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The Structure of Triaquabis(uracilato)cadmium(II)

BY ILPO MUTIKAINEN AND PAAVO LUMME

Department of Inorganic Chemistry, University of Helsinki, SF-00100 *Helsinki* 10, *Finland*

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Abstract

$C_8H_{12}CdN_4O_7$, $[Cd(C_4H_3N_2O_2)_2(H_2O)_3]$, is orthorhombic, space group $Fdd2$, with $a = 24{\cdot}833\ (8)$, $b = 9{\cdot}517\ (2)$, $c = 10{\cdot}420\ (3)$ Å, $Z = 8$. Final $R = 0{\cdot}018$ for 634 unique reflections. The coordination sphere about Cd is a trigonal bipyramid with the N(3) atoms of two symmetry-related uracilato monoanions and one water molecule occupying the equatorial sites at distances of 2·211 (4) and 2·269 (8) Å, respectively. The axial sites are occupied by two symmetry-related water molecules at 2·439 (4) Å. The coordination alters the uracil ring geometry by closing the angle at the coordination site, N(3), and widening the adjacent angles. The ring is also more non-planar than in uncoordinated uracil. The uracil rings form columns approximately along the [011] and $[01\bar{1}]$ directions. The rings in the columns are not parallel, but form angles of 8·72° with each other. The stacking pattern is characterized by minimal base overlap and the keto O atoms at C(2) point in the same direction. The Cd atoms and water molecules lie between the columns and the structure is held together by a hydrogen-bond network in which two water molecules and the N atom not involved in coordination act as donors and the exocyclic keto O atoms as acceptors.

Introduction

Few structural studies have been reported of metal complexes of uracil and thymine (Hodgson, 1977), owing to the weak coordination of the bases at low and neutral pH. At high pH, where they assume their enolic forms, there are several good coordination sites: the exocyclic O(2) and O(4) and the ring N(1) and N(3), both of which are deprotonated at pH > 9·5 (Nakanishi, Suzuki & Yamazaki, 1961).

One difficulty arising at high pH is the precipitation of the metals as hydroxides. This can be overcome by use of suitable complexation agents to keep the metals in solution. In the preparation of the Cu–thyminato complex, Kistenmacher, Sorrell & Marzilli (1975) used diethylenetriamine to form a soluble Cu complex and added thymine to this solution. We have used ammonia to form soluble metal complexes and to deprotonate the uracil base in the preparation of diamminediaquabis(uracilato)nickel(II) (Lumme & Mutikainen, 1980). Though ammonia is only useful with those metals that form soluble ammine complexes, it has the benefit of being a small molecule and causing only slight steric hindrance in the metal–uracil complexation.

In uracil and thymine both N(1) and N(3) are deprotonated at high pH and it is difficult to deduce the preferred coordination site. In fact, metal, reaction time and packing factors probably have a more pronounced influence on the site of coordination than the negligible difference in the nucleophilicities at the deprotonated ring N atoms (Snyder, Shulman & Neumann, 1970). In both Cu—thyminato and Ni—uracilato complexes, the coordination site is the deprotonated N(1). In our attempt to study the effect of the metal, we chose to use Cd because Cd^{2+} is not a transition-metal ion and the coordination is purely electrostatic. Cd, with its strong

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coordination to RNA and DNA, is also of biological interest (Wacker & Vallee, 1959).

In two Cd complexes with cytidine (Shiba & Bau, 1978; Clark & Orbell, 1978) and one with 1-methylcytosine (Gagnon, Beauchamp & Tranqui, 1979) the coordination site of the base is the ring N(3) atom which in cytosine is deprotonated. In the 1-methylthymine–Hg^{II} complex (Kosturko, Folzer & Stewart, 1974), prepared at high pH, the coordination site is also N(3), as it is in the 1-methylthyminato–Pt^{II} complex (Lock, Peresie, Rosenberg & Turner, 1978). In all these compounds N(1) has been blocked so that no coordination at that site is possible.

To study further the effect of metals in the complexation of the deprotonated uracil, where coordination is possible at both N(1) and N(3), we have prepared triaquabis(uracilato)cadmium(II) and undertaken its X-ray analysis.

Experimental

The complex was prepared by dissolving $CdCl_2.2H_2O$ and uracil (1:1 molar ratio) in a minimum amount of hot concentrated ammonia solution and slowly evaporating at room temperature. Colourless octagonal crystals precipitated during two weeks and were found suitable for X-ray work. Weissenberg photographs established the space group as orthorhombic *Fdd*2 from systematic absences $h + k, k + l = 2n + 1, k + l = 4n + 1$ and $l + h = 4n + 1$. The density was measured by flotation in a mixture of $CHCl_3$–CH_3I. The crystal selected for data collection was 0·50 × 0·25 × 0·25 mm. The cell parameters (Table 1) were determined by least squares from the adjusted angular settings of 17 reflections measured on a Syntex $P2_1$ diffractometer.

