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Structure of Adeninium Dinitrate, $C_5H_7N_5^{2+}.2NO_3^-$*†

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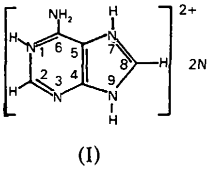
Abstract. $M_r = 261{\cdot}15$, orthorhombic, $P2_12_12_1$, $a = 4{\cdot}9880\,(3)$, $b = 9{\cdot}9376\,(5)$, $c = 19{\cdot}715\,(1)$ Å, $V = 977{\cdot}4\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}80\,(2)$, $D_x = 1{\cdot}77$ g cm^{-3}, Cu $K\alpha_1$ ($\lambda = 1{\cdot}54056$ Å), $\mu = 13{\cdot}15$ cm^{-1}, $T = 297\,(2)$ K, $R(F) = 0{\cdot}026$ with 1068 counter reflections. Crystals were prepared from a solution of adenine, $Cd(NO_3)_2$, and HNO_3. The base rings are protonated at positions 1 and 7 with a characteristic increase in the C—N—C bond angle relative to unprotonated adenine. The dication forms five hydrogen bonds with nitrate ions nearly in the same plane. The hydrogen-bonded groups form staggered-chain ribbons extending in the **b** direction.

Introduction. As part of a program of X-ray studies on metal complexes with nucleic acid constituents, structural analyses of an adenine–cadmium(II) complex (Wei & Jacobson, 1981) and of bis(adeninium) dinitrate monohydrate (Hingerty, Einstein & Wei, 1981) have been carried out in this laboratory.

In an attempt to prepare an adenine–cadmium complex, a product of unknown chemical formula was obtained from a solution containing adenine, HNO_3, and $Cd(NO_3)_2$, and it has been characterized by this X-ray analysis as $C_5H_7N_5^{2+}.2NO_3^-$ (I). Two other structures of diprotonated adenine salts include adenine dihydrochloride (Kistenmacher & Shigematsu, 1974) and adeninium sulfate (Langer & Huml, 1978). Stuctures of substituted diprotonated adenines include the N-oxide of adeninium sulfate (Prusiner & Sundaralingam, 1972) and 7-methyladenine dihydrochloride (Kistenmacher & Shigematsu, 1975).



(I)

Experimental. Preparation: 0·1032 g adenine (Calibiochem) and 4 ml 1*M* HNO_3 dissolved by heating, 1·52 ml 0·5*M* $Cd(NO_3)_2$ added, mixture heated to dryness, redissolved in HNO_3, 1·52 ml 0·5 *M* $Cd(NO_3)_2$ added, crystals appeared after 4 months. Unstable in air, water, chemical test for Cd negative, UV analysis on solution of dissolved crystal positive for adenine. Density by flotation in mixture of bromobenzene and bromoform, crystal dimensions 0·32 × 0·44 × 0·65 mm, contained in sealed capillary along with a drop of 2*M* HNO_3. Systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$ consistent with $P2_12_12_1$,§ Twelve reflections in 2θ range 101–131° used for least-squares refinement of lattice parameters (Busing, Ellison, Levy, King & Roseberry, 1968). Mosaic spread 0·2°, intensities measured with Picker four-circle diffractometer over 2θ range 1–136° by θ–2θ-step scan, relative e.s.d. of 400 reference reflection 2·7%, for reflections 060 and 0,0,10 relative e.s.d. 0·6%, transmission curves obtained for 101, 200, 400 reflections.

At the beginning of the analysis the chemical formula was unknown, but possibilities included $C_5H_5N_5.HNO_3.4H_2O$ and $C_5H_5N_5.2HNO_3$. The structure was solved by straightforward application of *MULTAN* (Germain, Main & Woolfson, 1971). Preliminary refinement was carried out with the block-diagonal least-squares program of Shiono (1971) modified to refine extinction parameters. Positions of the seven H atoms were found as the seven strongest peaks in a F_o–F_c synthesis. The intensity measurements were then corrected analytically for absorption by integration over the X-ray pathlengths (Busing & Levy, 1957). The range of corrections applied was 0·8 to 1·0.

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§ Counter measurements on a preliminary crystal had shown a prominent 009 reflection which was attributed to the Renninger effect, since it disappeared when the crystal was rotated 0·3° about the [001] axis.

