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The Structure of Diamminediaquabis(uracilato)nickel(II)

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Abstract

Crystals of $[Ni(C_4H_3N_2O_2)_2(H_2O)_2(NH_3)_2]$, $C_8H_{16}N_6NiO_6$, are triclinic, space group $P\bar{1}$, with $a = 6{\cdot}112\ (5)$, $b = 7{\cdot}101\ (3)$, $c = 8{\cdot}476\ (4)$ Å, $\alpha = 112{\cdot}53\ (4)$, $\beta = 83{\cdot}22\ (5)$, $\gamma = 107{\cdot}55\ (4)°$, $Z = 1$. The structure was refined to $R = 0{\cdot}067$ for 917 independent reflections. The coordination sphere about Ni is octahedral, with the two ammonia and two water ligands occupying the equatorial sites and two N(1)-coordinated uracil monoanions in the axial sites. The conformation of the N(1)-coordinated uracil monoanion differs from the uncoordinated form in having a slightly shorter N(1)—C(2) bond and a considerably longer C(2)—O(2) bond. The crystal structure consists of layers which are formed through hydrogen bonds in the ring planes. The layers are held together by a hydrogen-bond network in which the exocyclic O(4) atom acts as acceptor in two hydrogen bonds from the layer on one side and forms an intermolecular contact with a water molecule lying in the layer on the other side.

Introduction

Uracil and thymine and their nucleoside and nucleotide derivatives have barely protonated ring N atoms at low or neutral pH. Coordination to these N atoms is therefore less favourable than to ring N atoms in the other nucleic acid constituents which have at least one available lone pair (Kistenmacher, Sorrell & Marzilli, 1975).

The situation is different at high pH because uracil assumes its enolic form by losing the two ring N atom protons, and coordination of a metal ion becomes possible to N(1), N(3), O(2) or O(4). The favoured coordination site will depend on the metal, pH, reaction time, *etc.*

At low pH, uracil and dihydrouracil have been shown to bind $HgCl_2$ through the exocyclic O atom at C(4) of the pyrimidine ring (Carrabine & Sundaralingam, 1971). At high pH, complexation is probably to an unprotonated ring N atom. Three structural studies of thymine complexes, prepared at moderately high pH, have been published: 1-methylthyminato—Hg^{II} complex, in which the coordination site is N(3) (Kosturko, Folzer & Stewart, 1974); di-μ-(1-methylthyminato-N^3,O^4)-bis[*cis*-diammineplatinum(II)] dinitrate hydrate (Lock, Peresie, Rosenberg & Turner, 1978) in which the coordination sites are N(3) and O(4); and aqua(diethylenetriamine)(thyminato)copper(II) bromide dihydrate (Kistenmacher, Sorrell & Marzilli, 1975) in which the coordination site is N(1).

In a study of several pyrimidine complexes of Co and Ni, a crystalline uracil–Ni^{II} complex has been prepared at the very high pH of concentrated ammonium hydroxide solution (Weiss & Venner, 1969). Because no evidence of the actual coordination site was given and very few structural data on the coordination sites of uracil complexes are available, we have prepared this complex and undertaken its X-ray analysis.

Experimental

The complex was prepared by the method of Weiss & Venner (1969). The crystals exhibited severe multiple twinning, but when the crystallization was performed at 313 K, small single crystals were obtained.

Weissenberg photographs established the space group to be triclinic. Cell parameters were determined by least squares from the angular settings of 12 reflections measured on a Syntex $P2_1$ diffractometer (Table 1). The density was measured by flotation in a mixture of CCl_4 and CH_3I. The crystal selected for data collection was $0{\cdot}15 \times 0{\cdot}22 \times 0{\cdot}25$ mm. Intensity measurements were carried out at room temperature on

Table 1. *Crystal data*

$C_8H_{16}N_6NiO_6$
Triclinic $P\bar{1}$
$a = 6{\cdot}112\ (5)$ Å
$b = 7{\cdot}101\ (3)$
$c = 8{\cdot}476\ (4)$
$\alpha = 112{\cdot}53\ (4)°$
$\beta = 83{\cdot}22\ (5)$
$\gamma = 107{\cdot}55\ (4)$

$V = 323{\cdot}8$ Å^3
$M_r = 350{\cdot}96$
$Z = 1$
$D_m = 1{\cdot}81$ Mg m^{-3}
$D_c = 1{\cdot}80$
λ(Cu K) = 1·5418 Å
μ(Cu K) = 1·39 mm^{-1}

