analogue of BLM[9] but less negative than that of Cu(II)-BLM.

Summary. The following are the principal results and conclusions of this investigation.

(1) As part of a synthetic analogue approach to metallobleomycins, copper complexes (**4** and **5**) of two peptides (PypepH and PmpepH) resembling portions of the metal-chelating section of BLM have been isolated and structurally characterized. Prior to this report, no synthetic analogue has been isolated in crystalline form.

(2) In **5**, three of the five proposed BLM donor centers, namely a pyrimidine N, a peptide N, and an imidazole N, are coordinated to copper. A pyridine N replaces the pyrimidine N in the coordination sphere of copper in **4**. The remaining coordination sites around copper in both these complexes are filled by acetate ion and water. The presence of bulky groups on the pyrimidine ring in PmpepH leads to a monomeric copper complex whereas PypepH gives rise to an acetate-bridged dimer. Two distinctly different kinds of acetate coordination are observed in these two complexes. The coordination geometries of copper in **4** and **5** are square pyramidal and distorted octahedral, respectively.

(3) Apart from important structural data pertinent to the proposed structure of Cu(II)-BLM, **4** and **5** provide opportunities of correlating spectroscopic properties of synthetic analogues to their structures. Results from such attempts have raised questions regarding the proposed structure of Cu(II)-BLM based on the crystallographic data for Cu(II)-P-3A. The absorption and EPR spectra of **4** are remarkably similar to those of Cu(II)-BLM. This observation points out the possibility of a N_3O coordination in the basal plane of copper in Cu(II)-BLM. The spectral characteristics of **4** and **5** also suggest that a "typical" Cu(II)-BLM spectrum can arise from a few alternative structures where a N_5 coordination might not necessarily be present. Thus the apparent match in spectroscopic properties of synthetic analogues generated in situ and Cu(II)-BLM, reported in previous accounts, should not be taken as conclusive proof of the proposed structures.

Structural characterization of the copper complex of a synthetic fragment containing all the five proposed donor centers of BLM is in progress.

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Registry No. **1**, 11056-06-7; **2**, 103692-68-8; **3**, 103692-69-9; **4**, 103671-02-9; **5**, 103671-03-0; $[Cu(Pypep)(Cl)(H_2O)]_2$, 103671-04-1; $[Cu(Pmpep)(Br)]_2$, 103671-05-2; ethyl picolinate, 2524-52-9; histamine, 51-45-6; ethyl 2-methyl-5-bromopyrimidinecarboxylate, 83410-38-2.

Supplementary Material Available: Thermal parameters for non-hydrogen atoms (Table S1) and positional and thermal parameters for hydrogen atoms (Table S2) for $[Cu(Pypep)(CH_3COO)]_2 \cdot 1.46H_2O$ (**4**) and $[Cu(Pmpep)(CH_3COO)(H_2O)]$ (**5**) (2 pages). Ordering information is given on any current masthead page.

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Diplatinum(III) Complexes with Bridging 1-Methyluracil Ligands in Head-Tail Arrangement: Synthesis, Structures, and Solution Behavior

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The preparation, composition, and the solution behavior of a series of diplatinum(III) complexes of general formula $[X(NH_3)_2PtL_2Pt(NH_3)_2Y]Z_n \cdot mH_2O$ (L = 1-methyluracil anion, $C_5H_5N_2O_2$, or 5-chloro-1-methyluracil anion, $C_5H_4N_2O_2Cl$; X, Y = NO_2^-, NO_3^-, Cl^-, Br^-, H_2O, or combinations thereof; Z = NO_3^-, Cl^-, Br^-; $n = 2, 3$) are reported. The compounds are obtained by chemical oxidation (HNO_3, HNO_2, Cl_2) of the head-tail Pt(II) dimer *cis*-$[(NH_3)_2Pt(C_2H_5N_2O_2)]_2(NO_3)_2$ or via ligand exchange reactions of the Pt(III) dimers, respectively. The crystal structures of two modifications of $[(ONO_2)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2(OH_2)](NO_3)_3 \cdot mH_2O$ with $m = 3$ (**4**) and 2 (**5**) have been determined. **4** is triclinic, space group $P\bar{1}$, $a = 9.742$ (1) Å, $b = 12.436$ (2) Å, $c = 14.019$ (2) Å, $\alpha = 123.06$ (1)°, $\beta = 96.51$ (1)°, $\gamma = 93.66$ (1)°, $V = 1398.0$ Å^3, $Z = 2$; **5** is monoclinic, space group $P2_1/c$, $a = 14.202$ (2) Å, $b = 20.571$ (2) Å, $c = 9.760$ (1) Å, $\beta = 95.87$ (2)°, $V = 2836.4$ Å^3, $Z = 4$. As expected, the cations of both compounds are similar: Pt-Pt = 2.556 (1) Å (**4**), 2.560 (1) Å (**5**); Pt-OH_2 = 2.18 (1) Å (**4**), 2.17 (1) Å (**5**); Pt-ONO_2 = 2.14 (1) Å (**4**), 2.12 (1) Å (**5**). The structures are compared with the previously reported analogue with X = NO_2^- and Y = OH_2. In aqueous solution, axial X and Y ligands such as Cl^-, ONO_2^-, and NO_2^- readily undergo solvolysis with formation of the diaqua complex $[(OH_2)(NH_3)_2PtL_2Pt(NH_3)_2(OH_2)]^{4+}$. pK_a values of this complex have been determined as 3.5 and 6.7. At pH >2, diplatinum(III) complexes containing nitro ligands are spontaneously reduced to the diplatinum(II) starting compound. In a secondary reaction, evolution of N_2 is observed, presumably formed between NH_3 and NO_2^-. Diplatinum(III) complexes obtained through Cl_2 oxidation are special in that Cl_2 also attacks the uracil ring with substitution of H5 by Cl. Iodine has been found not to oxidize the diplatinum(II) precursor to the diplatinum(III) complex.

