

Ni₂O₄, 67722-53-6; C₄₀H₅₂F₂₄N₄Ni₂O₄, 67722-54-7; C₄₈H₆₈F₂₄N₄Ni₂O₄, 67722-55-8; C₁₆H₁₈CuF₁₂N₂O₂, 67722-56-9; C₁₇H₂₀CuF₁₂N₂O₂, 67722-57-0; C₁₈H₂₂CuF₁₂N₂O₂, 67722-58-1; C₂₀H₂₆CuF₁₂N₂O₂, 67722-59-2; C₂₄H₃₄CuF₁₂N₂O₂, 67722-60-5.

Supplementary Material Available: Table VI, a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

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Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007

Crystal and Molecular Structure of the Monoclinic Form of [Cd(5'-CMP)(H₂O)]_n¹

JANE K. SHIBA and ROBERT BAU*

Received June 9, 1978

Cadmium(II) 5'-cytidine monophosphate monohydrate sesquihydrate, prepared by the reaction of Na₂(5'-CMP) with Cd(NO₃)₂, crystallizes as fine needles in the monoclinic space group C₂, with $a = 31.480$ (12) Å, $b = 5.349$ (3) Å, $c = 25.200$ (9) Å, $\beta = 128.52$ (2)°, and $Z = 8$. The structure consists of a complex polymeric network in which each CMP group is coordinated to four different cadmium atoms and vice versa. The nucleotide chelates one Cd atom through N(3) and the carbonyl oxygen O(2) of the cytosine base and is further bonded to three other cadmiums through the phosphate group. The Cd atom is seven-coordinate, being connected to four oxygens from phosphate groups, two atoms from a cytosine base, and a water molecule. Average distances: Cd-O(phosphate) = 2.36 Å, Cd-N(3)(cytosine) = 2.33 Å, Cd-O(2)(cytosine) = 2.72 Å, and Cd-O(water) = 2.31 Å. The final R factor is 8.0% for 2359 independent reflections collected on a diffractometer.

Introduction

There has been a growing interest in the role of metals in biological processes. A considerable amount of research has been done on interactions between metal ions and nucleotides or polynucleotides, and many excellent reviews are now available on the subject.²⁻⁷

Cadmium, as well as many metals of the first transition series, has been found to be firmly coordinated to RNA, to the extent that it is not readily removed by the action of strong chelating agents.⁸ It has been suggested that some of these metals may have a role in stabilizing the configuration of RNA. An investigation of the cooling curves of DNA in the presence of Cd²⁺ ions has indicated strong binding of the metal ions to DNA. The decrease of the "melting point" of DNA in the presence of cadmium ions is thought to be due to the destabilizing influence of the cadmium ions arising from interactions between Cd²⁺ and the base portions of the DNA molecule.⁹

There has been relatively little spectral work done on the coordination of cadmium ions to cytosine derivatives, except for a Raman study indicating the absence of significant interaction between Cd²⁺ and cytidine.¹⁰ However, a fair amount is known about the binding of related metal ions such as Zn²⁺ and Hg²⁺ on cytosine and cytidine. ¹H NMR studies on these systems by Li and co-workers show that the predominant mode of coordination is through the N(3) atom of the pyrimidine ring.¹¹ This mode of binding has been confirmed by the results of X-ray crystallographic studies on cytosine and cytidine

complexes,¹²⁻¹⁷ while for 5'-CMP complexes simultaneous binding to both the N(3) position and the phosphate group seems to be the rule,¹⁸⁻²¹ with one exception which shows O(2) binding.²²

In order to get a clearer idea of the structural basis of the tight Cd²⁺/DNA binding, several groups of investigators have been studying the structures of cadmium nucleotide complexes by crystallographic methods. With 5'-GMP, cadmium forms discrete molecular complexes having the formula Cd(5'-GMP)(H₂O)₅, consisting of a cadmium ion octahedrally coordinated by the N(7) atom of the guanine base and five water molecules.²³ On the other hand, with 5'-CMP, cadmium forms orthorhombic crystals of empirical formula [Cd(5'-CMP)(H₂O)]·H₂O consisting of a polymeric network of [Cd(5'-CMP)(H₂O)] units.^{18,19} In this network each CMP molecule was found to be coordinated to Cd through the N(3) position of the pyrimidine ring and also through three oxygen atoms of the phosphate group. This structure will be discussed later.

Around the time the structure of the orthorhombic form of [Cd(5'-CMP)(H₂O)]_n was published^{18,19} we had independently isolated and solved the structure of a different crystalline modification (monoclinic) of this complex.¹ There are many similarities, and also distinct differences, between the two structures. Our results of the monoclinic form of [Cd(5'-CMP)(H₂O)]_n are described in this paper.

