Inorg. Chem. **1981**, *20*, 356-363

Contribution from the Biology Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830

X-ray Crystallographic Characterization of an Adenine–Cadmium(II) Complex, Di-μ-adeninium-di-μ-aquo-tetrakis(nitrato-O,O')dicadmium(II) Dinitrate, Containing a Cationic Nucleic Acid Base as a Bidentate Ligand[1]

CHIN HSUAN WEI* and K. BRUCE JACOBSON

Received August 13, 1980

The reaction of the monosodium salt of adenosine-5′-monophosphoric acid with cadmium nitrate in the presence of nitric acid has resulted in the formation of a binuclear cadmium complex of adenine, $[(C_5H_6N_5)Cd(NO_3)_2{\cdot}H_2O]_2(NO_3)_2$. The crystal structure of this complex has been characterized by single-crystal X-ray analysis based on counter data collected with an automated diffractometer. The crystals contain one centrosymmetric dimer in a reduced triclinic cell of symmetry $P\bar{1}$ and of dimensions a = 7.595 (2) Å, b = 9.539 (5) Å, c = 10.527 (5) Å, α = 101.37 (3)°, β = 108.69 (3)°, and γ = 107.42 (3)°. The structure was solved by the standard heavy-atom technique. Full-matrix least-squares refinement of the structure has led to a final value of the conventional discrepancy index, R_F, of 0.050 based on 1889 reflections with $F_o^2 \geq \sigma(F_o^2)$. The binuclear ion $[(C_5H_6N_5)Cd(NO_3)_2{\cdot}H_2O]_2^{2+}$ contains water-bridged, nitrated cadmium atoms each of which is coordinated to the N(3) atom of one adeninium moiety [Cd–N(3) distance 2.413 (7) Å] and to the N(9) atom of a centrosymmetrically related adeninium moiety [Cd–N(9) distance 2.349 (6) Å]. The Cd···Cd separation is 3.616 (2) Å, indicating that no appreciable metal–metal bonding is present. Since both N(3) and N(9) of each bidentate adeninium ligand are involved in coordination to the metals, the remaining nitrogen atoms, N(1) and N(7), are both protonated, giving rise to internal angles, enlarged as expected, of 124.3 (7) and 105.1 (7)°, respectively. The geometry around the cadmium atom can best be described as distorted octahedral, with two bridging-water oxygen atoms and two nitrate groups occupying the equatorial positions and the N(3) and N(9) atoms of different adeninium moieties occupying the axial positions. The water molecules in this structure serve as bridging ligands connecting two cadmium atoms [with Cd–O(water) distances of 2.397 (5) and 2.467(7) Å], as opposed to the water of solvation or terminal water ligands bound to metal as found in many other hydrated metal complexes of nucleic acid constituents. Each nitrate ion not bound to the metal is attached to the dimeric cation as a hydrogen-bond acceptor with four donors: a pyrimidine nitrogen atom, the exocyclic amino group, a water molecule, and an imidazole carbon atom. All hydrogen atoms of the adeninium ring as well as those of water molecules appear to take part in a network of hydrogen bonds with the neighboring nitrate groups; in this network linkages of the type N–H···O, O–H···O, and C–H···O are involved.

Introduction

It is well recognized that interactions of certain metal ions with nucleic acids are essential to a variety of biological processes in animals and plants;[2] hence there has been increasing interest toward understanding the stereochemistry of complexes formed between metal ions and nucleic acid bases, nucleosides, and nucleotides, as reflected by a recent review article by Marzilli et al. dealing with metal ion–nucleotide and metal ion–nucleic acid interactions.[3] In all cases, developing knowledge of binding sites of metals, site(s) of protonation or deprotonation of bases, and hydrogen bonding would be a first step in the elucidation of molecular mechanisms. Investigations of the complexes in solution have been extensively reviewed by Marzilli[4] and by Martin and Mariam,[5] whereas several comprehensive reviews concerning X-ray structural studies in the crystalline state have recently been published by Hodgson,[6] Swaminathan and Sundaralingam,[7] and Gellert and Bau.[8]

Cadmium is known to be an environmental pollutant. Chronically exposed humans exhibit several health problems,[9] including pulmonary emphysema, cardiovascular disease, interference with copper and zinc metabolism, anemia, reduced growth, gonadal damage and malfunction, liver and kidney damage, enlarged joints, scaly skin, reduced milk production, cancer, dental damage, enteritis, and gastritis. Once absorbed, cadmium has a long biological half-life: 15.7 years on average for the whole body.[10] It specifically inhibits or stimulates the catalytic activities of various enzymes.[11] Along with several other metal ions, cadmium has been observed to be one of the most potent in diminishing the fidelity of DNA synthesis in vitro.[12] Furthermore, this metal ion has opposing effects on DNA-dependent RNA polymerase: initiation is stimulated whereas elongation is inhibited.[13] Whether there is a correlation between the effects on DNA and RNA synthesis and the carcinogenic activity is not yet conclusive,[14] and indeed the mutagenic and carcinogenic properties of cadmium still remain unclear.[9a]

Although a large number of crystallographic results for the complexes of metal with nucleic acid constituents have been recorded to date,[6-8] only a few complexes of cadmium have been reported. Thus, structural analyses of two cadmium complexes with purine nucleotides, $Cd_2(5'\text{-}IMP)_3{\cdot}12H_2O$[15] and $[Cd(5'\text{-}GMP)(H_2O)_5]{\cdot}3H_2O$,[16] have revealed that in each case the cadmium binds to N(7) of the base, with a distorted octahedral geometry. In polymeric pyrimidine nucleotide complexes, $[Cd(5'\text{-}CMP)H_2O]{\cdot}H_2O$,[17] $[Cd(5'\text{-}CMP)(H_2O)_2]_n$

---

(1) (a) Research supported by the Office of Health and Environmental Research, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp. (b) Presented in part as paper PA18 at the Winter Meeting of the American Crystallographic Association, Eufaula, Ala., March 17–21, 1980.

(2) Eichhorn, G. L. *Inorg. Biochem.* **1973**, *2*, 1191–1243.

(3) Marzilli, L. G.; Kistenmacher, T. J.; Eichhorn, G. L. "Metal Ions in Biology"; Spiro, T. G., Ed.; Wiley: New York, 1980; Vol. 1, pp 179–250.

(4) Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255.

(5) Martin, R. B.; Mariam, Y. H. *Met. Ions Biol. Syst.* **1979**, *8*, 57–124.

(6) Hodgson, D. J. *Prog. Inorg. Chem.* **1977**, *23*, 211.

(7) Swaminathan, V.; Sundaralingam, M. *CRC Crit. Rev. Biochem.* **1979**, *6*, 245.

(8) Gellert, R. W.; Bau, R. *Met. Ions Biol. Syst.* **1979**, *8*, 1–55.

(9) (a) "Criteria for a Recommended Standard. Occupational Exposure to Cadmium". *DHEW* (*NIOSH*) *Publ.* (*U.S.*) **No. 76-192 1976**. (b) "Hazardous Wastes: A Risk Benefit Framework Applied to Cadmium and Asbestos". *U.S. Environ. Prot. Agency*, [*Rep.*] *EPA* **EPA-600/5-77-002 1977**.

(10) Zanzi, I.; Cohn, S. H.; Yasumura, S. *Science* (*Washington, D.C.*) **1979**, *205*, 323.

(11) Vallee, B. L.; Ulmer, D. D. *Annu. Rev. Biochem.* **1972**, *41*, 91.

(12) Sirover, M. A.; Loeb, L. A. *Science* (*Washington, D.C.*) **1976**, *194*, 1434.

(13) Hoffman, D. J.; Niyogi, S. K. *Science* (*Washington, D.C.*) **1977**, *198*, 512.

(14) Jacobson, K. B.; Turner, J. E. *Toxicology* **1980**, *16*, 1.

(15) Goodgame, D. M. L.; Jeeves, I.; Reynold, C. D.; Skapski, A. C. *Nucleic Acids Res.* **1975**, *2*, 1375.

(16) Aoki, K. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1454.

(17) Goodgame, D. M. L.; Jeeves, I.; Reynold, C. D.; Skapski, A. C. *Biochem. J.* **1975**, *151*, 467.

