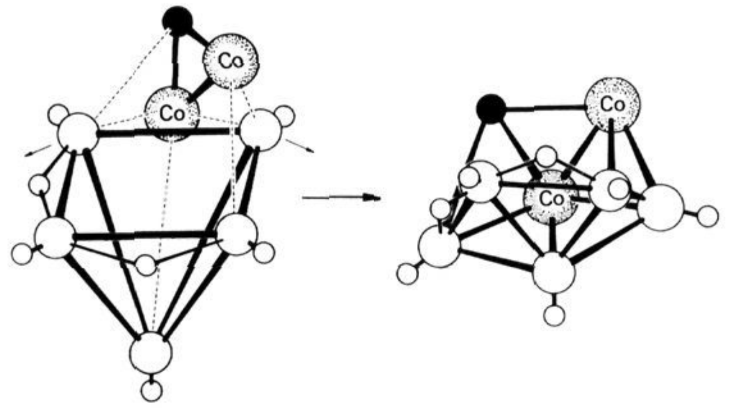

Figure 8. Scheme for the formation of 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$.

figure, leads directly to the structure observed for II.

The absence of boron cage degradation products along with the production of few, if any, other side products in the reactions used to obtain compounds I, II, and III, illustrates the significant synthetic advantages of the mild conditions employed in metal atom reactions. In addition, each of these compounds could be produced in reasonable quantities when cyclohexene sulfide was employed as a reactant, thus enabling future chemical investigations of their properties.

In contrast to the results obtained with pentaborane(9) and hexaborane(10) the reactions with decaborane(14) produced only the previously[2] known metallathiaborane 1,2-$(\eta\text{-}C_5H_5)CoSB_{10}H_{10}$ in low yield. This lower reactivity of decaborane(14) as well as the production of a nine-boron rather than a ten-boron species is consistent with our previous[4] investigations of the metal atom reactions of decaborane(14) and is probably linked to its greater stability compared to that of the smaller boranes.

Finally, it should also be noted that compounds I and III are two of the relatively few examples of dithiametallaboranes. In fact until recently[29,31] neither dithiaboranes or dithiametallaboranes had been isolated, even for large cage systems. The isolation of I and III illustrates that the metal atom technique may be used in the future to incorporate even larger numbers and types of heteroatoms into boron cage systems resulting in the production of new classes of hybrid clusters.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for support of this work.

Supplementary Material Available: Listings of structure factor amplitudes for compounds II and III (20 pages). Ordering information is given on any current masthead page.

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Unusual Platinum Complexes of Deprotonated 1-Methylcytosine: Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-diammineplatinum(II)) Dinitrate Dihydrate, $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2](NO_3)_2{\cdot}2H_2O$, and [Diaquahydrogen(1+)] [Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-nitrodiammineplatinum)(*Pt-Pt*)] Dinitrate, $(H_5O_2)[(NH_3)_2(NO_2)Pt(C_5H_6N_3O)_2Pt(NH_3)_2(NO_2)](NO_3)_2$

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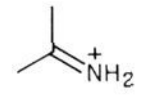
Abstract: The reaction of aqueous *cis*-$Pt(NH_3)_2(NO_3)_2$ with 1-methylcytosine yields a variety of products including the novel compounds bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-diammineplatinum(II)) dinitrate dihydrate, $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2](NO_3)_2{\cdot}2H_2O$ (A) and [diaquahydrogen(1+)] [bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-nitrodiammineplatinum)] dinitrate, $(H_5O_2)[(O_2N)(NH_3)_2Pt(C_5H_6N_3O_2)_2Pt(NH_3)_2(NO_2)](NO_3)_2$ (B), both of which contain the cytosine ligand deprotonated at the 4-NH_2 group. The crystal structures of both have been determined by X-ray diffraction. A has the space group $P2_1/c$ with cell dimensions $a = 9.887$ (3) Å, $b = 17.191$ (5) Å, $c = 15.532$ (4) Å, and $\beta = 116.40$ (2)° and has four formula units in the unit cell. Data for both compounds were collected by using Mo Kα radiation and a Syntex P2_1 diffractometer. Both crystal structures were determined by standard methods, and A was refined to $R_1 = 0.0739$ and $R_2 = 0.0953$ on the basis of 3248 independent reflections. B has space group $P\bar{1}$ with $a = 8.676$ (4) Å, $b = 10.877$ (4) Å, $c = 15.462$ (6) Å, $\alpha = 90.24$ (3)°, $\beta = 117.98$ (3)°, and $\gamma = 95.09$ (4)° and has two formula units in the unit cell. The final $R_1 = 0.0618$ and $R_2 = 0.0779$ was based on 2780 independent reflections. Both compounds contain a dimeric cation in which two square-planar arrays about each platinum atom lie very roughly parallel and these are bridged in the cis positions by the 1-methylcytosinato ligands through N^3 and N^4. The bridging ligands are arranged head to tail. In addition B has two axially bonded nitro groups (Pt–N = 2.12 (3), 2.13 (2) Å). The Pt–Pt distances are markedly different (Pt–Pt (A) = 2.981 (2) Å, (B) = 2.584 (1) Å), but the Pt–N distances (ammonia and 1-methylcytosine range 2.00 (2)–2.11 (3) Å) are normal.

Introduction

It has been generally accepted that the exocyclic group of cytosine is no site for metal coordination unless the NH_2 group is deprotonated.[2-5] This is because a good representation of the group is



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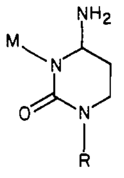
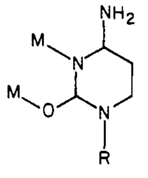
(1) (a) McMaster University. (b) Technical University of Munich.

The bond order for the C–N bond, based on the known bond length[6] and the Pauling bond length–bond order relationship,[7] is 1.6 and thus resonance forms which include the above structure must make an important contribution to the total structure. Apart from the positive charge on the nitrogen atom, the NH_2 group will at best be a hindered rotor and in the preferred position will be coplanar with the pyrimidine ring. In agreement with this picture, metal binding through N(3) of cytosine has been verified by X-ray crystallography in a number of cases (I).[8-13] In an even larger number of instances, additional interaction with the metal through oxygen donor atoms, either from the cytosine ring (II)[14-21] or, in nucleotide complexes, through the phosphate group,[22-24] has been observed. Metal coordination solely through the exocyclic oxygen of cytosine has been reported as well, both in the solid state[25] and in solution (III).[26] Recently, the first crystallographic example of metal coordination (ruthenium(III)) to the deprotonated exocyclic amine group of 1-methylcytosine has been reported (IV).[27] We now present evidence for yet another way of cytosine metal binding, namely, through both N3 and the deprotonated exocyclic amine group (V). One of the two dimeric platinum compounds described in this paper contains platinum in the usual oxidation state +2 and the other one in the unusual oxidation state +2.5.

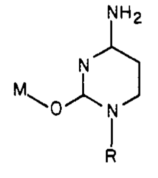
The only other dimeric compound of a similar type containing an unusual oxidation state is the platinum(III) sulfate bridged complex $K_2[Pt_2(SO_4)_4(H_2O)_2]$.[28] Although platinum coordination to N3 is favored,[29] binding of the *cis*-$Pt(NH_3)_2^{2+}$ moiety to the NH_2 group of cytosine has been suggested previously, either to the neutral NH_2 group at acidic pH[30] or to the deprotonated NH group at basic pH.[31]



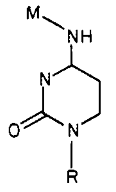
I



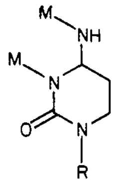
II



III



IV



V

Experimental Section

Compound A was prepared in two ways.

(1) $[(NH_3)_2Pt(OH)]_2(NO_3)_2$[32] and 2 equiv of 1-methylcytosine were stirred for a few minutes until the two compounds had dissolved (H_2O, 70 °C, $C = 0.066$ M Pt, stoppered flask). The pH of the solution was 6.8 when cooled to room temperature. Within 2 days (36 °C, stoppered flask), the solution became brownish and the pH rose to 8.7. Some black precipitate (~3 mg) was filtered off and the solution brought to pH 6 with 2 N HNO_3, concentrated in a rotary evaporator to a 40-mL volume, and kept at room temperature in a stoppered flask. After the mixture was cooled to 0 °C, 210 mg of the starting Pt compound was filtered off. The pH of the filtrate was then 6.5 and was brought back to 6.0 with diluted HNO_3. Within 2 days at room temperature (open beaker) crystals of the title compound A and the starting Pt compound had formed. They were filtered off and separated by means of dimethylformamide (DMF) (A dissolves forming a yellow solution; the Pt starting compound remains undissolved), and, after evaporation of DMF to dryness, A was recrystallized from H_2O. The first crop of A was 110 mg. The pH of the filtrate (6.25) was readjusted to 6.0 repeatedly, and additional crops of A were filtered off. Total yield of A was 450 mg after 2–3 weeks.

