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Heavy Transition Metal Complexes of Biologically Important Molecules. 4. Crystal and Molecular Structure of Pentahydrodioxonium Chloro(uracilato-*N*(*1*))(ethylenediamine)platinum(II) Chloride, $(H_5O_2)[PtCl(NH_2CH_2CH_2NH_2)(C_4H_5N_2O_2)]Cl$, and Chloro(thyminato-*N*(*1*))(ethylenediamine)platinum(II), $PtCl(NH_2CH_2CH_2NH_2)(C_5H_5N_2O_2)$

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The X-ray crystal structures have been determined of two platinum complexes in which platinum is bonded to the deprotonated N1 position of two pyrimidines. Pentahydrodioxonium chloro(uracilato-*N*(*1*))(ethylenediamine)platinum(II) chloride, $(H_5O_2)[PtCl(NH_2(CH_2)_2NH_2)(C_4H_5N_2O_2)]Cl$, is triclinic, $P\bar{1}$, with cell dimensions $a = 10.486$ (6) Å, $b = 8.073$ (4) Å, $c = 10.196$ (5) Å, $\alpha = 119.24$ (3)°, $\beta = 111.97$ (4)°, and $\gamma = 89.96$ (4)°, and has two formula units in the cell. The crystal structure was determined by standard methods and refined to $R_1 = 0.0488$ and $R_2 = 0.0566$ based on 3043 independent reflections. Chloro(thyminato-*N*(*1*))(ethylenediamine)platinum(II), $PtCl(NH_2(CH_2)_2NH_2)(C_5H_5N_2O_2)$, is triclinic, $P\bar{1}$, with cell dimensions $a = 7.884$ (1) Å, $b = 7.121$ (1) Å, $c = 10.768$ (2) Å, $\alpha = 93.57$ (2)°, $\beta = 114.00$ (2)°, and $\gamma = 101.58$ (2)°, and has two formula units in the cell. The crystal structure, which was determined similarly, refined to $R_1 = 0.0352$ and $R_2 = 0.0401$ on the basis of 2482 reflections. Both data sets were collected by using Mo Kα radiation and a Syntex $P2_1$ diffractometer. The molecular structures are remarkably similar and bond distances are normal (Pt–Cl = 2.298 (3), 2.299 (3) Å; Pt–N range 2.03 (1)–2.04 (1) Å). The only difference is the presence of an $H_5O_2^+$ unit (O(1)–O(3) = 2.59 (1) Å) in the uracil complex (and a compensating chloride ion), which is strongly hydrogen bonded to O4 of the uracilate ion (O(4)–O(1) = 2.47 (2) Å). The relationship of these compounds to the platinum pyrimidine blues is discussed.

Introduction

The original discovery of Rosenberg and co-workers of the potential antitumor activity of certain di- and tetravalent platinum complexes[3] and subsequent findings indicating a selective inhibition of DNA synthesis as a possible mode of action[4] inspired a renewed interest in the binding properties of heavy metals, and in particular of platinum, to nucleic acid constituents. During the course of such investigations it was found that reaction between the aquation products of the active *cis*-dichlorodiammineplatinum(II) and a series of 2,4-dihydroxopyrimidines resulted in the formation of a new group of potent antitumor agents.[5] Attempts to elucidate the nature and possible structure of these so called "platinum pyrimidine blues" have been undertaken but are still inconclusive.[6] In a related system with α-pyridone as ligand a crystalline compound was isolated and characterized, showing that the cyclic amide group is acting as a bridge between adjacent Pt atoms.[7]

Formation of these "platinum pyrimidine blues" was surprising because originally it had been assumed that no reaction occurred between *cis*-$Pt(a)_2Cl_2$ (a = NH_3 or other amines) or its aquated forms and uracil, thymine, or their derivatives,[8] though Russian investigators had reported complex formation with the lithium salt of 5-fluorouracil.[9] It was suggested that the slowness of the reaction, low pH, or chloride ion inhibition were responsible for earlier misinterpretations.[10] Recently, however, the isolation of a crystalline complex, *cis*-$[Pt(NH_3)_2(thymine\text{-}H)Cl]\cdot H_2O$,[6a] and of two kinds of uracil complexes (N(1) and N(3) coordinated) of the triammineplatinum(II) moiety[11] have been reported. Moreover several X-ray structure determinations have now been made of *cis*-diammineplatinum(II) complexes of both unsubstituted thymine[12,13] (binding site N(1)) and N(1) methylated thymine[14] and N(1)-methylated uracil[15] (binding site N(3)).

The complex-forming properties of uracil and its derivatives with metals other than platinum have been studied extensively and a variety of binding modes have been observed: copper(II) binds to N(1) of thymine[16] but to the phosphate group in 5-uridine monophosphate[17] and mercury(II) binds to N(3) of 1-methylthymine[18] and to C(4)O of uracil and dihydrouracil.[19] There is also an X-ray structure of a compound containing discrete K_2PdCl_6 and 1-propylthymine molecules with no direct bonding between the heavy metal and the thymine.[20] An even greater number of coordination possibilities of various metals has been deduced on the basis of spectroscopic measurements.[21]

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This obvious multiplicity of binding modes is not unexpected because uracil and its derivatives represent typical multisite ligands. In particular, the monoanions of unsubstituted uracil and thymine which occur in solution as N(1) and N(3) deprotonated tantomers and show a large degree of charge delocalization[22] make multiple coordination modes very likely.