0020-1669/81/1320-0356$01.00/0

(orthorhombic form),[18] and $[\mathrm{Cd(5'\text{-}CMP)(H_2O)_2}]_n$ (monoclinic form),[19] the cadmium atom has been found invariably to bind to N(3) of the base with pentacoordination[17,18] or pentagonal-bipyramidal configuration.[19] Although the metal binding also occurs at N(3) of a monomeric cytosine analogue, cadmium displays a different hexacoordination in dichlorobis(1-methylcytosine)cadmium(II).[20] In two additional cadmium complexes with purine analogues, bis(8-azahypoxanthinato)tetraaquocadmium(II)[21] and di-μ-chloro-dichlorobis(6-mercaptopurine)diaquodicadmium(II),[22] the cadmium ion has been shown to bind preferentially to N(7), with octahedral coordination. It is noteworthy that in most of these structures the cadmium is coordinated to one or more water molecules, except that no bridging water molecules have been reported. So far, no crystal structures of cadmium complexes with purine or pyrimidine bases or with an adenine nucleoside or nucleotide have been reported.

As part of a program of crystallographic studies on cadmium complexes with nucleotides, we have repeatedly attempted to crystallize a cadmium–adenosine monophosphate complex, without success. Instead, we have accidentally obtained a crystal specimen of an adenine complex containing cadmium. X-ray analysis of this spectrum has revealed the first known crystal structure of a cadmium complex with a purine base, $[(\mathrm{C_5H_6N_5})\mathrm{Cd(NO_3)_2{\cdot}H_2O}]_2(\mathrm{NO_3})_2$. Details of the structural investigation are presented in this report.

Experimental Section

A solution of 0.181 g of the monosodium salt of adenosine-5′-monophosphoric acid monohydrate (Sigma Chemical Co.) in 10 mL of water was added with stirring to 5 mL of an aqueous solution containing 0.144 g of cadmium nitrate tetrahydrate. A white gelatinous precipitate was dissolved by addition of 2 N $\mathrm{HNO_3}$ to give a clear solution at pH 3.2. This was heated to 60 °C for 15 min and then evaporated at 50 °C under vacuum nearly to dryness. The residue was redissolved in 5 mL of water with the aid of 0.1 mL of 2 N $\mathrm{HNO_3}$. Addition of aqueous ethanol (1:1) caused a massive precipitate,[23] which was filtered. The filtrate was kept in a petri dish for slow evaporation. After 5 months, formation of a few grains of irregular, elongated hexagonal-plate crystals was observed in a brownish viscous solution (pH ~2). Because of the limited amount of the crystals thus formed, complete elemental analysis was not performed. Prior to the X-ray investigation, however, a qualitative microanalysis showed the presence of cadmium in the crystal.[24] The UV spectrum indicated an absorbance maximum at 260 nm, which was later attributed to the presence of adenine.[25]

X-ray Data Collection. Preliminary film data showed that the crystals belong to the triclinic system, with space group either $P1$ or $P\bar{1}$.[26] Twelve strong reflections in the 2θ range of 100–110° were centered with an Oak Ridge computer-controlled diffractometer[27] by use of nickel-filtered Cu $K\alpha_1$ (λ = 1.540 51 Å) radiation. Cell parameters were refined by the least-squares method. A brief summary of crystal data and intensity collection is given in Table I.

Table I. Crystal Data and Intensity Collection for $[(\mathrm{C_5H_6N_5})\mathrm{Cd(NO_3)_2{\cdot}H_2O}]_2(\mathrm{NO_3})_2$

fw 905.13
space group C_i^1-$P\bar{1}$
a = 7.595 (2) Å
b = 9.539 (5) Å
c = 10.527 (5) Å
α = 101.37 (3)°
β = 108.69 (3)°
γ = 107.42 (3)°
V = 652.1 Å^3

Z = 1
D_{calcd} = 2.305 g cm^{-3}
D_{obsd} = 2.32 (2) g cm$^{-3\,a}$
$F(000)$ = 444
cryst dimens 0.05 × 0.17 × 0.38 mm
μ(Cu Kα) = 149.59 cm$^{-1\,b}$
transmission 0.138–0.479
temp 24 °C

radiation Cu Kα
takeoff angle 3°
scan type ω step–scan
reflctns measd $\pm h, \pm k, l^c$
2θ limits 1–120°
receiving aperture 21 cm from the cryst^d

scan step 0.025°/step
time per step 2 s
scan width 2.2–2.5°
2θ offset 0.5–1.25°^{d}
bkgd count time 88–100 s
no. of reflctns used 1889
no. of variables 255
data-to-parameter ratio 7.4

[a] Crystal density measured by flotation in mixtures of bromobenzene and bromoform. [b] Linear absorption coefficient for Cu Kα radiation. [c] Data collection based on the A-centered unit cell (see ref 26). [d] Aperture widths varied depending on the 2θ range (see text).

All of the crystals tested were of poor diffracting quality, but one of a few marginally acceptable specimens was chosen for data collection. The crystal, an irregular five-sided plate of dimensions 0.05 × 0.17 × 0.38 mm (crystal volume 0.0033 mm^3), was glued on the tip of a thin-glass fiber and was exposed to air during X-ray intensity collection. The longest dimension, corresponding to the c axis, was nearly parallel to the ϕ axis of the diffractometer. Narrow-source open-counter scans showed large mosaic spread about three reciprocal directions, ranging from 1.4 to 1.9°. In addition, they had multiple-peak, irregular mosaic distributions that made the accurate centering of reflections extremely difficult.

The intensities were measured by an ω step–scan technique, with (60° ≤ 2θ ≤ 120°) and without (1° ≤ 2θ ≤ 60°) nickel filter, in which three scans were performed for each reflection: a main scan with the detector set at the computed 2θ and two background scans with the detector offset lower and higher in 2θ. The total time spent on background measurement was equal to the time spent on the main scan. The receiving detector aperture and the 2θ offset were adjusted for different ranges of 2θ in the manner described by Einstein.[28] Throughout the data collection (at 40 kV and 18 mA), one standard reflection was measured for every 40 reflections.

Serious radiation deterioration of the crystal was observed during the course of data collection, as evidenced by the fact that the intensity of the standard steadily decreased. The data were collected over a period of 4 weeks (interrupted for 16 days for repair of the X-ray generator). The crystal decay was progressively more rapid toward the end of data collection, at which stage the intensity of the standard had decreased to 72% of the initial value. The measurements beyond a 2θ value of 120° were therefore abandoned.

A unique data set of 1922 nonzero intensities with 2θ ≤ 120° (equivalent to a minimum spacing of 0.89 Å) was obtained. Of these, the 1889 reflections which had corrected F_o^2 values greater than the corresponding standard deviations were subsequently utilized for the final least-squares refinement of the structure. Analytical absorption corrections were applied to the data according to the method of Busing and Levy.[29]

---

(18) Clark, G. R.; Orbell, J. D. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1815.

(19) Shiba, J. K.; Bau, R. *Inorg. Chem.* **1978**, *17*, 3484.

(20) Gagnon, C.; Beauchamp, A. L.; Tranqui, D. *Can. J. Chem.* **1979**, *57*, 1372.

(21) Purnell, L. G.; Estes, E. D.; Hodgson, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 740.

(22) Griffith, E. A. H.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1013.

(23) The precipitate was dissolved in 12 mL of water containing 0.1 mL of 2 N $\mathrm{HNO_3}$ (pH 3.2). As water evaporated, needle crystals resulted which were subsequently identified by X-ray diffraction patterns as adenosine 5′-monophosphate, the structure of which has previously been reported (Kraut, J.; Jensen, L. H. *Acta Crystallogr.* **1963**, *16*, 79).

(24) The analysis was carried out by a spot test procedure using ferrous dipyridyl iodide: Feigel, F. "Spot Tests"; Elsevier: Amsterdam, 1954; pp 90–91.

(25) The identification of adenine in the crystal was made by thin-layer chromatography (Eastman 13255, cellulose) using two solvent systems: (1) 1-butanol-HOAc-$\mathrm{H_2O}$ (4:1:1) and (2) 1-butanol–propionic acid–$\mathrm{H_2O}$ (50:25:35). The results indicated the absences of adenosine 5′-monophosphate, adenosine, ribose-5-phosphate, and inorganic phosphate. The adenine compounds were detected by UV light and the phosphate by an ammonium molybdate spray procedure that uses $\mathrm{HClO_4}$ to hydrolyze phosphate esters: Benson, A. A. *Methods Enzymol.* **1957**, *3*, 110.

