(2)	130·6
C(1′)–N(9)–C(8)	124	O(21)–P(2)–O(22)	117·9
C(1′)–O(1′)–C(4′)	108	O(21)–P(2)–O(23)	109·6
O(1′)–C(1′)–C(2′)	107	O(21)–P(2)–O(6′)	103·9
O(1′)–C(1′)–N(9)	105	O(22)–P(2)–O(23)	107·6
C(2′)–C(1′)–N(9)	108	O(22)–P(2)–O(6′)	113·5
O(2′)–C(2′)–C(1′)	110	O(23)–P(2)–O(6′)	103·4
		C(5′)–O(5′)–P(1)	123·2

Table 4. *Selected torsion angles* (°) *in the ADP molecule*

Sugar	
O(1′)–C(1′)–C(2′)–C(3′)	41 (1)
C(1′)–C(2′)–C(3′)–C(4′)	−37 (1)
C(2′)–C(3′)–C(4′)–O(1′)	23 (1)
C(3′)–C(4′)–O(1′)–C(1′)	3 (2)
C(4′)–O(1′)–C(1′)–C(2′)	−29 (1)
O(2′)–C(2′)–C(3′)–O(3′)	−39 (2)
O(1′)–C(1′)–N(9)–C(8)	33 (2)
O(1′)–C(1′)–N(9)–C(4)	−91 (1)
O(1′)–C(4′)–C(5′)–O(5′)	−63 (2)
C(3′)–C(4′)–C(5′)–O(5′)	57 (2)
Pyrophosphate	
C(4′)–C(5′)–O(5′)–P(1)	148 (1)
C(5′)–O(5′)–P(1)–O(6′)	−66 (1)
C(5′)–O(5′)–P(1)–O(11)	47 (1)
C(5′)–O(5′)–P(1)–O(13)	−179 (1)
O(5′)–P(1)–O(6′)–P(2)	158 (1)
P(1)–O(6′)–P(2)–O(21)	166 (1)
P(1)–O(6′)–P(2)–O(22)	37 (1)
P(1)–O(6′)–P(2)–O(23)	−80 (1)

Pseudorotation parameters: $P = 157°$, $\tau_{max} = 42°$.

Table 5. *The shorter intermolecular contacts* (Å) (*e.s.d.'s* 0·02 Å)

K···O(11^{i})	2·73	O(11)···O($W1^{iv}$)	3·20
O(13^{ii})	3·14	O($W1^{iii}$)	2·88
O(22^{i})	3·20	O($W2^{vii}$)	2·66
O(23^{i})	2·97	O(13)···O($W12^{viii}$)	2·81
O($2'^{iii}$)	2·84	O($W2^{viii}$)	2·73
N(3^{iii})	3·15	O(2′)···N(9)	3·15
O($W1^{iv}$)	2·80	O(W12)	3·26
O(21)···N(1^{iii})	2·66	O(W2)	2·63
N(6^{iv})	2·76	O(3′)···O($W1^{ix}$)	3·23
O(22)···N(6^{iii})	2·96	O($W1^{x}$)	2·98
O(23)···N(1^{v})	3·25	O(W12)	2·81
N(7^{iv})	2·78	O(W1)···O($W12^{xi}$)	3·40
		O($W12^{iii}$)	3·44

Symmetry code

None	x,y,z	(vi)	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
(i)	$\frac{1}{2}-x, \frac{1}{2}+y, -z$	(vii)	$1-x, 1-y, -1+z$
(ii)	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$	(viii)	$1-x, 1-y, z$
(iii)	$\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$	(ix)	$\frac{1}{2}+x, \frac{3}{2}-y, 1-z$
(iv)	$x, y, -1+z$	(x)	$\frac{1}{2}+x, \frac{1}{2}+y, 1-z$
(v)	$\frac{1}{2}-x, -\frac{1}{2}+y, -z$	(xi)	$-\frac{1}{2}+x, \frac{3}{2}-y, 1-z$