This present study is of importance because it proves that coordination of the (ethylenediamine)platinum(II) moiety to the N(1) position of uracil and thymine leads to complexes that are very stable even at strongly acidic pH. Moreover, the uracil complex represents the first example of a metal complex with deprotonated uracil for which an X-ray structure determination has been performed.

Experimental Section

A solution of 2 mmol of $[enPt(H_2O)_2](NO_3)_2$,[24] which was prepared by reacting $enPtCl_2$ with 2 equiv of $AgNO_3$ in water (25 mL), was reacted with 2 mmol of thymine (uracil) in 25 mL of water and kept at pH 7 on a 40 °C water bath in an open flask. The pH, which drops as reaction occurs, was initially adjusted hourly and later daily with 2 N NaOH solution. After about 10–14 days the orange-brown solution was concentrated to 3 mL and tan products were precipitated by the addition of 15 mL of ethanol and subsequent cooling for 4 h at 0 °C.[25] Yields for both thymine and uracil complexes were about 800 mg. The structure of these products is unclear at this moment, but preliminary studies show that they, like the "blues", are cationic, presumably polymeric species which are slightly paramagnetic as well and differ in their elemental analysis from preparation to preparation like the former.[26]

The isolated thymine (uracil) compound (300 mg) was then dissolved in 50 mL of 0.3 N (1.0 N) HCl, heated to 70 °C for 3 min and then allowed to evaporate slowly on a 40 °C water bath to 4 mL. The precipitate obtained at this stage consisted principally of crystals of the title compound. Further concentration of the filtrate gave other products which are listed below. The various compounds were separated mechanically under a microscope and identified by elemental analysis and/or IR spectroscopy. Separation of the title compounds by means of suitable solvents (H_2O, HCl, DMF) could only partially be achieved because of similar solubility properties or very low solubility of some of the coproducts. The following lists represent the major products obtained under the described procedure and may be incomplete.

Thymine system: (1) tan to reddish brown (size effect) crystals of the title compound (Anal. Calcd: C, 20.20; H, 3.16; N, 13.48; O, 7.70; Pt, 46.90; Cl, 8.53. Found: C, 19.84; H, 3.17; N, 13.09; O, 8.8; Pt, 46.6; Cl, 8.3. The crystals were treated with DMF to remove products (6) and (7) and then washed with 1 N HCl, water acetone, and ether and dried on a rotary pump vacuum. A 300-mg sample of thymine tan yielded 100 mg of the title compound.); (2) tan to reddish brown microneedles of a compound which analyzed as the monohydrate of the title compound (Anal. Calcd: C, 19.38; H, 3.49; N, 12.92; Pt, 44.97. Found: C, 19.51; H, 3.59; N, 12.82; Pt, 45.5. The compound showed distinct differences in the IR spectrum from the title compound.); (3) tan microcrystals of a compound with elemental analysis close to $enPt(C_5H_5N_2O_2)_2$; (4) pale yellow to colorless crystals of unknown composition; (5) colorless crystal plates of thymine; (6) yellow particles of $enPtCl_2$; (7) yellow particles of $enPtCl_4$. Uracil system: (1) colorless to yellowish crystals of the title compound (Anal. Calcd: C, 15.18; H, 3.35; N, 11.79; O, 13.49; Pt, 41.2; Cl, 14.97. Found: C, 14.75; H, 3.31; N, 11.15; O, 13.20; Pt, 41.7; Cl, 15.2. A 300-mg sample of uracil tan yields 140 mg of title compound. The crystals were washed with 6 N HCl and dried with acetone and ether. Washing with diluted HCl, water, or DMF resulted in an immediate loss of transparency of the crystals and a color change to white. It was noticed that no crystals of suitable size could be obtained when the starting HCl concentration was less than 1 N.); (2) colorless microneedles of unknown composition; (3) colorless crystals of uracil; (4) yellow crystals of $enPtCl_2$; (5) dichroic (red, yellow) crystals of $enPtCl_2 \cdot enPtCl_4$.

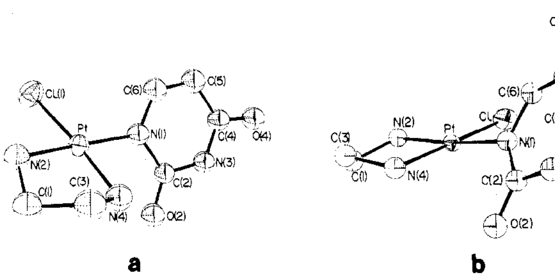

Figure 1. (a) The numbering of the atoms in the molecular unit chloro(uracilato-*N*(*1*))(ethylenediamine)platinum(II). (b) The numbering of the atoms in the molecular unit chloro(thyminato-*N*-(*1*))(ethylenediamine)platinum(II).

Collection of the X-ray Data. Crystals of the two compounds were selected after examination under a polarizing microscope for homogeneity. Precession photographs of both crystals showed the crystals were triclinic and Delaunay tests showed no hidden symmetry. Unit cell parameters were obtained from least-squares fit of χ, ϕ, and 2θ for 15 reflections for each compound in the range $20° < 2\theta < 35°$ recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation (λ 0.71069 Å at 20 °C). Crystal data and other numbers related to data collection are summarized in Table I. Densities were obtained by flotation in a diiodomethane–iodoethane mixture. Intensity data were also recorded on the Syntex $P2_1$ diffractometer using a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[27,28] Corrections were made for Lorentz–polarization effects and absorption.