(26) For convenience, however, an A-centered unit cell [a = 7.595 (2) Å, b = 18.717 (5) Å, c = 10.527 (5) Å, α = 95.82 (3)°, β = 108.69 (3)°, γ = 109.04 (3)°; unit cell volume twice that of the reduced unit cell] was chosen for data collection. The unit-cell vectors ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) of the reduced unit cell were related to those ($\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$) of the A-centered unit cell as follows: $\mathbf{a} = \mathbf{a}'$; $\mathbf{b} = -[\mathbf{a}' + {}^1/_2(\mathbf{b}' + \mathbf{c}')]$; $\mathbf{c} = \mathbf{c}'$.

(27) Busing, W. R.; Ellison, R. D.; Levy, H. A.; King, S. P.; Roseberry, R. T. "The Oak Ridge Computer-Controlled X-Ray Diffractometer", Report ORNL-4143; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1968.

(28) Einstein, J. R. *J. Appl. Crystallogr.* **1974**, *7*, 331.

Table II. Positional and Anisotropic Thermal Parameters ($\times 10^4$) for Nonhydrogen Atoms[a, b]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0.64930 (6)	0.65570 (5)	0.45755 (5)	205 (3)	182 (2)	105 (1)	26 (1)	50 (1)	39 (0.7)
O(W)	0.6157 (8)	0.3909 (9)	0.4597 (7)	207 (13)	188 (8)	107 (7)	57 (8)	65 (8)	49 (7)
N(1)	1.1209 (11)	0.8904 (9)	0.9123 (8)	241 (17)	176 (10)	139 (10)	5 (11)	56 (10)	39 (8)
C(2)	1.0056 (12)	0.8382 (11)	0.7717 (9)	270 (22)	233 (15)	129 (11)	54 (15)	70 (13)	43 (11)
N(3)	0.8410 (8)	0.7147 (7)	0.7074 (7)	173 (13)	173 (9)	122 (8)	−12 (9)	31 (8)	7 (7)
C(4)	0.7921 (12)	0.6360 (10)	0.7944 (8)	261 (19)	234 (13)	97 (9)	99 (14)	62 (11)	44 (9)
C(5)	0.9060 (11)	0.6787 (9)	0.9385 (8)	251 (19)	184 (11)	131 (10)	44 (12)	85 (12)	43 (8)
C(6)	1.0819 (12)	0.8131 (11)	1.0080 (9)	265 (20)	225 (13)	127 (11)	84 (14)	60 (12)	32 (10)
N(7)	0.8123 (12)	0.5721 (10)	0.9874 (9)	297 (20)	239 (13)	114 (10)	77 (13)	79 (12)	78 (9)
C(8)	0.6445 (12)	0.4689 (10)	0.8724 (8)	266 (20)	209 (13)	104 (10)	53 (14)	48 (12)	39 (9)
N(9)	0.6302 (8)	0.5043 (7)	0.7552 (6)	206 (14)	199 (10)	111 (8)	45 (10)	61 (9)	54 (7)
N(6)	1.1984 (12)	0.8674 (10)	1.1427 (7)	242 (17)	236 (12)	92 (8)	4 (8)	14 (10)	20 (8)
N(11)	0.6671 (13)	0.9541 (10)	0.4399 (9)	343 (22)	215 (13)	176 (12)	64 (14)	81 (14)	59 (10)
O(11)	0.5327 (11)	0.8274 (9)	0.3592 (8)	381 (20)	247 (12)	184 (10)	81 (14)	41 (12)	48 (9)
O(21)	0.6595 (18)	1.0706 (11)	0.4124 (15)	804 (45)	228 (14)	498 (29)	150 (22)	220 (30)	189 (18)
O(31)	0.7931 (14)	0.9458 (11)	0.5434 (10)	454 (25)	301 (15)	227 (14)	99 (17)	−31 (15)	45 (12)
N(22)	0.9545 (10)	0.6600 (8)	0.3458 (7)	212 (16)	203 (10)	127 (9)	20 (10)	38 (10)	35 (8)
O(12)	1.0796 (8)	0.6435 (8)	0.2989 (7)	241 (14)	280 (11)	199 (10)	87 (11)	140 (10)	68 (9)
O(22)	0.9620 (10)	0.6454 (8)	0.4614 (7)	329 (16)	273 (11)	137 (8)	49 (11)	105 (9)	81 (8)
O(32)	0.8166 (9)	0.6922 (9)	0.2773 (7)	245 (15)	306 (13)	169 (9)	108 (12)	43 (10)	43 (9)
N(33)	0.5355 (10)	0.2339 (8)	1.1017 (8)	243 (17)	176 (10)	133 (10)	39 (11)	66 (11)	36 (8)
O(13)	0.4494 (11)	0.1557 (9)	0.9738 (7)	379 (19)	260 (11)	122 (8)	−31 (12)	76 (10)	25 (8)
O(23)	0.6865 (9)	0.3526 (7)	1.1446 (7)	314 (17)	204 (10)	186 (9)	2 (11)	92 (10)	30 (8)
O(33)	0.4681 (10)	0.1844 (7)	1.1845 (7)	452 (20)	193 (9)	146 (8)	52 (11)	140 (11)	39 (7)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The estimated standard deviations of the last significant figures are given in parentheses in all tables and in the text.

Variances $\sigma^2(F_o^2)$ for use in least-squares weighting were estimated according to the empirical expression

$$\sigma^2(F_o^2) = A^2s^2[(G + B) + 0.0025(G - B)^2]/(Lp)^2$$

where A = correction factor on the intensity for absorption, s = scale factor on the intensity, G = gross count, B = background count, and Lp = Lorentz–polarization factor.

Solution and Refinement of the Structure. All least-squares refinements in this analysis were carried out on F^2, the function minimized being $\sum w|F_o^2 - sF_c^2|^2$, where the weights w are the reciprocals of the variances $\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for cadmium were taken from the tabulations of Ibers,[30] those for carbon, nitrogen, and oxygen from the tabulations of Berghuis et al.,[31] and those for hydrogen from Stewart et al.[32] The real and imaginary dispersion corrections of cadmium for Cu Kα radiation given by Cromer[33] were also included.

At the beginning of the structure determination the actual structural formula was unknown. From the crystallographic information, however, a plausible formula of $(AMP)_2Cd{\cdot}6H_2O$ was initially assumed, with two formula species per A-centered unit cell.[34] The interpretation of a three-dimensional Patterson function, calculated by the use of a fast Fourier routine,[35] resulted in positions for two independent cadmium atoms and two independent phosphorus atoms (the latter turned out to be water oxygens) in the initially assumed space group of $A1$. Successive Fourier syntheses and full-matrix least-squares refinements[36] revealed, in addition, two independent adenine moieties and six nitrate groups. Attempts to locate possible ribose rings, however, were not successful, and the presence of an adenosine moiety in the molecule was ruled out at this stage.

Table III. Positional and Isotropic Thermal Parameters for Hydrogen Atoms

	x	y	z	B, Å^2
H(1)	1.193 (20)	0.964 (16)	0.921 (14)	9 (4)
H(2)	1.022 (10)	0.906 (8)	0.717 (7)	3 (1)
H(7)	0.843 (12)	0.571 (9)	1.060 (9)	4 (1)
H(8)	0.545 (15)	0.358 (12)	0.870 (10)	6 (2)
H(6a)	1.309 (15)	0.950 (12)	1.187 (10)	5 (2)
H(6b)	1.158 (12)	0.813 (10)	1.198 (9)	5 (2)
H(a)	0.606 (17)	0.369 (13)	0.370 (14)	9 (3)
H(b)	0.671 (17)	0.367 (13)	0.502 (12)	5 (3)

An examination of the positional parameters enabled an assignment of one cadmium, one water oxygen, ten adenine atoms, and three nitrate groups as a half of the dimeric molecule, the other half being related by a crystallographic center of symmetry. Thus, the unit cell is centrosymmetric. Three cycles of isotropic refinement yielded a value of 0.124 for the conventional unweighted reliability index, $R_F = \sum||F_o| - s|F_c||/\sum|F_o|$. Further refinement, in which only cadmium was assigned anisotropic thermal parameters, markedly lowered the R_F value to 0.076. All hydrogen atoms were located at their expected positions in a difference Fourier map. The correct structural formula was then assigned as a dimeric species of adeniniumcadmium trinitrate monohydrate, $[(C_5H_6N_5)Cd(NO_3)_3{\cdot}H_2O]_2$.