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The final three cycles of refinement were carried out using the full-matrix program *ORXFLS*4 (Busing, Martin & Levy, 1962). Scattering factors were taken from *International Tables for X-ray Crystallography* (Cromer, 1974). Weights (w) used were reciprocals of variances $\sigma^2(F_o^2)$, which were estimated according to the empircal expression given elsewhere (Wei & Einstein, 1978). The C, N, O atoms were treated anisotropically, the H atoms isotropically. An isotropic extinction parameter was refined. On the final cycle the shift in the extinction parameter was $0{\cdot}3\sigma$. The other shifts did not exceed $0{\cdot}06\sigma$. For all 1068 reflections $wR = 0{\cdot}091$ and $S = 2{\cdot}32$; $F(000) = 536$. There were five reflections with measured intensities less than their e.s.d.'s. A $F_o - F_c$ synthesis exhibited no maxima exceeding 0·15 e Å^{-3}. The final positional parameters and isotropic thermal parameters (equivalent parameters for non-hydrogen atoms) are listed in Table 1.*

Discussion. The adenine rings are protonated at positions N(1) and N(7), in agreement with the results from adeninium sulfate (Langer & Huml, 1978) and adenine dihydrochloride (Kistenmacher & Shigematsu, 1974), and with predictions from extended Hückel calculations (Pullman, Kochanski, Gilbert & Denis, 1968). Bond lengths, angles (Fig. 1) and their corresponding e.s.d.'s were calculated using the program *ORFFE*4 (Busing, Martin & Levy, 1964). Table 2 lists C,N,O bond distances and angles for the weighted average of the three diprotonated compounds along with those for monoprotonated and unprotonated adenine. Among the three diprotonated compounds there are significant differences ($>3\sigma$) for the distances C(5)—C(6) and C(8)—N(9). One would expect that as N(7) becomes protonated, the five-membered ring should become more symmetrical, so that the distances C(8)—N(7) and C(8)—N(9) would become nearly equal. This is the case for the adeninium dinitrate structure. Examination of the packing in the other structures shows closer approach of neighboring groups to C(8), which may cause deviations. The major effect of the second protonation is to shorten the N(9)—C(8) distance and lengthen the N(9)—C(4) distance.

The significant change which occurs on adding the second proton is the increase of 3·8° in the C(5)—N(7)—C(8) angle, which is less than the increase of 5° stated by Ringertz (1972). This effect is accompanied by a decrease in the interior angles at neighboring C atoms. The adeninium dinitrate structure like the adeninium sulfate structure (Kistenmacher & Shigematsu, 1975) is a good test of ring planarity because the crystal symmetry does not constrain the adeninium ion to lie on a crystallographic mirror plane. The five-membered ring is planar within experimental error, but the six-membered ring deviates significantly from planarity with a maximum distance of 0·012 (1) Å from the plane. These deviations are not consistent with those of the adeninium sulfate structure. The angle

Table 1. *Positional and isotropic thermal parameters*

The e.s.d.'s for the least significant figures are given in parentheses in all tables and in the text. The equivalent isotropic temperature factors were calculated by the relation for C,N,O atoms $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$.

	x	y	z	B_{eq} or B (Å^2)
N(1)	0·2481 (3)	0·0685 (1)	0·40221 (7)	2·86 (4)
C(2)	0·0721 (4)	−0·0029 (2)	0·44105 (9)	3·03 (4)
N(3)	0·0580 (4)	−0·1335 (2)	0·44422 (7)	3·05 (4)
C(4)	0·2476 (4)	−0·1924 (2)	0·40564 (7)	2·66 (4)
C(5)	0·4368 (4)	−0·1303 (2)	0·36589 (7)	2·58 (4)
C(6)	0·4392 (4)	0·0123 (2)	0·36282 (8)	2·59 (4)
N(6)	0·6029 (4)	0·0855 (1)	0·32619 (8)	3·30 (4)
N(7)	0·5851 (4)	−0·2300 (1)	0·33463 (7)	2·75 (3)
C(8)	0·4876 (5)	−0·3467 (2)	0·35545 (8)	3·08 (4)
N(9)	0·2866 (4)	−0·3289 (1)	0·39794 (7)	2·87 (4)
N(10)	0·8826 (4)	−0·6239 (1)	0·27204 (7)	2·82 (3)
O(1)	0·9817 (5)	−0·5125 (1)	0·25941 (8)	4·62 (4)
O(2)	0·9883 (4)	−0·7300 (1)	0·25063 (7)	3·89 (4)
O(3)	0·6724 (3)	−0·6312 (1)	0·30542 (7)	3·59 (3)
N(11)	−0·0002 (4)	−0·6261 (1)	0·43750 (7)	2·90 (4)
O(4)	−0·0401 (5)	−0·5056 (1)	0·45577 (8)	5·23 (5)
O(5)	0·2057 (3)	−0·6511 (1)	0·40376 (7)	3·78 (3)
O(6)	−0·1594 (4)	−0·7133 (1)	0·45349 (8)	4·02 (4)
H(1)	0·238 (6)	0·163 (2)	0·404 (1)	3·5 (5)
H(2)	−0·040 (7)	0·059 (2)	0·469 (1)	4·9 (6)
H(9)	0·193 (7)	−0·393 (3)	0·417 (1)	5·3 (6)
H(8)	0·544 (5)	−0·432 (2)	0·339 (1)	2·9 (4)
H(7)	0·733 (6)	−0·229 (2)	0·301 (1)	3·9 (5)
H(61)	0·719 (7)	0·048 (3)	0·298 (1)	4·3 (6)
H(62)	0·605 (7)	0·164 (2)	0·330 (1)	4·4 (6)