Solution of the Structure. Both structures were solved in the same way. The coordinates of the platinum atom were found from a three-dimensional Patterson synthesis and a series of full-matrix least-squares refinements followed by three-dimensional electron density difference syntheses revealed all the nonhydrogen atoms. After refinement, the temperature factors of the platinum and chlorine atoms, which were previously isotropic, were made anisotropic. Tests were made at each stage to show the use of the increased parameters was significant.[29] Further refinement using full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error was about 0.2. No attempt was made to locate the hydrogen atoms. Cruickshank weighting schemes were used and corrections were made for secondary extinction using the method of Larson.[30] Throughout the refinement, the scattering curves were taken from ref 31 and anomalous dispersion corrections from ref 32 were applied to the curves for platinum and chlorine. The atom parameters for nonhydrogen atoms are listed in Tables II and III.

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Table I

compd	$(H_5O_2)Cl[Pt(NH_2CH_2CH_2NH_2)(C_4H_3N_2O_2)Cl]$	$[Pt(NH_2CH_2CH_2NH_2)(C_5H_5N_2O_2)Cl]$
cryst size	cylinder, 0.1 mm radius, 0.3 mm long	cube with truncated corners, roughly spherical, radius 0.1 mm
systematic absences	none	none
space group	$P\bar{1}$[a]	$P\bar{1}$
unit cell parameters (Å and deg)	$a = 10.486$ (6)	$a = 7.884$ (1)
	$b = 8.073$ (4)	$b = 7.121$ (1)
	$c = 10.196$ (5)	$c = 10.768$ (2)
	$\alpha = 119.24$ (3)	$\alpha = 93.57$ (2)
	$\beta = 111.97$ (4)	$\beta = 114.00$ (2)
	$\gamma = 89.96$ (4)	$\gamma = 101.58$ (2)
Z	2	2
ρ_{calcd}, g cm^{-3}	2.31	2.58
ρ_{obsd} g cm^{-3}	2.31 (2)	2.54 (2)
linear abs coeff, cm^{-1}	112.4	140.5
transmission coeff limits	3.68–5.90	3.98–6.90
std reflctns	(1) −3,−2,4; (2) 6,3,−4	(1) 1,1,−4; (2) 1,0,−2
counting esd and overall esd	(1) 2.0%, 3.4%	(1) 1.4%, 1.6%
	(2) 2.3%, 3.7%	(2) 1.8%, 2.0%
no. of independent reflctns	3043	2482
no. with $I > 3\sigma(I)$	2715	2263
$3\sigma(I) > I > \sigma(I)$	328	171
$I < \sigma(I)$		48
final R_1[b]	0.0488	0.0352
final R_2[b]	0.0566	0.0401
final shift in esd max	0.018	0.022
av	0.003	0.003
g (secondary extinction)	3.82×10^{-7}	4.94×10^{-7}
final difference map		
highest peak, location	1.62 e/Å^3, 0.93, 0.05, 0.13 1.52 e/Å^3, 0.08, 0.18, 0.30	1.22 e/Å^3, 0.05, 0.30, 0.15
lowest valley, location	−1.21 e/Å^3, 0, 0.05, 0.10 −1.20 e/Å^3, 0.98, 0.18, 0.30	−1.02 e/Å^3, 0.20, 0.40, 0.15
weighting scheme	$1/w = 9.486 - 0.4223\lvert F_o\rvert + 0.006507F_o^2$	$1/w = 6.5757 - 0.2709\lvert F_o\rvert + 0.003685F_o^2$

[a] This cell can be converted to the Delaunay reduced cell $a = 10.486$ (6) Å, $b = 8.073$ (4) Å, $c = 11.572$ (5) Å, $\alpha = 115.49$ (4)°, $\beta = 125.21$ (4)°, and $\gamma = 90.04$ (4)° by the matrix (100/0,−1,0/−1,0,−1). [b] $R_1 = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$. $R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{1/2}$.

Table II. Positional and Thermal Parameters (Å^2) and Anisotropic Temperature Factors[a] (Å^2) for Chloro(thyminato-*N(1)*)(ethylenediamine)platinum(II), $PtCl(C_5H_5N_2O_2)(NH_2CH_2CH_2NH_2)$ ($\times 10^3$)

atom	x	y	z	U
Pt	109.20 (4)	247.73 (4)	86.36 (3)	
Cl	237.8 (3)	310.0 (3)	−68.3 (2)	
N(2)	−158 (1)	238 (1)	−58.7 (6)	28 (1)
C(1)	−303 (1)	158 (1)	−9 (1)	35 (2)
C(3)	−221 (1)	216 (1)	145.8 (8)	35 (2)
N(4)	−25.8 (9)	185 (1)	210.3 (7)	32 (1)
N(1)	374.5 (9)	289.9 (9)	244.2 (6)	28 (1)
C(2)	422 (1)	171 (1)	340.9 (8)	29 (1)
O(2)	320 (1)	7 (1)	327.9 (6)	37 (1)
N(3)	588 (1)	240 (1)	456.2 (7)	31 (1)
C(4)	713 (1)	425 (1)	491.6 (8)	32 (1)
O(4)	851 (1)	472 (1)	603.1 (7)	46 (1)
C(5)	661 (1)	544 (1)	386.4 (8)	32 (1)
C(51)	784 (1)	743 (1)	407 (1)	41 (2)
C(6)	498 (1)	470 (1)	270.6 (8)	31 (1)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	20.3 (1)	20.6 (1)	20.6 (2)	3.0 (1)	4.9 (1)	3.0 (1)
Cl	40 (1)	39 (1)	34 (1)	9 (1)	19 (1)	12 (1)