The A-centered cell was transformed to the primitive cell,[26] and correct intensity data were recalculated with a liner absorption coefficient on the basis of experimentally derived structural formula. The continued refinement with all 24 nonhydrogen atoms assigned anisotropic thermal parameters yielded the R_F value of 0.054. The final refinement, in which all hydrogen atoms were included and treated isotropically, resulted in R_{F^2} (defined similarly to R_F) and $R_{wF^2} = [\sum w|F_o^2 - sF_c^2|^2/\sum wF_o^4]^{1/2}$ values of 0.083 and 0.137, respectively. The value of R_F stood at 0.050 (when all 1922 nonzero reflections were included, this value was also 0.050). Parameter shifts for the nonhydrogen atoms in the last cycle of the refinement were all less than 20% of the corresponding estimated standard deviations (esd's) except for the water oxygen atom (50% in x), whereas the maximum shift in the hydrogen parameters was 63% of the corresponding esd in x for H(b).[37] The standard deviation of an observation of unit

---

(29) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180.

(30) Ibers, J. A. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, Table 3.3.1B, p 211.

(31) Berghuis, I.; Haanappel, IJ. M.; Loopstra, B. O.; MacGillavry, C. H.; Veenendaal, A. L. *Acta Crystallogr.* **1955**, *8*, 478.

(32) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(33) Cromer, D. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1, p 149.

(34) This formula, $(C_{10}H_{13}N_5O_7P)_2Cd{\cdot}6H_2O$, corresponds to a molecular weight of 906.90, in close agreement with an estimated value of roughly 906.

(35) Levy, H. A. "Oak Ridge Fast Fourier Package, ORFFP3"; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1977.

(36) Busing, W. R.; Martin, K. O.; Levy, H. A. "OR FLS, a Fortran Crystallographic Least-Squares Program", Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1962.

(37) These shifts could have been decreased by carrying the refinement further. However, this was not attempted due to the high cost and to the observation that strong positional parameter correlations exist between the water oxygen atom and its accompanying hydrogen atoms, H(a) and H(b). It was felt that no significant change could result in the cadmium–adenine configuration.

Table IV. Interatomic Distances and Bond Angles in the Coordination Sphere of Cadmium and in the Nitrate Ions[a, b]

	dist, Å		angle, deg
Cd–O(W)	2.467 (7)	N(3)–Cd–N(9′)	150.7 (2)
Cd–O(W′)	2.397 (5)	O(W)–Cd–O(W′)	84.0 (2)
Cd–O(11)	2.343 (8)	MP1–Cd–MP2	92.4
Cd–O(31)	2.498 (10)	O(W)–Cd–MP2	89.7
Cd–MP1	2.189	O(W′)–Cd–MP1	93.9
Cd–O(22)	2.394 (7)	O(W)–Cd–MP1	177.2
Cd–O(32)	2.622 (7)	O(W′)–Cd–MP2	173.2
Cd–MP2	2.279	N(3)–Cd–O(W)	81.1 (2)
Cd–N(3)	2.413 (7)	N(3)–Cd–O(W′)	79.4 (2)
Cd–N(9′)	2.349 (6)	N(3)–Cd–MP1	100.4
Cd· · ·Cd′	3.616 (2)	N(3)–Cd–MP2	102.0
N(11)–O(11)	1.23 (1)	N(9′)–Cd–O(W)	76.6 (2)
N(11)–O(21)	1.22 (1)	N(9′)–Cd–O(W′)	79.6 (2)
N(11)–O(31)	1.23 (1)	N(9′)–Cd–MP1	101.3
N(11)–O	1.23 (av)	N(9′)–Cd–MP2	96.6
N(22)–O(12)	1.237 (9)	Cd–O(W)–Cd′	96.0 (2)
N(22)–O(22)	1.237 (9)	O(11)–N(11)–O(21)	118.4 (10)
N(22)–O(32)	1.228 (10)	O(21)–N(11)–O(31)	127.5 (11)
N(22)–O	1.234 (av)	O(31)–N(11)–O(11)	114.1 (9)
N(33)–O(13)	1.243 (10)	O–N(11)–O	120.0 (av)
N(33)–O(23)	1.220 (9)	O(12)–N(22)–O(22)	122.4 (7)
N(33)–O(33)	1.245 (9)	O(22)–N(22)–O(32)	117.5 (7)
N(33)–O	1.236 (av)	O(32)–N(22)–O(12)	120.1 (7)
		O–N(22)–O	120.0 (av)
		O(13)–N(33)–O(23)	120.5 (7)
		O(23)–N(33)–O(33)	121.4 (7)
		O(33)–N(33)–O(13)	118.1 (7)
		O–N(33)–O	120.0 (av)

[a] Atoms with primed symbols are related to the corresponding atoms with nonprimed symbols by a center of symmetry.

[b] MP1 designates the midpoint of O(11) and O(31) and MP2 the midpoint of O(22) and O(32).

weight, defined as $[w|\Delta F|^2/(n - p)]^{1/2}$, where n is the number of observations and p the number of parameters fitted to the data set, was 2.478. Although the final values of F_o and F_c suggested that no correction for secondary extinction was necessary, an isotropic extinction parameter[38] was incorporated in the final refinement, and a value of 0.003 (4) was obtained. A final difference Fourier map showed no residual peaks greater than 0.73 e/Å^3 (other than those in the vicinity of the cadmium atom, which ranged from 0.67 to 1.19 e/Å^3).

Final values of the atomic parameters and their esd's are given in Table II for nonhydrogen atoms and in Table III for hydrogen atoms. Bond lengths and angles around the cadmium atom and in the nitrate ions, calculated with the Busing–Martin–Levy program,[39] are given in Table IV. All figures were prepared by use of the Johnson program.[40] A list of observed and calculated structure amplitudes is available as supplementary material.

Results and Discussion

General Description of the Structure. Despite the fact that the crystal used was of poor quality, the molecular formula was unambiguously determined by X-ray analysis, and the coordination of the cadmium atom and its binding sites to the nucleic acid base were established with reasonable precision. The structure consists of a dimeric adeniniumcadmium dinitrate monohydrate cation, $[(C_5H_6N_5)Cd(NO_3)_2{\cdot}H_2O]_2^{2+}$, hydrogen bonded to the neighboring nitrate groups. The dication is electrically balanced by the nitrate ions associated with N(33) atoms. The dimeric molecule has crystallographic site symmetry C_i-1 in the triclinic lattice. The configuration of the dication (excluding hydrogen atoms) is depicted in Figure 1 with some pertinent bond lengths and bond angles, and its stereoscopic view is shown in Figure 2.

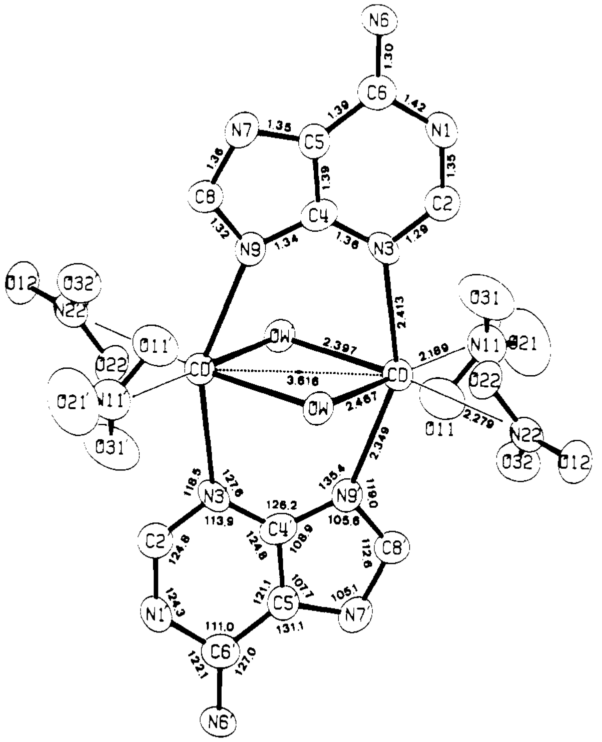

Figure 1. Bond lengths (Å) and bond angles (deg) for nonhydrogen atoms in the $[(C_5H_6N_5)Cd(NO_3)_2{\cdot}H_2O]_2^{2+}$ cation. The dication possesses crystallographic site symmetry C_i-$\bar{1}$. Unless otherwise stated, the esd's of bond lengths involving C and N atoms are 0.01 Å and those for bond angles range from 0.6 to 0.9°. The esd's for Cd–N–C angles are 0.5–0.6°. In this and in all subsequent figures, thermal ellipsoids enclose 33% probability.