Introduction

Dinuclear complexes of platinum in its unusual +3 oxidation state represent a relatively new class of coordination compounds. At present, two types of diplatinum(III) complexes are known, those with four bridging ligands, e.g. SO_4^{2-},[2] HPO_4^{2-} or $H_2PO_4^-$,[3] $H_2P_2O_5^{2-}$,[4] dithioacetate,[5] acetamide,[6] and pyrimidine-2-thione,[7] and those with two bridging ligands, e.g. acetate or derivatives,[8] pyrimidin-2-one,[9] 1-methyluracil,[10,11] and 1-methylcytosine.[12] Among the latter and with unsymmetrical ligands such as hydroxopyridine and pyrimidine derivatives, the two bridges may be oriented in a head-head or head-tail fashion. At least with 1-methyluracil ligands, these two types of complexes exhibit distinct differences in stability: while the head-tail dimers described subsequently are relatively stable in solution, the corre-

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sponding head–head dimers seem to be considerably less so.[11]

Previous studies on twofold bridged diplatinum(III) complexes have focused on structural aspects, e.g. the effect of the Pt–Pt bond on the Pt-(capping ligand) bond and vice versa (trans influence[9]), on the electrochemistry of these systems,[9a,c] and on displacement reactions of the axial ligands.[8b,c] Our particular interest in diplatinum(III) complexes containing the pyrimidine nucleobases uracil, thymine, and cytosine as bridging ligands stems from their suspected role as components of a class of potent antitumor agents, the so-called "platinum pyrimidine blues",[13] and the role as possible intermediates leading to the formation of the blues, respectively.

Experimental Section

Preparations. The starting compound, *cis*-$[(NH_3)_2Pt(C_5H_5N_2O_2)]_2(NO_3)_2$ (head–tail) (**1**), was prepared as previously reported.[14] The chloride salt of **1** was prepared by passing an aqueous solution of **1** (190 mg in 6 mL of H_2O) over an anion-exchange column in its Cl^- form and slow evaporation of the filtrate. Obtained were 150 mg of large, yellow crystal plates of **1a** together with 10 mg of colorless *cis*-$(NH_3)_2Pt(C_5H_5N_2O_2)Cl{\cdot}H_2O$.[14] Anal. Calcd for $[(NH_3)_2Pt(C_5H_5N_2O_2)]_2Cl_2{\cdot}4H_2O$ (**1a**): C, 14.10; H, 3.56; Cl, 8.33; Pt, 45.82. Found: C, 14.19; H, 3.44; Cl, 8.42; Pt, 46.0. The vibrational spectra (IR, Raman) of **1a** are very similar to those of **1** except for the anion modes of **1**.

The oxidation products of **1** (**1a**) described below were obtained via the following routes: oxidation with $NaNO_2/HNO_3$,[10] oxidation with concentrated nitric acid, and oxidation with chlorine. The first two routes gave a variety of products, at least seven, which differ in either the nature of X and Y capping ligands (OH_2, NO_2^-, ONO_2^-) in $[X(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2Y]^{n+}$ and/or the content of water of crystallization. The various forms were differentiated by the use of X-ray crystallography, vibrational and ^1H NMR spectroscopy, and elemental analysis. All characterized compounds were crystalline and had a uniform crystal habit as evident from inspection under a microscope, but the combinations of X and Y could not be established with certainty in all cases.

Oxidation with Nitrous Acid. A preliminary report on this method (addition of $NaNO_2$ to a sample and acidification with HNO_3) has appeared.[10] Three species were isolated: $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(NO_2)](NO_3)_2{\cdot}3H_2O$ (**2**) (1-MeU = 1-methyluracil anion, $C_5H_5N_2O_2$) as small, yellow cubes, $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}5H_2O$ (**3**) as large, pale yellow cubes that lose water of crystallization in air, and $[(ONO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}3H_2O$ (**4**) as orange-yellow cubes. **4** originally was formulated as $[(ONO_2)(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2{\cdot}4.5\text{-}H_2O$[10] but has now been shown by X-ray analysis to be in fact the mixed nitrato, aqua complex containing one coordinated water molecule and three free water molecules.

A modification of the preparation (300 mg of **1**, dissolved in 6 mL of H_2O, containing 100 mg of $NaNO_2$, pH adjustment to 0.2 by addition of 2 mL of 7 N HNO_3, crystallization at 3 °C in air) gave 10 mg of an unidentified yellow product (separated after 3 h), 130 mg of **3** together with 90 mg of **2** (collected after 10 h and separated by hand under a microscope), and 25 mg of **4** (collected after 17 days).

Oxidation with Concentrated Nitric Acid. In a typical experiment, 200 mg of finely powdered **1** was added to 1 mL of 14 N HNO_3 with stirring. After 1–2 min, during which the solution became orange-yellow, 1 mL of H_2O was added, and the solution was centrifuged from any undissolved material. Then the solution was transferred on a watch glass that was kept in an ice bath. Within 3 h of evaporation, tiny yellow crystals formed, which redissolved within 18 h, followed by formation of orange-yellow columns. After 5 days, 135 mg of this product was collected and briefly dried in air. Anal. Calcd for $[(ONO_2)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}2H_2O$ (**5**): C, 11.88; H, 2.80; N, 16.63. Found: C, 12.03; H, 2.87; N, 16.02.

Within 3–10 more days at 3 °C, a total of 45 mg of thin, yellow columns of another compound, **6**, were obtained, which analyzed as $Pt_2C_{10}H_{30}N_{12}O_{19}$ (Found: C, 11.78; H, 2.94; N, 16.40; O, 30.25).

From a more concentrated solution (200 mg of **1**, 0.75 mL of 14 N HNO_3, 1 mL of H_2O) under otherwise identical conditions, within 6 days 90 mg of **2** was collected. If the same sample was kept in a stoppered test tube instead of an open watch glass, within 9 days at 3 °C a mixture of two crystalline compounds had formed that consisted of about 100 mg of thin, yellow plates (transparent in air) of compound **7** and 10 mg of an unidentified product. The two species were separated by hand under a microscope. On the basis of its Raman spectrum (802 cm^{-1}, vs; 1299 cm^{-1}, s) and its behavior toward KBr (see below), a feasible description of **7** would be $[(NO_2)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}2H_2O$. Anal. Calcd: C, 12.07; H, 2.84; N, 16.90. Found: C, 11.70; H, 2.84; N, 17.15. Hence, **7** is believed to be another modification of **3**.

If the solution was even more concentrated (200 mg of **1**, 0.5 mL of 14 N HNO_3, 0.6 mL of H_2O), within a few hours at 3 °C transparent, yellow crystals formed. After 10 h, during which time the crystals had redissolved partly, 110 mg of air-stable crystals was collected. According to the Raman spectrum, this compound (**8**) contains coordinated NO_2^- (808 cm^{-1}, vs; 1302 cm^{-1}, s) and possibly coordinated ONO_2^- (745 cm^{-1}, m; 1031 cm^{-1}, m). Elemental analysis for C, H, and N (C, 11.16; H, 2.94; N, 17.16) suggests the presence of HNO_3 in the crystal lattice.