(2) An aqueous solution of *cis*-$Pt(NH_3)_2(NO_3)_2$[33] was reacted with 2 equiv of 1-methylcytosine (0.04 M based on Pt, 20 h at 40 °C, stoppered flask). The resulting solution of pH ~5 was adjusted to pH 6.0 with aqueous 2 N NaOH and concentrated to one-seventh of the volume by rotary evaporation. Slow evaporation gave several crystalline compounds (A, C–F) (in sequence of decreasing yields—*cis*-$[(NH_3)_2Pt(1\text{-}MeCyto)_2](NO_3)_2\cdot H_2O$, C (60%), *cis*-$[(NH_3)_2Pt(1\text{-}MeCyto)_2](NO_3)_2\cdot 1MeCyto$, D (15%), *trans*-$[(NH_3)_2Pt(1\text{-}MeCyto)_2](NO_3)_2$, E (2–5%), and compound A (2%), as well as a brown to purple amorphous material F.[34] Separation of the various products was achieved by fractional recrystallization utilizing differing solubilities in H_2O: E is very insoluble in H_2O and precipitates first and compounds D and A are moderately soluble in H_2O, whereas C and E are highly water soluble and do not precipitate until the reaction mixture is almost dry.

Preparation of B. Compound B was obtained according to procedure 2 described above. We have to admit that it has only proved possible to prepare B once, and so far we have been unable to reproduce the preparation of this compound. It was—to our knowledge—obtained in exactly the same way and at the same stage of the reaction as A, and we are presently varying the experimental conditions in an attempt to synthesize more of B for further investigations. At this moment we suspect that the conversion A → B is a spontaneous one. We did observe that in procedure 2 compound A sometimes crystallized as pale yellow to colorless crystals (as in procedure 1, yet sometimes as yellow-purple dichroic crystals). Infrared spectra did not reveal any difference between these

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Table I

compd	$C_{10}H_{28}N_{12}O_{10}Pt_2$	$C_{10}H_{28}N_{12}O_{10}Pt_2$	$C_{10}H_{28}N_{14}O_{14}Pt_2$
fw	866.59	866.59	959.60
cryst size		sphere of radius 0.05 mm	cylinder: $r = 0.075$ mm, $l = 0.25$ mm
systematic absences	$0k0, k = 2n + 1$ $h0l, l = 2n + 1$	$0k0, k = 2n + 1$ $h0l, l = 2n + 1$	
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$
unit cell parameters	$a = 9.88$ (1)Å $b = 17.17$ (2) Å $c = 15.52$ (1) $\beta = 116.38$ (6)°	$a = 9.887$ (3) Å $b = 17.191$ (5) Å $c = 15.532$ (4) $\beta = 116.40$ (2)°	$a = 8.676$ (4)Å $b = 10.877$ (4) Å $c = 15.462$ (6) Å $\alpha = 90.24$ (3)° $\beta = 117.98$ (3)° $\gamma = 95.09$ (4)°
volume, $Å^3$	2360 (4)	2365 (1)	1282 (1)
Z	4	4	2
ρ_{calcd}, g cm^{-3}	2.44	2.44	2.48
ρ_{obsd}, g cm^{-3}	2.41 (1)	2.41 (1)	2.48 (2)
linear abs coeff, cm^{-1}	125.3	125.3	110.7
abs coeff limits		2.392–2.350	3.650–4.330
max 2θ, quadrant	35°, $h, k, \pm l$	45°, $h, k, \pm l$	45°
std reflections	0,−4,1, −1,−3,1	0,−4,1, −1,−3,1	1,−2,3, 3,0,−8
overall esd	2.00%, 1.56%	2.01%, 2.03%	1.99%, 2.70%
temp, °C	22	22	22
no. of independent reflctns	1539	3248	3388
no. with $I > 3\sigma(I)$	1155	1631	2167
$3\sigma(I) > I > \sigma(I), F_c > F_o$	78	272	172
$3\sigma(I) > I > \sigma(I), F_o < F_c$	137	513	433
$I > \sigma(I)$ (rejected)	169	832	616
final R_1[a]	0.0436	0.0739	0.0618
final R_2[a]	0.0647	0.0953	0.0779
final shift in esd max	0.047	0.042	0.12
av	0.003	0.003	0.014
g (secondary extinction)	3.27×10^{-8}	2.10×10^{-8}	no extinction correction made
final difference map:			
highest peak, location	3.28 e/$Å^3$, 0.07, 0.20, 0.27 3.57 e/$Å^3$, 0.30, 0.20, 0.30	1.23 e/$Å^3$, 0.12, 0.23, 0.12 1.29 e/$Å^3$, 0.05, 0.20, 0.28	3.13 e/$Å^3$, 0.20, 0.82, 0.70 3.03 e/$Å^3$, 0.32, 0.22, 0.27
lowest valley, location	−2.52 e/$Å^3$, 0.18, 0.20, 0.17 −2.66 e/$Å^3$, 0.28, 0.20, 0.07	−1.17 e/$Å^3$, 0.27, 0.13, 0.12 −1.12 e/$Å^3$, 0.18, 0.13, 0.25	−2.60 e/$Å^3$, 0.02, 0.22, 0.37
weighting	$1/w = [\sigma(F)^2 + (0.056\|F_o\|)^2]$	$1/w = [\sigma(F)^2 + (0.069\|F_o\|)^2]$	$1/w = [\sigma(F)^2 + (0.03\|F_o\|)^2]$

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

two types of crystals. In contrast, compound B was obtained as deep yellow crystals and could be recrystallized from H_2O unchanged.

For elemental analysis cf. ref 35.

Measurement of the NMR Spectra. NMR spectra were measured either on a Varian EM390 spectrometer at 90 MHz, 34 °C (Figure 4a), or on a Varian EM360 spectrometer at 60 MHz, 27 °C (Figure 4b). The internal reference used was tetramethylsilane. The solution for spectrum Figure 4a was prepared by stirring 0.125 g of 1-methylcytosine in 10 mL of dimethyl sulfoxide for 3 h at 22 °C. The sample only dissolved slowly, so after 3 h saturation (~0.1 M) was assumed and the sample was used to obtain a spectrum. The solution for spectrum 4a (lower) was obtained by adding 0.410 g of K_2PtCl_4 (an equimolar amount) to the initial sample of 1-methylcytosine. After ~20 min a yellow solution developed. Spectrum 4a (lower) was obtained 1 h after the solution was mixed. For the spectra in Figure 4b the solvent was deuterated dimethyl sulfoxide, Me_2SO-d_6 and was dried over a 4-Å molecular sieve. Water of crystallization of A was removed by drying the Me_2SO solution with the same sieve.

Infrared spectra were recorded on a Perkin-Elmer 580 grating spectrometer, both as KBr pellets and Nujol mulls (CsI windows) from 4000 to 300 and 200 cm^{-1}, respectively. The spectra were calibrated by using polystyrene. Raman spectra were recorded on a Coderg PH1 with a krypton laser (647.1-nm) excitation. The spectra were calibrated by using indene. The deuterated analogue of A was prepared by repeated recrystallization from D_2O.

Collection of the X-ray Diffraction Data. Crystals of the two compounds were selected after examination under a polarizing microscope for homogeneity. Two crystals were chosen for A, and the structure was determined for both (see below). One crystal was chosen for B. Precession photographs of A showed it was monoclinic, with the unique absences of $P2_1/c$ whereas B was triclinic. A Delaunay test showed no hidden symmetry. Unit cell parameters were obtained from a least-squares fit of χ, Φ, and 2θ for 15 reflections for each crystal in the range $20° < 2\theta < 35°$ recorded on a Syntex P2$_1$ diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 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.[33,36] Corrections were made for Lorentz–polarization effects and absorption for the second crystal of A and B.

Solution of the Structure. Both structures were solved in the same way. The coordinates of the platinum atoms were found from three-dimensional Patterson syntheses 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 atoms, which were previously isotropic, were made anisotropic. Tests were made to show the use of increased parameters was significant.[37] Further refinement using full-matrix least-squares and minizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error was about 0.1. Secondary extinction was applied by using the method of Larson.[38] Throughout, the scattering curves were taken from ref 39, and anomalous dispersion corrections from ref 40 were applied to the curve for platinum. The atom parameters for nonhydrogen atoms are listed in Tables 2 and 3.[41–42]

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(35) Chemical analysis of A after recrystallization from water. Anal. Calcd: C, 13.9; H, 3.3; N, 19.4; O, 18.5; Pt, 45.0. Found: C, 13.9; H, 3.3; N, 19.4; O, 18.6; Pt, 44.5. Chemical analysis of B was incomplete and only in fair agreement with expected results because of the small quantity of sample available. Anal. Calcd: C, 12.5; H, 3.0; Pt, 40.7. Found: C, 13.2; H, 3.2; Pt, 39.6.