For metal–purine complexes containing base as a unidentate ligand, a strong preference for metal binding to N(9)[41] over N(7)[42] has been observed. In case N(9) is methylated, either the primary coordination site is at N(7),[43] with a sole observed exception at N(1),[44] or coordination takes place at both sites.[45] It appears that the N(3) site is the least basic relative to protonation in purine or 9-methylated purine,[6,7] and no crystal structures involving only N(3) bound to metals have been reported to date. The present binuclear cadmium complex contains cadmium atoms bridged by two water molecules as well as two bidentate adeninium ligands at N(3) and N(9), the least and the most basic sites relative to protonation in anionic adenine. However, this mode of base binding to metal is not unprecedented. In the structures of four known binuclear

---

(38) Coppens, P.; Hamilton, W. C. *Acta Crystallogr., Sect. A* **1970**, *A26*, 71.

(39) Busing, W. R.; Martin, K. O.; Levy, H. A. "OR FFE, a Fortran Crystallographic Function and Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1964.

(40) Johnson, C. K. "ORTEP-II: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1976.

(41) (a) Carrabine, J. C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1969**, *92*, 369. (b) de Meester, P.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1973**, 424. (c) de Meester, P.; Skapski, A. C. *Ibid.* **1973**, 1596. (d) Kistenmacher, T. J.; Marzilli, L. G.; Chang, C.-H. *J. Am. Chem. Soc.* **1973**, *95*, 5817. (e) Kistenmacher, T. J. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1610.

(42) Taylor, M. R. *Acta Crystallogr., Sect. B* **1973**, *B29*, 884.

(43) (a) Sletten, E. *J. Chem. Soc., Chem. Commun.* **1971**, 558. (b) Sletten, E.; Thorstensen, B. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2438. (c) Szalda, D. J.; Kistenmacher, T. J.; Marzilli, L. G. *Inorg. Chem.* **1975**, *14*, 2623. (d) Sletten, E.; Ruud, M. *Acta Crystallogr., Sect. B* **1975**, *B31*, 982. (e) Terzis, A.; Hadjiliadis, N.; Rivest, R.; Theophanides, T. *Inorg. Chim. Acta* **1975**, *12*, L5.

(44) McCall, M. J.; Taylor, M. R. *Biochim. Biophys. Acta* **1975**, *390*, 137.

(45) (a) de Meester, P.; Goodgame, D. M. L.; Skapski, A. C.; Warnke, Z. *Biochim. Biophys. Acta* **1973**, *324*, 301. (b) Lock, C. J. L.; Speranzini, R. A.; Turner, G.; Powell, J. *J. Am. Chem. Soc.* **1976**, *98*, 7865. (c) McCall, M. J.; Taylor, M. R. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1687. (d) Gagnon, P. C.; Beauchamp, A. L. *Ibid.* **1977**, *B33*, 1448. (e) Sletten, E.: Våland, E. *Ibid.* **1979**, *B35*, 840.

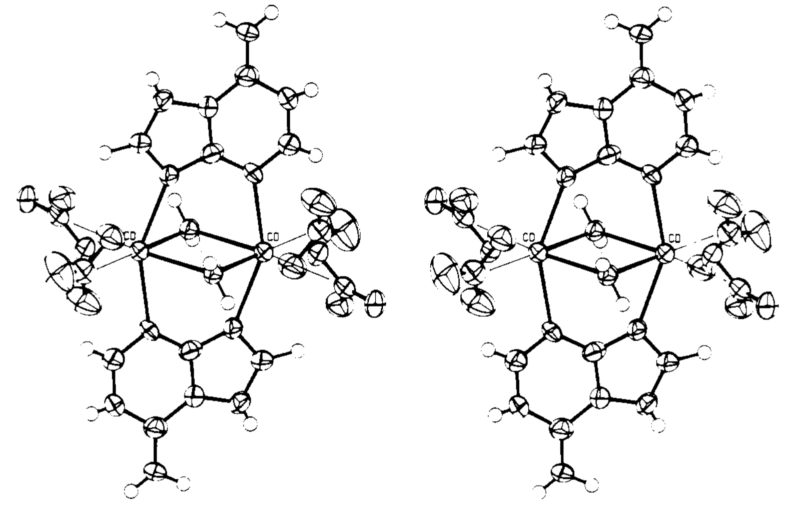

Figure 2. Stereoscopic view of the $[(C_5H_6N_5)Cd(NO_3)_2{\cdot}H_2O]_2^{2+}$ cation.

copper–adenine complexes, $[Cu_2(C_5H_4N_5)_4(H_2O)_2]{\cdot}6H_2O$,[46] the corresponding hypoxanthine complex, $[Cu_2(C_5H_4N_4O)_4Cl_2]Cl_2{\cdot}6H_2O$,[47] $[Cu_2(C_5H_5N_5)_4]Cl_2]Cl_2{\cdot}6H_2O$,[48] and $[Cu_2(C_5H_5N_5)_4(H_2O)_2](ClO_4)_4{\cdot}2H_2O$,[49] the copper atom is in square-pyramidal coordination with an apical ligand (water or chlorine) and four nitrogen atoms of four different adenine ligands in basal positions. In a similar binuclear silver–adenine complex, $[(C_5H_6N_5)Ag]_2(ClO_4)_2{\cdot}2H_2O$,[50] silver is strongly bonded to two nitrogen atoms of the centrosymmetrically related adeninium ligands and weakly bonded to three perchlorate oxygens. The nonbonding metal···metal separations for the four copper complexes range from 2.95 to 3.07 Å, and that for the silver complex is 3.00 Å. Since the single-bond metallic radius of cadmium is longer than those of copper and silver by 0.24 and 0.074 Å, respectively,[51] the nonbonding Cd···Cd separation is expected to be greater than those of Cu···Cu and Ag···Ag. The observed value of 3.616 (2) Å strongly suggests that no direct cadmium–cadmium bond interaction is present in this structure. Aside from the adenine ligand geometry, the existence of bridging water molecules presumably helps to account for this long Cd···Cd separation. Further examination reveals that the metal–N(3) distances (ranging from 2.01 to 2.04 Å) are systematically longer than the metal–N(9) distances (ranging from 1.99 to 2.01 Å) in three of the four copper complexes[46–48] (maximum difference: 8 esd's[46]) as well as in the silver complex[50] (3 esd's for the difference), in agreement with our observation that the Cd–N(3) distance of 2.413 (7) is longer than the Cd–N(9) distance of 2.349 (6) Å by approximately 7 esd's for the difference. While these results are still insufficient to warrant generalization,[49] this phenomenon has been attributed by Sletten[46,47] to the large amount of s character in the coordination orbital of the imidazole nitrogen, N(9). The structure of the cadmium complex can further be compared with that of the trinuclear copper–adenine complex $Cu_3Cl_8(C_5H_6N_5)_2{\cdot}4H_2O$,[52] in which each adenine moiety again acts as a bidentate ligand by coordinating through N(3) to one copper and through N(9) to another. The copper atoms are bridged by two chloride ligands. This Cu(II) complex, the Ag(I) complex,[50] and the present Cd(II) complex are the only complexes having cationic adenines[6] in which both N(3) and N(9) are involved in coordination to metal atoms and the remaining N(1) and N(7) atoms are both protonated.[53] The latter feature is also found in the case of a unidentate [coordinating via N(9)] adeninium complex of copper, $[Cu(C_5H_6N_5)_2Br_2]Br_2$.[41b] The protonations at N(1) and N(7) necessarily result in characteristic changes in molecular parameters involving these nitrogen atoms (see below).