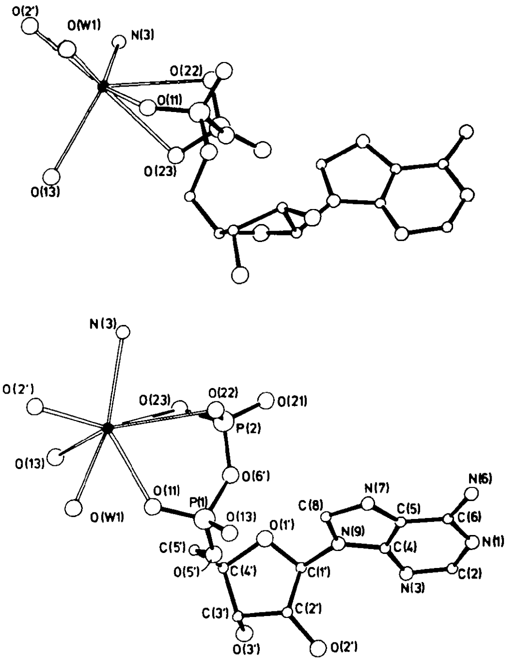

Fig. 1. Two views, at 90° to each other, of ADP with coordinated K^+. Top, projection along the C(1′)–O(1′)–C(4′) plane; bottom, projection on this plane. Covalent bonds are drawn as solid lines, coordinative bonds < 3·20 Å as open lines. Circles in increasing size represent C, N, O; K^+ is marked by a filled circle.

isomorphous RbADP salt contains only one formula unit of H_2O (Viswamitra *et al.*, 1976).

In the following the structure of KADP.$2H_2O$ is described and compared with ADP in the free-acid form (Viswamitra & Hosur, 1977), in RbADP.H_2O (Viswamitra *et al.*, 1976), in the ADP fragments of LiNAD$^+$.$2H_2O$ (Saenger, Reddy, Mühlegger & Weimann, 1977) and $Na_2ATP.12H_2O$ (Kennard *et al.*, 1971). Further, the geometries of the pyrophosphate groups of these ADP molecules will be described together with those in CDP, CDP–choline (Viswamitra, Seshadri, Post & Kennard, 1975) and $K_2UDP.3H_2O$ (Viswamitra, Post & Kennard, 1979).

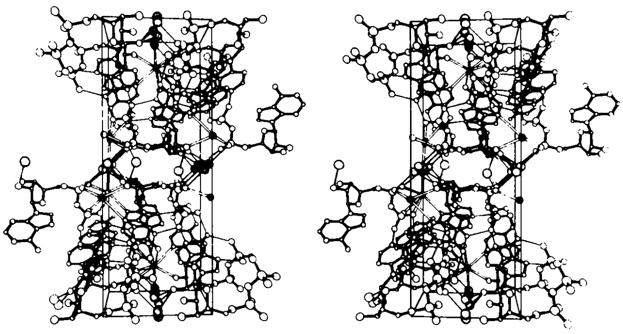

Fig. 2. Stereoplot of the unit cell (Johnson, 1965) viewed along **c**. Coordinative and hydrogen-bonding contacts are drawn with single lines, K^+ cations are indicated by filled circles and water molecules by stippling.

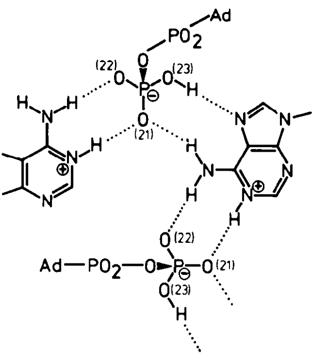

Fig. 3. A schematic drawing explaining the hydrogen-bonding scheme between terminal ADP phosphate groups and adenine heterocycles.

In KADP.$2H_2O$, the adenine heterocycle is *anti* to the ribose with torsion angle χ_{CN} = 33 (2)°, the ribose is in a C(2′)-*endo* envelope conformation with C(2′) 0·66 (1) Å out of the least-squares plane of the other four ring atoms which are coplanar within 0·14 (1) Å. A similar ribose puckering was observed in RbADP, in K_2UDP, in the ADP portion of LiNAD$^+$ while the free acids of ADP and ATP display the C(3′)-*endo* puckering mode (Table 6). As in all other naturally occurring ribonucleoside mono-, di- and triphosphates, the orientation about the C(4′)–C(5′) bond is *gauche,gauche* with φ_{OO}[O(1′)–C(4′)–C(5′)–O(5′)] = −63 (2)° and φ_{OC}[C(3′)–C(4′)–C(5′)–O(5′)] = 58 (2)°.

Two observations indicate that N(1) is protonated. First, the C(6)–N(1)–C(2) angle, 123 (1)° (Table 3), is significantly wider than the 118·6° found for a large number of unprotonated adenine heterocycles but

Table 6. *Comparison of bond lengths* (Å) *and angles* (°) *in pyrophosphate chains*

E.s.d.'s are in parentheses.