The intensity measurements were carried out at room temperature with graphite-monochromatized Mo $K\alpha$ radiation and the θ–2θ scan technique. The scan rate varied from 2·50 to 29·3° min^{-1}, depending on the number of counts measured in a fast preliminary scan. Up to a maximum value of $2\theta = 55°$, 768 reflections were measured, resulting in a set of 749 unique reflections. Of these, 634 were considered as observed [$I > 3\sigma(I)$]. Three strong reflections monitored periodically exhibited no significant variation. The intensities were corrected for Lorentz and polarization effects and an absorption correction was made from φ-scan data.

Table 1. *Crystal data*

$C_8H_{12}CdN_4O_7$
Orthorhombic, *Fdd*2
$a = 24{\cdot}833\ (8)$ Å
$b = 9{\cdot}517\ (2)$
$c = 10{\cdot}420\ (3)$
$V = 2462{\cdot}6$ Å^3

$M_r = 388{\cdot}6$
$Z = 8$
$D_m = 2{\cdot}10$ Mg m^{-3}
$D_c = 2{\cdot}10$
$\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å
$\mu(\text{Mo } K\alpha) = 1{\cdot}815$ mm^{-1}

Structure determination

In the space group *Fdd*2 with $Z = 8$, Cd atoms should occupy a special position 0,0,*z* of symmetry 2, and thus Cd was situated at 0,0,0 and its positional parameters were fixed. Successive difference syntheses, structure factor calculations and isotropic refinements revealed all the non-hydrogen atoms. After full-matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}024$ and a difference map revealed the positions of all the H atoms. Full-matrix refinement with all the non-hydrogen atoms anisotropic and H atoms isotropic gave a final $R = 0{\cdot}018$. After the last cycle the average shift/error was 0·029 and maximum 0·234. In the final difference map the largest residual peak was 0·37 e Å^{-3} in the vicinity of Cd. Unit weights were used at all stages. Scattering factors were obtained from Cromer & Mann (1968). The Cd was treated as Cd^{2+} and the anomalous-dispersion correction was applied (*International Tables for X-ray Crystallography*, 1974). Extinction was not regarded as being significant and no correction was made.

All calculations were performed on a Univac 1108 computer with XRAY 76 (Stewart, 1976).

Results and discussion

ORTEP drawings (Johnson, 1965) and the numbering scheme of the molecule are shown in Fig. 1. The

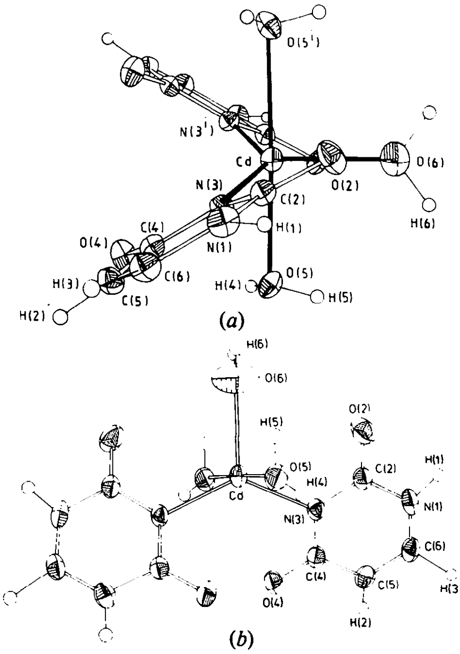

Fig. 1. *ORTEP* drawing with the numbering scheme of the triaquabis(uracilato)cadmium(II) molecule viewed (*a*) along *a* and (*b*) along *b*. 50% probability ellipsoids are shown for the non-hydrogen atoms.

packing of the molecules is shown in Fig. 2. The atomic coordinates and the equivalent values of the anisotropic temperature factor coefficients (Hamilton, 1959) are listed in Table 2,* bond lengths and angles in Table 3. The least-squares plane through the uracil ring and the distances of various atoms from the plane are given in Table 4 and the hydrogen-bond distances and angles in Table 5.