Recrystallization. Mixtures of **5** and **6** could be recrystallized (e.g. 110 mg, dissolved in 2 mL of 0.4 N HNO_3 at 25 °C, slow evaporation), giving a single product (90 mg of **4**) within 2 days.

Treatment with KI/I_2. No analytically pure product was obtained on treatment of **1** (0.1 mmol in 2 mL of H_2O) with an aqueous solution (2.5 mL) of KI (0.4 mmol) and I_2 (0.12 mmol). The brown precipitate (**10a**) that formed immediately (yields between 50 and 20 mg, depending on amount of washing water) gave highly variable iodine contents (between 3.6 and 5.6 I/Pt_2), despite identical IR spectra. According to IR spectra, 1-MeU bridging is preserved in **9a** (characteristic 630-cm^{-1} band), yet no oxidation to a diplatinum(III) complex has occurred (characteristic 1700-cm^{-1} band of Pt^{III} dimers missing). Moreover, the IR spectrum of **9a** is very similar to that of $[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_{0.5}I_{1.5}{\cdot}2H_2O$ (**10**), which was obtained by adding a fourfold excess of KI to an aqueous solution of **1** and immediately concentrating the solution in a stream of N_2 till crystallization started (yellow, transparent cubes). Anal. Calcd for **10**: C, 12.43; H, 2.72; I, 19.71. Found: C, 12.23; H, 2.64; I, 20.31.

We suggest that **9a** should be formulated as diplatinum(II) complex $[(NH_3)_2Pt(1\text{-}MeU)]_2(I^-)_m(I_3^-)_n$ with $n + m = 2$. The variable iodine content probably is a consequence of partial loss of I_2 from the triiodide ion. Support for this interpretation comes also from UV–vis spectra (see Results and Discussion) and from the fact that after filtration of **9a** no other oxidized product could be isolated, except slightly yellow crystals of *cis*-$(NH_3)_2Pt(1\text{-}MeU)I$ (**9b**). Anal. Calcd for **9b**: C, 12.48; H, 2.31; N, 11.65; Pt, 40.54. Found: C, 12.50; N, 2.30; N, 11.67; Pt, 40.5. The identity of **9b** (characteristic IR absorptions at 595 and 640 cm^{-1}) was unambiguously confirmed by alternative preparation from *cis*-$[(NH_3)_2Pt(1\text{-}MeU)(OH_2)]NO_3$[14] and KI.

Substitution of Axial Ligands by Cl^-. (i) A 50-mg sample of **3** was dissolved without warming in 1 mL of water, and to the intensely yellow solution (pH 2.8) was added 50 mg of solid NaCl. After 5 min at 22 °C, the sample was put on ice; after 2 h the precipitate was filtered off, washed with 1 mL of ice-cold water, and finally dried in air. The yield of the canary yellow cubes, which were transparent in air, was 30 mg. The Raman spectrum (solid state) of the product indicates the presence of $Pt\text{–}NO_2$ (813 cm^{-1}, vs; 1312 cm^{-1}, s) and of a small amount of ionic NO_3^- (1042 cm^{-1}, w). Consistent with this finding, elemental analysis

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Table I. List of Compounds Prepared[a]

1	*cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$
1a	*cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2Cl_2{\cdot}H_2O$
2	*cis*-$[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(NO_2)](NO_3)_2{\cdot}3H_2O$
3	*cis*-$[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}5H_2O$
4	*cis*-$[(ONO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}3H_2O$
5	*cis*-$[(ONO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}2H_2O$
7	*cis*-$[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}2H_2O$
9b	*cis*-$(NH_3)_2Pt(1\text{-}MeU)I$
10	*cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_{0.5}I_{1.5}{\cdot}2H_2O$
11	*cis*-$[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Cl](NO_3)_{0.5}Cl_{1.5}{\cdot}3H_2O$
12	*cis*-$[Cl(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Cl](NO_3)_{1.75}Cl_{0.25}{\cdot}4H_2O$

[a] Compounds of unclear composition (e.g. **6**, **8**, **9a**, **13**) are not included.

gives a higher N content and a lower Cl content than might be expected if Cl^- were the only counterion. Anal. Calcd for $[(NO_2)(NH_3)_2Pt(C_5H_5N_2O_2)Pt(NH_3)_2Cl]Cl_{1.5}(NO_3)_{0.5}{\cdot}3H_2O$ (**11**): C, 12.94; H, 3.05; N, 14.34; Cl, 9.55. Found: C, 13.01; H, 3.21; N, 14.09; Cl, 9.90. No other crystalline material was isolated on further evaporation of the filtrate.

(ii) A 200-mg sample of finely ground **1** was oxidized in 1 mL of 14 N HNO_3 (2 min); then 1 mL of H_2O was added and finally 200 mg of solid NaCl with stirring. After 2 min the sample was put on ice for 1 h; then the precipitate was filtered off, washed with 1 mL of 0.1 N HCl and 1 mL of ice-cold water, and finally dried in air. The yield of the canary yellow, microcrystalline material was 200 mg. If the sample was washed with a larger amount of water (4 × 1 mL), the yield decreased to 135 mg. IR and Raman spectra of samples obtained in either way indicate the presence of ionic NO_3^-, as does elemental analysis. Anal. Calcd for $[Cl(NH_3)_2Pt(C_5H_5N_2O_2)]_2(NO_3)_{1.75}Cl_{0.25}{\cdot}4H_2O$ (**12**): C, 12.39; H, 3.13; N, 14.10; Cl, 8.23; Pt, 40.27. Found: C, 12.44; H, 3.03; N, 14.15; Cl, 8.27 and 8.39; Pt, 40.0. Alternatively, **12** was obtained by dissolving **4** or **5** in a small volume of 0.1 N HCl and cooling the sample in an ice bath for several hours.

Oxidation with Cl_2. Treatment of **1a** with chlorine water (e.g. 100 mg of **1a** in 3 mL of water, 5 mL of Cl_2–water, pH 2.5) and slow evaporation of the intensely yellow solution gave primarily *cis*-$(NH_3)_2Pt(C_5H_5N_2O_2)Cl{\cdot}H_2O$[14] together with a small quantity of orange-yellow cubes that were not identified.