Environment of Cadmium. Each cadmium is surrounded by two adenine moieties [with binding at N(3) and N(9′)] (Figure 1), two bridging-water oxygens, and two nitrate groups. Using N(3) and N(9), the adenine moiety bichelates two symmetry-related cadmium atoms. The Cd–N distances of 2.413 (7) and 2.349 (6) Å, though significantly different (see above), are on the large margin found in other similar cadmium complexes with nucleic acid constituents (2.27–2.42 Å).[15–22] Most of these complexes,[15–19,21,22] as well as some other simpler cadmium compounds such as $Cd(NO_3)_2{\cdot}4H_2O$,[57] cadmium diacetate dihydrate,[58] and cadmium maleate dihydrate,[59] have one or more water molecules attached to cadmium atom. The Cd–O(water) distance varies from 2.23 Å in cadmium maleate dihydrate[59] to 2.40 Å in orthorhombic [Cd(5′-

---

(46) Sletten, E. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1480.
(47) Sletten, E. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1609.
(48) de Meester, P.; Skapski, A. C. *J. Chem. Soc. A* **1971**, 2167.
(49) Terzis, A.; Beauchamp, A. L.; Rivest, R. *Inorg. Chem.* **1973**, *12*, 1166.
(50) Gagnon, C.; Hubert, J.; Rivest, R.; Beauchamp, A. L. *Inorg. Chem.* **1977**, *16*, 2469.
(51) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 256.
(52) de Meester, P.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2400.
(53) Inasmuch as N(9) binds to the metal atom, the present complex offers little information concerning Cd–DNA interaction. Still, it is of interest to speculate regarding the formation of the binuclear adeninium–cadmium nitrate complex from the reaction of the monosodium salt of adenosine-5′-monophosphoric acid with $Cd(NO_3)_2$ in an excessive presence of HNO_3. It is well-known that the glycosyl bond of adenine nucleotide is sensitive to cleavage at low pH.[54] Since the reaction product was kept at acidic conditions (pH 2–3.2) for 5 months (see Experimental Section), the hydrolysis of the glycosyl linkage took place, resulting in the formation of adenine which formed the N(1)-protonated nitrate salt of the formula $(C_5H_6N_5^+NO_3^-)_2{\cdot}H_2O$, the structure of which has recently been determined in our laboratory.[55] Under the complex reaction conditions, it is conceivable that the tautomerism of adenine N(7)H $\rightleftarrows$ N(9) shifted toward N(7) protonation,[56] after which the cadmium ion was attached to the N(9) site with a pair of electrons furnished by N(9). This mode of metal binding is similar to but not identical with that of the structure of $C_5H_6N_5Cl_3Zn^{II}$,[42] in which another imidazole ring nitrogen N(7) is coordinated to the metal. Finally, this monomeric cadmium complex could dimerize, thus yielding the title complex. However, attempts to synthesize and crystallize the binuclear complex from the reaction of adenine with $Cd(NO_3)_2$ in the presence of HNO_3 have so far been unsuccessful.
(54) (a) Michelson, A. M. "The Chemistry of Nucleosides and Nucleotides"; Academic Press: New York, 1963; p 26. (b) Davidson, J. N. "The Biochemistry of the Nucleic Acids"; Academic Press: New York, 1972; p 70.
(55) Hingerty, B. E.; Einstein, J. R.; Wei, C. H. *Acta Crystallogr.*, in press.
(56) Dreyfus, M.; Dodin, G.; Bensande, O.; Dubois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 2369.
(57) Matković, B.; Ribar, B.; Zelenco, B.; Peterson, S. W. *Acta Crystallogr.* **1966**, *21*, 719.
(58) Harrison, W.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1972**, 956.
(59) Post, M. L.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1974**, 674.

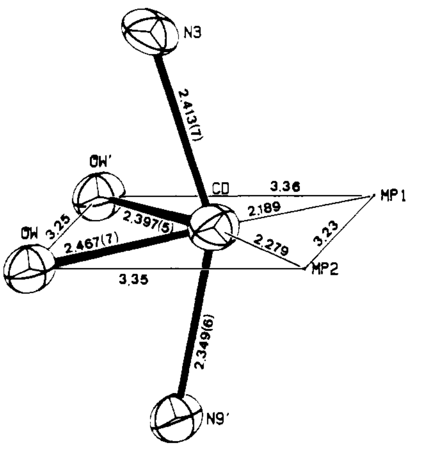

Figure 3. Coordination around the cadmium atom, showing the distorted octahedral geometry. For each of bonding nitrate groups, the midpoint (MP1 or MP2) of the two chemically equivalent oxygen atoms is taken as the coordination site.

Table V. Equations of Best Molecular Planes and Distances (Å) of Atoms from These Planes[a]

A: $0.6564X - 0.7343Y - 0.1732Z + 1.6265 = 0$
B: $0.8361X - 0.1671Y - 0.5226Z + 2.4482 = 0$
C: $-0.4265X - 0.7827Y - 0.4532Z + 6.4782 = 0$
D: $-0.5771X + 0.8057Y - 0.1330Z + 1.9998 = 0$
E: $-0.3452X + 0.0137Y - 0.9384Z + 4.9184 = 0$

Plane A	
N(1)	−0.013 (7)
C(2)	0.013 (7)
N(3)	0.004 (6)
C(4)	−0.007 (7)
C(5)	0.014 (7)
C(6)	0.004 (7)
N(7)	0.019 (7)
C(8)	−0.008 (6)
N(9)	−0.013 (6)
N(6)	−0.012 (6)
Cd[b]	−0.101 (9)
Cd′[b]	−0.081 (8)
O(W)[b]	1.532 (10)
O(W′)[b]	−1.713 (10)

Plane B	
N(11)	−0.009 (8)
O(11)	0.003 (3)
O(21)	0.003 (3)
O(31)	0.003 (3)

Plane C	
N(22)	0.000 (6)
O(12)	−0.000 (2)
O(22)	−0.000 (2)
O(32)	−0.000 (2)

Plane D	
N(33)	0.013 (6)
O(13)	−0.004 (2)
O(23)	−0.005 (2)
O(33)	−0.004 (2)

Plane E	
O(W)	−0.006
O(W′)	0.006
MP1	−0.006
MP2	0.006
Cd[b]	−0.044
O(11)[b]	1.001
O(31)[b]	−1.013
O(22)[b]	−0.865
O(32)[b]	0.876

[a] The coordinates X, Y, and Z (in Å) refer to a Cartesian system with unit vectors i along $b \times c^*$, j along b, and **k** along c^*.
[b] Values for atoms not included as members of the plane.

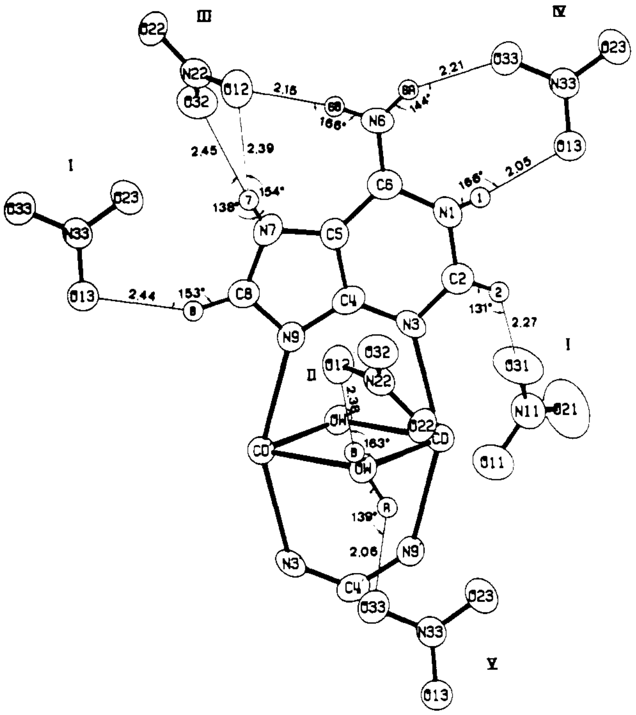

Figure 4. Possible hydrogen bonds between the dication and neighboring nitrate groups. Only those groups with interatomic H···O contacts of less than 2.45 Å are shown. For symmetry codes (I–V), refer to Table VI.

$CMP)(H_2O)_2]_n$,[18] an exceptionally long distance of 2.67 Å being reported in the structure of di-μ-chloro-bis(6-mercaptopurine)diaquodicadmium(II).[22] Unlike the terminal water ligand(s) in these cadmium compounds, the water molecules in the present structure are somewhat unusual in that each of them acts as a bridging ligand by donating two pairs of electrons to two metal atoms in a tetrahedral-array environment. The Cd–O(W) distances of 2.397 (5) and 2.467 (7) Å are significantly longer than the average of the commonly observed values. This observation is reminiscent of the well-known fact that in many transition-metal–carbonyl complexes, the distance of metal to bridging carbonyl carbon atom is usually longer than that of metal to terminal carbonyl carbon atom by the order of 0.1–0.2 Å.