Experimental Section

The cadmium-CMP complex was prepared in a similar manner

Table I. Crystal Data for $[\text{Cd}^{\text{II}}(5'-\text{CMP})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$

cryst type	monoclinic	cryst size	0.10 × 0.33
space group	C2		× 0.45 mm
<i>a</i>	31.480 (12) Å	variation in	0.777–1.152
<i>b</i>	5.349 (3) Å	transmission	
<i>c</i>	25.200 (9) Å	coeff (normalized	
β	128.52 (2)°	to an av of unity)	
cell vol	3320 (3) Å ³	2 θ upper limit used	48°
no. of molec	8	in data collection	
in unit cell		data collected	3774 reflcns
calcd density	1.92 g cm ⁻³	data used in the	2359 reflcns
obsd density ^a	1.98 (4) g	structure analysis	
	cm ⁻³	[<i>I</i> > 3 σ (<i>I</i>)]	
abs coeff (μ)	14.68 cm ⁻¹	final agreement	8.0%
for Mo K α		factor, <i>R</i>	
X-rays			

^a Obtained via flotation from a bromoform/hexane mixture.

to that reported by Ogawa and Sakaguchi.²⁴ Although other workers were subsequently able to obtain from this preparation crystals suitable for crystallographic study,^{18,19} in our experience we found that the literature method yielded needles too thin for diffraction work. In view of the well-known ability of urea to modify the crystal habit of salts grown from aqueous solution,²⁵ we repeated the preparation in the presence of urea in the reaction mixture. This yielded needles which were thicker and which turned out to have a different crystalline modification from those prepared conventionally.^{18,19} Several large crystals, growing in clusters, were obtained from a 20-mL aqueous solution of $\text{Cd}(\text{NO}_3)_2$ (0.0070 M), $\text{Na}_2(5'-\text{CMP})$ (0.0056 M), and urea (0.0025 M) at a pH of 6. The crystal used for data collection was a flat plate (0.10 × 0.33 × 0.45 mm) which was cleaved from a long planklike specimen. It was mounted on a glass fiber.

Preliminary photographs indicated the monoclinic space group C2. The alternative space groups *Cm* and *C2/m* were not considered in view of the chirality of the ribose groups. Accurate unit cell parameters were obtained by carefully centering 20 reflections on a Nonius CAD-3 automated diffractometer and are listed together with other relevant crystal data in Table I. The observed density and unit cell volume indicated two independent Cd(5'-CMP) molecules in the asymmetric unit. One unique quadrant of data was collected using Mo K α radiation up to a 2 θ limit of 48°. The scan speed used was 10°/min, the scan range being defined as $\Delta\theta = (1.2 + 0.15 \tan \theta)^\circ$. Each reflection was scanned between two and six times depending on the intensity of the reflection. If the counting rate exceeded 2500 counts/s, zirconium foil attenuators were automatically inserted. A takeoff angle of 4° was used. Three check reflections—(4,0,10), (17,1,9), (14,2,7)—were monitored at 35-reflection intervals during data collection and showed no significant intensity variations (maximum deviation $\pm 3\%$). Data reduction resulted in a total of 2359 reflections whose intensities are greater than 3 σ (*I*). The standard deviation of each intensity reading, σ (*I*), was estimated using the expression: $\sigma(I) = [(peak + background \text{ counts}) + 0.04^2(\text{net intensity})^2]^{1/2}$. Reflections were corrected for Lorentz and polarization effects. An empirical absorption correction was also applied,²⁶ with transmission coefficients varying between 0.777 and 1.152 (normalized to an average of unity).

The structure was solved by conventional heavy-atom methods: The coordinates of the two independent cadmium positions were determined from a Patterson map.²⁷ The other nonhydrogen positions were subsequently found from a series of difference-Fourier maps. Full-matrix isotropic-refinement cycles (with the cadmium and phosphorus atoms given anisotropic temperature factors) were performed separately on each independent molecule for several cycles. The final cycles of refinement included both independent molecules in a single matrix. The final agreement factors are $R_F = 0.080$, $R_{wF} = 0.094$, and $\text{GOF} = 1.88$.²⁸ In the refinement, the function minimized is $\sum w^2(F_o^2 - F_c^2)^2$, where $w = 1/\sigma(F_o^2)$. For the last least-squares cycle, the average shift/esd ratio for the refined parameters is less than 0.05. A final three-dimensional difference-Fourier map showed no residual peaks (other than those associated with the Cd atoms) greater than 1.0 e Å⁻³.