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Table II. Atom Parameters and Temperature Factors (Å^2) for Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-diammineplatinum(II)) Dinitrate Dihydrate (×10^3)

	x	*y*	*z*	*U*
Pt(1)	174.5 (1)	204.58 (7)	288.37 (8)	*a*
Pt(2)	232.2 (1)	212.36 (7)	115.83 (8)	*a*
N(11)	−22 (3)	268 (2)	234 (2)	46 (8)
N(12)	293 (3)	298 (2)	377 (2)	45 (8)
N(21)	411 (4)	286 (2)	169 (2)	55 (8)
N(22)	103 (3)	301 (1)	28 (2)	44 (7)
N(1)	573 (3)	88 (1)	482 (2)	40 (7)
C(1)	652 (5)	83 (2)	589 (3)	53 (11)
C(2)	437 (4)	123 (2)	439 (2)	39 (8)
O(2)	379 (3)	147 (1)	496 (2)	50 (6)
N(3)	373 (3)	144 (1)	346 (2)	22 (6)
C(4)	428 (4)	113 (2)	287 (2)	33 (8)
N(4)	373 (3)	128 (1)	195 (2)	24 (6)
C(5)	555 (4)	60 (2)	332 (2)	36 (8)
C(6)	630 (4)	53 (2)	424 (2)	41 (8)
N(1A)	−139 (3)	82 (1)	−77 (2)	28 (6)
C(1A)	−221 (4)	74 (2)	−181 (2)	32 (8)
C(2A)	−13 (3)	126 (2)	−33 (2)	32 (7)
O(2A)	31 (2)	161 (1)	−86 (2)	39 (6)
N(3A)	50 (3)	138 (1)	62 (2)	26 (6)
C(4A)	3 (3)	99 (1)	119 (2)	16 (6)
N(4A)	52 (3)	112 (2)	206 (2)	38 (7)
C(5A)	−118 (4)	43 (2)	76 (2)	41 (9)
C(6A)	−191 (4)	37 (2)	−26 (2)	33 (8)
N(7)	320 (5)	775 (2)	25 (3)	82 (12)
O(71)	401 (4)	796 (2)	104 (2)	89 (10)
O(72)	215 (4)	730 (2)	5 (2)	82 (9)
O(73)	343 (5)	793 (2)	−51 (3)	114 (13)
N(8)	139 (9)	458 (4)	202 (5)	127 (21)
O(81)	28 (12)	445 (6)	158 (7)	291 (51)
O(82)	133 (6)	537 (4)	208 (4)	163 (19)
O(83)	237 (8)	424 (4)	219 (4)	190 (27)
OH(1)	248 (5)	704 (2)	206 (3)	118 (14)
OH(2)	473 (4)	563 (2)	424 (3)	103 (12)

[a] Anisotropic temperatures U_{ij} were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where β_{ij}'s occur as a temperature effect from $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ and b_i and b_j are the reciprocal lattice vectors. For Pt(1), $U_{11} = 35.6$ (9), $U_{22} = 32.0$ (8), $U_{33} = 21.0$ (7), $U_{12} = -0.8$ (6), $U_{13} = 15.7$ (6), and $U_{23} = -4.3$ (6); for Pt(2), $U_{11} = 39.9$ (9), $U_{22} = 30.3$ (7), $U_{33} = 18.6$ (7), $U_{12} = -7.2$ (6), $U_{13} = 14.9$ (6), and $U_{23} = -0.3$ (6).

Table III. Atom Parameters and Temperature Factors (Å^2) for [Diaquohydrogen(1+)] [Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-nitrodiammineplatinum)(*Pt–Pt*)] Dinitrate (×10^3)

	x	*y*	*z*	*U*
Pt(1)	−33.5 (1)	162.56 (8)	305.05 (6)	*a*
Pt(2)	185.9 (1)	218.53 (8)	248.72 (6)	*a*
N(11)	−210 (3)	44 (2)	200 (1)	37 (5)
N(12)	75 (2)	15 (2)	396 (1)	32 (4)
N(21)	389 (3)	142 (2)	365 (1)	35 (5)
N(22)	143 (3)	60 (2)	163 (1)	37 (5)
N(1)	200 (3)	376 (2)	583 (2)	44 (5)
C(1)	220 (4)	362 (3)	683 (2)	57 (8)
C(2)	127 (3)	276 (2)	520 (2)	30 (5)
O(2)	82 (2)	182 (2)	541 (1)	41 (4)
N(3)	129 (2)	282 (2)	426 (1)	29 (4)
C(4)	219 (3)	381 (2)	409 (2)	33 (5)
N(4)	238 (2)	376 (2)	331 (1)	25 (4)
C(5)	275 (4)	492 (3)	473 (2)	50 (7)
C(6)	261 (3)	485 (2)	558 (2)	45 (6)
N(1A)	−148 (2)	377 (2)	−17 (1)	34 (5)
C(1A)	−165 (4)	374 (3)	−123 (2)	54 (7)
C(2A)	−23 (3)	310 (2)	46 (2)	37 (6)
O(2A)	83 (2)	263 (2)	28 (1)	48 (5)
N(3A)	−19 (2)	296 (2)	137 (1)	22 (4)
C(4A)	−148 (3)	335 (2)	156 (2)	38 (6)
N(4A)	−151 (3)	303 (2)	235 (1)	37 (5)
C(5A)	−278 (4)	413 (2)	82 (2)	49 (7)
C(6A)	−261 (3)	430 (2)	7 (2)	41 (6)
N(5)	−221 (2)	146 (2)	367 (1)	31 (5)
O(51)	−275 (2)	240 (2)	385 (1)	47 (4)
O(52)	−287 (2)	46 (2)	372 (1)	39 (4)
N(6)	375 (2)	286 (2)	205 (1)	25 (4)
O(61)	449 (2)	211 (2)	177 (1)	50 (5)
O(62)	431 (2)	393 (2)	218 (1)	53 (5)
N(7)	386 (5)	799 (4)	379 (3)	92 (10)
O(71)	286 (4)	694 (3)	329 (2)	132 (11)
O(72)	329 (5)	882 (4)	360 (3)	147 (13)
O(73)	504 (6)	744 (7)	428 (3)	161 (4)
N(8)	650 (3)	85 (2)	−49 (2)	48 (5)
O(81)	567 (2)	85 (2)	−139 (1)	55 (5)
O(82)	597 (3)	141 (2)	5 (1)	65 (6)
O(83)	779 (3)	30 (2)	−9 (1)	64 (6)
OH(1)	41 (4)	170 (3)	794 (2)	128 (11)
OH(2)	304 (4)	272 (3)	940 (2)	122 (10)

[a] Anisotropic temperature factor is defined in Table II. For Pt(1), $U_{11} = 0.0195$ (5), $U_{22} = 0.0290$ (6), $U_{33} = 0.0266$ (5), $U_{12} = 0.0030$ (4), $U_{13} = 0.0156$ (4), $U_{23} = -0.0010$ (4). For Pt(2), $U_{11} = 0.0190$ (5), $U_{22} = 0.0325$ (6), $U_{33} = 0.0263$ (5), $U_{12} = 0.0006$ (4), $U_{13} = 0.0147$ (4), and $U_{23} = 0.0039$ (4).

Results and Discussion

The stoichiometry of the Pt(+2.5)[74] (Pt(+2.5) means Pt at an oxidation state of +2.5) compound presented some difficulty since the analysis is incomplete and the actual formulation is based on crystallographic evidence and our knowledge of the chemicals present in the reaction solution. Our formulation as the title compound is based on the following arguments.

(a) The 1-methylcytosine is present as an anion deprotonated at N4 in both complexes. This seemed unlikely at first since the p*K* for deprotonation of the NH_2 group is 12.4,[43] yet the compounds were isolated from slightly acidic solutions. However, from ^{1}H NMR spectroscopic studies with a number of 1-methylcytosine complexes of platinum it becomes evident that there must be a substantial acidification of the NH_2 protons upon platinum coordination at N3.

(b) What were thought to be two water molecules are actually present as the $H_5O_2^+$ cation. The oxygen–oxygen distance of 2.50 (4) Å is much too short for a direct water–water hydrogen bond[44,45] and is close to the distance found previously[44,46] for a $H_5O_2^+$ unit.