Molecular parameters for nitrate groups in this structure are quite normal (Table IV). Close cadmium–oxygen distances for the two nitrate groups bound to the cadmium atom are as follows: 2.343 (8) and 2.498 (10) Å for O(11) and O(31), respectively, of one nitrate group; 2.394 (7) and 2.622 (7) Å for O(22) and O(32), respectively, of the second. Although these distances, compatible with those of 2.44 (2) and 2.59 (2) Å reported for $Cd(NO_3)_2 \cdot 4H_2O$,[57] have a range of 0.3 Å, they are all short enough to indicate definite Cd–O bonding interactions. The angles subtended at cadmium are 50.5 (5) and 49.4 (2)° for O(11)–Cd–O(31) and O(22)–Cd–O(32), respectively. It has been suggested by Bergman and Cotton[60] that when a chelating agent has a very short (<2.2 Å) intraligand distance, the mean position of the two chemically equivalent atoms can be considered to lie roughly at the vertex of one of the usual coordination polyhedra. Since in this structure the average O···O distance for the nitrate groups is 2.13 Å, this criterion can be applied to the two nitrate ligands, and the midpoints of the intraligands O(11)···O(31) and O(22)···O(32) were consequently assigned as MP1 and MP2, respectively. In this simplified representation, the cadmium coordination number was reduced from 8 to 6, and a very irregular coordination polyhedron (due to the actual dispositions of four nitrate oxygens) became a common octahedral geometry.[15,16,21,22,61,62] As can be seen in Figure 3, the $CdO_2(MP)_2N_2$ fragment of the molecule forms a distorted octahedron in which equatorial vertices are occupied by two water oxygens and two O···O midpoints, whereas two adeninium nitrogen atoms are at the axial positions. The four basal coordination sites are coplanar within 0.006 Å, and the cadmium atom is displaced from the plane by 0.044 Å toward the apical N(3) atom (Table V, E). Due to a long nonbonding Cd···Cd separation [3.616 (2) Å], however, the cadmium atom is pulled outward, and the resulting N–Cd–N angle subtended by nitrogen atoms of different adeniniums is 150.7 (2)°, showing a large deviation from linearity;[50] this results in an idealized C_{2v}-*mm* symmetry for the coordination sphere of cadmium.

Geometry of Adeninium Ligands. The adenine fused-ring system in the crystalline state is not required to be perfectly planar,[63] unless it is required by crystallographic symmetry

---

(60) Bergman, M. M.; Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1208.
(61) Braibanti, A.; Lanfredi, A. M. M.; Tiripicchio, A.; Bigoli, F. *Acta Crystallogr., Sect. B* **1969**, *B25*, 100.
(62) Bigoli, F.; Braibanti, A.; Pellinhelli, M. A.; Tiripicchio, A. *Acta Crystallogr., Sect. B* **1972**, *B28*, 962.
(63) Voet, D.; Rich, A. *Prog. Nucleic Acids Res. Mol. Biol.* **1970**, *10*, 183.

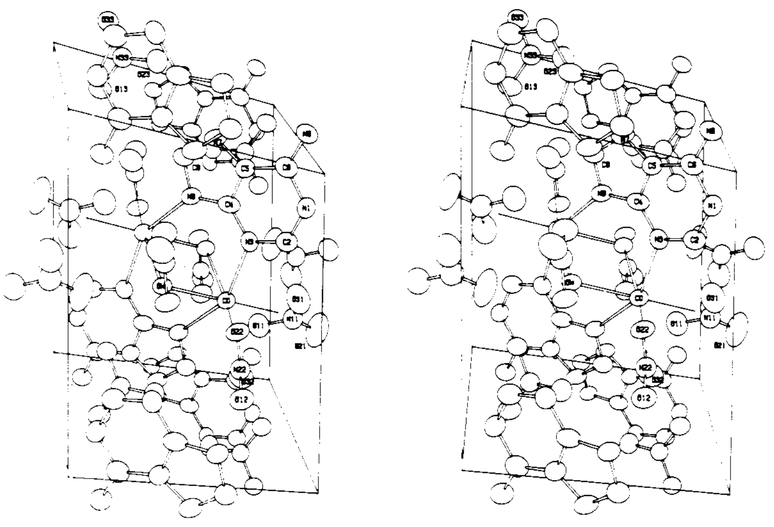

Figure 5. Stereoscopic pair showing the unit-cell packing. The axial system is right-handed. For sake of clarity, hydrogen atoms are not included, and only the basic atoms are labeled. The origin of the unit cell is in the lower-left rear corner, and the *c* axis is vertical.

to lie on a mirror plane.[43d,55,64] While significant nonplanarity of the pyrimidine ring has been observed,[42,45c,65] the imidazole ring is generally more planar.[45c,66,67] In this structure, the pyrimidine ring [including the exocyclic amino nitrogen atom, N(6)] is satisfactorily planar, with the maximum deviation from the least-squares plane of 0.013 Å for C(4), whereas the imidazole ring is planar within 0.005 Å. The dihedral angle between the two ring systems is 1.1°, within the normal range of 1–2° or even smaller found in most purines.[45c,64a,68] When all nine ring atoms and the exocyclic amino nitrogen atom are included in the plane calculation (Table V, A), the mean deviation from the least-squares plane is 0.011 Å, with the largest deviation of 0.019 (7) Å (within 3 esd's) for N(7). No abnormal folding along N(1)–C(5)[42] or C(2)–C(5)[45c] has been observed. The cadmium atoms are 0.09 Å (average) from this plane, and the two parallel adeninium moieties related by the center of symmetry are separated by 0.182 Å along the normal to their planes. The plane calculation also shows that the three nitrate groups are essentially planar (Table V, B–D).

It has been pointed out by Hodgson[6] that metal coordination at either N(3), N(7), or N(9) causes virtually no change in the internal angles at these atoms relative to their unsubstituted values. The attachment of protons to these atoms, however, causes a considerable increase in the internal angles. In this structure, protons are attached to both N(1) and N(7), giving rise to the enlarged internal angles of 124.3 (7) and 105.1 (7)°, respectively. The former value is closely similar to those reported for dibromodiadeniniumcopper(II) dibromide [124.6 (6)°],[41b] trichloroadeniniumzinc(II) [124.6 (3)°],[42] di-μ-adeninium-disilver(I) perchlorate monohydrate [124.8 (4)°],[50] octachlorodiadeniniumtricopper(II) tetrahydrate [124.3 (10)°],[52] adenine dihydrochloride [124.0 (2)°],[64a] and adeninium trichloromercurate(II) [125.0 (17) and 124.3 (17)°],[66] in agreement with the finding of Rao and Sundaralingam[69] that N(1) protonation increases the C(6)–N(1)–C(2) angle from 118–120° (for neutral) to approximately 123.5°. Also, the value for C(5)–N(7)–C(8) resembles 105.0 (6), 105.3 (4), and 105.3 (7)°, found in the structures of dibromodiadeniniumcopper(II) dibromide,[41b] di-μ-adeninium-disilver(I) perchlorate monohydrate,[50] and octachlorodiadeniniumtricopper(II) tetrahydrate,[52] respectively.

Table VI. Distances and Angles in the Hydrogen Bonds[a, b]

A–H· · ·B	dist, Å			angle, deg
	A· · ·B	A–H	H· · ·B	A–H· · ·B
N(1)–H(1)· · ·O(13)^{IV}	2.75 (1)	0.72 (13)	2.05 (14)	166 (14)
C(2)–H(2)· · ·O(31)^{I}	2.99 (1)	0.96 (7)	2.27 (7)	131 (5)
N(7)–H(7)· · ·O(12)^{III}	3.06 (1)	0.73 (8)	2.39 (9)	154 (8)
N(7)–H(7)· · ·O(32)^{III}	3.03 (1)	0.73 (8)	2.45 (8)	138 (7)
C(8)–H(8)· · ·O(13)^{I}	3.45 (1)	1.09 (10)	2.44 (10)	153 (7)
N(6)–H(6a)· · ·O(33)^{IV}	2.95 (1)	0.87 (10)	2.21 (10)	144 (8)
N(6)–H(6b)· · ·O(12)^{III}	3.04 (1)	0.91 (9)	2.15 (9)	166 (7)
O(W)–H(a)· · ·O(33)^{V}	2.81 (1)	0.90 (13)	2.06 (12)	139 (10)
O(W)–H(b)· · ·O(12)^{II}	2.99 (1)	0.64 (11)	2.38 (12)	163 (13)

[a] Symmetry codes: (I) x, y, z; (II) $-x, 1-y, 1-z$; (III) $x, y, 1+z$; (IV) $1+x, 1+y, z$; (V) $x, y, z-1$. [b] The criterion for inclusion is that the H· · ·B separation be less than 2.45 Å (see text).

