dimensions show that this carboxyl group is partially ionized, although to a lesser extent than that of glycine.

4.5. Salt or molecular complex?

We have noted previously, in discussing the structure of histidinium trimesate (Herbstein & Kapon, 1979), that Johnson & Rumon's (1965) rule applies to that compound and many others, i.e. salts are found when $\Delta pK_a > 3 \cdot 8$ and molecular complexes when $\Delta pK_a < 3 \cdot 8$. In histidine the relevant pK_1 value is that of the imidazole nitrogen (which accepts a proton from one of the TMA carboxyl groups), and the $H_3N^+-CH-COO^-$ zwitterion is not affected by the formation of the salt. In glycine.TMA.H₂O crystals the only possible proton acceptor in the glycine zwitterion is the ionized carboxyl group. TMA is a slightly stronger acid than glycine (pK_1 values, in dilute aqueous solution, are $2 \cdot 12$ and $2 \cdot 34$ respectively) and thus it is not surprising that the proton is shared almost equally between them. If these pK_1 values are relevant in the crystal, then one might expect the proton to be slightly closer to the glycine than to the TMA O atom; the converse is found in practice. The amino acids glycine, alanine, leucine, serine and glutamine all have pK_1 values for their carboxyl groups in the range $2 \cdot 17 - 2 \cdot 36$ (and have no other ionizable groups). Thus, if these amino acids form complexes of analogous type with TMA, we might expect them to have nearly symmetrical hydrogen bonds like those found in glycine.TMA.H₂O.

Glycine.TMA.H₂O can be classified as an acid salt if we take the cation to be the NH_3^+ group of the glycine molecule (present as a zwitterion), while the two anions are the partially ionized carboxyl groups of TMA and glycine, joined by a very short, nearly symmetrical, hydrogen bond.

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Structure of Bisadeninium Dinitrate Monohydrate, $(C_5H_6N_5^+.NO_3^-)_2.H_2O$*†

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Abstract

The title compound, $(C_5H_6N_5^+.NO_3^-)_2.H_2O$, is monoclinic, $P2_1/m$, with $a = 11 \cdot 705$ (2), $b = 6 \cdot 363$ (1), $c = 11 \cdot 280$ (1) Å, $\beta = 104 \cdot 241$ (6)°; $Z = 2$; $D_{calc} = 1 \cdot 690$, $D_{obs} = 1 \cdot 70$ (2) Mg m⁻³. The structure was refined by a full-matrix least-squares method to $R(F) = 0 \cdot 035$ for 1494 nonzero counter data to $0 \cdot 84$ Å. Analytical absorption and isotropic extinction corrections were applied. All hydrogen atoms were located and refined isotropically. E.s.d.'s of bond lengths and bond angles involving C, N, O atoms are $0 \cdot 002$ Å and $0 \cdot 2°$. The bases, and some of the other atoms, lie in the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. The two independent adeninium ions are both protonated at N(1), and are part of an

infinite hydrogen-bonded chain in the **a** direction. The bases are paired through hydrogen bonds, $N(9)H \cdots N(3)$ and $N(6)H \cdots N(7)$, where $N(6)$ is the exocyclic amino nitrogen, as found in some other adenine salts, in some oligonucleotides, and in the acid form of polyadenylic acid. Tautomerism was found to involve the hydrogen atoms of the $N(9)H \cdots N(3)$ bonds, with $N(9) \cdots HN(3)$ in 20% of the sites. Base stacking occurs between one of the two adeninium ions and its screw-related partners.

Introduction

As part of a program of X-ray studies on metal complexes with nucleic acid constituents, we have recently carried out the structural analysis of an adenine–cadium(II) complex (Wei & Jacobson, 1980). As a byproduct of the reaction of monosodium 5'-AMP with cadmium nitrate in the presence of nitric acid, we obtained crystals of unknown structural formula, which were subsequently characterized by X-ray analysis as a hydrated adeninium nitrate of formula $(C_5H_6N_5^+ . NO_3^-)_2 . H_2O$.

Attempts to synthesize the adenine–cadmium(II) complex in large quantity from the reaction of adenine with cadmium nitrate in the presence of nitric acid resulted only in the identical nitrate salt of adenine. In this paper, we present the results of a structural analysis of this bisadeninium dinitrate monohydrate. Several structures of other adenine salts, including adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974a), adenine dihydrochloride (Kisten-macher & Shigematsu, 1974b), adeninium sulfate (Langer & Huml, 1978a), adenine hydrobromide hemihydrate (Langer & Huml, 1978b), adeninium hemisulfate hydrate (Langer, Huml & Lessinger, 1978), and adeninium phosphate (Langer, Huml & Zachová, 1979), have appeared in the literature.