Description and Discussion of the Structure

Final positional and thermal parameters are listed in Table II, and distances and angles in the structure are given in Tables III and IV. A table of final observed and calculated structure

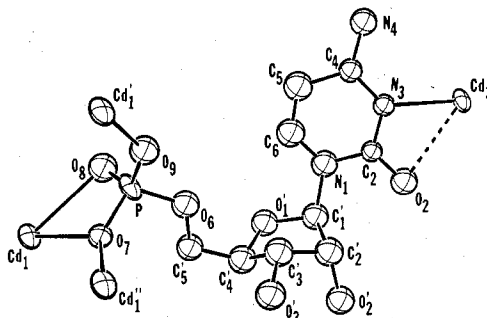


Figure 1. Coordination of a 5'-CMP molecule in $[\text{Cd}(5'-\text{CMP})(\text{H}_2\text{O})]_n$, showing one Cd atom being chelated by the N(3) and O(2) atoms of a cytosine ring and three other Cd atoms attached to the phosphate group of the nucleotide.

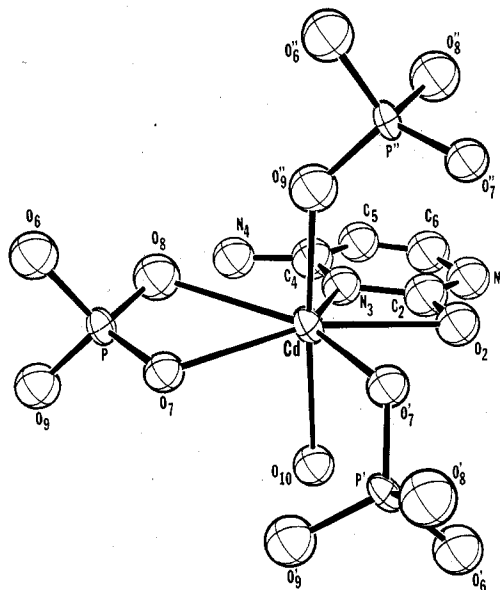


Figure 2. Coordination about the cadmium atom, showing the approximately pentagonal-bipyramidal geometry. Each cadmium atom is bonded to atoms from four different 5'-CMP ligands.

factors is available (supplementary material). There are two crystallographically independent $[\text{Cd}(5'-\text{CMP})(\text{H}_2\text{O})]$ units and three water molecules of crystallization per asymmetric unit. The structure consists of a complex three-dimensional network in which each cadmium atom is coordinated by four CMP molecules and vice versa.

The CMP molecules are essentially equivalent. One cadmium atom is chelated by the N(3) and O(2) atoms of the pyrimidine ring, while three other cadmium atoms are coordinated to the oxygen atoms of the phosphate group (Figure 1). The chelation from the cytosine rings is more obvious in the case of Cd(1) than Cd(2). For Cd(1), both Cd–N and Cd–O distances can be considered bonding [$\text{Cd}(1)\text{--N}(3) = 2.34$ (2) Å, $\text{Cd}(1)\text{--O}(2) = 2.58$ (2) Å], while for Cd(2) the Cd–O interaction is substantially weaker [$\text{Cd}(2)\text{--N}(3) = 2.32$ (2) Å, $\text{Cd}(2)\text{--O}(2) = 2.87$ (2) Å]. For both molecules, the C(5)'–O(6) bond relative to the ribose ring is in the gauche–gauche conformation, the configuration of the pyrimidine about the glycosidic C(1)'–N(1) bond is anti, and the puckering of the ribose ring is C(3)'-endo.

The coordination spheres about the cadmium atoms are, again, rather similar. The cadmium atoms are seven-coordinate²⁹ (Figure 2) and are bonded to (a) four phosphate oxygen atoms from three different CMP molecules, (b) the N(3) and O(2) cytosine atoms from a fourth CMP molecule, and (c) a water molecule. The coordination geometry is difficult to define precisely but can be very roughly described as a distorted pentagonal bipyramid, with the water molecule