	KADP (*a*)	RbADP (*b*)	ADP (*c*)	K_2UDP (*d*)		Na_2ATP (*e*)		LiNAD$^+$ (*f*)	CDP (*g*)	NaCDP–choline (*g*)
				Mol. *A*	Mol. *B*	Mol. *A*	Mol. *B*			
P(1)–O(6′)	1·65 (1)	1·64 (2)	1·60	1·617 (8)	1·597 (9)	1·52 (4)	1·54 (4)	1·56 (1)	1·58	1·60
P(2)–O(6′)	1·60 (1)	1·54 (2)	1·61	1·566 (7)	1·572 (9)	1·73 (4)	1·70 (4)	1·66 (1)	1·62	1·65
P(1)–O(6′)–P(2)	130·6 (7)	135 (1)	–	129·6 (5)	133·7 (5)	132 (2)	136 (2)	133 (1)	127·8	131·7

Comparison of some torsion angles (°)

	KADP (*a*)	RbADP (*b*)	ADP (*c*)	K_2UDP (*d*)		Na_2ATP (*e*)		LiNAD$^+$ (*f*) (adenosine part)	CDP (*g*)	NaCDP–choline (*g*)	5′AMP (*h*)
				Mol. *A*	Mol. *B*	Mol. *A*	Mol. *B*				
O(1′)–C(1′)–N(9)–C(8)	33	40·3	25·0	45·33	41·29	69	39	52	22·9	60·4	26
O(1′)–C(4′)–C(5′)–O(5′)	−63	−63·3	−65·9	−66·48	−65·17	−48	−58	−70	−60·2	−63·6	–
C(3′)–C(4′)–C(5′)–O(5′)	58	57·0	59·1	52·29	53·98	67	49	47	55·9	57·4	40
C(4′)–C(5′)–O(5′)–P(1)	148	147·1	–	172·35	176·51	224	224	163	–	–	177
O(5′)–P(1)–O(6′)–P(2)	158	–	–	−155·95	−121·22	164	−69	133	–	–	–
Range of e.s.d.'s	0·9–1·7°	1°	–	0·05–0·15°		5°		1°	–	–	–

References: (*a*) This study, (*b*) Viswamitra *et al.* (1976), (*c*) Viswamitra & Hosur (1977), (*d*) Viswamitra *et al.* (1979), (*e*) Kennard *et al.* (1971), (*f*) Saenger *et al.* (1977), (*g*) Viswamitra *et al.* (1975), (*h*) Kraut & Jensen (1963).

corresponds to the 123° derived for protonated adenine (Voet & Rich, 1970). Second, the N(1)···O(21) distance, 2·66 (2) Å (Table 5), indicates a hydrogen bond between these two groups which can only be of the N(1)H···O(22) type because O(22) is not protonated (see below).

The pyrophosphate group displays a staggered conformation with torsion angle O(5′)–P(1)–O(6′)–P(2), 158 (1)°, in the *trans* range (Table 4). The same conformational range was observed in some other diphosphates and in one of the two ATP molecules within the crystallographic asymmetric unit (Table 6) but in other pyrophosphate molecules, deviations in *gauche* ranges and even eclipsed conformations can occur as well (Saenger *et al.*, 1977). These data suggest that the pyrophosphate group is rather flexible and that it can adjust its geometry to the requirements of enzyme active sites interacting with it.

Of particular interest is the geometry within the pyrophosphate group. The P(1)–O(6′) and P(2)–O(6′) distances, 1·65 (1) and 1·60 (1) Å, deviate significantly from each other, and the P(1)–O(6′)–P(2) angle, 130·6 (6)°, is rather obtuse, as found in other pyrophosphate groups (Table 6). It is striking to find that in ADP itself both P–O distances are about equal, that in the isomorphous KADP and RbADP structures as well as in K_2UDP P(1)–O(6′) > P(2)–O(6′) and that in the other compounds listed in Table 6 P(1)–O(6′) < P(2)–O(6′). As there is no obvious correlation between molecular structures and P–O bond lengths, an explanation for this finding must be postponed until more data and/or theoretical calculations give a clear picture.

From the P–O distances to unesterified oxygens and from P–O···N or P–O···O distances, one can deduce that O(23) is protonated: P–O(23), 1·57 (1) Å, is the longest of all these P–O distances (Table 2) and O(23)···N(7), 2·78 (1) Å (Table 5), suggests the presence of an O(23)–H···N(7) hydrogen bond.

Alkali and alkaline-earth metal complexes with nucleic acid constituents exhibit three types of metal ion···hetero atom coordination: metal–base, metal–ribose and metal–phosphate (Swaminathan & Sundaralingam, 1979). From the ionic radius of K^+, 1·33 Å, and the atomic radii of O, 1·4 Å, and N, 1·5 Å (*Handbook of Chemistry and Physics*, 1971), K···O and K···N distances of 2·73 and 2·83 Å respectively are indicative of coordinative interactions. These criteria are only satisfied by the salt bridge $K^+\cdots{}^-$O(11), 2·73 (1) Å, Table 5, but all the other five nearest atoms to K^+, O(13), O(22), O(2′), N(3) and O(*W*1), are at distances from 2·80 to 3·20 Å and are therefore more loosely coordinated. If we consider all seven neighbours of K^+, then the three types of cation bonding to nucleic acid constituents are observed simultaneously in this crystal structure.