Experimental

Crystals prepared by the following method gave diffraction patterns identical with those of the crystal used in this study. To a solution of 0·209 g of adenine (Calbiochem) in 10 ml of water, 3 ml of an aqueous solution containing 0·476 g of cadmium nitrate was added with stirring (mol ratio 1:1). 150 μl of 2 M HNO_3, added to the mixture, resulted in pH ~2·0, and the content was kept in a water bath (325 K) overnight. After cooling to room temperature (297 K), lath-like crystals were collected by filtration and washed with water at 277 K. 293 mg of the dried title compound was obtained.

Preliminary cell parameters and systematic absences (for $0k0$, $k = 2n + 1$) were determined from Weissen-

Table 1. *Crystal data and intensity collection*

$(C_5H_6N_5^+ . NO_3^-)_2 . H_2O$	$Z = 2$
$M_r = 414.32$	$D_{calc} = 1.690 \text{ Mg m}^{-3}$
Space group $P2_1/m$	$D_{obs} = 1.70 (2)^*$
$a = 11.705 (2)$ Å	$F(000) = 452$
$b = 6.363 (1)$	$\mu(Cu K\alpha) = 1.268 \text{ mm}^{-1}$
$c = 11.280 (1)$	Transmission = 0.822–0.939
$\beta = 104.241 (6)^\circ$	$T = 297$ K
$V = 814.30$ Å^3	
Radiation Cu $K\alpha$	Total background time 24–96 s§
Take-off angle 3°	Number of unique nonzero
Scan type θ–2θ step scan	reflections 1494
2θ limits $1° - 132°$†	Number of reflections used in
2θ step size 0·05°	refinement 1373[‖]
Time per step 2–4 s	Number of variables 220
Scan width 1·6–1·8°‡	Data-to-variables ratio 6·2

* Determined by flotation in mixtures of bromobenzene and xylene.

† In the 130–132° range, only selected strong reflections were measured.

‡ The width of the α_1–α_2 separation was added.

§ Backgrounds were measured at the beginning and end of each scan. The longer times were used for higher 2θ ranges.

‖ Criteria used were $F_o^2 \geq \sigma(F_o^2)$ and $|\Delta F^2| \leq 4\sigma(F_o^2)$.

berg and precession photographs. Twelve strong reflections in the 2θ range of 118 to 129° were centered with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) with Ni-filtered Cu $K\alpha_1$ ($\lambda = 1.54051$ Å) radiation. Cell parameters were refined by the least-squares method. Crystal data are summarized in Table 1.

A colorless crystal with the shape of a four-sided prism of dimensions 0·06 × 0·07 × 0·66 mm was glued on the top of a thin glass fiber and was exposed to air during X-ray intensity data collection. The longest dimension, corresponding to the b axis, was nearly parallel to the φ axis of the diffractometer. The maximum mosaic spread of the crystal was estimated to be 0·6°. The intensities were measured up to a 2θ value of 132° (equivalent to a minimum spacing of 0·84 Å) with Ni-filtered Cu $K\alpha$ radiation at 40 kV and 18 mA, with the total estimated exposure time of 65 h. Intensities of standard reflections fluctuated ±2% during the course of data collection. Details of intensity collection are also given in Table 1. Absorption corrections were made by the method of Busing & Levy (1957). Weights (w) used in the least-squares refinement of the structure [in which some reflections were omitted (see Table 1)] are reciprocals of variances $\sigma^2(F_o^2)$, which were estimated according to the empirical expression given elsewhere (Wei & Einstein, 1978).

Solution and refinement of the structure

At the beginning of the analysis the actual structural formula was unknown. From the crystallographic

information, however, a plausible formula of AMP.$5H_2O$ was initially assumed. A three-dimensional Patterson function, calculated by the use of a fast Fourier program (Levy, 1977), showed that non-Harker sections were essentially flat; peaks were present only at sections $y = 0$ and $\frac{1}{2}$. These facts, plus the observation that the 020 reflection was particularly strong, suggested a layer-like structure in which virtually all atoms lie on planes separated by $\frac{1}{2}$ in the **b** direction. Attempts to locate adenine moieties were not successful, however.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Statistical averages of $|E^2 - 1|$ and $|E|$ were 1·030 and 0·774, corresponding to those for a centrosymmetric crystal [theoretical values for centrosymmetric: 0·968, 0·798; for acentrosymmetric: 0·736, 0·886, respectively (Karle, Dragonette & Brenner, 1965)]. However, in view of a slight degree of C centering, the statistical indications were not considered conclusive, and the space group was initially assumed to be $P2_1$. Calculation of a Wilson plot, in which two adenines and two nitrates were treated as spherically averaged rigid groups, gave an overall temperature factor of 2·8 $Å^2$. There are 209 reflections with $E > 1·49$ that were used for phase generation. Six symbols were required to solve the structure. The E map calculated from the sixth most consistent set of phase combinations gave a plausible solution, in which two adenine moieties were found to have a base-pair hydrogen-bonding configuration similar to that found in polyadenylic acid (Rich, Davies, Crick & Watson, 1961). Starting parameters for the two independent adenine groups were refined initially with a block-diagonal program (local modification of the program of Shiono, 1971) to give the conventional discrepancy index, $R(F)$, of 0·44. Successive difference-Fourier syntheses and least-squares refinements revealed, in addition, two nitrate groups and one water molecule. All atoms except for a pair of nitrate oxygens were found to be nearly coplanar at $y = \frac{1}{4}$. Anisotropic refinement of all 29 heavy atoms resulted in an $R(F)$ value of 0·072. All hydrogen atoms, found from a difference synthesis at their expected positions, were then included in the refinement with isotropic thermal parameters, which further lowered the $R(F)$ value to 0·041. Thus, the correct structural formula was established as $(C_5H_6N_5^+ . NO_3^-)_2 . H_2O$.