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a semi-automatic two-circle Stoe–Güttinger diffractometer with Ni-filtered Cu radiation and the ω-scan technique. The rotation axis was b, the scan range 3° and speed 1° $\min^{-1}$. Background counts of 30 s were taken at the beginning and end of each scan. The net intensity, I, and its e.s.d., $\sigma(I)$, were calculated as follows: $I = [P - 3(B_1 + B_2)]$ and $\sigma(I) = [P + (B_1 + B_2)]^{1/2}$, where P is the peak and B_1 and B_2 are the background counts. 1148 reflections were measured up to a maximum value of $2\theta = 145°$, and of the resulting set of 1033 unique reflections 917 were regarded as observed $[I > 2\sigma(I)]$. One strong reflection monitored periodically showed no significant variation of intensity. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure determination

In $P\bar{1}$, the Ni atom must lie on a centre of symmetry and the other atoms in general positions. All non-hydrogen atoms were located in a Fourier synthesis phased on Ni at 0,0,0. After full-matrix refinement, first with isotropic then with anisotropic temperature factors for the 11 non-hydrogen atoms, $R = \sum(||F_o| - |F_c||)/\sum |F_o|$ was 0·106. The scales were refined separately and the weights obtained from $w = 1/(10 + |F_o| + 0{\cdot}04|F_o|^2 + 0{\cdot}001|F_o|^3)$. At this stage a difference map with $\sin\theta/\lambda < 0{\cdot}475$ Å^{-1} revealed the positions of six H atoms. Two ammonia H atoms were not sharply defined and were located at expected positions with the aid of the one found from the map. The H atoms were given a common isotropic temperature factor, $U = 0{\cdot}05$ Å^2. Full-matrix least-squares refinement with the H parameters fixed and scales refined as a group resulted in a final $R = 0{\cdot}067$ and $R_w = 0{\cdot}093$. After the last cycle the average shift/error was 0·019 and maximum shift/error 0·076.

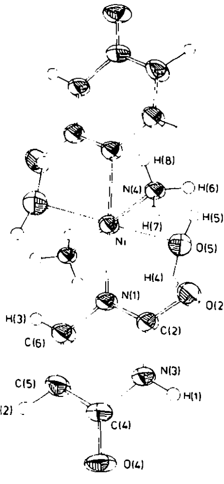

Fig. 1. *ORTEP* drawing showing the numbering scheme. 50% probability thermal ellipsoids are shown for the non-hydrogen atoms.

Scattering factors were obtained from Cromer & Mann (1968). Ni was treated as Ni^{2+} and an 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

An *ORTEP* drawing (Johnson, 1965) with the numbering scheme of the molecule is shown in Fig. 1. The intramolecular bond lengths and angles are illustrated in Fig. 2 and the packing of the molecules in Fig. 3. The atomic coordinates and U_{eq} (Hamilton, 1959) are in Table 2* and a comparison of the bond lengths and angles of the coordinated uracilato monoanion, uncoordinated uracil (Stewart & Jensen, 1967),

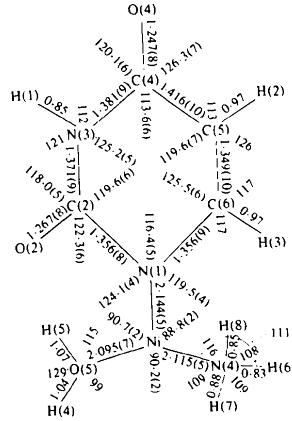

Fig. 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

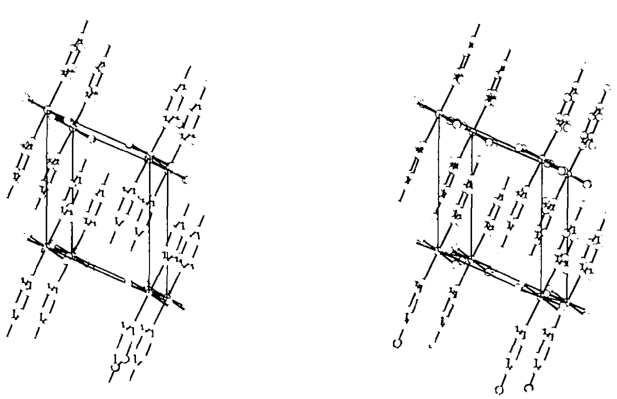

Fig. 3. Packing of the molecules viewed down **a**.

