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Crystal Structure of *cis*-Diammine(1-methylcytosine-*N3*)(thyminato-*N1*)platinum(II) Perchlorate, *cis*-$[Pt(NH_3)_2(C_5H_5N_2O_2)(C_5H_7N_3O)]ClO_4$, and Its ^1H NMR and Vibrational Spectra and Those of the Corresponding Mono- and Trihydrates

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The X-ray crystal structure of diammine(1-methylcytosine-*N3*)(thyminato-*N1*)platinum(II) perchlorate, $[Pt(NH_3)_2(C_5H_7N_3O)(C_5H_5N_2O_2)]ClO_4$, $C_{10}H_{18}ClN_7O_7Pt$, has been determined. Crystals are monoclinic, *C*2/*c*, with cell dimensions $a = 20.071$ (13) Å, $b = 12.514$ (4) Å, $c = 16.442$ (5) Å, and $\beta = 118.25$ (3)° and has eight formula units in the unit cell. The crystal structure was determined by standard methods and refined to $R_1 = 0.054$ and $R_2 = 0.069$, on the basis of 4409 reflections. The data were collected with use of Mo Kα radiation and a Syntex $P2_1$ diffractometer. The geometry about platinum is square planar with the rings very roughly at right angles to each other and the square plane. The pyrimidine ligands are oriented in such a way that the exocyclic NH_2 group of 1-methylcytosine and the exocyclic O(2) group of thymine are both at the same side of the platinum coordination plane and hydrogen bonded to each other. Bond lengths (Pt-N range 2.025 (9)-2.08 (1) Å) and angles are normal. IR and Raman solid-state spectra of this compound as well as those of the corresponding mono- and trihydrates are studied in order to evaluate the effects of crystal packing and hydrogen bonding on the vibrational modes of the heterocyclic ligands. In solution, the three compounds are identical as indicated by Raman and ^1H NMR spectra.

Introduction

Uracil and thymine anions exist in solution in an equilibrium of N(1)- and N(3)-deprotonated tautomers.[2] With respect to metal coordination of these tautomers, Inagaki and Kidani have isolated both N(1)- and N(3)-coordinated complexes of uracil with the triammineplatinum(II) moiety.[3] We have recently shown that in dimethylformamide, DMF, a *cis*-diammineplatinum(II) compound with N(1)-bound thymine, *cis*-$PtCl(C_5H_5N_2O_2)(NH_3)_2$, is formed in high yield.[4] Upon removal of the chloride and reaction with 1-methylcytosine, different crystalline products of composition $[Pt(C_5H_5N_2O_2)(C_5H_7N_3O)(NH_3)_2]ClO_4{\cdot}xH_2O$ ($x = 3, 1, 0$) have been obtained. The structure of the trihydrate has been reported.[4] It shows the *cis*-$Pt(NH_3)_2^{2+}$ moiety bound to N(1) of thymine and N(3) of 1-methylcytosine, arranged in centrosymmetrically related pairs with strong hydrogen bonds through N(3)-H(3)-O(2) of neighboring thymine ligands. The monohydrate is readily obtained as a powder from the trihydrate when kept in air and in crystalline form from aqueous solution. All three compounds exhibit a series of differences in their solid-state IR and Raman spectra. As we have shown for related (ethylenediamine)platinum(II) complexes of thymine,[5] differences in hydrogen bonding, crystal packing, and solvent molecules can affect the typical ring vibrations of heterocyclic compounds markedly.

In continuation of this work, we herewith report the crystal structure of anhydrous *cis*-diammine(1-methylcytosine-*N3*)(thyminato-*N1*)platinum(II) perchlorate and compare the infrared and Raman spectra of the three species. As shown by ^1H NMR and Raman spectroscopy, the three compounds are identical in solution.

Experimental Section

Preparation. The preparation of the trihydrate has been reported, as has the formation of the monohydrate as a powder.[4] Needle-shaped crystals of the monohydrate were obtained by reacting *cis*-$[PtCl(Thy\text{-}H)(NH_3)_2]{\cdot}H_2O$[4] and 1-methylcytosine ($c_{Pt} = 0.008$ M, H_2O, 40 °C, 14 days), filtering off some unreacted Pt starting material, and adding the equivalent amount of $AgClO_4{\cdot}H_2O$ to remove all chloride. After filtration of AgCl and concentration to one-sixth of its original volume, the solution was allowed to evaporate at room temperature. Colorless needles were washed with a small amount of water and air-dried. The yield was 52% after 2 weeks of crystallization.

The anhydrate was obtained in a way similar to that of the formation of the trihydrate, except with crystallization at 40 °C instead of 22 °C as in the case of the trihydrate. After 1 day of crystallization, the yield was 48% of colorless to slightly yellow cubes. Anal. Calcd: C, 20.75; H, 3.14; N, 16.94; O, 19.35. Found: C, 20.75; H, 3.20; N, 16.72; O, 19.43.

We admit that recrystallization of the three species represented a problem, since it proved impossible to selectively isolate one of the three compounds from solution. Obviously, there are a number of variables such as temperature, concentration, ionic strength of the solution, and quickness of the crystallization process that are of importance in deciding which of the hydrated species is formed preferentially.

Apparatus. IR spectra were recorded on a Perkin-Elmer 580 as Nujol mulls (CsI windows) and KBr pellets and calibrated against polystyrene. The spectra shown were recorded on an extended scale with a maximum resolution of 1.3 cm^{-1}.