Intensity data were reprocessed with the correct linear absorption coefficient, and the refinement on F^2 was continued with the full-matrix least-squares program *ORXFLS4* (Busing, Martin & Levy, 1962). The strong secondary extinction for the 020 reflection was corrected by incorporating an isotropic extinction parameter in the following refinement. It became increasingly evident, from the following observations, that two oxygens of one nitrate group were disordered. The difference synthesis showed peaks approximately

related to O(11) and O(21) by a mirror at $y = \frac{1}{4}$. Furthermore, these oxygens had very large β_{22} thermal parameters, corresponding to root-mean-square displacements along y of 0·45 and 0·52 Å, while the corresponding displacements for 20 adeninium atoms ranged between 0·17 and 0·25 Å. If, on the other hand, the structure was refined in $P2_1/m$, with most atoms, including O(11) and O(21), on the mirror plane at $y = \frac{1}{4}$ (for details, see below), the difference synthesis showed, for each of these oxygens, a negative peak at $y = \frac{1}{4}$ and two mirror-related positive peaks off that plane. Thus, observations in both space groups led to the assumption of disorder in the O(11) and O(21) positions.

Refinement was continued in $P2_1$, with two positions, initially about $\frac{1}{3}$ Å above and below the plane at $y = \frac{1}{4}$, for the disordered oxygen atoms. O(11) above the plane and O(21) below, forming a nitrate group with O(31) and N(1), were constrained to have the same occupancy, m, while O(11′) and O(21′) had occupancies $1 - m$; m was initially 0·5. These nitrate groups were maintained approximately planar by constraints corresponding to the equation: $3y[N(1)] = y[O(11)] + y[O(21)] + y[O(31)]$, and the corresponding equation involving O(11′) and O(21′). Although the $R(F)$ value reached 0·033 for 1416 reflections with $F_o^2 \geq \sigma(F_o^2)$ after three cycles of full-matrix refinement, convergence was still distant, as the matrix was ill-conditioned.*

The assumed space group was then changed to $P2_1/m$, because of the following considerations. (*a*) All the nonhydrogen atoms deviated from the plane at $y = \frac{1}{4}$ by less than 0·05 Å, except for pairs of atoms which were approximately mirror-related by that plane: two pairs of disordered oxygens of one nitrate group, O(22) and O(22′) of the second nitrate, and the two water hydrogens. (*b*) The assumption of the mirror plane would eliminate much correlation between parameters of the disordered oxygens. (*c*) The intensity statistics agreed with the assumption.

Refinement in $P2_1/m$ led rapidly to convergence. In this space group, approximate planarity of the disordered nitrate group was maintained by the constraint: $y[O(11)] = \frac{1}{2} - y[O(21)]$. In a difference synthesis calculated at this stage, the two highest peaks (0·22 and 0·19 e $Å^{-3}$) were in appropriate positions for hydrogens attached to N(3)'s of the two adeniniums, indicating possible tautomerism of the type N(9)H···N(3) ⇌ N(9)···HN(3).† In order to test this

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hypothesis, refinement was continued with partially occupied hydrogens, H(91) and H(92) at N(9) sites, and H(31) and H(32) at N(3) sites. The positional parameters for H(31) and H(32), as obtained from the difference synthesis, were not varied, whereas those of H(91) and H(92) were varied. The multiplicities, m, of H(91) and H(92) were constrained to be equal, and those of H(31) and H(32) to be $\frac{1}{2} - m$. The temperature factors of these four H atoms were constrained to be equal. Thus, with the addition of one occupancy and the deletion of one temperature factor, the number of varied parameters remained the same. The refinement converged with $m = 0.40$ (1) [equivalent to 80% occupancy for the major sites, H(91) and H(92)]. For the two refinements (with and without tautomerism), we may compare the resulting values of $R(F)$, $R(F^2)$ and $R_w(F^2)$ [defined as $(\sum w|F_o^2 - sF_c^2|^2/\sum wF_o^4)^{1/2}$,

where s is the scale factor] for 1416 reflections with $F_o^2 \geq \sigma(F_o^2)$: 0.0326, 0.0354 and 0.0993 for the former and 0.0335, 0.0383 and 0.1031 for the latter. The assumption of tautomerism was therefore accepted.[*] At the end of refinement with this model, $R(F)$, $R(F^2)$ and $R_w(F^2)$ had values of 0.029, 0.033 and 0.074, respectively, for 1373 reflections with $F_o^2 \geq \sigma(F_o^2)$ and $|F_o^2 - sF_c^2| \leq 4\sigma(F_o^2)$, used in the refinement. For all 1494 nonzero reflections, the $R(F)$ value was 0.035. Parameter shifts for the nonhydrogen atoms in the last cycle of the refinement were all less than 2% of the corresponding estimated standard deviations (e.s.d.'s), whereas the maximum shift in the H parameters [for H(12)] was 5% of the corresponding e.s.d. A final difference synthesis showed peaks ranging from 0.17 to -0.20 e Å^{-3}. Scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C, N and O; Stewart, Davidson & Simpson (1965) for H.