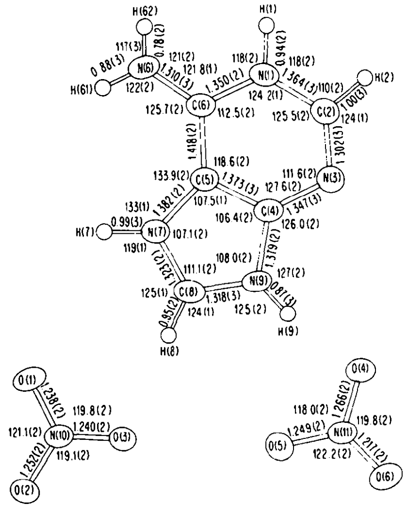

Fig. 1. Bond distances (Å) and bond angles (°) with their e.s.d.'s for diprotonated adenine and the two independent nitrate ions.

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* Lists of structure factors, anisotropic thermal parameters, a stacking diagram, molecular least-squares planes, and hydrogen-bond parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38106 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparison of bond lengths* (Å) *and angles* (°) *for diprotonated adenine* (H_2Ade^{2+}), *monoprotonated adenine* ($HAde^+$), *and unprotonated adenine* (Ade)

	(1) H_2Ade^{2+}	(2) $HAde^+$	(3) Ade
N(1)—C(2)	1·362	1·360	1·332
C(2)—N(3)	1·299	1·305	1·315
N(3)—C(4)	1·352	1·362	1·349
C(4)—C(5)	1·373	1·378	1·365
C(5)—C(6)	1·411	1·411	1·404
C(6)—N(1)	1·358	1·368	1·346
C(5)—N(7)	1·380	1·382	1·388
N(7)—C(8)	1·324	1·315	1·297
C(8)—N(9)	1·329	1·359	1·365
N(9)—C(4)	1·374	1·358	1·370
C(6)—N(6)	1·305	1·309	1·341
N(1)—C(2)—N(3)	125·6	125·4	128·8
C(2)—N(3)—C(4)	111·8	112·1	111·0
N(3)—C(4)—C(5)	127·1	127·2	126·9
C(4)—C(5)—C(6)	119·0	118·3	115·4
C(5)—C(6)—N(1)	112·5	113·5	118·1
C(6)—N(1)—C(2)	124·0	123·6	119·8
N(1)—C(6)—N(6)	120·9	120·7	119·1
C(5)—C(6)—N(6)	126·6	125·9	122·7
C(4)—C(5)—N(7)	107·4	110·8	110·7
C(5)—N(7)—C(8)	107·3	103·5	104·4
N(7)—C(8)—N(9)	110·6	113·4	113·4
C(8)—N(9)—C(4)	107·9	105·6	104·8
N(9)—C(4)—C(5)	106·7	105·6	104·8
N(3)—C(4)—N(9)	126·2	127·2	128·3
C(6)—C(5)—N(7)	133·5	130·9	133·9

(1) Weighted average of three H_2Ade^{2+} structures.

(2) Average of five studies for $HAde^+$ (Hingerty, Einstein & Wei, 1981).

(3) Average of a number of adenine structures (Voet & Rich, 1970).

between the planes of the five- and six-membered rings is 0·89 (9)°.

The nitrate ions show some deviations from D_{3h} symmetry. The N(11)—O(6) bond length of 1·217 (2) Å is significantly shorter than the other N—O bonds (see Fig. 2). O(6) is the only O atom which does not participate in hydrogen bonding. The nitrate groups are both essentially planar.

As in the other diprotonated adenine structures, the base ring forms hydrogen bonds only with the anions. The five H atoms attached to N atoms form hydrogen bonds with five O atoms in the nitrate groups lying roughly in the same plane. The staggered arrays of adeninium and nitrate ions form ribbons, extending in the **b** direction and nearly parallel to the (105) plane.

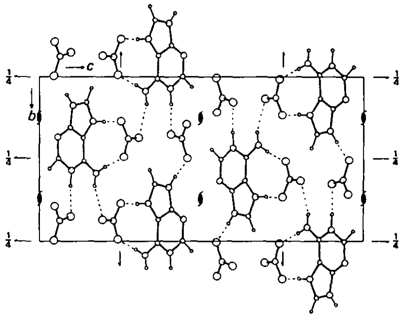

Fig. 2. Projection of the unit cell along [100]. Hydrogen bonds are indicated by dashed lines.

The spacing between least-squares adeninium planes is 3·14 Å. The adeninium cation lies opposite to a nitrate ion in the adjacent layer, so that the layers are held together by Coulombic attractions.

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