Raman spectra were taken with use of krypton laser excitation (647.1 nm) and recorded on a Coderg PH1 spectrometer, which had been calibrated against indene. Spectral slit widhts were 4 cm^{-1} or less in the solid-state spectra and 6-8 cm^{-1} in the solution spectra. Reported Raman intensities refer to signal heights.

^1H NMR spectra were recorded on a Varian EM360 spectrometer at 60 MHz in dimethyl-d_6 sulfoxide, Me_2SO, as solvent. Tetramethylsilane was used as internal standard; the temperature was 27 °C. Me_2SO was dried over 4-Å molecular sieve. Water of crystallization of the tri- and monohydrates was removed by means of molecular sieve after the compound was dissolved in Me_2SO.

Collection of the X-ray Data. A crystal was selected after examination under the polarizing microscope for homogeneity. Precession photographs showed the crystal was monoclinic, *C*2/*c* or *Cc*. The centrosymmetric space group was assumed and justified by satisfactory solution of the structure. Unit-cell parameters were obtained from a fit of χ, ϕ, and 2θ for 15 reflections recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). Crystal data and other numbers related to data collection are summarized in Table I. The density was obtained by flotation in a diiodomethane-iodoethane mixture. Intensity data were recorded on the $P2_1$ diffractometer using a coupled θ(crystal)-2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[6,7] Corrections were made for Lorentz-polarization effects and absorption.

Solution of the Structure. The coordinates of the platinum atom were found from a three-dimensional Patterson synthesis, and a series

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(1) (a) McMaster University. (b) Technical University of Munich.

(2) Lippert, B. *J. Raman Spectrosc.* **1979**, *8*, 274 and references therein.

(3) Inagaki, K.; Kidani, Y. *Bioinorg. Chem.* **1978**, *9*, 157.

(4) Lippert, B.; Pfab, R.; Neugebauer, D. *Inorg. Chim. Acta* **1979**, *37*, 1495.

(5) Lippert, B. *J. Raman Spectrosc.* **1980**, in press.

(6) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1977**, *16*, 1525.

(7) Hughes, R. P.; Krishnamachari, N.; Lock, C. J. L.; Powell, J.; Turner, G. *Inorg. Chem.* **1977**, *16*, 314.

0020-1669/81/1320-2381$01.25/0

Table I. Crystal data

compd	$[Pt(NH_3)_2(C_5H_7N_3O)(C_5H_5N_2O_2)](ClO_4)$, $C_{10}H_{18}ClN_7O_7Pt$
fw	578.84
cryst size, mm	sphere, $r = 0.10$
systematic abs	hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$
space group	$C2/c$
unit cell parameters (Å and deg)	$a = 20.071$ (13), $b = 12.514$ (4), $c = 16.442$ (5), $\beta = 118.25$ (3)
V, Å^3	3638 (3)
Z	8
ρ_{calcd}, g cm^{-3}	2.114
ρ_{obsd}, g cm^{-3}	2.12 (1)
linear abs coeff, cm^{-1}	83.1
abs factor limits	3.150–2.550
max 2θ, reflctns collected	55°, $h,k,\pm l$
std reflctns, esd	2,0,–4, 1.0%; 2,4,–8, 2.1%
temp, °C	22
no. of independent reflctns	4409
no. of reflctns with $I > 3\sigma(I)$	2535
$3\sigma(I) < I < \sigma(I)$, $F_c > F_o$	373
$3\sigma(I) < I < \sigma(I)$, $F_c < F_o$	707
$I < \sigma(I)$, rejected	794
no. of variables	116
final R_1, R_2[a]	0.054, 0.069
final shift/error max, av	0.076, 0.009
g (secondary extinction)	3.749×10^{-9}
final difference map	
highest peak, e/Å^3; location	1.6; 0.90, 0.20, 0.60
lowest valley, e/Å^3; location	–1.1; 0.10, 0.30, 0.95
weighting	$w = (\sigma_F^2 + (0.05F_o)^2)^{-1}$
error in an observn of unit wt	1.02

[a] $R_1 = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$; $R_2 = [(\Sigma w(|F_o| - |F_c|)^2)/\Sigma w F_o^2]^{1/2}$.

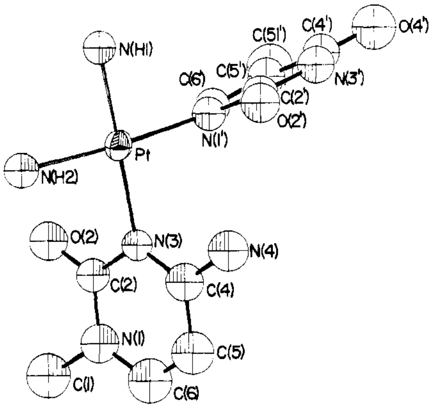

Figure 1. The cation *cis*-diammine(1-methylcytosine-*N3*)(thyminato-*N1*)platinum(II), showing the atom numbering.