The atomic positional parameters from the last cycle of refinement are given in Table 2 for nonhydrogen atoms and in Table 3 for H atoms (positional and isotropic thermal parameters). The anisotropic thermal parameter terms β_{12} and β_{23} were constrained to be zero

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[*] The Hamilton (1964) R-factor test cannot be applied, since the number of variables was the same for the two refinements. As an indication of the significance of the ratio, 1.038, for $R_w(F^2)$, we note that the hypothesis that no tautomerism exists could have been rejected at the 0.001 confidence level even if 52 additional parameters had been varied in the tautomeric model. With 1416 observations and 220 varied parameters, there are 1196 degrees of freedom, and $\mathscr{R}_{52,1196,0.001} = 1.037$ (Pawley, 1970).

Table 2. *Positional* $(\times 10^4)$ *and equivalent isotropic thermal parameters* (Å^2) *for nonhydrogen atoms*

The e.s.d.'s of the least significant figures are given in parentheses in all tables and in the text. For all atoms, $y = \frac{1}{4}$, except for O(11), O(21) and O(22), for which $y = 0.3006$ (4), 0.1994 (4) and 0.4168 (3), respectively. Equivalent isotropic thermal parameters were calculated from the corresponding anisotropic thermal parameters and unit-cell parameters by the relation $B = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$ (Hamilton, 1959).

(*a*) Adeninium ions

	x	z	B
N(11)	−70 (1)	8329 (1)	3.3
C(21)	994 (2)	8066 (2)	3.7
N(31)	1165 (1)	6967 (1)	3.2
C(41)	144 (1)	6087 (2)	2.7
C(51)	−990 (1)	6264 (1)	2.7
C(61)	−1117 (1)	7470 (1)	2.8
N(61)	−2121 (1)	7793 (2)	3.3
N(71)	−1812 (1)	5162 (1)	2.8
C(81)	−1178 (2)	4353 (1)	3.0
N(91)	8 (1)	4865 (1)	2.7
N(12)	3759 (1)	3014 (1)	2.7
C(22)	2653 (2)	3207 (2)	3.0
N(32)	2412 (1)	4274 (1)	3.0
C(42)	3404 (1)	5206 (1)	2.7
C(52)	4559 (1)	5112 (1)	2.6
C(62)	4761 (1)	3934 (2)	2.6
N(62)	5801 (1)	3687 (1)	3.0
N(72)	5329 (1)	6262 (1)	2.7
C(82)	4624 (2)	7005 (2)	2.9
N(92)	3462 (1)	6420 (1)	2.8

(*b*) Nitrate ions and water

	x	z	B
N(1)	−249 (1)	1217 (1)	3.6
O(11)	579 (2)	779 (1)	4.4
O(21)	−1193 (2)	521 (2)	7.1
O(31)	−102 (1)	2330 (1)	5.7
N(2)	6411 (1)	780 (1)	4.1
O(22)	6453 (1)	1337 (1)	7.3
O(32)	6300 (1)	−339 (1)	6.2
W	3617 (2)	618 (2)	5.3

Table 3. *Positional* $(\times 10^3)$ *and isotropic thermal parameters* (Å^2) *for hydrogen atoms*

For all atoms, $y = \frac{1}{4}$, except for H(W) [$y = 0.347$ (4)]. The positional parameters of H(31) and H(32) were not adjusted (see text). The temperature factors of H(91), H(92), H(31) and H(32) were constrained to be equal.

(*a*) Adeninium ions

	x	z	B
H(11)	−1 (2)	913 (2)	4.1 (5)
H(21)	168 (2)	873 (2)	4.9 (5)
H(31)	180	693	2.2 (3)
H(61a)	−285 (2)	721 (2)	4.0 (5)
H(61b)	−218 (2)	848 (3)	5.0 (6)
H(81)	−151 (2)	353 (2)	2.9 (4)
H(91)	52 (2)	450 (2)	2.2 (3)
H(12)	383 (2)	228 (2)	4.0 (5)
H(22)	202 (2)	243 (2)	3.3 (4)
H(32)	180	444	2.2 (3)
H(62a)	646 (2)	433 (2)	3.7 (5)
H(62b)	592 (2)	296 (2)	3.6 (4)
H(82)	490 (2)	786 (2)	3.6 (4)
H(92)	291 (2)	673 (2)	2.2 (3)