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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 35370 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* (×10⁴) *and equivalent values of the anisotropic temperature factor coefficients* (×10⁴)

	x	y	z	U_{eq} (Å²)
Ni	0	0	0	28
N(1)	−133 (9)	−1521 (9)	−2728 (6)	29
C(2)	−2064 (11)	−2836 (12)	−3618 (8)	33
O(2)	−3937 (9)	−3416 (10)	−2889 (6)	49
N(3)	−1996 (10)	−3639 (10)	−5369 (7)	36
C(4)	−78 (13)	−3220 (13)	−6353 (8)	37
O(4)	−215 (10)	−3994 (9)	−7942 (6)	43
C(5)	1919 (13)	−1894 (13)	−5382 (9)	42
C(6)	1795 (12)	−1141 (12)	−3661 (9)	38
O(5)	−2430 (9)	1516 (10)	−55 (7)	47
N(4)	2656 (9)	2569 (9)	−279 (6)	27
H(1)	−3232	−4193	−5951	
H(2)	3315	−1835	−6063	
H(3)	3191	−192	−3038	
H(4)	−1900	1833	−1167	
H(5)	−2833	2567	1167	
H(6)	3893	2256	−522	
H(7)	2820	3654	694	
H(8)	2426	3050	−1000	

Table 3. *Comparison of the bond lengths* (Å) *and angles* (°) *in the* N(1)-*coordinated uracil monoanion* (*LM*), *uracil* (*Stewart & Jensen*, 1967; *SJ*) *and two forms of uridine* (*Green et al.*, 1975; *GM*)

	LM	SJ	GM	
N(1)–C(2)	1·356 (8)	1·371 (3)	1·376	1·366
C(2)–N(3)	1·371 (9)	1·376 (2)	1·371	1·369
C(2)–O(2)	1·267 (8)	1·215 (2)	1·227	1·217
N(3)–C(4)	1·381 (9)	1·371 (2)	1·387	1·374
C(4)–C(5)	1·416 (10)	1·430 (3)	1·423	1·419
C(4)–O(4)	1·247 (8)	1·245 (2)	1·232	1·229
C(5)–C(6)	1·349 (10)	1·340 (2)	1·333	1·335
C(6)–N(1)	1·356 (9)	1·358 (2)	1·369	1·369
N(1)–C(2)–N(3)	119·6 (6)	114·0 (1)	115·5	115·3
N(1)–C(2)–O(2)	122·3 (6)	123·7 (2)	121·7	122·6
N(3)–C(2)–O(2)	118·0 (5)	122·3 (2)	122·8	122·2
C(2)–N(3)–C(4)	125·2 (5)	126·7 (2)	126·4	127·2
N(3)–C(4)–C(5)	113·6 (6)	115·5 (1)	114·3	114·0
N(3)–C(4)–O(4)	120·1 (6)	119·2 (2)	120·1	118·8
C(5)–C(4)–O(4)	126·3 (7)	125·3 (2)	125·6	127·2
C(4)–C(5)–C(6)	119·6 (7)	118·9 (2)	120·0	120·0
N(1)–C(6)–C(5)	125·5 (6)	122·3 (2)	123·0	122·9
Ni*–N(1)–C(2)	124·1 (4)	115·1 (1)	117·4	117·0
Ni*–N(1)–C(6)	119·5 (4)	122·1 (1)	122·0	122·4

* C(1′) of the ribose ring in uridine and the H atom at N(1) in uracil.

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

The equation of the plane is expressed in direct space as $-3{\cdot}08719X + 6{\cdot}92403Y - 3{\cdot}28529Z = -0{\cdot}13152$. Displacements from the plane are in Å with e.s.d.'s in parentheses.

N(1)*	0·015 (6)	C(6)*	−0·010 (8)
C(2)*	−0·006 (8)	O(2)	−0·069 (6)
N(3)*	−0·008 (8)	O(4)	0·042 (6)
C(4)*	0·014 (9)	Ni	0·132 (4)
C(5)*	−0·005 (9)		

* Atoms included in the calculation of the plane.

Table 5. *Distances* (Å) *and angles* (°) *in interactions of the type* D–H···A

D	H	A	$D\cdots A$	H···A	D–H···A
N(3)	H(1)	O(2)[a]	2·846 (7)	2·048	155
N(4)	H(8)	O(4)[b]	2·852 (10)	2·091	149
O(5)	H(4)	O(4)[b]	2·918 (9)	2·014	143
N(4)	H(7)	O(2)[c]	2·676 (8)	2·197	119
Other interaction					
O(5)	H(5)	O(4)[d]	2·966 (8)	2·369	114

Symmetry position of atom A: (a) $-x-1, -y-1, -z-1$; (b) $-x, -y, -z-1$; (c) $-x, -y, -z$; (d) $x, y+1, z+1$.

and two forms of uridine (Green, Rosenstein, Shiono, Abraham, Trus & Marsh, 1975) is made in Table 3. The least-squares plane through the uracil ring and the distances of various atoms from the plane are shown in Table 4 and intermolecular contacts and hydrogen bonds in Table 5.