[a] Anisotropic temperature factors U_{ij} were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where the β_{ij}'s appear as a temperature effect of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ and $\mathbf{b}_i$ and $\mathbf{b}_j$ are the reciprocal lattice vectors.

Table III. Positional and Thermal Parameters (Å^2) and Anisotropic Temperature Factors[a] (Å^2) for Chloro(uracilato-*N(1)*)(ethylenediamine)platinum(II) Pentahydrodioxonium Chloride, $[PtCl(C_4H_3N_2O_2)(NH_2CH_2CH_2NH_2)](H_5O_2)Cl$ ($\times 10^3$)

atom	x	y	z	U
Pt	−12.90 (4)	115.37 (5)	207.21 (4)	
Cl(1)	127.6 (3)	−77.9 (4)	269.9 (4)	
Cl(2)	676.0 (3)	374.2 (4)	342.0 (3)	
N(1)	−187 (1)	−48 (1)	166 (1)	37 (2)
C(2)	−311 (1)	−102 (1)	29 (1)	33 (2)
O(2)	−320 (1)	−78 (1)	−83 (1)	43 (1)
N(3)	−430 (1)	−194 (1)	19 (1)	38 (2)
C(4)	−432 (1)	−230 (1)	132 (1)	40 (2)
O(4)	−553 (1)	−317 (1)	100 (1)	46 (2)
C(5)	−305 (1)	−173 (2)	272 (1)	49 (2)
C(6)	−191 (1)	−82 (1)	282 (1)	44 (2)
N(2)	154 (1)	298 (1)	258 (1)	41 (2)
C(1)	105 (1)	431 (2)	196 (1)	49 (2)
C(3)	−23 (1)	479 (2)	223 (2)	58 (3)
N(4)	−123 (1)	298 (1)	153 (1)	46 (2)
O(1)	−555 (9)	−397 (1)	304 (1)	54 (2)
O(3)	−475 (1)	−105 (2)	606 (1)	72 (2)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	29.1 (2)	32.8 (2)	33.0 (4)	3.5 (1)	11.6 (1)	16.7 (1)
Cl(1)	43 (1)	54 (1)	65 (2)	13 (1)	17 (1)	40 (1)
Cl(2)	48 (1)	58 (1)	37 (1)	10 (1)	14 (1)	17 (1)

[a] Anisotropic temperature factors U_{ij} were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where the β_{ij}'s appear as a temperature effect of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ and $\mathbf{b}_i$ and $\mathbf{b}_j$ are the reciprocal lattice vectors.

Results and Discussion

The two platinum-containing molecules are shown in Figure 1, and selected interatomic distances and angles are given in Tables IV and V. As can be seen, the structures are very similar. Each platinum atom is surrounded by the four bonded ligand atoms in a rough square plane (see Table VI) and the planar uracilate and thyminate (Table VI) groups are twisted so as to bring the O(2) atoms close to N(4) of the ethylenediamine groups, presumably to form weak hydrogen bonds. The interatomic distances and angles involved are very similar (uracil, thymine; N(4)–O(2) = 2.90 (1), 3.07 (1) Å; Pt–N(4)–O(2) = 77.2 (3), 76.5 (3)°; C(3)–N(4)–O(2) = 161 (1), 164.9 (5)°; C(2)–O(2)–N(4) = 91.1 (5), 86.9 (5)°) and

Table IV. Selected Interatomic Distances (Å) and Angles (Deg) for Chloro(thyminato-*N(1)*)(ethylenediamine)platinum(II) Chloride, $PtCl(C_5H_5N_2O_2)(NH_2CH_2CH_2NH_2)$