(*b*) Water

	x	z	B
H(W)	374 (2)	19 (2)	9.2 (8)

by symmetry (Peterse & Palm, 1966) for nonhydrogen atoms at the special position.*

Discussion

The reaction of neutral adenine with acids yields the monoprotonated cation, in which the proton is found to be at the N(1) site. This has been demonstrated by three-dimensional X-ray studies of several inorganic salts of adenine, including adenine hydrochloride hemihydrate, $(C_5H_6N_5^+ . Cl^-).0 \cdot 5H_2O$ (Kistenmacher & Shigematsu, 1974a), adenine hydrobromide hemihydrate, $(C_5H_6N_5^+ . Br^-).0 \cdot 5H_2O$ (Langer & Huml, 1978b), adeninium hemisulfate hydrate, $(C_5H_6N_5^+ . HSO_4^-). H_2O$ (Langer, Huml & Lessinger, 1978) and adeninium phosphate, $C_5H_6N_5^+ . H_2PO_4^-$ (Langer, Huml & Zachová, 1979).

The adenine fused-ring system in the crystalline state is not required to be perfectly planar (Voet & Rich, 1970). In this investigation, however, the adeniniums were assumed to lie on a crystallographic mirror plane. Similar situations have previously been encountered in cases of adenine dihydrochloride (Kistenmacher & Shigematsu, 1974b), 7-methyladenine dihydrochloride (Kistenmacher & Shigematsu, 1975), and tetraaqua-bis(9-methyladenine)copper(II) dichloride dihydrate (Sletten & Ruud, 1975). In this structure, however, two nitrate oxygen atoms O(11) and O(21) are disordered with respect to the mirror plane, and O(22) and H(W) atoms are mirror-related to the corresponding partner atoms, thus destroying the perfect layer structure. Still,

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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 35590 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
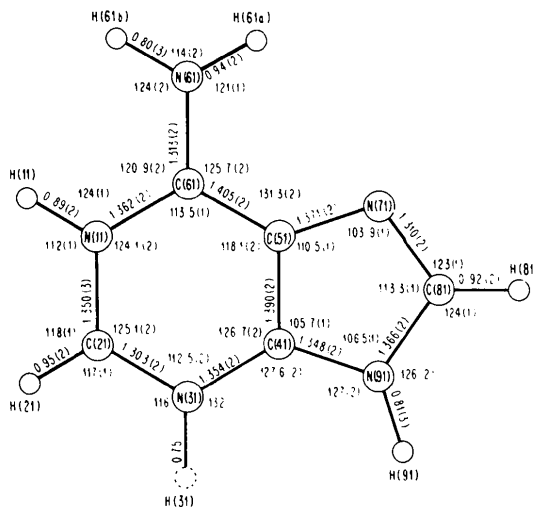
most of the atoms are on the mirror plane, resulting in the particularly strong intensity for the 020 reflection.

The numbering scheme of the adeninium ions is shown in Fig. 1, and that of the nitrate ions and water in Fig. 2. Bond lengths, bond angles, and their corresponding e.s.d.'s were calculated by the program $ORFFE4$ (Busing, Martin & Levy, 1964), and are also given in the figures. These bond lengths and bond angles differ negligibly from the corresponding parameters obtained from refinement of a model in which no tautomerism was assumed. For nonhydrogen atoms, the largest difference was 0·003 Å for a bond distance and 0·2° for a bond angle. The average differences were 0·001 Å and 0·1°.

Only a few of the bond lengths and angles differ significantly in the two independent adeniniums (Fig. 1). The N(1)—C(2) distances differ by 0·015 Å or 4·4 e.s.d.'s (for the difference). The C(5)—N(7) distances differ by 0·014 Å or 4·7 e.s.d.'s. The former difference
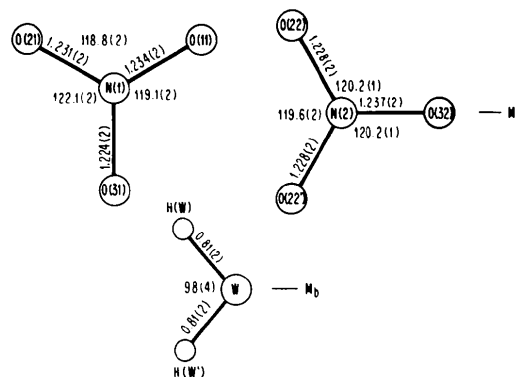

Fig. 2. Molecular parameters of nitrate ions and water molecule. Atoms with primed symbols are related to the corresponding atoms with unprimed symbols by a crystallographic mirror plane at $y = \frac{1}{4}$.
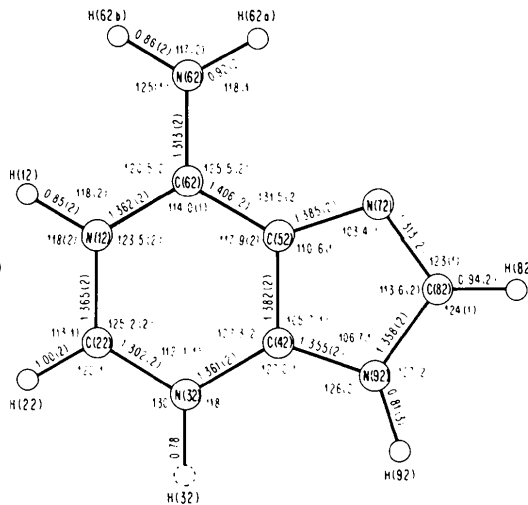

Fig. 1. Numbering scheme with bond lengths (Å) and bond angles (°) for adeninium ions. Atoms shown by dashes represent the minor H sites.