Table II. Final Atomic Parameters for $[\text{Cd}^{\text{II}}(\text{5}'\text{-CMP})(\text{H}_2\text{O})]\cdot 1.5\text{H}_2\text{O}^{\text{a}}$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å
Cd(1)	0.18568 (6)	0.50000 (0) ^b	0.95490 (7)	
Cd(2)	0.23368 (6)	0.38827 (37)	0.42153 (6)	
N(1)	0.238 (1)	-0.183 (4)	0.283 (1)	4.4 (4)
	0.542 (1)	0.339 (4)	0.788 (1)	5.1 (4)
C(2)	0.246 (1)	-0.325 (4)	0.332 (1)	3.3 (4)
	0.589 (1)	0.230 (5)	0.839 (1)	4.4 (5)
O(2)	0.287 (1)	-0.283 (3)	0.390 (1)	4.3 (3)
	0.633 (1)	0.306 (3)	0.854 (1)	4.5 (3)
N(3)	0.212 (1)	-0.499 (4)	0.318 (1)	3.4 (3)
	0.591 (1)	0.048 (4)	0.877 (1)	4.7 (4)
C(4)	0.169 (1)	-0.540 (4)	0.256 (1)	3.4 (4)
	0.545 (1)	0.952 (6)	0.860 (1)	5.4 (6)
N(4)	0.133 (1)	-0.731 (5)	0.241 (1)	4.9 (4)
	0.549 (1)	0.762 (5)	0.896 (1)	6.3 (5)
C(5)	0.158 (1)	-0.387 (6)	0.200 (1)	5.6 (6)
	0.495 (1)	0.078 (6)	0.809 (1)	5.5 (6)
C(6)	0.195 (1)	-0.226 (6)	0.216 (1)	5.4 (5)
	0.492 (1)	0.252 (8)	0.771 (2)	7.3 (8)
C(1')	0.279 (1)	0.015 (6)	0.301 (1)	4.9 (5)
	0.546 (1)	0.551 (8)	0.748 (2)	8.4 (9)
O(1')	0.257 (1)	0.192 (4)	0.249 (1)	5.7 (4)
	0.497 (1)	0.682 (5)	0.715 (1)	7.2 (5)
C(2')	0.332 (2)	0.917 (10)	0.319 (2)	9.2 (9)
	0.534 (2)	0.397 (11)	0.681 (2)	10.1 (10)
O(2')	0.377 (1)	0.076 (7)	0.364 (2)	7.1 (7)
	0.569 (2)	0.548 (13)	0.675 (2)	17.5 (14)
C(3')	0.319 (1)	-0.058 (8)	0.255 (2)	8.0 (8)
	0.488 (1)	0.451 (6)	0.634 (1)	5.7 (6)
O(3')	0.363 (1)	-0.056 (9)	0.250 (2)	12.8 (9)
	0.480 (1)	0.431 (9)	0.572 (2)	13.7 (10)
C(4')	0.290 (1)	0.236 (6)	0.229 (1)	5.3 (6)
	0.470 (1)	0.686 (6)	0.646 (1)	6.0 (6)
C(5')	0.255 (1)	0.283 (6)	0.154 (1)	5.3 (5)
	0.405 (1)	0.701 (6)	0.607 (1)	5.9 (6)
P	0.2040 (2)	0.0386 (10)	0.0415 (3)	
	0.3304 (2)	0.4329 (9)	0.5906 (3)	
O(6)	0.230 (1)	0.063 (3)	0.118 (1)	4.7 (3)
	0.391 (1)	0.473 (3)	0.620 (1)	4.3 (3)
O(7)	0.241 (1)	0.168 (3)	0.031 (1)	3.2 (3)
	0.294 (1)	0.560 (3)	0.522 (1)	3.5 (3)
O(8)	0.153 (1)	0.185 (4)	0.002 (1)	6.4 (4)
	0.322 (1)	0.555 (3)	0.636 (1)	4.5 (3)
O(9)	0.200 (1)	0.764 (4)	0.031 (1)	5.3 (4)
	0.325 (1)	0.147 (3)	0.586 (1)	3.5 (3)
O(10)	0.181 (1)	0.247 (3)	0.877 (1)	4.0 (3)
	0.305 (1)	0.111 (3)	0.464 (1)	4.3 (3)
O(11)	0.043 (1)	0.130 (6)	0.100 (1)	9.5 (6)
O(12)	0.113 (1)	0.639 (9)	0.038 (2)	13.5 (10)
O(13)	0.377 (1)	0.426 (11)	0.456 (2)	16.1 (12)

atom	$10^4\beta_{11}^{\text{c}}$	$10^4\beta_{22}^{\text{c}}$	$10^4\beta_{33}^{\text{c}}$	$10^4\beta_{12}^{\text{c}}$	$10^4\beta_{13}^{\text{c}}$	$10^4\beta_{23}^{\text{c}}$
Cd (1)	19 (1)	195 (5)	25 (1)	-1 (2)	30 (1)	-4 (3)
Cd (2)	17 (1)	179 (5)	17 (1)	1 (2)	22 (1)	-1 (2)
P	22 (1)	157 (21)	30 (2)	9 (8)	41 (3)	-15 (10)
	14 (1)	113 (21)	18 (1)	2 (6)	18 (2)	-4 (8)

^a Where applicable, the coordinate for molecule one is given on the first line and that of molecule two is on the second. ^b The *y* value of Cd(1) was arbitrarily set equal to 1/2 to define the origin of the unit cell. ^c Anisotropic temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

and the O(9) atom of one of the phosphate groups defining the axial ligands.

The Polymeric Network. The way in which the $[\text{Cd}(\text{CMP})(\text{H}_2\text{O})]$ units are assembled to form the three-dimensional framework of the crystal is rather interesting. The most striking feature is the presence of large cylindrical channels aligned parallel to the *b* axis (Figure 3). These channels are filled by various water molecules, as will be described later. The walls of the channel are composed of rings of $[\text{Cd}(\text{CMP})(\text{H}_2\text{O})]_4$ units, with each ring consisting of the sequence $[-\text{Cd}_1-(\text{CMP})_1-\text{Cd}_2-(\text{CMP})_2-\text{Cd}_1-(\text{CMP})_1-\text{Cd}_2-(\text{CMP})_2-]$.