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 were made anisotropic. Tests were made at each stage to show the use of increased parameters was significant.[8] Further refinement using full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, was terminated when the maximum shift per error was <0.1. No attempt was made to locate the hydrogen atoms. Correction was made for secondary extinction by using the method of Larson.[9] Throughout the refinement, the scattering curves were from ref 10, and anomalous dispersion corrections from ref 11 were applied to the curves for platinum and chlorine. The atom parameters for nonhydrogen atoms are listed in Table II.[12]

Table II

Atomic Positional Parameters (×10^4) and Isotropic Temperature Factors (Å^2 × 10^3)

atom	x	y	z	U
Pt	3901.4 (2)	2423.4 (3)	969.3 (3)	*a*
N(H1)	3879 (5)	3942 (7)	1399 (7)	43 (2)
N(H2)	3138 (6)	2034 (8)	1446 (7)	49 (2)
N(1)	3273 (6)	–651 (9)	–178 (8)	59 (3)
C(2)	3283 (7)	409 (9)	18 (8)	45 (3)
N(3)	3957 (5)	877 (7)	643 (6)	38 (2)
C(4)	4573 (8)	298 (11)	1032 (10)	58 (3)
C(5)	4561 (10)	–801 (13)	792 (12)	73 (4)
C(6)	3931 (10)	–1229 (14)	250 (12)	79 (5)
C(1)	2532 (10)	–1145 (13)	–794 (12)	78 (4)
O(2)	2703 (5)	940 (7)	–361 (6)	59 (2)
N(4)	5239 (7)	786 (9)	1642 (8)	66 (3)
N(1′)	4574 (6)	2915 (8)	422 (7)	45 (2)
C(2′)	5281 (7)	3229 (10)	945 (9)	51 (3)
N(3′)	5667 (6)	3680 (8)	534 (8)	55 (3)
C(4′)	5351 (8)	3863 (10)	–403 (10)	56 (3)
C(5′)	4606 (8)	3495 (10)	–949 (9)	55 (3)
C(6′)	4248 (7)	3039 (10)	–514 (9)	49 (3)
O(2′)	5613 (5)	3083 (7)	1797 (7)	62 (2)
O(4′)	5762 (6)	4261 (9)	–676 (8)	78 (3)
C(51)	4247 (11)	3638 (14)	–1966 (13)	85 (5)
Cl	2170 (2)	4249 (3)	2803 (3)	*a*
O(11)	2516 (15)	3350 (22)	2747 (2)	211 (10)
O(12)	2774 (18)	4946 (24)	3132 (22)	251 (13)
O(13)	1726 (21)	4367 (27)	3255 (25)	292 (16)
O(14)	1654 (20)	4597 (24)	1901 (23)	255 (13)

Anisotropic Temperature Factors (×10^4)[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	271 (2)	383 (2)	372 (2)	27 (2)	123 (2)	10 (2)
Cl	556 (21)	717 (22)	869 (27)	137 (17)	295 (20)	–41 (19)

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

Results and Discussion

The molecular cation is shown in Figure 1, and selected interatomic distances are given in Table III. The arrangement of the ligands around the platinum is a rough square plane, but the ligating atoms are significantly out of the ideal square plane (N(1) -0.07 (1) Å, N(2) +0.09 (1) Å, N(3) -0.06 (1) Å, N(1′) +0.08 (1) Å), which passes through the platinum atom. Pt–N distances (2.025 (9)–2.08 (1) Å) are within the range we have observed previously.[13,14] The 1-methylcytosine ligand is bonded to platinum in the normal manner by N(3), and the thyminate anion is bonded to platinum through N(1′) as we have observed previously.[14,13] The ligand rings are planar within the errors, and only C(1) (–0.10 (2) Å) and Pt (–0.137 (1) Å) of the exocyclic atoms lie significantly outside the cytosine plane. All the exocyclic atoms of the thyminate ion

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(8) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

(9) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(10) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, p 72 ff.

(11) Cromer, D. T. Reference 10: ref 6, Table 2.3.1, pp 149–150.

(12) All calculations were carried out on CDC-6400 or CYBER 170/730 computers. Initial data treatment used programs from the XRAY 76 package (Stewart, J. M. "The XRAY 76 System Technical Report TR-446"; Computer Science Center, University of Maryland: College Park, Md., 1976). The structure was solved with use of SHELX (Sheldrick, G. M. "SHELX, A Programme for Crystal Structure Solution and Refinement"; University of Cambridge: Cambridge, England, 1976). Final refinement and difference maps used the full-matrix, least-squares program CUDLS and Fourier program SYMFOU, written internally by J. S. Stephens and J. S. Rutherford, respectively. Plane and interplanar angles were calculated with use of NRC-22 (Pippy, M. E.; Ahmed, F. R. "NRC-22"; National Research Council of Canada: Ottawa, 1978). Diagrams were prepared by using ORTEP-II (Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1976).

(13) Faggiani, R.; Lippert, B.; Lock, C. J. L. *Inorg. Chem.* **1980**, *19*, 295 and references therein.

(14) Lock, C. J. L.; Speranzini, R. A.; Powell, J. *Can. J. Chem.* **1976**, *54*, 53.

Table III. Selected Interatomic Distances (Å) and Angles (Deg)[a]