Bond distances for the adeninium ligand appear to be less sensitive to protonation than bond angles. The observed bond lengths conform to the view that in the imidazole ring the double bonds are delocalized, while in the pyrimidine ring the bond C(2)–N(3) has considerable double-bond character. The reason that the N(1)–C(6) bond [1.42 (1) Å] is longer than the C(5)–C(6) bond [1.39 (1) Å] (the reverse of the normal situation) is not obvious. Due to the lack of high accuracy in atomic parameters, however, we deem the bond distances for the adeninium ring obtained in this structure to be in the acceptable range.

Hydrogen Bonding and Packing. All hydrogen atoms of the adeninium rings as well as those of the water molecules appear to be involved in hydrogen bonding with neighboring nitrate oxygen atoms. In Figure 4, nitrate groups which are in close contact with hydrogen atoms of the asymmetric unit are shown with O···H distances. Complete information regarding these possible hydrogen bonds are tabulated in Table VI. The criterion used for inclusion of an interaction is that the H···O separation is less than 2.45 Å, even if the C···O, N···O, and O···O separations exceed the sum of the van der Waals radii of 3.0 Å for C···O, 2.9 Å for N···O, and 2.8 Å for O···O.[70] Although this value of 2.45 Å is somewhat smaller than 2.6 Å (sum of the van der Waals radii of H and O), which

---

(64) (a) Kistenmacher, T. J.; Shigematsu, T. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1528. (b) Kistenmacher, T. J.; Shigematsu, T. *Ibid.* **1975**, *B31*, 211.

(65) Langer, V.; Huml, K. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2229.

(66) Authier-Martin, M.; Beauchamp, A. L. *Can. J. Chem.* **1975**, *53*, 2345.

(67) Langer, V.; Huml, K. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1148.

(68) (a) Kistenmacher, T. J.; Shigematsu, T. *Acta Crystallogr., Sect. B* **1974**, *B30*, 166. (b) Langer, V.; Huml, K. *Ibid.* **1978**, *B34*, 1157. (c) Langer, V.; Huml, K. *Ibid.* **1978**, *B34*, 1881.

(69) Rao, S. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1970**, *92*, 4963.

(70) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968; p 16.

Inorg. Chem. **1981**, *20*, 363-372

Hamilton and Ibers[70] suggested as a criterion for existence of a hydrogen bond, it excludes the resulting C–H···O, N–H···O, and O–H···O angles of less than 126°, a value which is considered to be unrealistically small. It can be seen in Figure 4 that oxygens of the non-metal-bonding nitrate ion [containing N(33)] act as acceptor sites through H(1) and H(6a) of the adeninium moiety and the H(a) atom of the water molecule. The existence of this weakly binding nitrate ion in the molecule may explain in part the rather unstable nature of the crystal to X irradiation. It is noted that the imidazole carbon atom C(8) is also involved in a short contact with one of the nitrate oxygen atoms. This type of weak interaction involving the C(8)–H group has previously been observed in a number of structures (see ref 43c, and references cited therein, and ref 55).

Shown in Figure 5 is a stereoscopic view of the unit-cell packing.

Acknowledgment. We are most pleased to acknowledge the partial financial support of this research by Oak Ridge National Laboratory through the Exploratory Studies Program. We are indebted to Dr. B. Pal for helpful discussion on the chemistry of nucleic acid and its constituents. Thanks are also due to Drs. G. M. Brown and J. R. Einstein for their criticism of the paper.

Registry No. $[(C_5H_6N_5)Cd(NO_3)_2{\cdot}H_2O]_2(NO_3)_2$, 75626-83-4; adenosine-5′-monophosphoric acid monosodium salt, 132-00-3.

Supplementary Material Available: A table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Chemical Applications of Topology and Group Theory. 9. The Symmetries of Coordination Polyhedra[1]

R. B. KING

Received May 9, 1980

The point groups of three-dimensional polyhedra with n vertices including those of importance as coordination polyhedra in ML_n complexes are considered as subgroups of the fully symmetric permutation group P_n with $n!$ elements. The terms in the cycle index of P_n are first classified into those forbidden and those allowed for three-dimensional symmetry operations. Subsets of the allowed cycle index terms of P_n can then be chosen in different ways to correspond to the permutations representing symmetry operations in different families of polyhedra with n vertices. Thus the point groups D_{3h}, C_{4v}, and D_5 for the five-vertex figures trigonal bipyramid, square pyramid, and planar pentagon, respectively, can be obtained from the fully symmetric group P_5 by deletion of the (4 + 5)-fold, the (3 + 5)-fold, and the (3 + 4)-fold rotation terms, respectively. For coordination numbers 6, 8, and 9, subgroups Q_n of the fully symmetric group P_n can be found which span all of the symmetries of the chemically feasible polyhedra for these coordination numbers. Thus for coordination number 6, the octahedral group O_h or $P_3[P_2]$ is an effective Q_6 since it spans the symmetries of all possible six-coordinate polyhedra except for the pentagonal pyramid, which is not feasible as a coordination polyhedron. Similarly, for coordination number 8, the wreath product group $P_4[P_2]$ with 384 elements corresponding to the symmetries of the four-dimensional analogue of the octahedron is an effective Q_8 since it spans the symmetries of all of the chemically reasonable eight-coordinate polyhedra including the cube, square antiprism, and hexagonal bipyramid. For coordination number 9, the pair group $P_2[P_3]^{(2)}$ with only 72 elements spans as well as the fully symmetric P_9 group with 9! = 362 880 elements the symmetries of the chemically feasible nine-coordinate polyhedra.

Introduction

In 1969 I published a topological method for generating possible polyhedra for coordination numbers 4–9, inclusive.[2] This approach considered maximum symmetry polyhedra with numbers of vertices (v), edges (e), and faces (f) satisfying the relationships $e + 2 = v + f$ (Euler's relationship), $2e \geq 3f$, $3v \leq 2e$, and $4 \leq v \leq 9$ and avoiding polyhedra containing one or more pentagonal or higher polygonal faces. Among such polyhedra those corresponding to the various possible sp^3d^n hybrids were next examined. Such polyhedra with minimum flexibilities (number of possible different sp^3d^n hybrids), maximum symmetries, and maximum numbers of faces were found to be favored in actual ML_n complexes.

This topological approach for generating polyhedra is attractive since a small number of rather elementary principles and assumptions provides a basis for extracting from the large numbers of possible polyhedra[3,4] those of chemical significance. Furthermore, combination of this topological approach[2] with rather elementary interligand electrostatic repulsion calculations in ML_n complexes[5–12] removes the need for some of the more difficultly justifiable assumptions of the topological treatment[2] including particularly the assumptions of flexibility minimization and avoidance of faces with five or more edges. Nevertheless, the topological approach of my earlier paper,[2] despite possible improvements, has the following inherent limitations for generating chemically significant coordination polyhedra. (1) In the cases of less symmetrical coordination complexes the question of which of several relatively unsymmetrical idealized coordination polyhedra most closely represents that found in an actual structure (such as that found by an X-ray diffraction study) may be ambiguous. (2) Ste-

---

(1) For part 8 of this series see R. B. King, *Theor. Chim, Acta*, **56**, 269 (1980).

(2) R. B. King, *J. Am. Chem. Soc.*, **91**, 7211 (1969).

(3) B. Grünbaum, "Convex Polytopes", Interscience, New York, 1967.

(4) P. J. Federico, *J. Comb. Theory*, **7**, 155 (1969).

(5) D. L. Kepert, *Prog. Inorg. Chem.*, **25**, 42 (1979).

(6) D. L. Kepert, *Prog. Inorg. Chem.*, **24**, 179 (1978).

(7) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(8) D. G. Blight and D. L. Kepert, *Theor. Chim. Acta*, **11**, 51 (1968).

(9) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, **11**, 1556 (1972).

(10) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).

(11) R. V. Parish and P. G. Perkins, *J. Chem. Soc. A*, 345 (1967).

(12) R. B. King, *J. Am. Chem. Soc.*, **92**, 6455 (1970).

0020-1669/81/1320-0363$01.00/0