Table III. Distances (Å) and Angles (deg) around the Cadmium Atoms (See Figure 2)

	Cd(1)	Cd(2)
Distances		
Cd-N(3)	2.34 (2)	2.32 (2)
Cd...O(2)	2.58 (2)	2.87 (2)
Cd...C(2)	2.86 (2)	2.95 (2)
Cd-O(7')	2.29 (2)	2.20 (1)
Cd-O(7)	2.38 (1)	2.72 (2)
Cd-O(8)	2.62 (2)	2.28 (2)
Cd-O(9)''	2.19 (2)	2.22 (2)
Cd-O(10)	2.30 (2)	2.32 (2)
Angles		
N(3)-Cd-O(2)	53.5 (7)	48.8 (6)
N(3)-Cd-O(9)''	97.2 (8)	95.6 (7)
N(3)-Cd-O(8)	78.6 (8)	85.2 (6)
N(3)-Cd-O(7)	131.6 (7)	128.4 (7)
N(3)-Cd-O(7')	136.0 (7)	142.2 (6)
N(3)-Cd-O(10)	88.4 (7)	102.1 (7)
O(2)-Cd-O(7')	82.5 (6)	80.3 (5)
O(2)-Cd-O(7)	164.1 (6)	166.8 (5)
O(2)-Cd-O(8)	132.0 (7)	130.7 (6)
O(2)-Cd-O(9)''	96.4 (6)	101.2 (6)
O(2)-Cd-O(10)	82.5 (6)	87.5 (6)
O(7)-Cd-O(7)	90.3 (5)	89.4 (5)
O(7)-Cd-O(8)	145.5 (6)	145.9 (6)
O(7)-Cd-O(9)''	88.4 (7)	84.6 (6)
O(7)-Cd-O(10)	83.8 (6)	81.0 (6)
O(7)-Cd-O(8)	56.7 (7)	57.5 (5)
O(7)-Cd-O(9)''	97.6 (6)	86.0 (6)
O(7)-Cd-O(10)	82.6 (5)	82.7 (6)
O(8)-Cd-O(9)''	86.6 (7)	99.8 (7)
O(8)-Cd-O(10)	99.9 (7)	86.1 (7)
O(9)''-Cd-O(10)	172.2 (8)	161.7 (5)

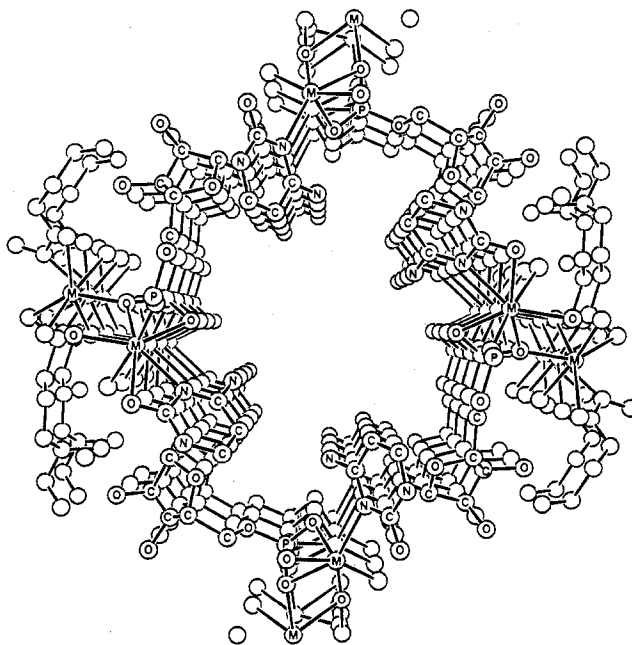


Figure 3. Plot of the large cylindrical channel in the structure, as viewed along the *b* axis of the crystal. A crystallographic twofold axis passes down the center of the channel. The channel is lined by rings by tetrameric $[\text{Cd}(\text{5}'\text{-CMP})(\text{H}_2\text{O})]_4$ units and is partially filled with water molecules of crystallization (not shown) which are hydrogen-bonded to the N(4) amine groups and some of the phosphate oxygen atoms. The $[\text{Cd}(\text{5}'\text{-CMP})(\text{H}_2\text{O})]_4$ rings are further cross-linked by tight $[-\text{Cd}-\text{O}-\text{Cd}-\text{O}-]_n$ spirals, which are shown at the top, bottom, left, and right portions of the diagram.