(c) The two coordinated groups in the axis positions seem certain to be nitro groups. It is not clear exactly how they are formed, although Stanko et al.[47] have shown that $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$ can be partially photodecomposed to Pt(III) and NO_2^-. The shape of the ion and the temperature factors of the atoms are consistent with the nitro group formulation.

(d) A platinum state of 2.50 is consistent with the bond length of 2.584 (1) Å. Interatomic distances in dimeric platinum complexes for various oxidation states of platinum are 2.970 Å for +2.0 (average from ref 48 and 49 and this work), 2.843 Å for +2.25 (average from ref 50), 2.584 Å for +2.50 (this work), and

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(41) All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATRDN were from the X-RAY 77 package and were used for preliminary data treatment. The full-matrix least-squares program, CUDLS, Fourier program, SYMFOU, and least-squares planes program, PALS, were written locally by J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams were prepared by using the program ORTEP-II by: Johnson, C. K., U.S. Atomic Energy Commission Report ORNL-5138, 1976.

(42) The parameters used here for $C_{10}H_{28}N_{12}O_{10}Pt_2$, A, related to crystal 2 in Table I (sphere of radius 0.05 mm). The parameters for crystal I have been deposited.

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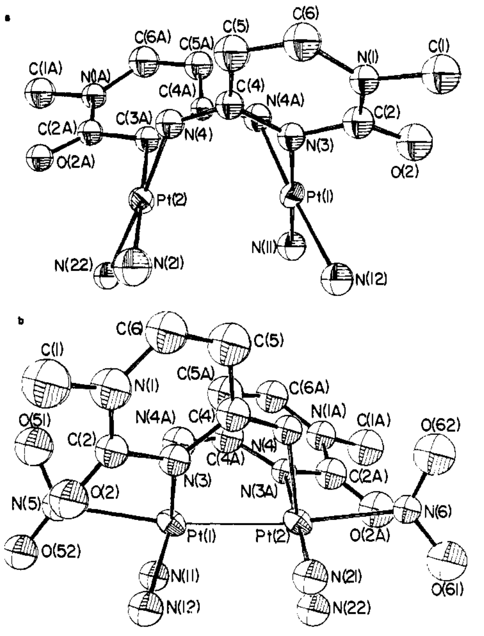

Figure 1. (A) The molecular cation $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2]^{2+}$. (B) The molecular cation $[O_2N(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2NO_2]^+$.

2.466 Å for +3.0 (from ref 28).

(e) Analysis, although incomplete, is consistent with the formulation.

The molecular cations are illustrated in Figure 1, and selected interatomic distances and angles are given in Table IV. The basic structure of the cations is very similar, comprising two platinum atoms, each bound to two ammonia molecules and the Pt-Pt pair bridged by two cytosinate anions bonded through N3 and the deprotonated 4-NH_2 group. The cytosinate anions are arranged head-to-tail and thus the structures are very like those of the platinum(II)-1-methylthyminate[48] and platinum(II)-1-methyluracilate[49] complexes.

The major differences in the cations lie in the change in platinum-platinum distances from 2.981 (2) Å for the Pt(II) complex to 2.584 (1) Å for the Pt(+2.5)[74] complex. In addition the platinum atom increases its coordination to six in the Pt(+2.5) complex from four in the Pt(II) complex by bonding through the nitrogen atom to an axial nitrite ion. (We consider there to be a Pt-Pt bond in the Pt(+2.5) complex but not in the Pt(II) complex.)

Clearly with a major change in the platinum-platinum distance there must be changes in the bridging framework and these are illustrated in Table V. Bond lengths and bond angles are presented for the 1-methylthyminate[48] and 1-methyluracilate complexes[49] and the two title compounds. Apart from the change in the Pt-Pt distance there is no evidence of any bond length change. There do appear to be angular changes, however. In the Pt(+2.5) compound the angles N3-C4-O4(N4)[51] are about 5° larger than the corresponding angle in the Pt(II) compounds. C4-O4(N4)-Pt2 is about 5° larger and Pt1-Pt2-O4(N4) is about 5° smaller. Pt-N3-C4 is 4° larger and Pt2-Pt1-N3 2° smaller. All of these changes are in the expected direction for a shortened Pt-Pt distance. Clearly the major changes take place in the angles involving the exocyclic N4(O4) atom.

The shortening of the Pt-Pt distance and the presence of the axial NO_2 groups also causes major changes in the twist angles of various groups. Thus the dihedral angle between the square planes is reduced to 21° for B from 34° for A, and there is an increasing rotation of the two square planes from the eclipsed position from 16° for A to 25° for B. The dihedral angle between the two pyrimidine planes remains about the same in the two complexes (A, 77°, B 77°), but the pyrimidine rings are twisted much more from the N3-Pt-Pt and N4-Pt-Pt planes in B (N3, 34.6, 28.5; N4, 31.4, 33.2°) compared to those in A (N3, 16.1, 17.5; N4, 21.0, 23.5). As can be seen in Figure 1, this is to reduce the contact between the exocyclic O2 atom and the nitrogen atom of the nitro groups. Even then the nonbonding N-O distances are 2.74 (2) and 2.70 (2) Å which are considerably shorter than N-O nonbonding distances we normally observe, which are typically 3.0-3.3 Å. Surprisingly, although the Pt-N(NO_2) distances are slightly longer than normal, the Pt-Pt-N(NO_2) angles are close to 180°, but the NO_2 groups themselves are bent off the Pt-Pt axis such that both platinum atoms lie about 0.3 Å out of the plane of the NO_2 group and the oxygen atoms are moved further from O2 of the cytosine group. The NO_2 groups have somewhat different orientations with respect to the ligand atoms in the square plane. The oxygen atoms of N(5)O(51)O(52) lie between the N(3), N(4A) and N(11), N(12) pairs at roughly 50° to Pt(1)-N(3) and Pt(1)-N(4A) and 40° to Pt(1)-N(11) and Pt(1)-N(12) while the oxygen atoms of N(6)O(61)O(62), although still between the equivalent pairs of atoms are much closer to the eclipsed position (roughly 20° to Pt(2)-N(4) and Pt(2)-N(22) and roughly 70° to Pt(2)-N(3A) and Pt(2)-N(21)). Bond lengths and angles in the nitro group are similar to those observed previously when it is bonded to a transition metal.[52,53]

The bond distances and angles within cytosinate rings do not differ significantly from published values,[6] although there seems to be some changes between the exocyclic angles in A and B, as we have noted above. Further, as the results in Table VI show, the exocyclic atoms can be quite significantly out of the plane of the pyrimidine ring. We assume this is caused by packing effects.

The Pt-N distances for the ammonia groups (trans to N3, 2.05 Å average, 2.03 (3)-2.08-(2) Å range; trans to N4, 2.06 Å average, 2.05 (2)-2.11 (3) Å range) are longer than we have observed previously where the trans ligand was a bridging hydroxide group (2.03 Å average, 1.97 (5)-2.06 (2)-Å range)[32,54] or nitrate ion (1.995 Å average, 1.99 (1)-2.00 (1)-Å range).[33] This is presumably because of the larger trans influence of the 1-methylcytosinate anion.

As can be seen in Table IV, hydrogen bonding is clearly a major factor in holding the crystal together. In A, evidence for intramolecular hydrogen bonding is slight, although there may be some between the ammonia groups and N4 and O2. The molecules are arranged (Figure 3) so that Pt(1)-Pt(2) is roughly along *c*. The molecules are then stacked into chains along *b* so that the ammonia groups of one molecule are pointed at the pyrimidine rings of the adjacent molecules. One chain is centered at about $z = {}^1/_4$, while the other, which points in the opposite direction is at $z = {}^3/_4$. The adjacent molecules in a chain are bonded primarily through the N(8) nitrate group. O(83) is bonded to N(21) and N(12) in one molecule and N(4A) in the next. O(82) is also bonded through OH(1) to O(71) and O(72) of the N(7) nitrate group. The N(7) nitrate is stacked parallel to the planes of the pyrimidine rings in adjacent molecules along b but is only in contact with the first (LH bottom in the diagram) since another pyrimidine ring from a molecule related to the first by a *c* glide, *a* translation, is interleaved between the N(7) nitrate and the other cation along *b*. In the *c* direction the two chains are extensively hydrogen bonded, a few of the hydrogen bond links being N(4A)-OH(2)-OH(2)^1-N(4A)^1, N(4A)-OH(2)-OH(2)-O(72)-N(7)-O(71)-N(12), N(21), O(2)-N(21), N(22), and O(2a)-N(11), N(12). In the *a* direction, because of the interleaving of the pyrimidine rings, which provides primarily C-H and H-C contacts, there are few short hydrogen bonding links, but there are still long-range NH_3-NO_3-H_2O contacts holding the molecules together.