The metal-ion coordination is similar in the isomorphous KADP.$2H_2O$ and RbADP.H_2O crystal structures but some significant differences remain. Thus, Rb^+ is coordinated to both unesterified oxygens of P(1) and to two oxygens of the P(2) phosphate group of one ADP and to N(3) and O(2′) of an adjacent molecule, but not to H_2O. The $Rb^+\cdots$O distances, 2·85 to 3·33 Å, and $Rb^+\cdots$N, 3·19 Å, are comparable to the described $K^+\cdots X$ distances if the larger ionic radius for Rb^+, 1·47 Å, is taken into account. In RbADP.H_2O, the water molecule is hydrogen bonded to O(2′) of one ADP and to P(1) oxygens of a symmetry-related ADP and located approximately in the position of O(*W*2) in

KADP.$2H_2O$ which is similarly hydrogen bonded, Table 5. The additional O(*W*1) found in the latter crystal structure is twofold disordered, the molecule being statistically distributed over sites O(*W*1), O(*W*12) (Table 1). These are located within a cage formed by phosphate P(1), by K^+, ribose and the fully occupied water O(*W*2). The position of the disordered water is vacant in the RbADP.H_2O crystal structure, probably because K^+ with a radius of 1·33 Å is substituted by the larger Rb^+, 1·47 Å. Since this difference, however, is only small compared to the volume filled by the two statistical water sites, it might well be that later refinement locates another molecule of water of crystallization in the Rb^+ complex.

The crystal packing, Fig. 2, is determined by hydrophilic regions filled with K^+, H_2O, ribose phosphate and interspersed hydrophobic regions formed by adenine heterocycles. These are involved in an interesting H-bonding pattern with terminal phosphate groups belonging to two neighbouring, symmetry-related ADP molecules. One of these phosphates accepts two hydrogen bonds from N(1)H and N(6)H, the other accepts one hydrogen bond from N(6)H and donates one hydrogen bond to N(7). Or, *vice versa*, one phosphate group is linked by four hydrogen bonds to two adenine moieties (see the schematic drawing Fig. 3). It should be noted that these N—H···O and O—H···N interactions are not only of the hydrogen-bonding type but contain salt-like contributions due to the negative and positive charges residing in phosphate and adenine groups.

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Note: Following the submission of this paper we learned of a report on the same structure by Swaminathan & Sundaralingam (1980) (following paper). The two independently determined crystal structures of KADP.$2H_2O$ described here (I) and by Swaminathan & Sundaralingam (II) are, in a broad sense, indentical but differ in some details. With reference to individual atomic positions, the two half-occupied water molecules [O(*W*1) and O(*W*12)] are found to be located *near* the diad axis in (I) but on the diad in (II). The results show lower temperature factors for these atoms in (I) (4·8 and 3·5 Å^2) than in (II) (7·91 and 7·88 Å^2), which appears to suggest that, as assumed in (I), these water molecules are in fact located slightly off the diad axis. Otherwise, the atomic coordinates and temperature factors are similar within 3σ but the standard deviations in (I) are generally 25 to 50% higher than in (II). This is due to the better refinement in (II): $R = 6{\cdot}2\%$ and $R_w = 7{\cdot}6\%$ for 1384 observed reflections compared to $R = 12{\cdot}4\%$ and $R_w = 9{\cdot}3\%$ in (I) for all 1726 measured data. As to bond distances they agree in a few cases [N(7)—C(8); C(2)—N(3); N(3)—C(4); N(9)—C(1′)] better in (II) than in (I) with the average values given for protonated adenine by Voet & Rich (1970) but in (I) there also occur some large deviations, *viz.* C(6)—N(6), 1·394 (13) Å [average 1·315 (5) Å] and C(4)—N(9), 1·416 (13) Å [average 1·366 (16) Å]. It is clear that in both crystal structures the limited data sets, having $2\theta_{\max} = 120$ to 127° (Cu $K\alpha$), and the large proportion (about 25%) of weak, unobserved data obtained from only small, needle-shaped crystals have led to structure determinations which are not entirely satisfactory from the point of view of accuracy. In the case of KADP, however, it is not so much the bonding geometry as the conformational and coordination aspects that are of interest, both of which have been evaluated by the two studies.

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