In addition to these large channels, there are also tight $[-\text{Cd}-\text{O}-\text{Cd}-\text{O}-]_n$ spirals which form cross-links between the large channels. Four of these tight spirals are visible in Figure 3. The $[-\text{Cd}-\text{O}-\text{Cd}-\text{O}-]_n$ spirals are, like the large channels,

Table IV. Average Distances (Å) and Angles (deg) in the 5'-CMP Ligands

Distances			
N(1)-C(2)	1.34 (2)	C(2)'-O(2)'	1.44 (3)
C(2)-O(2)	1.24 (2)	C(2)''-C(3)'	1.31 (3)
C(2)-N(3)	1.32 (2)	C(3)''-O(3)'	1.46 (3)
N(3)-C(4)	1.32 (2)	C(3)''-C(4)'	1.59 (3)
C(4)-N(4)	1.35 (2)	C(4)''-C(5)'	1.57 (2)
C(4)-C(5)	1.46 (2)	C(4)''-O(1)'	1.41 (2)
C(5)-C(6)	1.30 (2)	C(5)''-O(6)	1.40 (2)
C(6)-N(1)	1.40 (2)	P-O(6)	1.57 (1)
N(1)-C(1)'	1.54 (2)	P-O(7)	1.52 (1)
C(1)''-C(2)'	1.60 (3)	P-O(8)	1.48 (1)
C(1)''-O(1)'	1.40 (2)	P-O(9)	1.51 (1)
Angles			
N(1)-C(2)-O(2)	118 (1)	N(3)-C(4)-C(5)	119 (1)
N(1)-C(2)-N(3)	121 (1)	N(4)-C(4)-C(5)	121 (1)
O(2)-C(2)-N(3)	121 (1)	C(4)-C(5)-C(6)	119 (1)
C(2)-N(3)-C(4)	120 (1)	C(5)-C(6)-N(1)	119 (1)
N(3)-C(4)-N(4)	119 (1)	C(6)-N(1)-C(2)	121 (1)
C(6)-N(1)-C(1)'	122 (1)	N(1)-C(1)''-C(2)'	109 (1)
C(2)-N(1)-C(1)'	118 (1)	N(1)-C(1)''-O(1)'	108 (1)
C(1)''-C(2)''-O(2)'	105 (2)	C(5)''-C(4)''-O(1)'	109 (2)
C(1)''-C(2)''-C(3)'	102 (2)	C(3)''-C(4)''-O(1)'	98 (2)
O(2)''-C(2)''-C(3)'	107 (2)	C(4)''-O(1)''-C(1)'	112 (2)
C(2)''-C(3)''-O(3)'	114 (2)	O(1)''-C(1)''-C(2)'	105 (2)
C(2)''-C(3)''-C(4)'	108 (2)	C(4)''-C(5)''-O(6)	108 (2)
O(3)''-C(3)''-C(4)'	111 (2)	C(5)''-O(6)-P	120 (1)
C(3)''-C(4)''-C(5)'	115 (2)		
O(6)-P-O(7)	108.7 (5)	O(7)-P-O(8)	106.9 (5)
O(6)-P-O(8)	108.0 (5)	O(7)-P-O(9)	113.4 (5)
O(6)-P-O(9)	102.8 (5)	O(8)-P-O(9)	116.6 (6)
Torsion Angles ^a			
O(6)-C(5)''-C(4)''-O(1)'	(ϕ_{OO})	-70	
O(6)-C(5)''-C(4)''-C(3)'	($\phi_{\text{OC}} = \psi$)	38	
C(5)''-C(4)''-C(3)''-O(3)'	(ψ')	78	
C(5)''-C(4)''-C(3)''-C(2)'		-154	
O(1)''-C(4)''-C(3)''-O(3)'		-167	
O(1)''-C(4)''-C(3)''-C(2)'	(τ_3)	-40	
C(4)''-C(3)''-C(2)''-O(2)'		-76	
C(4)''-C(3)''-C(2)''-C(1)'	(τ_2)	34	
O(3)''-C(3)''-C(2)''-O(2)'		47	
O(3)''-C(3)''-C(2)''-C(1)'		157	
O(2)''-C(2)''-C(1)''-O(1)'		93	
O(2)''-C(2)''-C(1)''-N(1)		-150	
C(3)''-C(2)''-C(1)''-O(1)'	(τ_1)	-17	
C(3)''-C(2)''-C(1)''-N(1)		99	
O(1)''-C(1)''-N(1)''-C(2)'	(χ_{CN})	-161	
C(4)''-O(1)''-C(1)''-C(2)'	(τ_0)	-9	
C(4)''-O(1)''-C(1)''-N(1)		-126	
C(5)''-C(4)''-O(1)''-C(1)'		148	
C(3)''-C(4)''-O(1)''-C(1)'	(τ_4)	27	
P-O(6)-C(5)''-C(4)''	(ϕ)	-171	

^a The symbols used to define the torsion angles are those given by W. Saenger, *Angew. Chem., Int. Ed. Engl.*, 12, 591 (1973); *Angew. Chem.*, 83, 680 (1973).

aligned along the *b* axis of the unit cell, which happens to be physically the long axis of the actual crystalline sample. One can thus imagine a rapid crystal growth process along the direction of these channels giving rise to the needle-shaped habit of these crystals.