		Distances			
Pt-N(H1)	2.035 (9)	Pt-N(H2)	2.08 (1)	Pt-N(3)	2.025 (9)
Pt-N(1′)	2.04 (1)	N(1)-C(2)	1.36 (2)	C(2)-N(3)	1.38 (1)
N(3)-C(4)	1.31 (2)	C(4)-C(5)	1.43 (2)	C(5)-C(6)	1.27 (2)
C(6)-N(1)	1.37 (2)	N(1)-C(1)	1.48 (2)	C(2)-O(2)	1.22 (2)
C(4)-N(4)	1.38 (2)	N(1′)-C(2′)	1.32 (2)	C(2′)-N(3′)	1.37 (2)
N(3′)-C(4′)	1.38 (2)	C(4′)-C(5′)	1.41 (2)	C(5′)-C(6′)	1.36 (2)
C(6′)-N(1′)	1.37 (2)	C(2′)-O(2′)	1.25 (2)	C(4′)-O(4′)	1.22 (2)
C(5′)-C(51)	1.48 (2)	Cl-O(11)	1.35 (3)	Cl-O(12)	1.37 (3)
Cl-O(13)	1.41 (5)	Cl-O(14)	1.42 (3)		
		Possible Hydrogen-Bond Distances			
N(H1)-O(2)^{i}	2.81 (2)	N(H1)-O(2′)^{ii}	2.85 (2)	N(H1)-O(4′)^{iii}	2.79 (2)
N(H2)-O(2)^{i}	3.10 (2)	N(H2)-O(2)	3.00 (2)	N(H2)-O(2′)^{ii}	3.08 (2)
N(4)-O(2′)	2.95 (2)	N(4)-O(14)^{iv}	3.05 (3)	N(3′)-O(12)^{ii}	3.26 (3)
		Angles			
N(H1)-Pt-N(H2)	87.0 (5)	N(H1)-Pt-N(3)	175.7 (5)	N(H1)-Pt-N(1′)	89.9 (5)
N(H2)-Pt-N(3)	91.1 (5)	N(H2)-Pt-N(1′)	174.4 (4)	N(3)-Pt-N(1′)	92.3 (5)
C(6)-N(1)-C(2)	119 (1)	N(1)-C(2)-N(3)	119 (1)	C(2)-N(3)-C(4)	120 (1)
N(3)-C(4)-C(5)	121 (1)	C(4)-C(5)-C(6)	119 (2)	C(5)-C(6)-N(1)	122 (2)
C(6)-N(1)-C(1)	123 (1)	C(1)-N(1)-C(2)	118 (1)	N(1)-C(2)-O(2)	120 (1)
O(2)-C(2)-N(3)	121 (1)	C(2)-N(3)-Pt	116.3 (7)	Pt-N(3)-C(4)	123.9 (8)
N(3)-C(4)-N(4)	118 (1)	N(4)-C(4)-C(5)	121 (1)	C(6′)-N(1′)-C(2′)	120 (1)
N(1′)-C(2′)-N(3′)	119 (1)	C(2′)-N(3′)-C(4′)	123 (1)	N(3′)-C(4′)-C(5′)	117 (2)
C(4′)-C(5′)-C(6′)	118 (1)	C(5′)-C(6′)-N(1′)	123 (1)	C(6′)-N(1′)-Pt	117.8 (9)
Pt-N(1′)-C(2′)	122 (1)	N(1′)-C(2′)-O(2′)	122 (1)	O(2′)-C(2′)-N(3′)	119 (1)
N(3′)-C(4′)-O(4′)	116 (1)	O(4′)-C(4′)-C(5′)	127 (1)	C(4′)-C(5′)-C(51)	119 (2)
C(51)-C(5′)-C(6′)	123 (1)	O(11)-Cl-O(12)	100 (2)	O(11)-Cl-O(13)	127 (2)
O(11)-Cl-O(14)	109 (2)	O(12)-Cl-O(13)	113 (2)	O(12)-Cl-O(14)	107 (2)
O(13)-Cl-O(14)	101 (2)				

[a] Atoms are related to those in Table I as follows: (i) $^{1}/_{2} - x, {}^{1}/_{2} - y, -z$; (ii) $1 - x, y, {}^{1}/_{2} - z$; (iii) $1 - x, 1 - y, -z$; (iv) $^{1}/_{2} + x, y - {}^{1}/_{2}, z$.

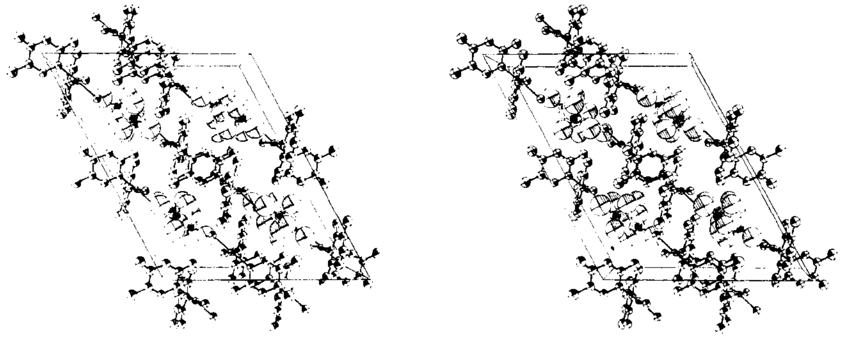

Figure 2. Packing of the cations and anions within the unit cell. *c* and *a** are parallel to the bottom and sides of the page, respectively, and the view is down *b*.

are coplanar. The ligand rings are very roughly at right angles to the square plane and each other (square plane–cytosine 62.9 (5)° (cf. 72°[4]), square plane–thymine 104.3 (5)° (cf. 114°[4]), cytosine–thymine 82.7 (5)°), because of the steric repulsion of the exocyclic groups and because of the fact that the two rings are linked through an N(4)···O(2′) hydrogen bond (2.95 (2) Å). Another intramolecular hydrogen bond is between N(H2) and O(2) (3.10 (2) Å). Bond lengths and bond angles within the 1-methylcytosine and thyminate groups agree extremely well with values we have obtained previously.[13,14] The hydrogen bonding to the two ammonia groups is quite different. N(H1) is involved in three relatively strong hydrogen bonds (N–O range 2.79 (2)–2.85 (2) Å), whereas the three hydrogen bonds from N(H2) are much weaker (N–O range 3.00 (2)–3.10 (2) Å). The hydrogen bonds from N(4) are of similar strength (N–O 2.95 (2), 3.05 (3) Å) while that from N(3′) is very weak (N(3′)–O(12) 3.26 (3) Å).[15]

The packing of the cations and anions in the crystal is shown in Figure 2.