The Cd *coordination sphere*

The Cd atom is pentacoordinated to two uracilato monoanions at N(3) and to three water molecules, one of which is at the special position 0,0,–0·2178. Although the compound was prepared in concentrated ammonia solution, no ammonia molecules were present in the complex. The Cd coordination sphere is a distorted trigonal bipyramid, with the water O(6) atom in the special position and N(3) and N(3^{i}) occupying the equatorial sites. The Cd—O(6) length is 2·269 (8), the Cd—N(3) length 2·211 (4) Å, and the angles O(6)—Cd—N(3) and N(3)—Cd—N(3^{i}) are 112·7 (1)

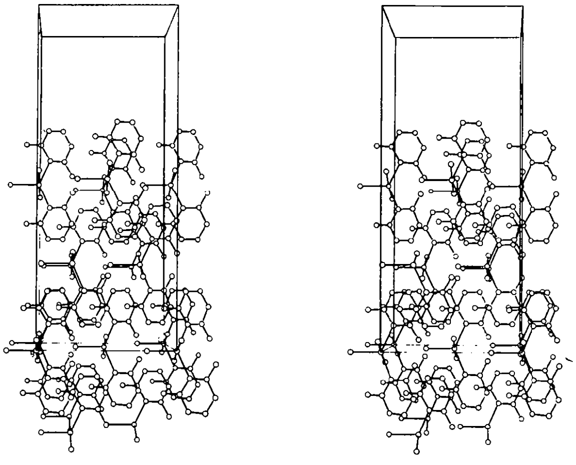

Fig. 2. The packing of the molecules viewed down *b*.

Table 2. *Fractional atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms*; $\times 10^3$ *for* H) *and* U_{eq} ($\text{Å}^2 \times 10^4$)

E.s.d.'s are given in parentheses.

	x	y	z	U_{eq}
Cd	0	0	0	270
N(1)	−1710 (2)	939 (5)	716 (5)	324
C(2)	−1231 (2)	533 (6)	144 (7)	264
N(3)	−765 (2)	781 (4)	819 (4)	235
C(4)	−766 (2)	1479 (6)	1948 (5)	260
C(5)	−1268 (2)	1941 (6)	2483 (9)	308
C(6)	−1728 (2)	1629 (6)	1846 (6)	305
O(2)	−1228 (2)	−34 (6)	−921 (4)	421
O(4)	−329 (1)	1695 (4)	2537 (6)	368
O(5)	349 (2)	2395 (5)	47 (5)	353
O(6)	0	0	−2178 (8)	869
H(1)	−199 (2)	96 (7)	12 (10)	
H(2)	−125 (2)	255 (8)	327 (5)	
H(3)	−215 (2)	186 (6)	251 (10)	
H(4)	34 (2)	265 (7)	−84 (7)	
H(5)	56 (2)	247 (9)	40 (7)	
H(6)	−3 (4)	−85 (7)	−277 (8)	

Table 3. *Interatomic distances* (Å) *and angles* (°)

(*a*) Primary coordination sphere about the Cd atom

Cd—N(3)	2·211 (4)	N(3)—Cd—N(3^{i})	134·6 (2)
Cd—O(5)	2·439 (4)	N(3)—Cd—O(6)	112·7 (1)
Cd—O(6)	2·269 (8)	N(3)—Cd—O(5)	89·0 (1)
		O(6)—Cd—O(5)	91·2 (1)
		O(5)—Cd—O(5^{i})	177·7 (2)

(*b*) Uracilato ligand

N(1)—C(2)	1·386 (7)	C(6)—N(1)—C(2)	122·6 (5)
C(2)—O(2)	1·234 (0)	N(1)—C(2)—N(3)	117·1 (6)
C(2)—N(3)	1·375 (7)	N(1)—C(2)—O(2)	120·9 (5)
N(3)—C(4)	1·351 (7)	N(3)—C(2)—O(2)	122·0 (5)
C(4)—C(5)	1·434 (7)	C(2)—N(3)—C(4)	121·8 (4)
C(4)—O(4)	1·264 (6)	N(3)—C(4)—C(5)	119·5 (5)
C(5)—C(6)	1·355 (8)	N(3)—C(4)—O(4)	120·0 (5)
C(6)—N(1)	1·349 (8)	O(4)—C(4)—C(5)	120·5 (5)
		C(4)—C(5)—C(6)	118·4 (7)
		C(5)—C(6)—N(1)	120·4 (5)

(*c*) Hydrogen atoms

N(1)—H(1)	0·94 (9)	O(5)—H(4)	0·96 (7)
C(5)—H(2)	1·01 (6)	O(5)—H(5)	0·64 (6)
C(6)—H(3)	1·27 (7)	O(6)—H(6)	1·02 (8)
C(6)—N(1)—H(1)	123 (5)	H(4)—O(5)—H(5)	123 (7)
C(2)—N(1)—H(1)	111 (5)	H(4)—O(5)—Cd	102 (4)
C(4)—C(5)—H(2)	117 (3)	H(5)—O(5)—Cd	113 (7)
C(6)—C(5)—H(2)	125 (3)	H(6)—O(6)—H(6^{i})	105 (6)
C(5)—C(6)—H(3)	113 (4)	H(6)—O(6)—Cd	127 (4)
N(1)—C(6)—H(3)	126 (4)		