The hydrogen-bonding pattern (Table V) involving the water molecules of crystallization is largely confined to the large cylindrical channel. Water molecule O(11) is hydrogen-bonded to the N(4) amino groups of two adjacent cytosine bases and O(12) is hydrogen-bonded to two phosphate oxygen atoms, O(9) and O(8). One other set of water molecules, O(13), are hydrogen-bonded to (a) the O(2)' ribose atom and the O(2) cytosine atom of one molecule, (b) the O(3)' ribose atom of another molecule, and (c) a water ligand.

Comparison between the Orthorhombic^{18,19} and Monoclinic Forms of $[\text{Cd}(\text{CMP})(\text{H}_2\text{O})]_n$. As mentioned earlier, there are many similarities as well as distinct differences between the

Table V. Hydrogen-Bonding Contacts^a Involving the Water Molecules of Crystallization

hydrogen-bonded atoms	dist,		hydrogen-bonded atoms	dist, A
	A	hydrogen-bonded atoms		
O(11)···N(4) ^b (cytosine)	2.95	O(13)···O(10) (H ₂ O ligand)		2.94
O(11)···N(4) ^b (cytosine)	3.02	O(13)···O(2) (cytosine)		2.71
O(12)···O(9) (phosphate)	2.93	O(13)···O(3)' (ribose)		2.69
O(12)···O(8) (phosphate)	3.12	O(13)···O(2)' (ribose)		2.98

^a Contacts below 3.2 Å. ^b Water molecule O(11) bridges the 4-NH₂ groups of two different cytosine rings.

two forms of $[\text{Cd}(\text{CMP})(\text{H}_2\text{O})]_n$. The main areas of similarity are (a) the fact that both structures are polymeric, with essentially similar modes of attachment (e.g., each Cd is coordinated to one CMP molecule through its cytosine base and to three other CMP molecules through their phosphate groups; each Cd atom also has one directly coordinated water molecule) and (b) the presence of large cylindrical channels through the crystal cross-linked by cadmium-phosphate-cadmium spirals.

The differences include the following: (a) $[-\text{Cd}-\text{O}-\text{Cd}-]$ spirals are present in the monoclinic form of $[\text{Cd}(\text{CMP})(\text{H}_2\text{O})]_n$. Although the $[-\text{Cd}-\text{O}-\text{P}-\text{O}-\text{Cd}-]$ spirals reported in orthorhombic form can also be envisaged here (consider, for example, sequences such as Cd(1)''-O(9)-P-O(7)-Cd(1)'' or Cd(1)''-O(9)-P-O(8)-Cd(1) as shown in Figure 1), the $[-\text{Cd}-\text{O}-\text{Cd}-]$ type spirals observed in our structure are as far as we can tell not present in the orthorhombic form.^{18,19} (b) The cadmium ions in the monoclinic form are seven-coordinate while those in the orthorhombic form are five-coordinate. This, however, is a rather subjective difference, since as pointed out in footnote 29, the coordination number depends on one's definition of bond distance. (c) A crystallographic difference between the two structures, besides the dissimilarity of the space groups, is the fact that there are two independent molecules per asymmetric unit in the monoclinic form as opposed to one in the orthorhombic form. (d) The density of the monoclinic crystals [$\rho(\text{calcd}) = 1.92 \text{ g cm}^{-3}$] is distinctly different from that of the orthorhombic crystals [$\rho(\text{calcd}) = 2.11 \text{ g cm}^{-3}$],^{18,19} indicating a more "open" structure for the monoclinic compound.

The Cytosine-Cadmium Chelate. Szalda, Marzilli, and Kistenmacher have discussed in some detail the question of when a cytosine ligand is considered chelating or not.¹⁵ In the present complex there is reason to consider the interaction between CMP and Cd(1) as a true example of chelation, but for Cd(2), the significantly longer Cd(2)-O(2) distance makes this assignment questionable. In Table VI, we have tabulated the M-N(3) and M-O(2) distances of a number of metal complexes of cytosine and cytosine derivatives. As expected, the M-N(3) interaction is in almost all cases the dominant interaction, while the M-O(2) distances span a wide range of values. The difference between the M-N(3) and M-O(2) distances in monoclinic $[\text{Cd}(5' \text{-CMP})(\text{H}_2\text{O})]_n$ is significantly smaller than those in other compounds, suggesting that the present compound approaches the true N(3)-O(2) chelating condition more closely than previous structures.