Table 4. *Comparison of bond lengths* (Å) *and angles* (°) *for* N(1)-*protonated adenine*

	(a)	(b)	(c)	(d)	(e)	Average
N(1)–C(2)	1·374	1·371	1·359, 1·352	1·351	1·350, 1·365	1·360
C(2)–N(3)	1·289	1·309	1·314, 1·309	1·306	1·303, 1·302	1·305
N(3)–C(4)	1·358	1·363	1·364, 1·363	1·370	1·354, 1·361	1·362
C(4)–C(5)	1·377	1·378	1·378, 1·374	1·364	1·390, 1·382	1·378
C(5)–C(6)	1·403	1·408	1·408, 1·415	1·429	1·405, 1·406	1·411
C(6)–N(1)	1·360	1·366	1·371, 1·389	1·366	1·362, 1·362	1·368
C(6)–N(6)	1·311	1·311	1·309, 1·304	1·305	1·313, 1·313	1·309
C(5)–N(7)	1·377	1·382	1·395, 1·388	1·378	1·371, 1·385	1·382
N(7)–C(8)	1·320	1·316	1·324, 1·314	1·305	1·310, 1·313	1·315
C(8)–N(9)	1·351	1·355	1·366, 1·363	1·355	1·366, 1·358	1·359
N(9)–C(4)	1·360	1·357	1·364, 1·365	1·357	1·348, 1·355	1·358
N(1)–C(2)–N(3)	125·1	124·6	125·5, 126·1	126·0	125·1, 125·2	125·4
C(2)–N(3)–C(4)	112·0	111·8	112·3, 112·2	111·6	112·5, 112·1	112·1
N(3)–C(4)–C(5)	127·8	127·8	126·4, 126·8	127·6	126·7, 127·3	127·2
C(4)–C(5)–C(6)	117·7	118·3	119·0, 118·9	118·0	118·1, 117·9	118·3
C(5)–C(6)–N(1)	113·8	113·2	113·6, 113·2	113·3	113·5, 114·0	113·5
C(6)–N(1)–C(2)	123·5	124·3	123·2, 122·8	123·6	124·1, 123·5	123·6
N(1)–C(6)–N(6)	120·8	121·2	119·6, 120·9	120·7	120·9, 120·5	120·7
C(5)–C(6)–N(6)	125·5	125·6	126·8, 125·9	126·0	125·7, 125·5	125·9
C(4)–C(5)–N(7)	111·3	110·8	110·6, 110·9	111·0	110·5, 110·6	110·8
C(5)–N(7)–C(8)	103·1	103·3	103·5, 103·6	103·5	103·9, 103·4	103·5
N(7)–C(8)–N(9)	113·6	113·6	113·1, 113·3	113·5	113·3, 113·6	113·4
C(8)–N(9)–C(4)	106·8	106·6	107·1, 106·6	106·4	106·5, 106·7	106·7
N(9)–C(4)–C(5)	105·2	105·7	105·7, 105·6	105·7	105·7, 105·7	105·6
N(3)–C(4)–N(9)	126·9	126·5	127·9, 127·6	126·7	127·6, 127·0	127·2
C(6)–C(5)–N(7)	131·0	130·9	130·4, 130·2	131·1	131·3, 131·5	130·9

References: (*a*) Adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974*a*); e.s.d.'s 0·004 Å for bond lengths, 0·2° for bond angles. (*b*) Adenine hydrobromide hemihydrate (Langer & Huml, 1978*b*); e.s.d.'s 0·004 Å, 0·3°. (*c*) Adeninium hemisulfate hydrate (Langer, Huml & Lessinger, 1978); e.s.d.'s 0·004 Å, 0·3°. (*d*) Adeninium phosphate (Langer, Huml & Zachová, 1979); e.s.d.'s 0·005 Å, 0·4°. (*e*) This work; e.s.d.'s 0·002 Å, 0·2°.

might possibly have arisen because of the different chemical environments of N(11) and N(12), and C(21) and C(22) (see below), but no such explanation could apply to the second case. Since this structure has two independent adeniniums, both protonated at N(1), a comparison of bond lengths and bond angles with those of other N(1)-protonated adeniniums of different salts, determined with sufficient accuracy, is summarized in Table 4. It can be seen that the molecular parameters of adenine frameworks for these five different salts agree well in every detail. Despite the existence of a disordered nitrate ion and the observed tautomerism involving base–base hydrogen bondings, molecular parameters of our present structure are in accord with the corresponding average values within 0·012 Å in bond lengths and 0·6° in bond angles. The average deviation of all the bond lengths from the corresponding mean values is 0·005 Å, and that of bond angles is 0·2°.