Treatment of **1** (200 mg in 3 mL of H_2O) with Cl_2 gas (1–2 min) gave a canary yellow precipitate of **12**. Within 1–2 more min of continued Cl_2 bubbling, this precipitate redissolved and the solution turned deep red. At this stage, the solution was briefly put on a rotavapor to remove excess Cl_2; then the pH (1.0) was brought to $\simeq 0$ by means of HCl and the solution kept at 22 °C. Within 12 h the sample had changed its color to orange, and on further evaporation 50 mg of orange-red crystals of **13** (brick red appearance when dry) was isolated. Later fractions, which had a color shaded toward orange-yellow, were identical with the first fraction according to the IR spectra, but elemental analyses were somewhat variable, giving ratios of C:H:N:Cl = 10:(25 ± 1):(7.8 ± 0.2):(5.9 ± 0.3) (four different samples). ^1H NMR spectra (cf. Results and Discussion) indicated that substitution of H5 of the 1-MeU ligands by Cl had occurred (cf. also ref 15), suggesting that the bulk material of **13** consisted of $[Cl(NH_3)_2Pt(C_5H_4N_2O_2Cl)]_2Cl_2{\cdot}(H_2O)_n$. Attempts to purify **13** by recrystallization from H_2O, from NaCl solution, or from HCl were unsuccessful as yet.

In Table I, the proposed or verified compositions of the various complexes are listed.

Apparatus. IR spectra were recorded as KBr pellets and Nujol mulls (CsI windows) on Perkin-Elmer 577 and 580 grating spectrometers, Raman spectra on a Coderg PH1 with krypton laser excitation (647.1 nm), ^1H NMR spectra (D_2O) on a JEOL JNM-FX 60 FT ($[N(CH_3)_4]BF_4$ as internal standard, shifts referenced to sodium 3-(trimethylsilyl)propanesulfonate), and UV–vis spectra on a Cary 17D. Reported pD values were obtained by adding 0.4 to the pH meter reading. Potentiometric titrations were carried out on a Metrohm E 536 potentiograph, and the mass spectroscopic study (sample dissolved in Ar-saturated water) on a Varian MAT 311 A. Preliminary electrochemical studies (voltage scan generator Wenking Model VSG 83, laboratory potentiostat Wenking Model LB 81) of **1** were performed in aqueous solutions (1 N KNO_3, pH 1.0 (HNO_3)) with a Pt sheet (0.4 cm^2) and a calomel electrode.

Crystallography. The X-ray measurements for **4** and **5** were carried out on a Philips-PW 1100 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71067 Å) at room temperature. The unit cell dimensions were calculated from 39 reflections (θ range 13–20°) for **4** and 18 reflections (θ range 14–20°) for **5** centered on the diffractometer. Crystal data and other numbers related to data collection are summarized in Table II. Intensity data for both compounds were collected with $\theta/2\theta$ scans, corrected for Lorentz and polarization effects and, at a later stage, for absorption by using the method of Walker and Stuart.[16] Transmission factors were in the range 0.61–1.0 for **4** and 0.59–1.0 for **5**. The coordinated Pt atoms in **4** and **5** were found in a three-dimensional Patterson map. The other non-hydrogen atoms were located by subsequent ΔF syntheses. Hydrogen atoms were ignored during the structure determinations. The Pt atoms were refined with anisotropic temperature factors and the remaining atoms with isotropic temperature factors. Complex scattering factors for atoms were taken from ref 17 and 18. The atomic parameters for **5** are listed in Table III; those for **4** are given in the supplementary material. For the Pt atoms, the equivalent isotropic temperature factors were calculated from the U_{ij} values by $U_{eq} = {}^1/_3\sum U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$ (U_{ij} in Å^2). The SHELX program package[19] was used in the determination of the structures.

Table II. Crystallographic Data of the Trihydrate (**4**) and Dihydrate (**5**) of $[(NO_3)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2(OH_2)](NO_3)_3$

	4[a]	**5**
compd	$C_{10}H_{30}N_{12}O_{20}Pt_2$	$C_{10}H_{28}N_{12}O_{19}Pt_2$
fw	1028.59	1010.58
space group	$P\bar{1}$	$P2_1/c$
a, Å	9.742 (1)	14.202 (2)
b, Å	12.436 (2)	20.571 (2)
c, Å	14.019 (2)	9.760 (1)
α, deg	123.06 (1)	90.0
β, deg	96.51 (1)	95.87 (2)
γ, deg	93.66 (1)	90.0
V, Å^3	1398.0	2836.4
Z	2	4
d_{calcd} g cm^{-3}	2.443	2.367
d_{measd}, g cm^{-3}	2.43	2.38
cryst size, mm	0.2 × 0.2 × 0.1	0.2 × 0.1 × 0.1
μ, cm^{-1}	96.9	95.5
θ range, deg	2–23	2–23
no. of unique refl	3886	3935
no. of refl used in calcns	3548 ($F_o > 2\sigma(F_o)$)	3471 ($F_o > 2\sigma(F_o)$)
no. of params	187	183
R	0.060	0.059
$R_w(F)$	0.068	0.067

[a] An alternative unit cell for **4**, obtained from Dirichlet reduction, is a = 9.742 (1) Å, b = 12.436 (2) Å, c = 12.688 (2) Å, α = 67.83 (1)°, β = 79.17 (1)°, γ = 86.34 (1)°.

Results and Discussion

As described in detail in the Experimental Section, the composition of complexes of type $[X(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Y](NO_3)_n{\cdot}mH_2O$ with X and Y = NO_2^-, ONO_2^-, or OH_2 and with n = 2 or 3 depends on the specific crystallization conditions applied. Not only are different combinations of X and Y possible, but also different modifications (with m values variable, cf. X-ray results). Complexes **2**–**8** most likely do not represent all possible reaction products to be isolated from HNO_2 and HNO_3 solutions. Unless crystal structures were performed (**3**,[10] **4**, **5**), the assignment of complex composition usually was based on spectroscopic methods and on reactivity patterns, respectively.