The basic structure consists of intersecting layers of cations parallel to the *bc* (centered at $x = 0, {}^{1}/_{2}$) and *ab* planes (centered at $z = 0, {}^{1}/_{2}$) and arranged such that the thyminate groups lie roughly parallel to the *ac* plane and the cytosine groups roughly parallel to $(1\bar{1}0)$. The perchlorate ions lie in the channels formed by the layers. Within the layers in the *b* direction, the cations are arranged in centrosymmetric pairs such that the thymine molecules lie parallel at a distance of about 3.4 Å, thus maximizing ring π–π interactions. A further hydrogen-bonding interaction exists between N(H1) on each molecule and O(4′) on the other. Between sets of pairs of molecules in the *b* direction, the interaction is of van der Waals type. In the *c* direction adjacent cations are held together by N(H1)···O(2′)^{ii} and N(H2)···O(2′)^{ii} hydrogen bonds, while in the *a* direction the hydrogen bonds are N(H1)···O(2)^{i} and N(H2)···O(2)^{i}. The reason for the large thermal motion of the perchlorate is now obvious. The symmetric perchlorate ion is sitting in the voids in the channel relatively free to librate, the only constraints being interaction with the adjacent perchlorate ions along the channel and two relatively weak hydrogen bonds N(4)···O(14) and N(3′)···O(12).

Spectroscopy

A comparison of the solid-state IR and Raman spectra of the trihydrate, the monohydrate, and the anhydrate of *cis*-diammine(1-methylcytosine-*N3*)(thyminato-*N1*)platinum(II)

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[15] Brown, I. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 24.

Table IV. Most Intense Raman Bands[a] and IR Counterparts[b] of Thymine (T) and 1-Methylcytosine (C) Ligands in the Three Types of *cis*-[(Thy-H)(1-MeCyto)$(NH_3)_2$Pt]ClO_4

anhydrate (solid)		trihydrate (solid)		monohydrate (solid)		soln (H_2O)	
Raman	IR	Raman	IR	Raman	IR	Raman	mode
1670 (2.5)	1670 vs			1667 (1.0)	1670 s, sh	1676 (4.9)[c]	C
1648 (3.1)							T
1630 sh	1635 vs	1626 (1.2)	1620 vs, sh			1633 (6.3)[c]	
1622 sh	1620 vs			1629 (2.0)			
1614 (2.1)		1612 (3.5)		1612 (3.4)	1610 s	1610 sh	T, C
1602 sh							
1538 (1.7)	1542 s	1545 (1.3)	1545 s	1545 (1.8)	1545 s	1545 (1.7)	C
1479 (1.0)	1478 m[d]	1480 (1.2)	*e*	1472 (1.1)	1480 m[d]	1480 (1.0)	C, T
1386 (1.3)	1390 s[d]	1390 (1.5)	*e*	1400 (1.2)	1406 s	1390 (2.5)	T (?)
1375 (1.2)	1378 s[d]	1367 (1.0)					
1347 (10)	1349 w	1348 (10)	1343 m	1348 (10)	1348 vw	1352 (10)	T
1255 (7.1)	1262 m, sh	1257 (6.0)	1257 w, sh	1249 (7.3)	1250 w, sh	1259 (7.5)	C
1214 (4.7)	1218 m	1215 (3.7)	1219 m	1214 (5.2)	1219 m	1218 (6.5)	T
1205 (2.2)	1206 m		1206 m	1206 (3.3)	1204 m		
1169 (3.3)	1165 sh	1183 (2.9)	1183 vw, sh	1179 (3.3)	1178 vw, sh	1188 (6.6)	T
1157 (2.0)	1158 m	1175 (2.2)	1171 w	1163 (1.5)	1168 vw, sh	1153 sh (?)	C
996 (2.0)	1000 w	1003 (1.7)	1000 w	1004 (1.0)	1006 vw	1000 (3.0)	T
		985 (1.0)	983 w	991 (1.4)			C (?)
				837 (1.8)		830 (4.2)	C, T
828 (2.7)	831 s	831 (2.3)	833 s	828 (3.2)	832 s		
793 (6.6)	786 m (?)	793 (7.0)	799 m	796 (7.0)	799 m, sh	794 (9.5)	C
			796 m, sh		796 m		
758 (5.0)		770 (5.3)	765 m	765 (7.5)	762 m	768 (7.6)	T
645 (3.3)	648 s	647 (3.4)	649 s	651 (4.0)	652 s	643 (4.5)	C
633 (4.7)				641 (4.0)			T
609 (2.0)	613 m	610 (1.0)		608 (1.5)			T
585 (1.9)	591 w	581 (1.0)	582 w	583 (2.2)	586 w	583 (1.7)	C
581 (1.4)							
489 (4.4)	492 m	491 (2.7)	493 w, sh	488 (4.0)	492 w	487 (3.1)	T
477 (3.3)	481 m	478 (2.8)	480 m	477 (4.0)	481 m	479 (4.3)	C
430 (1.6)	431 s	421 (1.3)	423 m	427 (1.0)	425 s	424 (1.0)	C
				421 (1.0)			

[a] Only Raman bands with intensity $I = 1.0$ relative to strongest Raman band with intensity $I = 10$. [b] Nujol mulls unless otherwise indicated; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. [c] Superimposed with water peak. [d] KBr disk because of Nujol absorption. [e] No IR data because of Nujol absorption and alteration of compound in KBr disk.