Distances					
Pt–Cl	2.299 (3)	Pt–N(2)	2.033 (6)	Pt–N(4)	2.038 (9)
N(2)–C(1)	1.48 (1)	C(1)–C(3)	1.52 (1)	C(3)–N(4)	1.48 (1)
Pt–N(1)	2.036 (5)	N(1)–C(2)	1.36 (1)	C(2)–O(2)	1.245 (9)
C(2)–N(3)	1.356 (8)	N(3)–C(4)	1.399 (9)	C(4)–O(4)	1.218 (9)
C(4)–C(5)	1.44 (1)	C(5)–C(51)	1.49 (1)	C(5)–C(6)	1.352 (9)
C(6)–N(1)	1.38 (1)				
Possible Hydrogen Bond Distances					
O(2)–N(2)^a	2.92 (1)	O(2)–N(3)^b	2.94 (1)	N(4)–O(4)^c	2.78 (1)
N(4)–O(2)	3.07 (1)				
Angles					
Cl–Pt–N(1)	91.5 (2)	Cl–Pt–N(2)	91.4 (2)	Cl–Pt–N(4)	175.4 (2)
N(1)–Pt–N(2)	172.4 (3)	N(1)–Pt–N(4)	93.0 (3)	N(2)–Pt–N(4)	84.3 (3)
Pt–N(2)–C(1)	110.1 (5)	N(2)–C(1)–C(3)	109.7 (6)	C(1)–C(3)–N(4)	109.5 (8)
C(3)–N(4)–Pt	109.6 (6)	Pt–N(1)–C(2)	124.2 (5)	N(1)–C(2)–O(2)	123.0 (6)
N(1)–C(2)–N(3)	117.4 (6)	O(2)–C(2)–N(3)	119.6 (7)	C(2)–N(3)–C(4)	127.2 (7)
N(3)–C(4)–O(4)	120.3 (8)	N(3)–C(4)–C(5)	114.0 (6)	O(4)–C(4)–C(5)	125.7 (7)
C(4)–C(5)–C(51)	120.2 (6)	C(4)–C(5)–C(6)	117.3 (7)	C(51)–C(5)–C(6)	122.5 (8)
C(5)–C(6)–N(1)	126.3 (8)	C(6)–N(1)–Pt	116.6 (5)	C(6)–N(1)–C(2)	117.7 (5)
Possible Hydrogen Bond Angles					
Pt–N(4)–O(4)^c	97.5 (3)	C(3)–N(4)–O(4)^c	97.7 (5)	C(4)^c–O(4)^c–N(4)	133.2 (6)
Pt^a–N(2)^a–O(2)	121.6 (4)	C(1)^a–N(2)^a–O(2)	100.0 (4)	C(2)–O(2)–N(2)^a	117.0 (6)
C(2)^b–N(3)^b–O(2)	117.3 (5)	C(4)^b–N(3)^b–O(2)	115.2 (4)	C(2)–O(2)–N(3)^b	123.0 (5)
Pt–N(4)–O(2)	76.5 (3)	C(3)–N(4)–O(2)	164.9 (5)	C(2)–O(2)–N(4)	86.9 (5)

$^{a-c}$ Atomic coordinates are related to those given in Table II by the transformations (*a*) $-x, -y, -z$; (*b*) $1-x, -y, 1-z$; (*c*) $1-x, 1-y, 1-z$.

Table V. Selected Interatomic Distances (Å) and Angles (Deg) for Chloro(uracilato-*N(1)*)(ethylenediamine)platinum(II) Pentahydrodioxonium Chloride, $[PtCl(C_4H_3N_2O_2)(NH_2CH_2CH_2NH_2)](H_5O_2)Cl$

Distances					
Pt–Cl(1)	2.298 (3)	Pt–N(2)	2.03 (1)	Pt–N(4)	2.03 (1)
N(2)–C(1)	1.50 (2)	C(1)–C(3)	1.48 (2)	C(3)–N(4)	1.48 (2)
Pt–N(1)	2.04 (1)	N(1)–C(2)	1.37 (1)	C(2)–O(2)	1.217 (16)
C(2)–N(3)	1.40 (2)	N(3)–C(4)	1.33 (2)	C(4)–O(4)	1.291 (15)
C(4)–C(5)	1.40 (1)	C(5)–C(6)	1.35 (2)	C(6)–N(1)	1.35 (2)
O(4)–O(1)	2.47 (2)	O(1)–O(3)	2.59 (1)		
Possible Hydrogen Bond Distances					
Cl(2)–N(3)^a	3.16 (1)	Cl(2)–O(1)^b	3.08 (1)	Cl(2)–N(4)^c	3.23 (1)
Cl(2)–N(2)^d	3.29 (1)	N(4)–O(2)	2.90 (1)	N(2)–O(2)^a	2.93 (1)
O(2)–O(3)^e	2.86 (2)				
Angles					
Cl(1)–Pt–N(1)	91.9 (3)	Cl(1)–Pt–N(2)	92.0 (3)	Cl(1)–Pt–N(4)	175.3 (3)
N(1)–Pt–N(2)	175.0 (3)	N(1)–Pt–N(4)	92.8 (4)	N(2)–Pt–N(4)	83.4 (4)
Pt–N(2)–C(1)	110.4 (6)	N(2)–C(1)–C(3)	106.8 (4)	C(1)–C(3)–N(4)	109.6 (11)
C(3)–N(4)–Pt	108.5 (8)	Pt–N(1)–C(2)	119.9 (9)	N(1)–C(2)–O(2)	124 (1)
N(1)–C(2)–N(3)	117 (1)	O(2)–C(2)–N(3)	119.7 (8)	C(2)–N(3)–C(4)	125.2 (8)
N(3)–C(4)–O(4)	115.5 (9)	N(3)–C(4)–C(5)	118 (1)	O(4)–C(4)–C(5)	127 (1)
C(4)–C(5)–C(6)	117 (1)	C(5)–C(6)–N(1)	126 (1)	C(6)–N(1)–Pt	121.5 (6)
C(6)–N(1)–C(2)	118 (1)	C(4)–O(4)–O(1)	115.5 (8)	O(4)–O(1)–O(3)	116.3 (5)
Possible Hydrogen Bond Angles					
C(2)–N(3)–Cl(2)^a	109.2 (7)	C(4)–N(3)–Cl(2)^a	124.6 (6)	O(3)–O(1)–Cl(2)^b	102.2 (4)
Pt–N(4)–Cl(2)^c	102.8 (5)	C(3)–N(4)–Cl(2)^c	111.4 (8)	Pt–N(2)–Cl(2)^d	112.2 (5)
C(1)–N(2)–Cl(2)^d	99.1 (5)	Pt–N(4)–O(2)	77.2 (3)	C(3)–N(4)–O(2)	161 (1)
C(2)–O(2)–N(4)	91.1 (5)	Pt–N(2)–O(2)^a	110.3 (3)	C(1)–N(2)–O(2)^a	106.1 (8)
O(4)–O(1)–Cl(2)^b	105.9 (4)				