Vibrational Spectra. The IR spectra in all cases provided an unambiguous method to establish the integrity of the dinuclear, 1-MeU-bridged unit.[20] In particular, the 1-MeU mode around 630 cm^{-1} was indicative of N3,O4 bridging, very similar to the situation in the diplatinum(II) complex.[10] Raman spectra, recorded whenever possible, confirmed this finding and in addition

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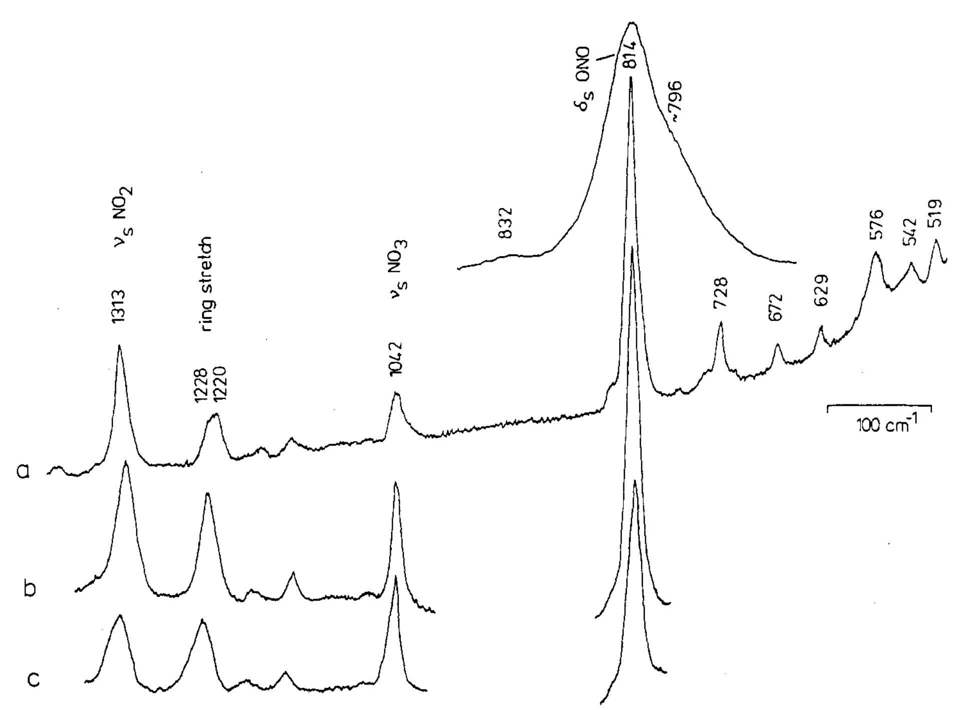

Figure 1. Sections of Raman spectra of $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2\cdot 3H_2O$ (**2**): (a) solid state (f = 4 cm^{-1}; insert f = 2 cm^{-1}, expanded), the δ_s(ONO) mode at 814 cm^{-1} superimposed with the ring breathing mode at ca. 796 cm^{-1}; (b) solution spectrum (H_2O, 0.3 M, pH 2.5, f = 8 cm^{-1}) immediately after dissolving; (c) solution spectrum after 40 h at 22 °C (same conditions).

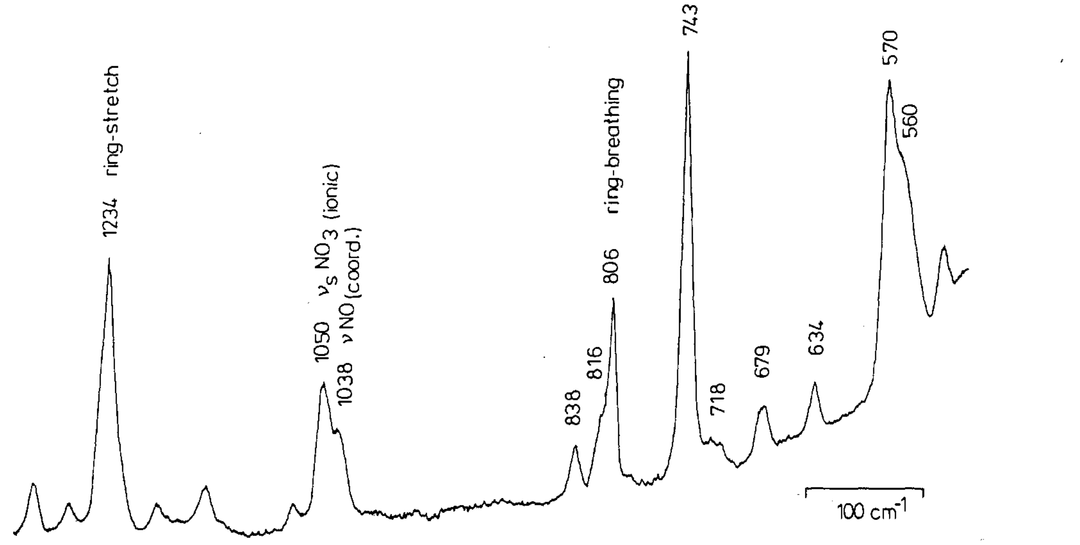

Figure 2. Section of Raman spectrum (solid state, f = 6 cm^{-1}) of $[(NO_3)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3\cdot 3H_2O$ (**4**), with unusual intensity of nitrato mode at 743 cm^{-1}.

provided other ring modes characteristic of N3,O4 bridge formation, e.g. the ring stretching mode around 1220–1235 cm^{-1}.

Complexes containing nitro ligands were particularly easily recognized by their Raman spectra because of the high intensity of $\nu_s(NO_2)$ and δ_s(ONO) modes.[21] The positions of these vibrations around 1300–1320 and 800–815 cm^{-1} are slightly at lower energy as compared to nitro complexes of Pt^{II} and Pt^{IV}.[22] As a typical example, the Raman spectrum of **2** with X = Y = NO_2 and n = 2 is given in Figure 1. From the solution spectrum it became evident that **2** was unstable in water (pH 2.5), losing NO_2^- with time. This finding was consistent with the electronic spectra (cf. supplementary material) and with the ^{1}H NMR results (see below).

The Raman spectra (solid state) of **4** and **5** (X = ONO_2^-, Y = OH_2, n = 3) were remarkable in that one mode, at 743 cm^{-1} (**4**) and 749 cm^{-1} (**5**), respectively, which presumably was due to the nitrato ligand (possibly δ(ONO)), was of an unexpected high intensity (Figure 2). It is noted that with *cis*-$(NH_3)_2Pt(ONO_2)_2$, for example, the two ONO modes (bending and planar rocking) occurring in the 700–800-cm^{-1} range, are of weak to moderate intensity only.[24] The position of the NO stretch (with O being coordinated to Pt) at 1038 cm^{-1} (**4**) and 1048 cm^{-1} (**5**) is close to (**4**) or identical with (**5**) the value of ν(NO) of ionic NO_3^-.[25]

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(21) (a) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978; pp 220–223.