perchlorate reveals a series of differences in positions, relative intensities, and number of bands. It is evident, however, that the spectra of the tri- and monohydrates show a higher degree of similarity than does the anhydrate with the two hydrates. In Figures 3 and 4, examples of such differences are shown. Figure 3 depicts the range between 750 and 850 cm^{-1} with the intense ring breathing modes of the cytosine and thymine rings in the Raman spectrum; Figure 4 shows the 1100–1300 cm^{-1} range which includes, among others, the intense Raman absorption caused by the ring stretching modes. In Table IV, the most intense Raman absorptions caused by thymine and cytosine vibrations are listed and partially assigned. Assignment of these bands is based on comparison with related compounds with N(3)-bound 1-methylcytosines such as *cis*-[PtCl$(NH_3)_2$(1-MeCyto)]NO_3[16] and *cis*-[PtCl$(NH_3)_2$(1-MeCyto)]Cl[17] and N(1)-bound thymines such as [PtCl(Thy-H)(en)][5] and *cis*-[PtCl(Thy-H)$(NH_3)_2$]H_2O.[4] Additional strong Raman bands caused by ClO_4^- and the Pt–NH_3 stretching modes are not given in this table.

The trihydrate[4] crystallizes in space group $P2_1/c$ with four molecules in the unit cell. Pairs of molecules are bonded through two short N(3)–H···O(2) hydrogen bonds into dimers with a center of inversion. As a consequence, the A vibrational modes of the "free" cation (C_1 symmetry) are coupled to give A_g and A_u crystal modes (C_i symmetry of the "free" dimer and C_i site symmetry). With the A_g modes being Raman active and the A_u modes IR active, noncoincidence is observed for a great number of bands. Coupling between adjacent dimers might lead to further doubling of the modes (C_{2h} factor group, A_g + B_g (Raman), A_u + B_u (IR)), but this is not generally observed. Possible exceptions are the ring-breathing mode of cytosine—three of four noncoincident bands expected for factor group coupling are observed, namely, at 799 (IR), 796 (IR), and 793 cm^{-1} (Raman)—and the split thymine mode around 1215 cm^{-1}. The magnitudes of splittings caused by intermolecular coupling within the dimer are in the order of 1–5 cm^{-1} with the exception of the aforementioned thymine

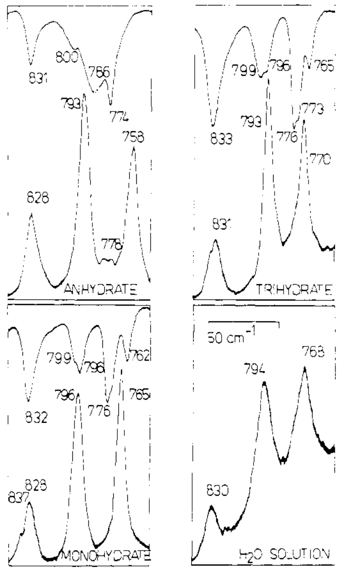

Figure 3. IR (Nujol) and Raman bands between 750 and 850 cm^{-1}.

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(16) Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1981**, *20*, 335.

(17) Lippert, B.; Lock, C. J. L., to be submitted for publication.

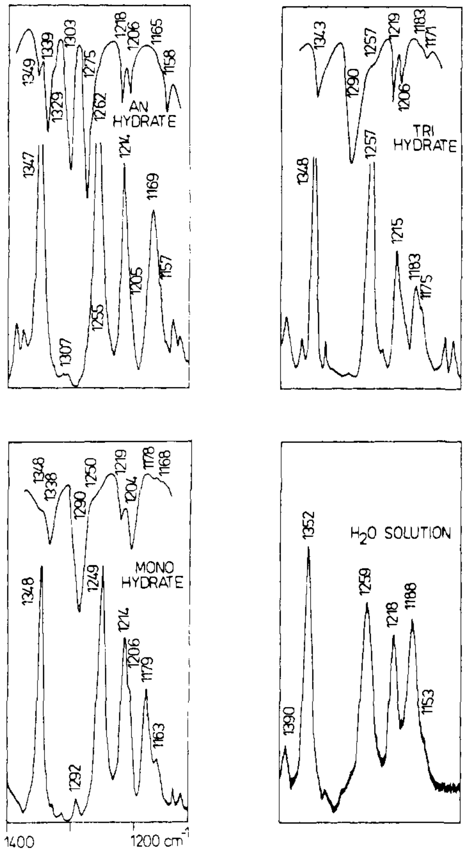

Figure 4. IR (Nujol) and Raman bands between 1150 and 1350 cm^{-1}.

mode around 1215 cm^{-1}. With neutral thymine[18] as well as the thymine monoanion (N(1) deprotonated),[19] which form similar hydrogen-bonded aggregates, splitting caused by intermolecular coupling is generally found to be larger,[5] frequently 4–10 cm^{-1} and occasionally 10–19 cm^{-1}. The apparent decrease in intermolecular coupling in the hydrogen-bonded Pt dimer as compared to that of neutral thymine and potassium thyminate must primarily be a consequence of the damping effect of the heavy metal. If it were only caused by the lengthening of the hydrogen bonds—2.85 (3) Å in the Pt dimer compared to 2.838 and 2.842 Å in thymine monohydrate and 2.807 (6) Å in potassium thyminate—one might expect only a small change similar to that observed when going from potassium thyminate to neutral thymine.