$^{a-e}$ Atoms are related to those given in Table I by the transformations (*a*) $-x, -y, -z$; (*b*) $1+x, 1+y, z$; (*c*) $1+x, y, z$; (*d*) $1-x, 1-y, 1-z$; (*e*) $x, y, z-1$.

consistent with Brown's[33] hydrogen bond relationships. The dihedral angles between the square planes and the pyrimidine planes are 50° (uracil) and 56° (thymine). Comparison of equivalent bond distances and angles in the two structures shows very few significant differences. The bond angles in the ethylenediamine groups are close to the tetrahedral angle and only C(3)–C(1)–N(2) for the uracil complex (106.8 (4)°) differs significantly from 109.45° and from the corresponding angle in the thymine complex (109.7 (6)°). There are some significant differences in bond lengths and angles within the pyrimidine rings and these are all associated with C(4),O(4) and apparently arise because of the very strong hydrogen bond from the $H_5O_2^+$ group to O(4) in the uracil compound (O(1)–O(4) = 2.47 (2) Å). Thus C(4)–O(4) is longer in the uracil complex than in the thymine complex (1.291 (15) vs. 1.218 (9) Å) whereas the N(3)–C(4) and C(4)–C(5) distances are shorter (1.33 (2) vs. 1.399 (9) Å and 1.40 (1) vs. 1.44 (1) Å). Further, the C(2)–O(2) and C(4)–O(4) distances, which are not significantly different in the thymine complex, differ by 3.4σ for the uracil complex, even though the errors are greater in the latter. Differences are also observed in the angles

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[33] Brown, I. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 24.