Table 4. *The least-squares plane for the pyrimidine ring*

The equation is expressed in direct space as $1{\cdot}8854X + 8{\cdot}3122Y - 5{\cdot}0125Z = 0{\cdot}112$. Asterisks denote atoms defining the plane. Displacements from the plane are in Å and e.s.d.'s are given in parentheses.

N(1)*	−0·013 (5)	C(4)*	−0·004 (5)	O(2)	0·089 (5)
C(2)*	0·026 (6)	C(5)*	0·018 (6)	O(4)	−0·037 (5)
N(3)*	−0·018 (5)	C(6)*	−0·009 (5)	Cd	−0·112 (5)

Table 5. *Distances and angles in interactions of the type D*—H···*A*

D	H	*A*	*D*—H (Å)	*D*···*A* (Å)	H···*A* (Å)	*D*—H···*A* (°)
O(5)	H(4)	O(4)[a]	0·96 (9)	2·756	1·799	174
O(5)	H(5)	O(2)[b]	0·64 (6)	2·797	2·160	174
N(1)	H(1)	O(4)[c]	0·94 (9)	2·869	2·082	140

Symmetry position of atom *A*: (*a*) $-x, -y+\frac{1}{2}, z+\frac{1}{2}$; (*b*) $x+\frac{1}{4}, -y+\frac{1}{4}, z+\frac{1}{4}$; (*c*) $x-\frac{1}{4}, -y+\frac{1}{4}, z-\frac{1}{4}$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35397 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England

and 134·6 (2)°, respectively. Because of the symmetry, the Cd atom lies in the equatorial plane. The axial positions are occupied by the water O(5) and O(5$^{\mathrm{i}}$) atoms, at a distance of 2·439 (4) Å from Cd.

The Cd—ligand bond lengths agree well with those found in other Cd complexes, though the Cd—O(5) length is rather long for a pentacoordinated Cd complex.

The trigonal bipyramid in this compound is less distorted from its ideal geometry than in other Cd complexes (Harrison & Trotter, 1972; Post & Trotter, 1974; Clark & Orbell, 1978), the O(5)—Cd—O(5$^{\mathrm{i}}$) angle being 177·7 (2)°.

The Cd coordination sphere is blocked by the exocyclic keto O atoms of the two uracilato ligands, so that no more ligands can coordinate to Cd. The exocyclic O(2) and O(4) are at distances of 3·196 (4) and 3·202 (4) Å, respectively, and must lie on opposite sides of the equatorial plane because the angle between the uracilato ligand and the plane is 32·8°.

The uracilato ligand structure

The N(3) coordination alters the uracil ring geometry by closing slightly the C(2)—N(3)—C(4) angle and opening the adjacent angles. This same trend can be observed in the N(1)-coordinated Cu–thyminato and Ni–uracilato complexes, in both of which the angle at the coordination site closes and the adjacent angles get wider. The bond lengths do not differ significantly from those of uncoordinated uracil (Stewart & Jensen, 1967), but the uracil ring is more non-planar, the largest deviations from the least-squares plane through the uracil ring being for C(2), 0·026 (6), and C(5), 0·018 (6) Å. The exocyclic keto O(2) and O(4) atoms and Cd are considerably out of the ring plane, the deviations being 0·089 (5), −0·037 (5) and −0·112 (5) Å, respectively.

Molecular arrangement and hydrogen-bond system

The uracil rings form columns approximately along the [001] and $[01\bar{1}]$ directions. The rings in the columns are not parallel, but form angles of 8·72° with each other. The average distance between rings is 3·2 Å. As is commonly found in the crystal structures of pyrimidines (Bugg, Thomas, Sundaralingam & Rao, 1971), the stacking of the bases is not extensive and the keto O atoms at C(2) point in the same direction. The Cd atoms and coordinated water molecules lie between these columns. The columnar network is held together by hydrogen bonds formed between the two H atoms of O(5) and the exocyclic keto O atoms of the pyrimidine rings. The keto O(4) also forms a hydrogen bond with N(1$^{\mathrm{i}}$). The coordinated water molecule at the special position 0,0,−0·2178 (8) does not form any hydrogen bonds nor intermolecular contacts within 3·2 Å. The details of the hydrogen bonds are given in Table 5.

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