Structure of Adeninium Dinitrate, C₅H₇N₂⁺.2NO₃⁻

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(Received 17 May 1982; accepted 10 August 1982)

Abstract. $M_r = 261.15$, orthorhombic, $P2_12_12_1$, $a = 4.9880 (3)$, $b = 9.9376 (5)$, $c = 19.715 (1)$ Å, $V = 977.4 (1)$ Å³, $Z = 4$, $D_m = 1.80 (2)$, $D_x = 1.77$ g cm⁻³, Cu Ka ($\lambda = 1.54056$ Å), $\mu = 13.15$ cm⁻¹, $T = 297 (2)$ K, $R(F) = 0.026$ with 1068 counter reflections. Crystals were prepared from a solution of adenine, Cd(NO₃)₂, and HNO₃. 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, HNO₃, and Cd(NO₃)₂. 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.

Experimental. Preparation: 0·1032 g adenine (Calibiochem) and 4 ml 1M HNO₃ dissolved by heating, 1·52 ml 0·5M Cd(NO₃)₂ added, mixture heated to dryness, redissolved in HNO₃, 1·52 ml 0·5M Cd(NO₃)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 x 0·44 x 0·65 mm, contained in sealed capillary along with a drop of 2M HNO₃. Systematic absences h00, $h = 2n + 1$, 0k0, $k = 2n + 1$, 00l, $l = 2n + 1$ consistent with $P2_12_12_1$,§ Twelve reflections in $2\theta$ 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 $2\theta$ range 1–136° by $\theta$–$2\theta$-step scan, relative e.s.d. of 0·00 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 C₅H₇N₂.HNO₃.4H₂O and C₅H₇N₂.2HNO₃. 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.

§ 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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0108-2701/83/010088-03$01.50

‡ Support from GLCA-ACM Oak Ridge Science Semester Program.
The final three cycles of refinement were carried out using the full-matrix program ORXFLS4 (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 empirical 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 0.3σ. The other shifts did not exceed 0.06σ. For all 1068 reflections \(\text{wR} = 0.091\) and \(S = 2.32; F(000) = 536\). 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, 1975). The adeninium dinitrate structure (Cromer, 1974) 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. Among the three diprotonated compounds there are significant differences (>3σ) 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 shows closer approach of neighboring groups than the adeninium sulfate structure (Kistenmacher & Shigematsu, 1975), 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 ORFFE4 (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. The angle C(5)–C(6)–C(8) is less than the increase of 3.8° in the second protonation is to shorten the N(9)–C(8) distance and lengthen the N(9)–C(4) distance.

![Fig. 1. Bond distances (Å) and bond angles (°) with their e.s.d.'s for diprotonated adenine and the two independent nitrate ions.](image)
Table 2. Comparison of bond lengths (Å) and angles (°) for diprotonated adenine (H₂Ade²⁺), mono-
protonated adenine (H⁺Ade⁺), and unprotonated adenine (Ade)

<table>
<thead>
<tr>
<th></th>
<th>H₂Ade²⁺</th>
<th>H⁺Ade⁺</th>
<th>Ade</th>
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<tr>
<td>N(1)--C(2)</td>
<td>1.362</td>
<td>1.360</td>
<td>1.332</td>
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<td>1.352</td>
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<td>1.358</td>
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<td>1.411</td>
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<td>C(5)--N(7)</td>
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<tr>
<td>N(7)--C(8)</td>
<td>1.324</td>
<td>1.315</td>
<td>1.297</td>
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<tr>
<td>C(8)--N(9)</td>
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<td>1.365</td>
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<td>N(9)--C(4)</td>
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<tr>
<td>C(6)--N(6)</td>
<td>1.365</td>
<td>1.369</td>
<td>1.341</td>
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(1) Weighted average of three H₂Ade²⁺ structures.
(2) Average of five studies for H⁺Ade⁺ (Hingerty, Einstein & Wei, 1981).
(3) Average of a number of adenine structures (Voet & Rich, 1970).

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.

References