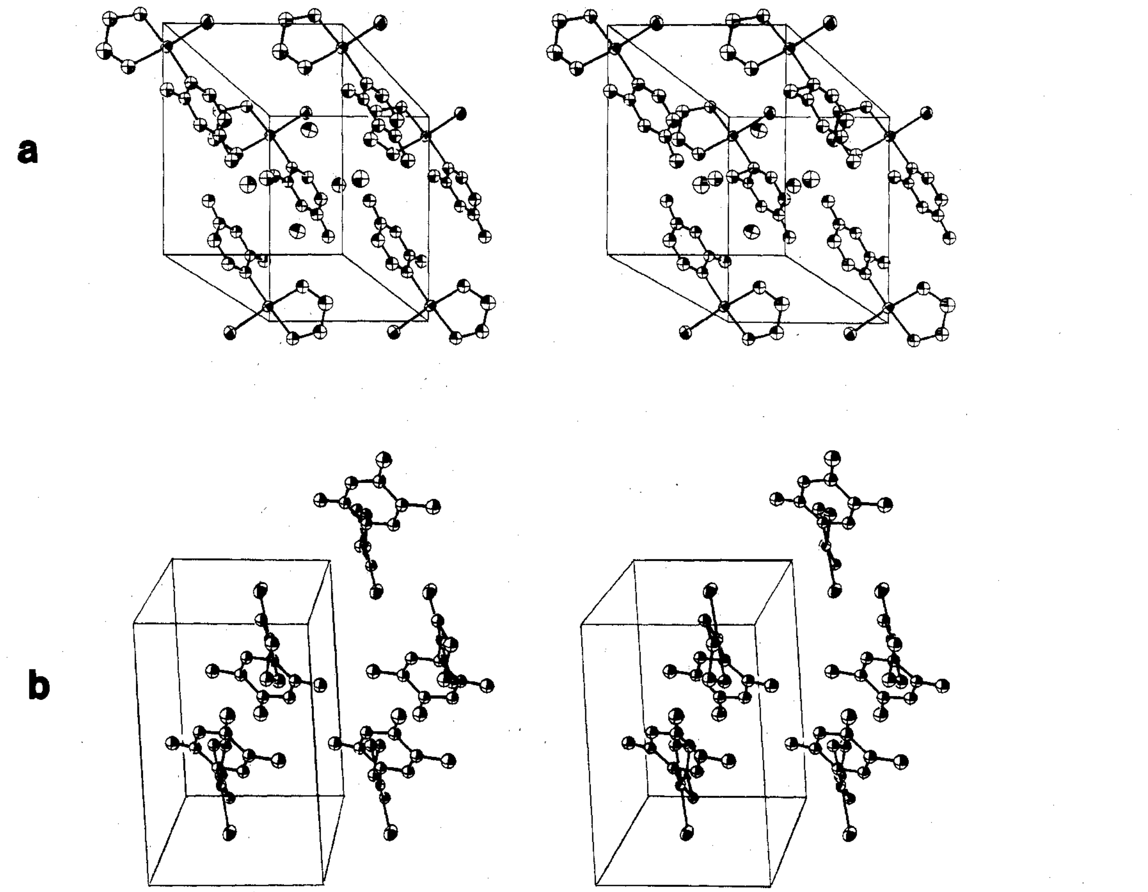

Figure 2. Stereogram (pair of stereoscopic projections) of the contents of the unit cells, plus other molecules to illustrate the packing, of (a) pentahydrodioxonium chloro(uracilato-*N*(*1*))(ethylenediamine)platinum(II) chloride, **b** and **c*** × **b** are parallel to the bottom and side of the page, respectively, and the view is along **c***, and (b) chloro(thyminato-*N*(*1*))(ethylenediamine)platinum(II), **b** and **a*** × **b** are parallel to the bottom and top of the page, respectively, and the view is along **a***.

Table VI. Deviation from Best Least-Squares Planes for the Title Compounds

uracil	Pt[a]Cl(1)N(1)N(2)N(4)	Pt, −0.02; Cl(1), −0.03; N(1), 0.03; N(2), 0.04; N(4), −0.04
thymine	Pt[a]Cl(1)N(1)N(2)N(4)	Pt, −0.05; Cl(1), −0.07; N(1), 0.07; N(2), −0.08; N(4), −0.08
uracil	N(1)C(2)O(2)[a]N(3)C(4)-O(4)[a]C(5)C(6)	N(1), −0.01; C(2), 0.00; O(2), −0.01; N(3), 0.00; C(4), 0.00; O(4), 0.00; C(5), −0.01; C(6), 0.01
thymine	N(1)C(2)O(2)[a]N(3)-C(4)O(4)[a]C(5)C(51)[a]C(6)	N(1), −0.01; C(2), −0.01; O(2), −0.08; N(3) 0.02; C(4), −0.02; O(4), −0.08; C(5), 0.00; C(51), 0.01; C(6), 0.01

[a] These atoms are given no weight in the refinement. All other atoms are given unit weights. Errors in parameters are as follows: Pt, 0.001; Cl(1), 0.003; others, 0.02 Å.

around C(4), N(3)–C(4)–O(4) being significantly smaller in the uracil complex (115.5 (9) vs. 120.3 (8)°) and N(3)–C-(4)–C(5) being larger (118 (1) vs. 114.0 (6)°).

It is of interest to compare the structure of the thyminate ion bonded to platinum with the thyminate ion in potassium thyminate trihydrate[35] and the protonated ion in thymine monohydrate.[36] Bond distances in the platinum complex do not differ significantly from those in either species (except for C(4)–O(4) in the thyminate ion) although agreement is better with those in thymine (differences vary by 0.16σ[34] to 1.91σ, average 0.80σ) rather than the thyminate ion (differences vary by 1.02σ to 3.01σ, average 2.02σ). The bond angles show exactly the opposite effect, however. Angles in the platinum complex do not differ significantly from those in the thyminate anion (differences 0.25σ to 2.21σ, average 1.25σ), whereas there are larger differences in certain angles in thymine. C(6)–N(1)–C(2) is smaller for the platinum complex (difference 8.75σ) whereas adjacent internal ring angles are larger (C(5)–C(6)–N(1), 7.35σ; N(1)–C(2)–N(3), 5.00σ). As a consequence of the last the O(2)–C(2)–N(3) angle is smaller in the platinum complex (6.22σ). We have already commented on the angular difference between the thyminate ion and thymine.[35] The difference is caused by the exocyclic proton bonded to N(1), an effect shown by Singh[37] to be general for exocyclic organic or hydrogen groups bonded to the pyrimidine ring. It is clear that this effect is not observed when platinum is the exocyclic bonded group, and as we have noted before for a platinum–cytosine complex,[38] although the $Pt^{II}L_3$ group is an electrophile, its coordination, unlike that of a proton, has very little effect on the pyrimidine ring structure.

The crystal of the uracil complex comprises neutral molecules of chloro(uracilato-*N*(*1*))(ethylenediamine)platinum(II) and pentahydrodioxonium and chloride ions. Hydrogen bonding is of prime importance in deciding the crystal packing and this is illustrated in Figure 2a. In the **b** direction, molecules are arranged so that the pyrimidine rings are interleaved forming a chain centered about the $x = {}^1/_2$, $z = 0$

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(34) σ for comparison of bonds and angles is given by $\sigma = (\sigma_1{}^2 + \sigma_2{}^2)^{1/2}$ where σ_1 and σ_2 are the individual errors in bonds or angles.
(35) Lock, C. J. L.; Pilon, P.; Lippert, B. *Acta Crystallogr.*, in press.
(36) Gerdil, R. *Acta Crystallogr.* **1961**, *14*, 333.
(37) Singh, C. *Acta Crystallogr.* **1965**, *19*, 861.
(38) Lock, C. J. L.; Speranzini, R. A.; Powell, J. *Can. J. Chem.* **1976**, *54*, 53.