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(51) We use the nomenclature N1, C2, etc. based on the IUPAC standard nomenclature for pyrimidine rings, when we do not wish to differentiate between the rings. When referring to specific atoms, we use N(1), C(2), N(1A), etc.

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Table IV. Selected Interatomic Distances (Å) and Angles (Deg) in Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-diammineplatinum(II)) Dinitrate Dihydrate (A) and [Diaquohydrogen(1+)] [Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-nitrodiammineplatinum)(*Pt–Pt*)] Dinitrate

	distance			distance	
atoms	A	B	atoms	A	B
Pt(1)–Pt(2)	2.981 (2)	2.584 (1)	Pt(1)–N(11)	2.06 (3)	2.07 (2)
Pt(1)–N(12)	2.11 (3)	2.05 (2)	Pt(2)–N(21)	2.03 (3)	2.08 (2)
Pt(2)–N(22)	2.06 (3)	2.07 (2)	Pt(1)–N(3)	2.04 (2)	2.00 (2)
Pt(1)–N(4A)	2.06 (3)	2.00 (2)	Pt(2)–N(3A)	2.06 (3)	2.06 (2)
Pt(2)–N(4)	2.01 (2)	2.02 (2)	Pt(1)–N(5)		2.12 (3)
N(1)–C(1)	1.50 (1)	1.49 (4)	N(1A)–C(1A)	1.46 (4)	1.57 (4)
N(1)–C(2)	1.34 (5)	1.34 (3)	N(1A)–C(2A)	1.36 (4)	1.35 (3)
C(2)–O(2)	1.32 (6)	1.17 (3)	C(2A)–O(2A)	1.25 (5)	1.23 (4)
C(2)–N(3)	1.34 (4)	1.46 (4)	C(2A)–N(3A)	1.35 (4)	1.41 (4)
N(3)–C(4)	1.38 (5)	1.37 (3)	N(3A)–C(4A)	1.35 (5)	1.38 (4)
C(4)–N(4)	1.31 (4)	1.29 (4)	C(4A)–N(4A)	1.23 (4)	1.28 (3)
C(4)–C(5)	1.45 (5)	1.45 (4)	C(4A)–C(5A)	1.44 (4)	1.50 (3)
C(5)–C(6)	1.29 (5)	1.37 (5)	C(5A)–C(6A)	1.42 (5)	1.26 (5)
C(6)–N(1)	1.40 (6)	1.38 (4)	C(6A)–N(1A)	1.36 (5)	1.37 (4)
Pt(2)–N(6)		2.13 (2)	N(5)–O(51)		1.24 (3)
N(5)–O(52)		1.21 (3)	N(6)–O(61)		1.27 (3)
N(6)–O(62)		1.20 (3)	N(7)–O(71)	1.18 (5)	1.35 (5)
N(7)–O(72)	1.22 (6)	1.05 (6)	N(7)–O(73)	1.34 (8)	1.17 (5)
N(8)–O(81)	1.02 (12)	1.23 (3)	N(8)–O(82)	1.07 (11)	1.30 (4)
N(8)–O(83)	1.35 (10)	1.21 (2)			

Possible Hydrogen Bonding Distances

atoms	distance	atoms	distance	atoms	distance
		A			
N(11)–N(4A)	2.87 (4)	N(11)–O(2A)[a]	2.86 (4)	N(11)–OH(1)[b]	2.98 (7)
N(12)–O(2)	3.07 (4)	N(12)–O(2A)[a]	2.97 (5)	N(12)–O(83)	3.13 (8)
N(12)–O(71)[c]	2.90 (6)	N(21)–O(2)[d]	2.81 (5)	N(21)–N(4)	2.80 (4)
N(21)–O(83)	3.21 (9)	N(21)–O(71)[c]	3.18 (5)	N(22)–O(2)[d]	3.11 (5)
N(22)–O(2A)	2.88 (4)	N(22)–O(72)[e]	3.01 (5)	N(4)–OH(2)[c]	3.09 (6)
N(4A)–O(82)[b]	2.99 (8)	O(72)–OH(1)	3.04 (6)	O(73)–OH(2)[f]	2.90 (6)
O(82)–OH(1)	3.10 (8)	O(71)–OH(1)	3.08 (7)	OH(2)–OH(2)[g]	3.06 (6)
		B			
O(2)–N(12)	2.86 (3)	O(2)–N(12)[j]	2.85 (3)	O(2A)–N(22)	2.95 (3)
O(2A)–OH(2)[p]	2.83 (5)	N(22)–OH(1)[j]	3.09 (4)	N(22)–O(83)[k]	3.02 (2)
N(22)–O(83)[l]	2.95 (4)	N(4A)–O(61)[k]	3.21 (3)	N(22)–O(81)[l]	3.25 (3)
N(21)–O(52)[o]	3.04 (3)	N(12)–O(2)[j]	2.86 (3)	N(12)–O(52)[j]	3.28 (2)
N(12)–OH(1)[j]	3.24 (4)	N(12)–O(72)[m]	2.99 (6)	N(11)–OH(1)[j]	2.84 (4)
N(11)–O(82)[k]	2.93 (3)	N(11)–O(83)[k]	3.18 (4)	N(11)–O(81)[h]	2.99 (3)
N(21)–O(72)[m]	2.82 (5)	N(21)–O(73)[g]	3.11 (5)	N(21)–O(51)[o]	2.88 (3)

	angle			angle	
atoms	A	B	atoms	A	B
Pt(2)–Pt(1)–N(11)	98 (1)	97.7 (7)	Pt(1)–Pt(2)–N(2)	98 (1)	93.2 (7)
Pt(2)–Pt(1)–N(12)	106 (1)	100.1 (7)	Pt(1)–Pt(2)–N(22)	109 (1)	99.7 (7)
Pt(2)–Pt(1)–N(3)	83.8 (8)	83.6 (7)	Pt(1)–Pt(2)–N(3A)	81.5 (8)	85.0 (6)
Pt(2)–Pt(1)–N(4A)	77 (1)	82.2 (7)	Pt(1)–Pt(2)–N(4)	77 (1)	83.0 (6)
Pt(2)–Pt(1)–N(5)		171.0 (5)	Pt(1)–Pt(2)–N(6)		172.9 (5)
N(11)–Pt(1)–N(12)	91 (1)	90.2 (7)	N(21)–Pt(2)–N(22)	89 (1)	89.2 (7)
N(11)–Pt(1)–N(3)	178 (1)	177.6 (8)	N(21)–Pt(2)–N(3A)	179 (1)	177.8 (9)
N(11)–Pt(1)–N(4A)	88 (1)	87.9 (7)	N(21)–Pt(2)–N(4)	88 (1)	90.5 (7)
N(11)–Pt(1)–N(5)		86.2 (9)	N(21)–Pt(2)–N(6)		86.8 (8)
N(12)–Pt(1)–N(3)	87 (1)	91.6 (7)	N(22)–Pt(2)–N(3A)	91 (1)	92.4 (7)
N(12)–Pt(1)–N(4A)	177 (2)	177.2 (8)	N(22)–Pt(2)–N(4)	174 (1)	177.2 (9)
N(12)–Pt(1)–N(5)		88.0 (9)	N(22)–Pt(2)–N(6)		87.4 (8)
N(3)–Pt(1)–N(4A)	94 (1)	90.3 (7)	N(3A)–Pt(2)–N(4)	93 (1)	88.1 (6)
N(3)–Pt(1)–N(5)		92.2 (8)	N(3A)–Pt(2)–N(6)		94.8 (7)
N(4A)–Pt(1)–N(5)		89.8 (9)	N94)–Pt(2)–N(6)		89.8 (8)
Pt(1)–N(3)–C(2)	122 (3)	119 (1)	Pt(2)–N(3A)–C(2A)	116 (2)	120 (2)
Pt(1)–N(3)–C(4)	120 (2)	120 (2)	Pt(2)–N(3A)–C(4A)	123 (2)	119 (2)
Pt(1)–N(4A)–C(4A)	131 (3)	126 (2)	Pt(2)–N(4)–C(4)	131 (2)	123 (2)
Pt(1)–N(5)–O(51)		120 (2)	Pt(2)–N(6)–O(6)		120 (1)
Pt(1)–N(5)–O(52)		120 (2)	Pt(2)–N(6)–O(62)		121 (2)
O(51)–N(5)–O(52)		119 (2)	O(61)–N(6)–O(62)		118 (2)
C(1)–N(1)–C(2)	119 (4)	117 (2)	C(1A)–N(1A)–C(2A)	123 (3)	114 (2)
C(1)–N(1)–C(6)	122 (3)	121 (2)	C(1A)–N(1A)–C(6A)	115 (3)	124 (2)
C(6)–N(1)–C(2)	118 (3)	122 (2)	C(6A)–N(1A)–C(2A)	122 (3)	122 (2)
N(1)–C(2)–O(2)	117 (3)	123 (3)	N(1A)–C(2A)–O(2A)	117 (3)	124 (3)
N(1)–C(2)–N(3)	123 (4)	118 (2)	N(1A)–C(2A)–N(3A)	121 (4)	116 (3)
O(2)–C(2)–N(3)	119 (3)	119 (2)	O(2A)–C(2A)–N(3A)	122 (3)	120 (2)
C(2)–N(3)–C(4)	118 (3)	120 (2)	C(2A)–N(3A)–C(4A)	121 (3)	122 (2)
N(3)–C(4)–N(4)	124 (3)	118 (2)	N(3A)–C(4A)–N(4A)	123 (3)	118 (2)
N(3)–C(4)–C(5)	117 (3)	119 (3)	N(3A)–C(4A)–C(5A)	119 (3)	118 (3)