(22) (a) Burmeister, J. L.; Timmer, R. C. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1973. (b) LePostollec, M.; Mathieu, J. P.; Pulet, H. *J. Chim. Phys. Phys.-Chim. Biol.* **1963**, *60*, 1319.

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(25) As to the other Raman-active modes of the coordinated ONO_2^- ligand, comparison with **12** (X = Y = Cl$^-$) suggests that bands at 1265 and 1294 cm^{-1} (each m) and 1479 and 1499 cm^{-1} (w and m) might be attributed to $\nu_s(NO_2)$ and $\nu_{as}(NO_2)$, respectively.

Table III. Positional Parameters and Temperature Factors (Å^2) for $[(NO_3)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2(OH_2)](NO_3)_3 \cdot 2H_2O$ (**5**)^a

atom	x	y	z	U_{11}
Pt1	0.2614 (1)	0.0401 (1)	0.3587 (1)	0.028 (1)
Pt2	0.2429 (1)	0.0968 (1)	0.1240 (1)	0.024 (1)
N10	0.1421 (9)	0.0732 (6)	0.4393 (12)	0.035 (3)
N11	0.3431 (9)	0.1104 (6)	0.4622 (12)	0.037 (3)
O10	0.3041 (8)	−0.0156 (5)	0.5437 (11)	0.045 (2)
N20	0.1005 (9)	0.1011 (6)	0.0936 (12)	0.036 (3)
N21	0.2477 (10)	0.1917 (6)	0.1821 (13)	0.040 (3)
N22	0.2661 (10)	0.1216 (6)	−0.1821 (13)	0.038 (3)
O20	0.2181 (8)	0.1382 (4)	−0.0753 (10)	0.036 (2)
O21	0.2450 (9)	0.1517 (5)	−0.2848 (12)	0.052 (3)
O22	0.3257 (9)	0.0801 (5)	−0.1655 (11)	0.046 (2)
N1A	0.1140 (11)	−0.1345 (7)	0.2618 (14)	0.047 (3)
C1A′	0.0550 (20)	−0.1823 (13)	0.3329 (27)	0.092 (7)
C2A	0.1399 (13)	−0.0769 (8)	0.3224 (16)	0.043 (4)
O2A′	0.1288 (10)	−0.0691 (6)	0.4442 (14)	0.068 (3)
N3A	0.1888 (10)	−0.0336 (6)	0.2538 (13)	0.039 (3)
C4A	0.1989 (11)	−0.0397 (6)	0.1230 (13)	0.025 (3)
O4A′	0.2347 (7)	0.0041 (4)	0.0510 (9)	0.030 (2)
C5A	0.1705 (13)	−0.0999 (8)	0.0532 (17)	0.046 (4)
C6A	0.1293 (13)	−0.1468 (9)	0.1267 (18)	0.049 (4)
N1B	0.5341 (10)	0.1102 (6)	0.0580 (13)	0.043 (3)
C1B′	0.5924 (16)	0.1534 (10)	−0.0220 (22)	0.069 (6)
C2B	0.4403 (11)	0.1303 (7)	0.0674 (14)	0.032 (3)
O2B′	0.4099 (8)	0.1798 (5)	0.0191 (10)	0.038 (2)
N3B	0.3856 (10)	0.0892 (6)	0.1438 (12)	0.037 (3)
C4B	0.4298 (12)	0.0360 (7)	0.2128 (15)	0.035 (3)
O4B′	0.3797 (7)	0.0025 (5)	0.2872 (9)	0.034 (2)
C5B	0.5220 (12)	0.0153 (7)	0.1948 (15)	0.038 (3)
C6B	0.5724 (13)	0.0561 (8)	0.1132 (17)	0.047 (4)
N3O	0.0915 (10)	0.2288 (6)	0.4247 (13)	0.041 (3)
O3O	0.0534 (10)	0.1965 (6)	0.3267 (14)	0.068 (3)
O31	0.1777 (9)	0.2193 (5)	0.4579 (11)	0.050 (3)
O32	0.0506 (9)	0.2715 (6)	0.4867 (12)	0.055 (3)
N4O	0.0601 (15)	0.5004 (11)	0.2639 (21)	0.087 (6)
O4O	0.0213 (13)	0.4787 (8)	0.3624 (18)	0.093 (5)
O41	0.0404 (13)	0.5561 (9)	0.2209 (19)	0.104 (5)
O42	0.1340 (18)	0.4767 (11)	0.2216 (24)	0.134 (7)
N5O	0.5771 (16)	0.3600 (9)	0.0734 (19)	0.074 (5)
O5O	0.5157 (16)	0.3347 (10)	0.1313 (22)	0.123 (6)
O51	0.6566 (17)	0.3455 (10)	0.1087 (22)	0.125 (7)
O52	0.5542 (11)	0.4039 (7)	−0.0132 (16)	0.076 (4)
O60	0.4295 (9)	0.2261 (6)	0.3206 (12)	0.058 (3)
O61	0.2217 (25)	−0.1249 (18)	0.7086 (40)	0.236 (14)

^{a}For the Pt atoms the equivalent isotropic temperature factors are given.

Reactions with Cl$^-$, Br$^-$, I$^-$. It was noticed that during IR sample preparation (KBr pellets or Nujol mulls with CsI windows) or after recording of the IR spectra most of the compounds had reacted with KBr or CsI, as evident from a color change of the KBr disk (from yellow to orange or orange-brown) or a brownish coating of the window material. Exceptions were compounds **2** (X = Y = NO_2^-), **11** (X = NO_2^-, Y = Cl$^-$), and **12** (X = Y = Cl$^-$), which did not show any color change. As shown by UV-visible spectroscopy, the color of the KBr samples was due to an intense absorption at 376 nm (ϵ 36 000), attributed to the Br–Pt–Pt–Br chromophore (cf. supplementary material). Unlike in the solid state, in aqueous solution of pH 4–5, Cl$^-$ and NO_2^- ligands were also substituted by Br$^-$. In the case of nitro complexes **2** and **3**, the intensity of the 376-nm band depended on the time Br$^-$ was added after dissolving the nitro complex: Aged solutions produced only weak absorptions on addition of excess Br$^-$, indicating that reduction of the diplatinum(III) complex had occurred.[26] The Br-capped diplatinum(III) complex is unstable in solutions of pH 4–5, as evident from the gradual decay of the 376-nm absorption with time. The presence of NO_2^- (from **2** and **3**) accelerated this process markedly.