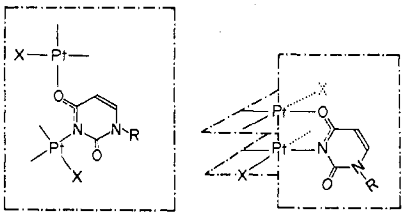

Figure 3. Possible arrangements of 2,4-dihydroxopyrimidine bridges: R = H or CH_3, X = terminal ligand (OH, H_2O, 2,4-dihydroxopyrimidine, etc.) or bridging ligand (OH, 2,4-dihydroxopyrimidine, etc.).

line. These chains contact in the **a** direction about the $x = 0$ plane primarily through ethylenediamine–Cl(1) interactions not involving hydrogen bonds, but there is a hydrogen bond between N(4) and O(2) in adjacent molecules along **a**, related by the inversion center at 0, 0, 0. In the **c** direction the $H_5O_2^+$ unit (O(1)–O(3)) links molecules related by the **c** translation, O(1) being strongly bonded to O(4) of one molecule while O(3) is less strongly bonded to O(2) of the next. Cl(2) is an important link in the hydrogen bonding network being bonded to O(1), to N(4) in the molecule related to that bonded to O(1) by the **b** translation, to N(3) in the molecule interleaved between these two, and to N(2) in the molecule related to the second by the **c** translation.

Hydrogen bonding is less pronounced, but still important, in crystal packing of the thymine complex which is shown in Figure 2b. Pairs of molecules are bonded through two N(3)–H···O(2) interactions into dimers, very much like the pyrimidine pairs observed in potassium thyminate trihydrate,[35] though there the interactions were N3–H···O4. Along the **b** directions the dimers are canted and stacked like tiles on a roof. Each dimer is hydrogen bonded to the next dimer by N(4)–H···O(4) hydrogen bonds. The remaining hydrogen bond interaction is between N(2) in one molecule and O(2) in another molecule related by an **a** + **c** translation. The main interactions between the chains of dimers in the **c** direction involve chlorine and ethylenediamine contacts. In the **a** direction interactions involve the overlap of the pyrimidine rings and the interleaving of the ethylenediamine groups. Because of the smaller amount of hydrogen bonding in the thymine complex the crystal packing is more efficient than in the uracil complex, which has extensive hydrogen bonding, and this is shown in the significantly greater density of the thymine complex. Why one compound should crystallize with the $H_5O_2^+$ and Cl^- units extra is not possible to say. The difference is not surprising since the two compounds were crystallized at different pHs. This was not for any good scientific reason other than one obtained good crystals under these conditions. Probably both compounds can be crystallized with and without the extra units if sufficient care is taken.

There is a strong resemblance between the (ethylenediamine)platinum(II) complexes described here and the corresponding thymine complex[6a,12] of the *cis*-diammineplatinum(II) moiety. The compounds are prepared in analogous ways from the corresponding "tans" and "blues", respectively; they have platinum bonded through N(1) of the pyrimidine base, and they show a remarkable stability at acidic pH. This high stability of the Pt–N(1) pyrimidine bond toward acid treatment does not rule out the existence of Pt–N(3) pyrimidine bonds in platinum "blues" and "tans", however. Both types of binding might be expected from the tautomerism of uracil and thymine anions[22] and have been observed in the triammineplatinum(II) system.[11] However, it appears that Pt–N(3) pyrimidine bonds are less stable in strongly acidic medium. This is based on the observation that HCl decomposes both "blues" and "tans" of 1-methylated uracil and thymine completely under conditions (pH ~0, 40–80 °C) identical with those applied for the isolation of N(1) bonded uracil and thymine complexes of $enPt^{II}$ and *cis*-$(NH_3)_2Pt^{II}$. It is possible, however, to prepare *cis*-diammineplatinum(II) complexes of 1-methylthymine and 1-methyluracil but at neutral pH.[14,15] We have shown that these compounds are dimeric with pyrimidine anions in head to tail arrangement, binding through N(3) and O(4). It is possible[14] that in the alternate head to head arrangement further polymerization and oxidation occur to give a "blue" similar to the structure found in the α-pyridone blue of Lippard et al.[7] The fact that the "pyrimidine blues" keep their color and EPR signals in concentrated solutions[6a] makes it reasonable to assume pyrimidine bridge formation between more than two platinum atoms. Bridge formation could occur, as in the α-pyridone blue structure, via ring-N and exocyclic O in both "blues" and "tans" in essentially the same way, the difference being only the position of the heterocycle plane relative to the coordination planes of the two Pt atoms that are bridged. The two extreme positions possible are indicated in Figure 3. The arrangement with the ring approximately perpendicular to the two platinum planes (Figure 3, right) leads to short Pt–Pt distances of 3 Å or less. With increasing bulkiness of the amine ligands, a twisting toward an arrangement similar to that shown in Figure 3 (left) might be expected. This model may explain the difference in color between "tans" and "blues". The question still remains whether in the "tans" and "blues" of unsubstituted 2,4-dihydroxopyrimidines only N(3)–O(4) bridging is occurring or whether the N(1) bonded ligand can act as a bridge as well.

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Registry No. $(H_5O_2)Cl[Pt(NH_2CH_2CH_2NH_2)(C_4H_3N_2O_2)Cl]$, 72016-77-4; $[Pt(NH_2CH_2CH_2NH_2)(C_5H_5N_2O_2)Cl]$, 72016-75-2; $[enPt(H_2O)_2](NO_3)_2$, 52241-27-7.

Supplementary Material Available: Listings of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.