In monohydrate, for which the crystal structure is unknown, the center of inversion appears to be preserved. A number of IR and Raman bands are clearly noncoincident with band separations similar to those observed for the trihydrate. Spectra can be analyzed on the basis of C_i site symmetry since there is no clear indication for additional coupling between more than two cations. From the way the monohydrate was obtained from the trihydrate (cf. Experimental Section), and consistent with the data of the vibrational spectra, it is assumed that the hydrogen-bonded dimer structure (C_i molecular symmetry) is retained in the monohydrate.

As mentioned above, differences between the spectra of the two hydrous forms and the anhydrate are more pronounced than between those of the two hydrates. This refers not only to areas of H_2O absorptions such as the IR range between 3500 and 3600 cm^{-1} but also to areas with ligand modes around 1300 and 700–800 cm^{-1}, for example. IR and Raman bands generally do not coincide in the spectra of the anhydrate. Coupling is usually about 1–4 cm^{-1} with few exceptions (such as the cytosine stretching mode (1255 (Raman), 1262 cm^{-1} (IR)) and the already mentioned thymine mode around 1215 cm^{-1}). The observed splitting is probably caused by hydrogen bonding. The magnitude of this interaction in the anhydrate is similar to that observed for the trihydrate where coupling is assumed to occur through two strong hydrogen bonds. With two cations each being interrelated through an inversion center, coupling between corresponding modes is expected to lead to noncoincident IR and Raman bands.

Besides hydrogen-bonding, crystal-packing, and coupling effects, a π-back-bonding mechanism between the metal and the heterocyclic ring may also contribute to the observable differences in the vibrational spectra. Since heterocyclic ring vibrations generally involve motions of the ring as a whole rather than of individual groups of it, any change in the π-electron system should be reflected in changes of a number of ring vibrations. Even though this is observed, the differences in angles between the ligand plane and the Pt coordination plane—which are important for the overlap of suitable d orbitals of the metal with π^* orbitals of the heterocycle—in the trihydrate and anhydrate cannot be considered large enough to evaluate the possible relevance of such an influence.

As to the effect of platinum on the two most intense Raman modes of the heterocyclic rings, the ring stretching and breathing modes, the following is observed. For 1-methylcytosine the ring stretch at 1275 cm^{-1} $(H_2O)^{20}$ and 1261 cm^{-1} (solid) is shifted to 1259 cm^{-1} (H_2O) and 1249–1257 cm^{-1} (solid) in the platinum compounds and the ring breathing mode from 781 cm^{-1} $(H_2O)^{20}$ and 771 cm^{-1} (solid) to 794 cm^{-1} (H_2O) and 793–796 cm^{-1} (solid). For thymine the ring stretch at 1348 cm^{-1} $(H_2O)^{21}$ and 1345 cm^{-1} (solid)[5] is shifted to 1352 cm^{-1} (H_2O) and 1347–1348 cm^{-1} (solid) in the platinum compounds and the ring breathing vibration from 761 cm^{-1} $(H_2O)^2$ and 756 cm^{-1} (solid)[5] to 768 cm^{-1} (H_2O) and 758–770 cm^{-1} (solid).

The perchlorate anions occupy sites of C_1 symmetry in the trihydrate and of C_2 in the anhydrate. As a consequence of the reduction of symmetry from T_d (free ion) to C_1 and C_2, respectively, a splitting of the E mode into two and of the F_2 modes into three components is expected. Moreover, all nine modes become both IR and Raman active. Splitting of the ν_3 mode of free ClO_4^- around 1100 cm^{-1} is observed in all three compounds;[16,22] splitting of the ν_4 mode of free ClO_4^- is well observable only for the monohydrate (630, 625, 620 cm^{-1}) whereas it is unresolved in the two other compounds. The symmetric Cl–O stretching mode (ν_1 of free ClO_4^-) is weakly IR active in all three compounds (around 935 cm^{-1}) and very strong in the Raman spectra. The symmetric bending mode (ν_2 of free ClO_4^-), which frequently is too weak in the IR spectra to be observed,[23] is tentatively assigned to the Raman band around 469 cm^{-1}, since it is the only one not having an IR counterpart in the 400–500 cm^{-1} range.

In solution, the three compounds are identical. This can be seen from Raman and ^1H NMR spectra. In the ^1H NMR spectra (Me_2SO-d_6) signals are observed for 1-methylcytosine at 8.69 and 8.45 (NH_2), 7.68 (H(6), doublet), 5.62 (H(5), doublet), and 3.34 ppm (N–CH_3). For the thyminato ligand signals are observed at 10.5 (NH), 7.1 (H(6)), and 1.64 ppm (CH_3). For the *cis*-$(NH_3)_2$ groups signals are observed at 4.15 and 3.98 ppm. The mode of platinum binding to the hetero-

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(18) (a) Gerdil, R. *Acta Crystallogr.* **1961**, *14*, 333. (b) Ozeki, K.; Sakabe, N.; Tanaka, J. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1038.

(19) Lock, C. J. L.; Pilon, P.; Lippert, B. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2533.

(20) Lord, R. C.; Thomas, G. J., Jr. *Spectrochim. Acta, Part A* **1967**, *23A*, 2551.

(21) This refers to the N(1)-deprotonated tautomer of thymine in H_2O. Identification is by the method outlined in ref 2.

(22) Kong, P.-C; Theophanides, T. *Inorg. Chem.* **1974**, *13*, 1981.