Conclusion

There have now been several structure determinations reported on cadmium-nucleotide complexes and those of the related metal zinc. Cadmium and zinc are both considered to be of the "phosphate and base" binding category,^{4,5} and, with only one exception so far, this conclusion has been confirmed in crystallographic studies. The structures of $[\text{Zn}(5' \text{-IMP})(\text{H}_2\text{O})]_n$,³⁰ $[\text{Cd}_2(5' \text{-IMP})_3(\text{H}_2\text{O})_6]_n$,³¹ $[\text{Zn}(5' \text{-CMP})(\text{H}_2\text{O})]_n$,²⁰ and the two forms of $[\text{Cd}(5' \text{-CMP})(\text{H}_2\text{O})]_n$,^{18,19} discussed in this paper have all been of the polymeric variety involving extensive metal-phosphate as well

Table VI. Comparison between the M-N(3) and M-O(2) Distances in Various Metal-Cytosine Complexes and Related Compounds^a

	M-	M-	diff,	ref
	N(3), A	O(2), A		
Cu(cytosine) ₂ Cl ₂	1.95	2.74	0.79	12
Cu(cytosine)(glycylglycine)	1.97	2.88	0.91	12
Cu(cytosine)(glycylglycine)	1.979	2.819	0.84	13
Cu(cytidine)(glycylglycine)	1.979	2.819	0.840	14
Cu(cytidine)(glycylglycine)	2.01	2.74	0.73	15
[Cu(cytosine)(N'-salicylidene-N'-methylethylenediamine)]NO ₃	2.008	2.772	0.764	16
Pd(1-methylcytosine) ₂ Cl ₂	2.031	3.015	0.984	17
[Co(5'-CMP)(H ₂ O)] _n	1.99	2.64	0.65	18
[Cd(5'-CMP)(H ₂ O)] _n	2.32	2.92	0.60	18
(orthorhombic)				
[Cd(5'-CMP)(H ₂ O)] _n	2.327	<i>b</i>		19
(orthorhombic)				
[Cd(5'-CMP)(H ₂ O)] _n	2.34	2.58	0.24	this work
(monoclinic)	2.32	2.87	0.55	this work
[Zn(5'-CMP)(H ₂ O)] _n	2.04	2.69	0.65	20
[Pt(5'-CMP)(ethylenediamine)] ₂	2.06	2.99	0.93	21
[Mn(5'-CMP)(H ₂ O)] _n		2.08 ^c		22

^a For an earlier tabulation, see ref 15. ^b Value not reported.

^c [Mn(5'-CMP)(H₂O)]_n is the only compound in this table showing metal-cytosine binding through O(2) and not through N(3).

as metal-base binding. The lone exception is the structure of monomeric [Cd(5'-GMP)(H₂O)]₂,²³ which shows bonding between Cd and the N(7) atom of the purine ring but no direct cadmium-phosphate bonding.

As far as complexes of CMP with metals are concerned, there is mounting evidence to suggest that the N(3) atom of cytosine is not as strong a ligand as the N(7) atom of guanine and that M-N(3) binding often needs to be augmented by phosphate-metal bonding for added stability. This pattern has been found repeatedly in the polymeric structures of [Cd(5'-CMP)(H₂O)]_n,^{18,19} [Co(5'-CMP)(H₂O)]_n,¹⁸ and [Zn(5'-CMP)(H₂O)]_n,²⁰ and in the dimeric structure of [Pt(NH₂CH₂CH₂NH₂)(5'-CMP)]₂.²¹ It remains for future crystallographic work to determine if this is indeed a consistent pattern in metal-5'-CMP complexes.

Acknowledgment. This research was supported by NIH Grants CA-17367 and AM-15846, and computer time was provided by the USC Computer Center. R.B. acknowledges support from a NIH Research Career Development Award (CA-00015). We also thank Mr. Donald L. Tipton for computational assistance, Dr. G. R. Clark for supplying material prior to publication, and Dr. R. B. Saillant for suggesting to us the use of urea to modify crystal habit.

Registry No. [Cd^{II}(5'-CMP)(H₂O)]·1.5H₂O, 67761-40-4.

Supplementary Material Available: A listing of the observed and calculated structure factors of [Cd(5'-CMP)(H₂O)]·1.5H₂O (12 pages). Ordering information is given on any current masthead page.

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- The coordination number depends somewhat on one's definition of a bonding distance. For the seven-coordinate structure depicted in Figure 2, bonding distances range from 2.19 to 2.62 Å in the case of Cd(1) and from 2.20 to 2.87 Å in the case of Cd(2). On the other hand, if a 2.4 Å limit constitutes one's definition of a bonding distance, then both metal atoms would be considered five-coordinate.
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