Table IV (*Continued*)

atoms	angle		atoms	angle	
	A	B		A	B
N(4)-C(4)-C(5)	120 (4)	122 (2)	N(4A)-C(4A)-C(5A)	118 (3)	124 (3)
C(4)-C(5)-C(6)	121 (4)	117 (3)	C(4A)-C(5A)-C(6A)	119 (4)	115 (3)
C(5)-C(6)-N(1)	119 (3)	122 (2)	C(5A)-C(6A)-N(1A)	118 (3)	127 (2)
O(71)-N(7)-O(72)	125 (6)	118 (4)	O(71)-N(7)-O(73)	123 (5)	92 (3)
O(72)-N(7)-O(73)	112 (4)	150 (4)	O(81)-N(8)-O(82)	102 (8)	120 (2)
O(81)-N(8)-O(83)	129 (10)	122 (3)	O(82)-N(8)-O(83)	127 (8)	118 (2)

[a-r] Atoms are related to those in Tables II and III by the following relationships: (a) $x, {}^1/_2 - y, {}^1/_2 + z$; (b) $-x, y - {}^1/_2, {}^1/_2 - z$; (c) $1 - x, y - {}^1/_2, {}^1/_2 - z$; (d) $x, {}^1/_2 - y, z - {}^1/_2$; (e) $-x, 1 - y, -z$; (f) $x, 1.5 - y, z - {}^1/_2$; (g) $1 - x, 1 - y, 1 - z$; (h) $x, 1.5 - y, {}^1/_2 + z$; (i) $1 - x, {}^1/_2 + y, {}^1/_2 - z$; (j) $-x, -y, 1 - z$; (k) $x - 1, y, z$; (l) $1 - x, -y, -z$; (m) $x, y - 1, z$; (n) $-x, -y, -z$; (o) $1 + x, y, z$; (p) $x, y, z - 1$; (q) $-x, 1 - y, 1 - z$; (r) $x, y, 1 + z$.

Table V. Comparison of Bond Lengths and Angles within the Bridging Framework of a Series of Dimeric Platinum–Pyrimidine Complexes

	distance, Å				
	Pt-Pt	Pt-N3	N3-C4	C4-O4(N4)	Pt-O4(N4)
Pt(II)-1-methylthymine[a]	2.974 (1)	2.064 (8)	1.30 (2)	1.26 (2)	2.037 (7)
		2.014 (9)	1.35 (2)	1.29 (1)	2.013 (7)
Pt(II)-1-methyluracil[b]	2.954 (2)	2.041 (13)	1.37 (3)	1.28 (4)	2.026 (18)
		2.046 (15)	1.34 (3)	1.25 (4)	2.060 (16)
Pt(II)-1-methylcytosine[c]	2.981 (2)	2.04 (2)	1.38 (5)	1.31 (4)	2.01 (2)
		2.06 (3)	1.31 (4)	1.23 (4)	2.06 (3)
average	2.970	2.04	1.34	1.27	2.03
Pt(+2.5)-1-methylcytosine[c]	2.584 (1)	2.00 (2)	1.37 (3)	1.29 (4)	2.02 (2)
		2.06 (2)	1.29 (4)	1.28 (3)	2.00 (2)
average		2.03	1.33	1.285	2.01

	angle, deg				
	Pt-Pt-N3	Pt-N3-C4	N3-C4-O4(N4)	C4-O4(N4)-Pt	O4-Pt-Pt
Pt(II)-1-methylthymine[a]	79.6 (3)	125.1 (8)	123 (1)	129.5 (8)	78.7 (3)
	81.6 (3)	124.9 (7)	121 (1)	130.6 (8)	77.4 (3)
Pt(II)-1-methyluracil[b]	82.4 (7)	122 (2)	122 (2)	129 (1)	77.1 (6)
	82.6 (8)	121 (2)	125 (2)	127 (1)	76.6 (6)
Pt(II)-1-methylcytosine[c]	83.8 (8)	120 (2)	124 (3)	131 (2)	77 (1)
	81.5 (8)	123 (2)	123 (3)	131 (3)	77 (1)
average	81.9	123	123	130	77.3
Pt(+2.5)-1-methylcytosine[c]	83.6 (7)	120 (2)	118 (2)	123 (2)	83.0 (6)
	85.0 (6)	119 (2)	118 (2)	126 (2)	82.2 (7)
average	84.3	119.5	118	124.5	82.6

[a] See ref 28. [b] See ref 29. [c] This work.

Table VI. Least-Squares Planes through Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-diammineplatinum(II)) Dinitrate Dihydrate (A) and [Diaquohydrogen (1+)] [Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-nitrodiammineplatinum)] Dinitrate (B)

no.	plane	distance of atoms from plane, Å	
		A	B
1	N(11)N(12)N(3)N(4A)Pt(1)[a]	N(11), 0.02; N(12), −0.02; N(3), 0.02; N(4A), −0.02; Pt(1), 0.03	N(11), 0.00; N(12), 0.00; N(3), 0.00; N(4), 0.00; Pt(1), 0.15
2	N(21)N(22)N(3A)N(4)Pt(2)[a]	N(21), −0.05; N(22), 0.04; N(3A), −0.04; N(4), 0.05; Pt(2), −0.04	N(21), −0.04; N(22), 0.04; N(3A), −0.04; N(3), 0.04; Pt(2), −0.01
3	N(1)C(2)N(3)C(4)C(5)C(6)Pt(1)[a] C(1)[a]O(2)[a]N(4)[a]Pt(2)[a]	N(1), 0.07; C(2), −0.10; N(3), 0.04; C(4), 0.05; C(5), −0.08; C(6), 0.03; Pt(1), −0.09; C(1), 0.20; O(2), −0.22; N(4), 0.16; Pt(2), 0.73	N(1), 0.06; C(2), 0.00; N(3), −0.07; C(4), 0.08; C(5), −0.02; C(6), −0.05; Pt(1), −0.70; C(1), 0.32; O(2), 0.14; N(4), 0.20; Pt(2), 0.55
4	N(1A)C(2A)N(3A)C(4A)C(5A)C(6A), Pt(2)[a] C(1A)[a]O(2A)[a]N(4A)[a]Pt(1)[a]	N(1A), −0.05; C(2A), 0.06; N(3A), −0.02; C(4A), −0.03; C(5A), 0.04; C(6A), 0.00; Pt(2), 0.04; C(1A), −0.12; O(2A), 0.09; N(4A), −0.19; Pt(1), −0.86	N(1A), −0.03; C(2A), −0.02; N(3A), 0.06; C(4A), −0.05; C(5A), −0.01; C(6A), 0.05; Pt(2), 0.37; C(1A), −0.33; O(2A), −0.06; N(4A), −0.17; Pt(1), −0.78
5	N(5)O(51)O(52)Pt(1)[a]		Pt(1), −0.30
6	N(6)O(61)O(62)Pt(2)[a]		Pt(2), 0.30

[a] Atoms given no weight in determining the best plane; other atoms are given unit weight. Errors in atom positions about 0.02 Å except for the nitrate groups for A ≈ 0.05 Å.