(23) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111.

cyclic rings can be inferred from $^{195}Pt-^{1}H$ coupling data: H(6) of the thymine ligand exhibits sidebands caused by coupling with the ^{195}Pt isotope ($J = 37$ Hz), as does the NH signal ($J = 20$ Hz). The relative magnitudes of coupling constants indicate that the site of platinum coordination is closer to H(6) than to the NH group, caused by N(1) being the site of platination. The H(5) signal of 1-methylcytosine is coupled not only to H(6) ($J = 8$ Hz) but also to ^{195}Pt ($J = 20$ Hz). This is consistent with N(3)–platinum binding.[22] The H(5) and H(6) signals and the NH_2 signal of 1-methylcytosine are shifted downfield upon platination. The shifts for H(5) and H(6) are relatively minor (approximately 0.1 ppm each); the NH_2 signal shift, however, is substantial (1.50 and 1.75 ppm). It reflects the acidification of the amino protons on platinum coordination at N(3), which is sufficient to allow even substitution of a proton for a second platinum.[23] Splitting of the cytosine amino group signal in a 1:1 ratio indicates nonequivalence of the two protons. It probably is a consequence of the increased hindrance of the NH_2 group to rotation about the C4–N4 bond on platinum binding at N(3).[24] The proton signals of the two NH_3 groups cis to each other are nonequivalent as well and also exhibit ^{195}Pt coupling of approximately 52 Hz each. Only the low-field satellites overlap with the $N-CH_3$ signal of 1-methylcytosine.

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Registry No. *cis*-$[Pt(NH_3)_2(C_5H_7N_3O)(C_5H_5N_2O_2)]ClO_4$, 73103-92-1.

Supplementary Material Available: A listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

(24) Kan, L. S.; Li, N. C. *J. Am. Chem. Soc.* **1970**, *92*, 4823.

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Preparation and X-ray Structure of *trans*-Dioxo(1,4,8,11-tetraazacyclotetradecane)technetium(V) Perchlorate Hydrate

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The preparation, properties, and X-ray structure of *trans*-$[Tc(cyclam)O_2]ClO_4\cdot H_2O$ are described. The yellow complex crystallizes in space group $P\bar{1}$ with two independent molecules per unit cell, each having a crystallographically imposed center of symmetry: $a = 9.964$ (3) Å, $b = 9.473$ (2) Å, $c = 11.815$ (3) Å, $\alpha = 101.38$ (2)°, $\beta = 112.54$ (2)°, $\gamma = 113.50$ (2)°, $Z = 2$, $\rho_{\text{exptl}} = 1.72$ g cm^{-3}, $\rho_{\text{calcd}} = 1.728$ g cm^{-3}. The structure was solved by using 2671 data having $F > 3\sigma_F$; final $R = 0.040$, $R_w = 0.055$. The average Tc–O distance is 1.751 (4) Å, and the average Tc–N distance is 2.125 (11) Å.

Introduction

Technetium-99m is one of the most common radionuclides used for imaging in diagnostic nuclear medicine. For most in vivo uses, the metal, which is available as pertechnetate, must be complexed in a reduced form by ligands which produce complexes that are stable in body fluids and, in the most ideal cases, result in specific biodistributions. At the same time, other criteria must be met such as rapid excretion from the body, etc. As noted by Deutsch,[2] both synthetic Tc chemistry and chemistry of Tc pharmaceuticals are poorly understood. In fact, only recently have inorganic chemists applied their talents to the rational design of technetium complexes of potential pharmaceutical interest.

Recent experiments have shown that robust complexes of ^{99m}Tc, generated from $^{99m}TcO_4^-$ by Sn(II), $Na_2S_2O_4$, or electrochemical reduction, are rapidly formed with macrocyclic tetraaza ligands.[3-5] Because of the relative ease with which the chelate ring sizes, ligand charge and ring substituents can be varied in this class of ligands, these observations suggested that a major advance in the design of complexing agents might be made and investigations in this area are under way. However, one of the difficulties with tracer level experiments is that characterization and subsequent study of the chemistry of the species formed is very difficult because of the extremely low ^{99m}Tc concentrations (i.e., $<10^{-8}$ M) used. In addition, the possibility of forming a ^{99m}Tc complex with impurities in the presumed ligand[6] makes it imperative that the chemistry observed at the tracer level be related to macroscopic technetium chemistry by using long-lived ^{99}Tc. This report concerns the preparation and structure determination of the perchlorate salt of $[^{99}Tc(C_{10}H_{24}N_4)O_2]^+$, the species believed to be formed under similar conditions at the tracer level. This is the first *trans*-dioxotechnetium complex to be structurally characterized, and it has the longest metal–nitrogen bond distances of any cyclam complex whose structure is known. Both of these points are considered further in the Discussion.

Experimental Section

Cyclam was purchased from Strem Chemicals, Inc., and purified by recrystallization from chlorobenzene. Technetium-99 was pur-

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(2) Deutsch, E. "Proceedings of Second International Symposium on Radiopharmaceuticals", Seattle, Washington, 1979; Sorenson, J. A., Ed.; Society of Nuclear Medicine, Inc.: New York, 1979; p 127.

(3) Simon, J.; Ketring, A. R.; Troutner, D. E.; Volkert, W. A.; Holmes, R. A. *Radiochem. Radioanal. Lett.* **1979**, *38*, 133.

(4) Troutner, D. E.; Simon, J.; Ketring, A. R.; Volkert, W. A.; Holmes, R. A. *J. Nucl. Med.* **1980**, *21*, 443.

(5) Simon, J.; Troutner, D. E.; Volkert, W. A.; Holmes, R. A. *Radiochem. Radioanal. Lett.*, in press.

(6) DePamphilis, B. V.; Jones, A. G.; Davis, M. A.; Davison, A. *J. Am. Chem. Soc.* **1978**, *100*, 5570.

0020-1669/81/1320-2386$01.25/0