Table IV. ^{1}H NMR Chemical Shifts of Dinuclear Complexes in D_2O^a

	CH_3	H5	H6	pD
1 (1a)	3.40	5.90	7.44	1–7
2	3.52	6.21	7.95	3
3	3.54, 3.51	6.23, 6.20	7.94	2.3
4, 5	3.53	6.20	7.94	1.9
11	3.50	6.12	7.92	2
12	3.53	6.10	7.91	3.3

^{a}H5 and H6 doublets each ($^3J \simeq 7.3$ Hz for diplatinum(III) complexes)

Comparison of the electronic spectra of the dichloro complex, **12**, and the mixed nitrato, aqua complex, **4** (**5**), strongly suggested that in dilute solution solvolysis of the axial ligands is extensive; hence the equilibrium

$$[X\text{-}Pt\text{-}Pt\text{-}Y] + 2H_2O \rightleftharpoons [H_2O\text{-}Pt\text{-}Pt\text{-}OH_2] + X + Y$$

was far to the right. Addition of excess Cl$^-$ expectedly shifted the equilibrium in the other direction and permitted isolation of the dichloro complex, **12**, on a preparative scale. Similarly, the mixed nitro, chloro complex, **11**, was prepared by adding NaCl to a solution containing the nitro, aqua complex, **3**, and taking advantage of the relatively low solubility of **11**.

The reaction of nitrato and aqua groups containing diplatinum(III) complexes with CsI most likely does not involve a ligand exchange (OH_2 or ONO_2^- vs. I$^-$) but rather a redox process in which the diplatinum(III) species acts as an oxidizing agent. For example, I_2 has been qualitatively detected (reaction with starch) when **4** (**5**) was added to an aqueous solution of KI (pH 1 or 7). UV-visible spectra confirmed the formation of I_3^- (absorptions at 350 and 288 nm) under these conditions and suggested the process

$$[(H_2O)(NH_3)_2Pt^{III}(1\text{-MeU})]_2^{4+} + 2I^- \rightarrow [(NH_3)_2Pt^{II}(1\text{-MeU})]_2^{2+} + I_2 + 2H_2O$$

and

$$I_2 + I^- \rightarrow I_3^-$$

These results are consistent with preliminary results from cyclic voltammetry studies, which gave a E_p of 0.75 V vs. SCE for the oxidation of **1**, and with findings (cf. Experimental Section) that I_2/KI did not oxidize diplatinum(II) complex **1** but only precipitated it as a complex iodide salt and, in a slower secondary reaction, caused cleavage to the mononuclear complex *cis*-$(NH_3)_2Pt(1\text{-MeU})I$:

$$[(NH_3)_2Pt(1\text{-MeU})]_2^{2+} + 2I^- \rightarrow 2\,cis\text{-}(NH_3)_2Pt(1\text{-MeU})I$$

^{1}H NMR Spectra. ^{1}H NMR chemical shifts of the various diplatinum(III) complexes are listed in Table IV. In D_2O solution all compounds studied changed with time, but as compared to diplatinum(III) complexes with head–head-arranged 1-MeU ligands,[11] the head–tail isomers were considerably more stable. The ^{1}H NMR resonances of the 1-MeU ligands consisted of doublets for H5 and H6 ($^2J \simeq 7$–7.5 Hz) and singlets for N–CH_3. In general, coupling between the ^{195}Pt isotope at N3 and the proton at C5 was detectable ($^5J \simeq 8$ Hz), but coupling between the ^{195}Pt isotope at O4 and the proton at H6 ($^5J \simeq 5.6$ Hz) was only occasionally well resolved (e.g. Figure 3b). While coupling between ^{195}Pt and H5 is markedly reduced when going from the diplatinum(II) starting complex **1** ($^5J \simeq 14$–15 Hz)[20] to the diplatinum(III) complexes, as might be expected from the lowering of Pt 6s contribution to the Pt–(1-MeU) interaction on oxidation,[27] coupling between ^{195}Pt and H6 is virtually unaffected. As to the chemical shifts of 1-MeU resonances, only H5 was moderately sensitive to variations in the nature of the capping axial ligands,

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(26) Diplatinum(II) complex **1** (λ 279 nm, ϵ 17 100) expectedly does not produce a yellow color with Br$^-$ but is only slowly cleaved to give the monomer *cis*-$(NH_3)_2Pt(1\text{-MeU})Br$.

(27) (a) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1971**, *10*, 1717. (b) Pregosin, P. S.; Omura, H.; Venanzi, L. M. *J. Am. Chem. Soc.* **1973**, *95*, 2047.

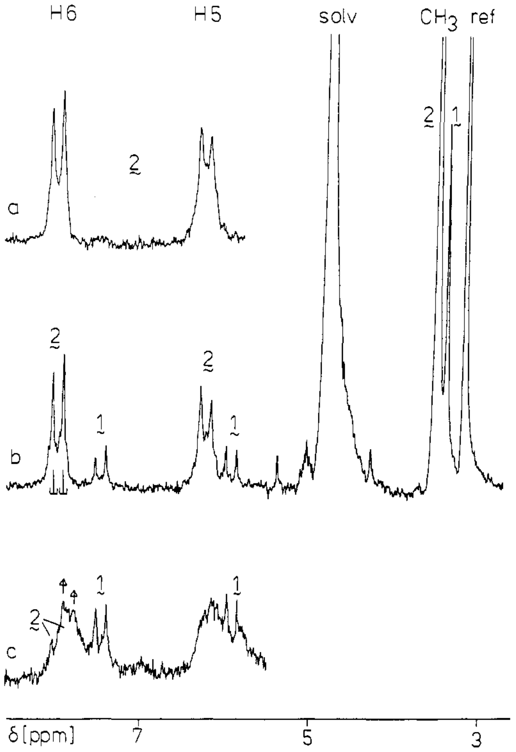

Figure 3. ^1H NMR spectra (D_2O) of $[(NO_2)(NH_3)_2Pt(1\text{-MeU})]_2(NO_3)_2$ (**2**) (0.04 M): (a) immediately after dissolving (pD 3.0); (b) after 12 h at 30 °C (pD dropped to 1.9) with new resonances due to diplatinum(II) complex **1**; (c) at 5 d (22 °C) after spectrum (b). Besides **1** and **2**, new resonances of an unidentified species (arrows) have appeared, accompanied by evolution of N_2.

thus confirming the conclusions from structural work on diplatinum(III) complexes that indicated relatively weak interactions between the diplatinum(III) core and the axial ligands (see below).