Internal bond angles at purine-ring N atoms increase by the order of 5° with protonation (Ringertz, 1972). The angles at N(3) of the present compound and all others in Table 4 agree well with the average value, 112·6°, for an unprotonated N(3). The angles at N(9), listed in Table 4, are all between 106·4 and 107·1°, toward the lower end of the range, 105–111°, for a

protonated N(9). No discernible difference exists, between the present structure and the others in Table 4, in the N(3) and N(9) bond angles, as might have been expected for a partial proton shift from N(9) to N(3). We cannot explain this discrepancy. A neutron diffraction analysis could resolve the question of tautomerism. The effect of protonation at N(1) sites is reflected, as in all other cases, in the characteristic increase in the internal angles.

The molecular parameters for the two nitrate groups are in the expected ranges. Least-squares-plane calculations show that the disordered nitrate ion [associated with N(1)], to which a constraint roughly corresponding to planarity was applied, is planar within 0·003 (1) Å, and the second nitrate ion within 0·009 (2) Å.

Tautomerism involving N(91)H···N(32) ⇌ N(91)···HN(32) and N(31)···HN(92) ⇌ N(31)H···N(92), as derived from X-ray evidence, is shown in Fig. 3. Base pairing involving the major H sites (80% occupancy), H(91) and H(92), is shown in (*a*), and that involving the minor H sites (20% occupancy), H(31) and H(32), is given in (*b*). Since the N(3) site of adenine is known to be least basic relative to protonation, the protonation at the N(3) site appears unusual. This mode of base pairing, N(3)···N(9), has
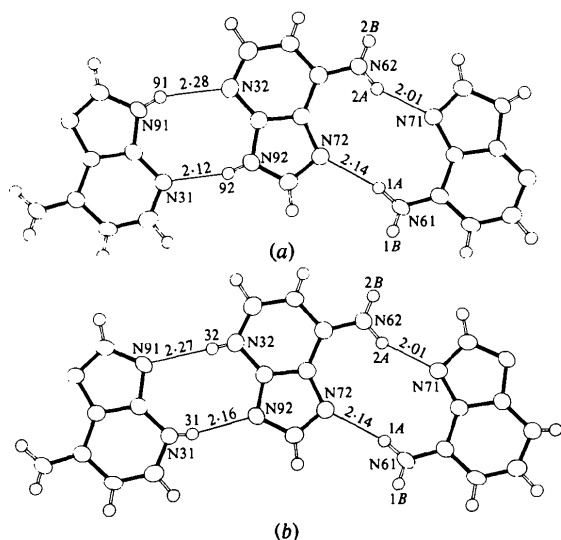
Fig. 3. Scheme of base pairings. The major N(9)H···N(3) base pairing (80% occupancy) is shown in (a), and the minor H(9)···HN(3) base pairing (20% occupancy) is given in (b). Another mode of base pairing N(6)H···N(7) can be seen on the opposite side of each adeninium ion. Figures with thermal ellipsoids were prepared with ORTEP-II (Johnson, 1976).

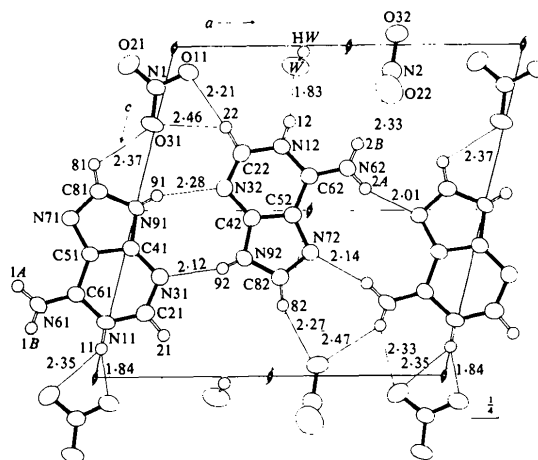

Fig. 4. Two-dimensional projection in the y direction of the structure at $y = \frac{1}{4}$. Hydrogen bonds are shown by solid lines, but those involving H(W) are not shown (see Table 5).

Table 5. Hydrogen bonds (A—H···B)

The criterion for inclusion in this table was that H···B < 2·6 Å. E.s.d.'s, except for bonds involving H(31) and H(32), are of the order of: A···B 0·002 Å; A—H and H···B 0·02 Å; $\angle A$ H···B 2°.

Symmetry code: (i) $x, y, 1 + z$; (ii) x, y, z; (iii) $-1 + x, y, z$; (iv) $-1 + x, y, 1 + z$; (v) $1 + x, y, z$; (vi) $1 - x, 1 - y, -z$.