In **B**, evidence for intramolecular hydrogen bonding is also slight, although it may occur between O(2)–N(12) and O(2A)–N(22). In the *b* direction at $y = {}^1/_2$ there is very little hydrogen bonding, contact being primarily between the pyrimidine rings. At $y = 0$, there is extensive hydrogen bonding but this is primarily of such a type as to provide bonding along *a* and *c* as

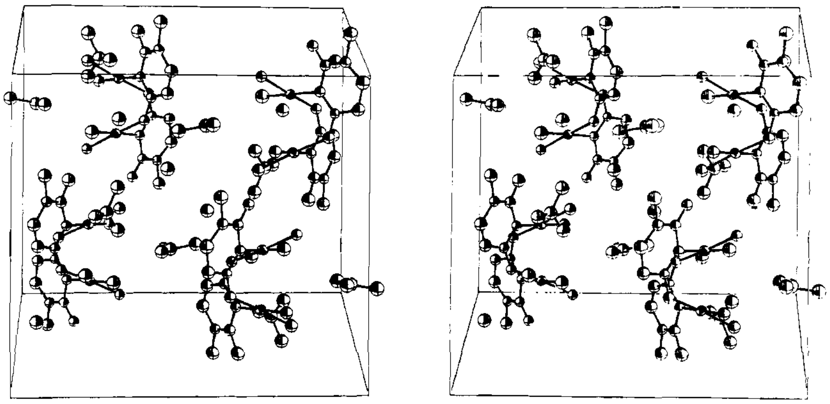

Figure 2. The unit cell contents of $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2](NO_3)_2{\cdot}2H_2O$. *b* and *c* are parallel to the bottom and sides of the page, respectively, and the view is down *a**.

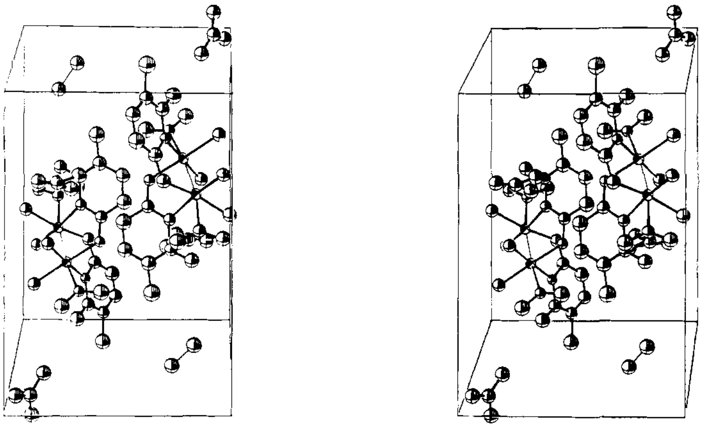

Figure 3. The unit cell contents of $(H_5O_2)[NO_2(NH_3)_2Pt(C_5H_6N_3O_2)_2Pt(NH_3)_2(NO_2)](NO_3)_2$. *b* and $b \times c \times b$ are parallel to the bottom and sides of the page, respectively, and the view is down *a**.

well as *b*; it is not possible to consider the three components separately. Thus both the $H_5O_2^+$ and N(8) nitrate groups are involved in bonding between a molecule and one related by inversion at $^1/_2$, 1, 1 and an *a* translation. One chain is O(2)–$H_5O_2^+$–N(21), N(22) and the other is ammonia groups—N(8) nitrate–ammonia groups. The N(7) nitrate group is bonded through O(73) to N(21) in the molecule depicted on the lhs of Figure 3 and through O(72) and N(21), N(22) in a molecule related by inversion at 0, $^1/_2$, $^1/_2$. O(61) in one molecule is bonded to N(4A) in a molecule related by the *a* translation, and O(51) and O(52) are bonded to ammonia groups in molecules related by the *a* translation and inversion at 1, 1, $^1/_2$.

Metal coordination at N(3) of cytosine leads to a downfield shift of the NH_2 resonance as a consequence of an increased acidity of this group.[55] As shown in Figure 4a, the NH_2 resonance of 1-methylcytosine at 6.95 ppm (δ scale) is shifted to lower field by 1.75 and 1.33 ppm upon reaction with K_2PtCl_4 in dimethyl sulfoxide. Crystallographic evidence suggests the existence of *trans*-dichloro(dimethyl sulfoxide-*S*)(1-methylcytosine-N^3)platinum(II)[8] in this solution. Similar downfield shifts have been observed for *cis*-$[Pt(NH_3)_2$(1-methylcytosine)(thymine-H)$]^+$ [56] (1.75 and 1.50 ppm) and *cis*-$[Pt(NH_3)_2$(1-methylcytosine)(9-ethylguanine)$]^{2+}$ [57] (1.6 ppm) and for complexes of other metals such as zinc (~1 ppm)[58] and mercury (~1.3 and 1.6 ppm).[59] Protonation of N3 causes even larger shifts.[60] Splitting of the NH_2 signal shows the two protons are no longer chemically equivalent, probably because rotation of the NH_2 group has stopped by metal binding. This effect has been observed previously.[59,61]

Simpson,[3] in a UV spectrophotometric study on the complexation of mercury(II) with cytidine, found that besides the marked decrease in p*K* of the NH_2 group on mercuration at N3 there was evidence of a pH-independent deprotonation of the NH_2 group involving CH_3HgOH. We have demonstrated previously[32,54,62] that OH-bridged *cis*-diammineplatinum(II) complexes are formed under the reaction conditions used here and are stable even under mildly acid conditions. It therefore seems possible that a similar metal hydroxide assisted deprotonation may be taking place as well as the previously mentioned lowering of the p*K* of the NH_2 group. Metal-assisted deprotonation of amines in weakly basic, neutron, or slightly acidic solutions, although not common, has been reported before, e.g., for gold,[63] copper,[64] and platinum(IV).[65-67] Similar reactions for platinum in nonaqueous solvents have also been reported.[68]

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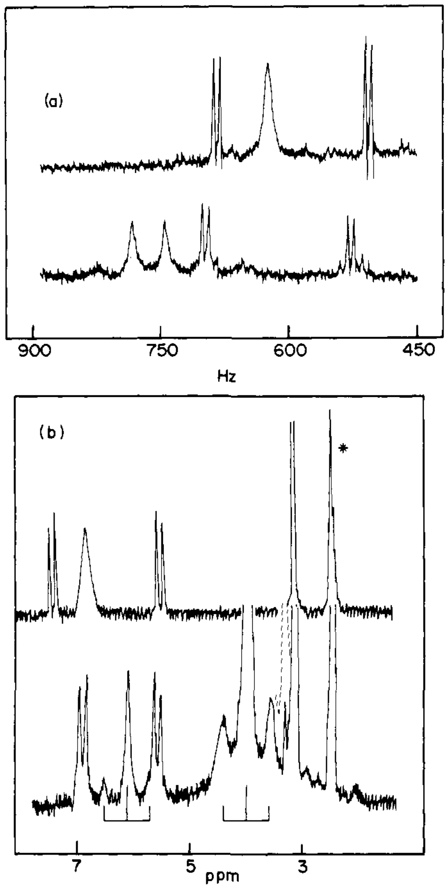

Figure 4. (A) Portions of the proton NMR spectra of (upper) 1-methylcytosine in dimethyl sulfoxide and (lower) 1-methylcytosine and K_2PtCl_4 in dimethyl sulfoxide. (B) Proton NMR spectra of (upper) 1-methylcytosine in dimethyl sulfoxide and (lower) the Pt(II) dimer (A) $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2](NO_3)_2$ in dimethyl sulfoxide. Both taken at $C = 0.13$ M. The dotted signal indicates the H_2O signal before drying over 4-Å molecular sieve. The asterisk denotes the solvent signal. Internal standard of tetramethylsilane was used as a standard for all spectra.

Upon deprotonation and formation of a Pt–NH bond, the NH signal for A (Figure 4b) appears upfield (6.16 ppm) relative to 1-methylcytosine, implying the p*K* of the remaining proton is greater. ^{195}Pt coupling is observed ($^2J_{^{195}\mathrm{Pt}-^1\mathrm{H}}$ = 52 Hz).

Platination of 1-methylcytosine at N3 alone (Figure 4a) usually leads to a slight downfield shift of both H6 and H5 signals[69] compared to the case for the free ligand, but in the Pt(II) dimer (A) (Figure 4c) there is a considerable upfield shift of the H6 doublet, from 7.55 ppm in 1-methylcytosine to 6.98 ppm in A, although the H5 doublet remains unchanged. ^{195}Pt coupling, frequently observed when N3 is the only coordination site,[69] is not observed for A. A similar upfield shift for the H6 signal has been observed previously for a silver–cytidine complex believed to contain deprotonated cytidine.[5]

Signals from the protons of the *cis*-$(NH_3)_2$ groups are observed at 4.03 ppm with sidebands caused by coupling with the ^{195}Pt isotope ($^2J_{^{195}\mathrm{Pt}-^1\mathrm{H}}$ = 53 Hz).

A signal caused by the protons of water of crystallization is observed at 3.33 ppm and disappears upon drying over molecular sieve. No effects on the signals of the NH and NH_3 groups are observed when the sample is dried. The N-CH_3 signal of 1-methylcytosine at 3.2 ppm is not shifted in complex A.