The Ni coordination sphere

The Ni atom is involved in octahedral coordination and is situated at the centre of a plane defined by the ammonia molecules, N(4) and $N(4^{i})$, and the water molecules, O(5) and $O(5^{i})$. The octahedron is completed by two centrosymmetrically situated uracil-ring N(1) and $N(1^{i})$ atoms which occupy the axial positions in the coordination sphere.

The Ni–N lengths are 2·115 (6) and 2·114 (5) Å for the ammonia and uracil-ring N atoms, respectively, and the Ni–O length is 2·095 (7) Å. These may be compared with the Ni–N distances of 2·107 (3) and 2·082 (3) Å and the Ni–O distance of 2·103 (3) Å in diaquabis(2,2′-biimidazole)nickel(II) dinitrate (Mighell, Reimann & Mauer, 1969).

The angles N(1)–Ni–N(4), N(1)–Ni–O(5) and N(4)–Ni–O(5), with values 88·8 (2), 90·7 (2) and 90·2 (2)° respectively, indicate regular geometry.

The uracilato ligand structure

Besides the exact site of coordination, it is also of interest to study the effects of coordination on the uracil moiety. Several accurate structural analyses of uracil and uridine and their substituted homologues have been made, and thus a detailed comparison for the various substituents at the N(1) position is possible. It has been suggested that the major bond-length differences in going from thymine to 1-methylthymine are an increase in the N(1)–C(2) length and a decrease in the C(2)–O(2) length because C is more electronegative than H (Hoogsteen, 1963). The contraction of N(1)–C(2) and lengthening of C(2)–O(2) for the thymine monoanion in the N(1)-coordinated Cu^{II}–

thyminato complex support this trend (Kistenmacher, Sorrell & Marzilli, 1975).

The values which we have determined for the N(1)-coordinated uracilato monoanion are compared with those of uracil (Stewart & Jensen, 1967) and the two forms of uridine (Green *et al.*, 1975) in Table 3. The N(1)-coordinated uracilato monoanion has a slightly shorter N(1)—C(2) bond, 1·356 (8) Å, compared with those in uracil, 1·371 (3) Å, and uridine, 1·376 and 1·366 Å. C(2)—O(2), 1·267 (8) Å, is considerably longer than in uncoordinated uracil, 1·215 (2) Å, and uridine, 1·227 and 1·217 Å.

The bond-length trend just discussed and further comparisons in Table 3 are in agreement with the conclusions drawn for the Cu^{II}–thyminato complex, and it is evident that the electronegativity of the $[Ni^{II}(H_2O)_2(NH_3)_2]^{2+}$ ion is less than for a ribose moiety or even a proton.

The deviations of atoms from the least-squares plane through the uracil ring are shown in Table 4. The ring is planar within experimental error. The Ni atom is considerably out of the ring plane, 0·132 (4) Å, causing small distortions in the uracilato anion. The most pronounced distortion is the bending of the exocyclic keto O(2) and O(4) atoms out of the ring plane by –0·069 (6) and 0·042 (6) Å, respectively.

Molecular arrangement and hydrogen-bond system

The arrangement of the molecules in the unit cell, as viewed down *a*, is shown in Fig. 3. The molecules form layers through hydrogen bonds between N(3) and $O(2^i)$. The exocyclic O(2) is also an acceptor in an intramolecular hydrogen bond with N(4) and thus the geometry in the vicinity of O(2) is approximately trigonal.

The uracil rings in the layers are 3·48 Å apart and the layers are held together by intermolecular contacts, in which each exocyclic O(4) atom has three closest neighbours: N(4) and $O(5^i)$ of one molecule and $O(5^{ii})$ of the molecule on the opposite side of the pyrimidine ring plane. Hydrogen bonds are formed with the first two, with $A\cdots H$ distances of 2·091 and 2·014 Å and $D—H\cdots A$ angles of 148·8 and 143·7°, respectively. The third contact is weaker with an $O(4)\cdots O(5^i)$ distance of 2·966 Å and $O(4)\cdots H(5)—O(5^i)$ angle of 113·7°. The geometry about O(4) is roughly tetrahedral. The pyrimidine ring overlap is small and thus consistent with the trend noticed for pyrimidine bases (Bugg, Thomas, Sundaralingam & Rao, 1971).

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