A	H	B	A···B (Å)	A—H (Å)	H···B (Å)	$\angle A$—H···B (°)
N(11)	H(11)	O(11^i)	2·699	0·89	1·84	160
N(11)	H(11)	O(21^i)	3·089	0·89	2·35	140
N(31)	H(31)	N(92^{ii})	2·903	0·75	2·16	168
N(61)	H(61a)	N(72^{iii})	3·059	0·94	2·14	166
N(61)	H(61b)	O(21^i)	3·018	0·80	2·33	146
N(61)	H(61b)	O(32^{iv})	3·126	0·80	2·47	140
C(81)	H(81)	O(31^{ii})	2·864	0·92	2·37	114
N(91)	H(91)	N(32^{ii})	3·047	0·81	2·28	157
N(12)	H(12)	W^{ii}	2·667	0·85	1·83	167
C(22)	H(22)	O(11^{ii})	3·198	1·00	2·21	171
C(22)	H(22)	O(31^{ii})	3·133	1·00	2·46	124
N(32)	H(32)	N(91^{ii})	3·047	0·78	2·27	178
N(62)	H(62a)	N(71^v)	2·879	0·92	2·01	157
N(62)	H(62b)	O(22^{ii})	3·120	0·86	2·33	152
C(82)	H(82)	O(32^i)	3·153	0·94	2·27	156
N(92)	H(92)	N(31^{ii})	2·903	0·81	2·12	163
W	H(W)	O(22^{vi})	3·045	0·81	2·26	162
W	H(W)	O(32^{vi})	3·201	0·81	2·57	135

been observed in adeninium hemisulfate hydrate (Langer, Huml & Lessinger, 1978) and adeninium phosphate (Langer, Huml & Zachová, 1979). Fig. 3 also exhibits the second mode of base pairing, N(61)H···N(72) and N(62)H···N(71), which has been found previously in the structures of adenine dihydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974a), adenine hydrobromide hemihydrate (Langer & Huml, 1978b), adeninium hemisulfate hydrate (Langer, Huml & Lessinger, 1978), polyadenylic acid (Rich, Davies, Crick & Watson, 1961), more refined models of two pH-dependent double helical forms of polyriboadenylic acid (Finch & Klug, 1969), CpA, a dinucleoside monophosphate (Westhof & Sundaralingam, 1979), and ApApA, a trinucleoside diphosphate (Suck, Manor & Saenger, 1976). The adeninium ions in this structure are thus linked together in alternative fashion by these two different modes of base pairings, forming an infinite hydrogen-bonded chain in the **a** direction. A third mode of base–base hydrogen bond, of the type N(3)···HN(6), has been reported by Kistenmacher & Shigematsu (1974b) in adenine dihydrochloride.

The molecular arrangement on the mirror plane at $y = \frac{1}{4}$ is shown in Fig. 4, which illustrates a complex hydrogen-bond scheme. All H atoms except for H(21) attached to C(21) appear to participate in the hydrogen bonding with electronegative acceptor atoms as well as water oxygens. It is noteworthy that the structure contains four CH···O hydrogen bonds involving C(8)H donors in both adeniniums, and a C(2)H donor

in a bifurcated interaction. That N(11) and C(21) are in different chemical environments to N(12) and C(22) in this two-dimensional array of molecules may contribute in part to the observed, significant difference between N(11)–C(21) and N(12)–C(22) bond lengths. However, the cause of the significant difference between N(71)–C(51) and N(72)–C(52) bond lengths is not immediately apparent. Also, as may be seen in Fig. 4, pairs of adeninium ions are related roughly by noncrystallographic diad axes along the y direction [$x = 0·179$ (7) and $z = 0·567$ (7) for the two adeninium ions in the asymmetric unit]. Details of hydrogen-bond parameters are tabulated in Table 5.
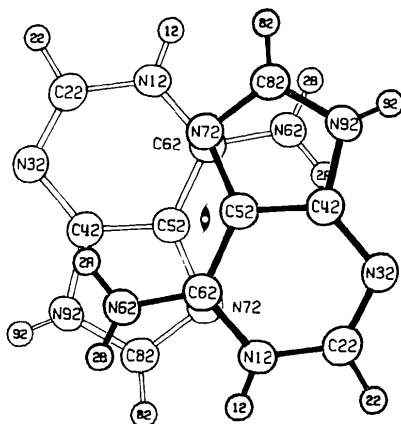
Fig. 5. Base stacking between one adeninium ion and its partner related by the screw axis at $x = \frac{1}{2}$ and $z = \frac{1}{4}$.

Shown in Fig. 5 is the base stacking between one of the two adeninium ions and its screw-related ($x = \frac{1}{2}$, $z = \frac{1}{4}$) partner. The shortest contact in the stacking interaction occurs between C(62) and N(72) (3·22 Å) in this figure. The other adeninium ion is not involved in base stacking. One oxygen atom O(31) of a nitrate ion lies over the pyrimidine ring of this adeninium, 3·27 Å from N(11).

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