When the Raman spectra (solid state) of 1-methylcytosine complexes of the *cis*-diammineplatinum(II) moiety are compared, a number of differences between corresponding ligand bands are observed depending on whether N3 coordination takes place or bridge formation via N3 and NH4 as in A. For example, a prominent shift occurs for the very intense in-plane "ring-deformation-stretch" mode.[70] It absorbs at 771 cm^{-1} in the free ligand, at 793 and 794 cm^{-1}, respectively, in the N3-bonded cytosine complexes *cis*-$[Pt(NH_3)_2(1\text{-MeCyto})Cl]Cl$, (G) and *cis*-$[Pt(NH_3)_2(1\text{-MeCyto})_2]Cl_2$ (H), and at 817 cm^{-1} in the Pt(II) dimer A. The most intense Raman band, a ring-stretching mode[70] which absorbs at 1250 cm^{-1} in C, 1256 cm^{-1} in D, and at 1247 cm^{-1} in A, appears not to be useful for a differentiation of the various compounds. However, in compound A this mode is quite sensitive to deuteration and shifts by 30 cm^{-1} to higher energy, whereas the corresponding modes in G and H are shifted only insignificantly (+5 cm^{-1}) when being deuterated. Another intense 1-methylcytosine band at 627 cm^{-1} (free ligand) is observed around 645 cm^{-1} in G and H but at 633 cm^{-1} in A.

Although a Raman spectrum for compound B could not be obtained, there is some evidence from the infrared spectrum that the ligand modes are changed similarly in both A and B. For example, the Raman bands of A at 1247 and 633 cm^{-1}, which are also IR active, are observed at the same wavenumbers in the IR spectrum of B. Generally, the infrared spectra of A and B resemble each other quite closely over a wide range. However, there are additional bands in the spectrum of B in the 1300–1400-cm^{-1} range and around 800 cm^{-1} as well as changes around 1650 and 500 cm^{-1}. The additional bands are observed in regions where vibrations of coordinated NO_2 groups are usually observed.[71] Among the IR and Raman bands of A between 1700 and 1300 cm^{-1}, two bands appear to be sensitive to deuteration: the IR band at 1505 cm^{-1} is slightly shifted to 1490 cm^{-1} and the 1305-cm^{-1} band to 1030 and 1015 cm^{-1}, but no shift of the 1410-cm^{-1} band was detected. Since the 1305-cm^{-1} band is assigned to a $\delta_s(NH_3)$ mode, the 1410-cm^{-1} band is tentatively interpreted as arising mainly from a NH-bending mode. NH_3 modes for A are observed at 3280 and 3200 cm^{-1} ($\nu(NH_3)$), around 1305 cm^{-1} ($\delta_s(NH_3)$), and 870 cm^{-1} ($\delta_r(NH_3)$).[72] These modes are identified by means of their deuteration shifts to 2460, 2350 ($\nu(ND_3)$), 1030, 1015 ($\delta_s(ND_3)$), and 670 cm^{-1} ($\delta_r(ND_3)$). These shifts show substantial deviations from the theoretical $2^{1/2}$ shifts for harmonic oscillators, thus indicating involvement of the NH_3 protons in hydrogen bonding (cf. Table IV). The 1305-cm^{-1} Raman band, as well as its deuterated counterpart, exhibits a remarkable intensity (about 15% of the strongest Raman band) not observed in other *cis*-$Pt(NH_3)_2^{2+}$ compounds.[32] Another NH_3 mode ($\delta_d(NH_3)$), expected around 1600 cm^{-1}, is not observed since it is masked by the intense cytosine modes in this region. A shoulder around 1240 cm^{-1} in the IR spectrum of the deuterated compound is assigned to this mode.

The symmetry of the NO_3^- ion (D_{3h}) is lowered to C_1 in both A and B. Thus all four fundamentals can be both infrared and Raman active (RA), and the two E′ modes can split. For A IR activation of the ν_1 mode is observed (1045 (vs) cm^{-1} (RA), w (IR))[73] as is the splitting of ν_4 in the Raman spectrum (736, 706 (vw) cm^{-1} (RA), 735 (vw) cm^{-1} (IR)), but splitting of ν_3 (1388 (vs) cm^{-1} (IR), not observed (RA)) is not observed. There is, however, an unexpected splitting of the ν_2 mode (828 (s), 835 (s) cm^{-1} (IR), vw (RA)). This may arise from factor group coupling since there are two nitrate ions in the asymetric unit. The splitting is observed in the spectrum of the deuterated compound as well.

Conclusion

We have shown that the *cis*-$Pt(NH_3)_2^{2+}$ moiety can bind to 1-methylcytosine through both N3 and the exocyclic amine group

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[72] Abbreviations: ν = stretching; δ_d = degenerate deformation; δ_s = symmetric deformation; ρ_r = rocking vibration.

[73] Abbreviations: vs = very strong; s = strong; w = weak; vw = very weak; IR = infrared; RA = Raman.

with resultant deprotonation of the latter. Deprotonation occurs at neutral pH and even in slightly acidic medium. It is possible that the exocyclic NH_2 group of N9-substituted adenines may act in a similar fashion. This work reveals yet another possible way in which the anticancer drug *cis*-$(NH_3)_2PtCl_2$ may interact with DNA bases.

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Supplementary Material Available: A table of atomic parameters and temperature factors for A and listings of structure factor amplitudes for A and B (31 pages). Ordering information is given on any current masthead page.

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^{15}N NMR Spectrum of a 1,1-Diazene. *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene[1]

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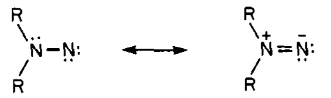
Abstract: The low-temperature ^{15}N NMR spectrum of the 1,1-diazene, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**1**), is reported. The ^{15}N double- and mono-labeled 1,1-diazenes **1a** and **1b** were synthesized. The nitrene and amino nitrogens of **1** have resonances in dimethyl ether at −90 °C at 917.0 and 321.4 ppm, respectively, downfield from anhydrous $^{15}NH_3$, affording a chemical shift difference of 595 ppm for the directly bonded nitrogen nuclei. The chemical shift of the ring nitrogen is consistent with an amino nitrogen whose lone pair is largely delocalized. The large downfield shift of the nitrene nitrogen is consistent with a large paramagnetic term due to a low-lying n → π* transition.

Introduction

1,1-Diazenes (aminonitrenes, *N*-nitrenes) unlike their more stable 1,2-diazene isomers (azo compounds) are usually not isolated or detected by spectroscopic methods but rather are assumed intermediates on the basis of a substantial body of chemical evidence.[5] Recently, the synthesis and direct observation of



persistent[6] 1,1-diazenes, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**1**)[7] and *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene,[8] were reported. The infrared and electronic spectra and kinetics of decomposition of these 1,1-diazenes[7,8] allowed the first comparison of experiment with theory on the nature of the bonding and the relative energies of the states of the parent 1,1-diazene (H_2N–N).[9]

^{15}N NMR spectroscopy has proven to be a sensitive probe of the electronic environment of nitrogen nuclei.[10] With the availability of persistent 1,1-diazenes, we have obtained the first ^{15}N magnetic resonance spectrum of a 1,1-diazene. The low-temperature ^{15}N NMR spectrum of *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**1**)[7] reveals the different electronic environments

Scheme I

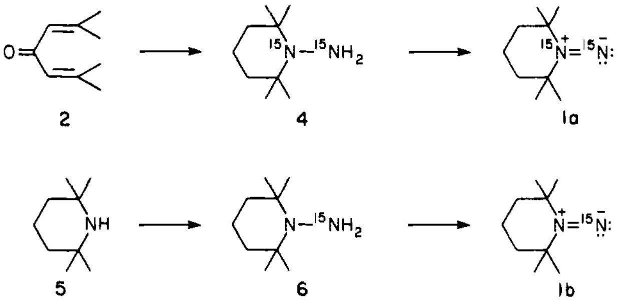
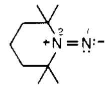
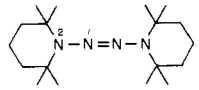


Table I

compd		$^{15}N1$	$^{15}N2$
	δ^a	917.0	321.4
	J^b	15.5	15.5
	NOE	−0.2	−5
	δ	419.5	164.6
	J	6.4	6.4
	NOE	−2	−5

[a] Downfield from external anhydrous ammonia, at 25 °C using a 1:4 $CH_3{}^{15}NO_2$:CD_2Cl_2 mixture as a secondary standard at 380.7 ppm. [b] Error in coupling constants is ±0.6 Hz. Error in chemical shift is ±0.5 ppm.

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[3] National Science Foundation Postdoctoral Fellow.

[4] National Science Foundation Predoctoral Fellow.

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