In the following, the solution behavior of three selected diplatinum(III) complexes as studied by ^1H NMR spectroscopy will be discussed briefly.

(i) $[(NO_2)(NH_3)_2Pt(1\text{-MeU})_2Pt(NH_3)_2(NO_2)](NO_3)_2$ (2). In aqueous solution (pD 3), **2** underwent a spontaneous reduction to the Pt^{II} starting complex, **1**, as evident from the appearance of the corresponding ^1H NMR resonances (Figure 3) and the loss of coordinated nitro groups (cf. Figure 1 and UV spectra (supplementary material)). A feasible description of the reaction that takes into account the observed drop in pH, would be

$$[(NO_2)(NH_3)_2Pt^{III}(1\text{-MeU})]_2^{2+} + H_2O \rightarrow [(NH_3)_2Pt^{II}(1\text{-MeU})]_2^{2+} + NO_3^- + NO_2^- + 2H^+$$

At a later stage of the reaction, the formation of a new, yet unidentified species was observed, with its H6 resonances (7.75 and 7.89 ppm) clearly discernible. It was noticed that the spectroscopic changes were accompanied by the evolution of a colorless gas. Using mass spectroscopy, we found that the gas formed was N_2, and we assume that it is formed as

$$NH_3 + NO_2^- + H^+ \rightarrow N_2 + 2H_2O$$

Although we do not know at present whether NH_3, while still coordinated to Pt or after displacement from the complex, is oxidized to N_2, we note that in the related head–head diplatinum(III) system we recently observed a rather facile substitution of ammine ligands by chloride.[11a]

(ii) $[(NO_2)(NH_3)_2Pt(1\text{-MeU})_2Pt(NH_3)_2(OH_2)](NO_3)_3$ (3). As previously shown,[10] the ^1H NMR spectrum of **3** (D_2O, pD 1.6) reflects the inequivalence of the two Pt centers by exhibiting two sets of H5 and CH_3 resonances. Within 15 h at 30 °C, however, only single sets of 1-MeU resonances were observed, which had chemical shifts practically identical with that of **4** (**5**). This suggests that, similar to the case of **2**, the nitro ligand comes off from the diplatinum(III) complex and is replaced by an aqua ligand. With time, new resonances appeared (only H6 signals at 7.74 and 7.88 ppm well observable), but after 48 h the amount of this product did not exceed 5–10% of **2**. There was some evolution of N_2 yet no clear indication for the formation of **1** at pD 1.6. However, if the initial pD was raised to 3, again reduction to **1** was observed (distribution of **3**:**1** after 14 h at 30 °C was 2:1).

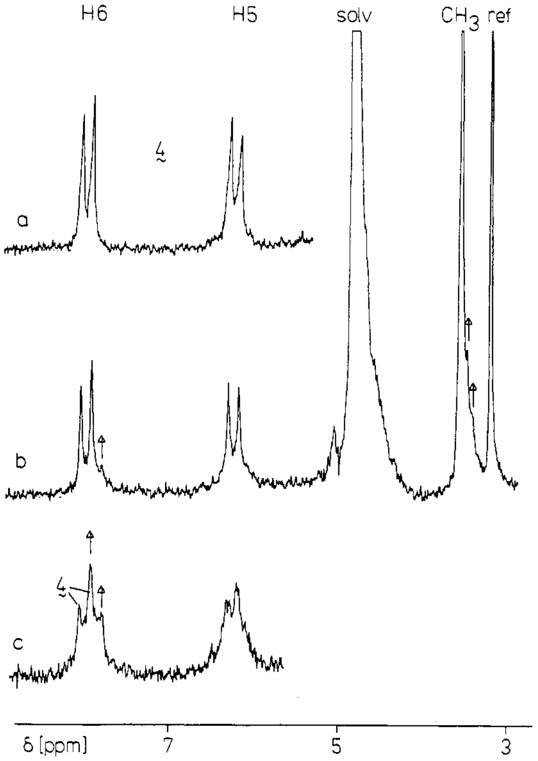

Figure 4. ^1H NMR spectrum of $[(NO_3)(NH_3)_2Pt(1\text{-MeU})_2Pt(NH_3)_2(OH_2)](NO_3)_3 \cdot 3H_2O$ (**4**) (0.03 M): (a) immediately after dissolving in D_2O (pD 1.9); (b) after 5 h at 30 °C with new resonances due to an unidentified species (arrows); (c) after 28 h at 30 °C (pD unchanged).

Addition of acid (DNO_3, pD $\simeq$0) to an aqueous solution of **3** readily converted the mixed nitro, aqua complex to the diaqua complex (as shown by NMR), which, at pD 0 and room temperature, was stable for days. Similar substitution reactions of nitro groups in the presence of acid have been reported for Pt^{II} complexes before.[28]

(iii) $[(ONO_2)(NH_3)_2Pt(1\text{-MeU})_2Pt(NH_3)_2(OH_2)](NO_3)_3$ (4 (5)). Expectedly, the ^1H NMR solution spectra (D_2O) of **4** and **5** were identical. There was strong indication from the electronic spectra (see above), the ^1H NMR spectrum (unlike **3**, single sets of resonances), and the potentiometric titration (two titratable H_2O groups, see below) that on dissolving **4** (**5**) in water the nitrato groups are immediately replaced by aqua ligands. As mentioned before, solutions of **4** and **5** were stable for days at pD 0, but at pD 2 (30 °C) resonances due to other species began to appear (Figure 4). There was no observed reduction of the diplatinum(III) complex as with nitro complexes **2** and **3**.

Addition of NaCl to an aqueous solution of **4** or **5** resulted in an immediate spectroscopic change with H6 and H5 resonances shifted upfield by 0.02 and 0.10 ppm and in partial precipitation of compound **12** (X = Y = Cl^-).

Reaction with Cl_2. Cleavage of dinuclear complex **1a** to the mononuclear compound *cis*-$(NH_3)_2Pt(1\text{-MeU})Cl \cdot H_2O$ was the preferred reaction in moderately acidic solutions of chlorine water, very similar to the reaction of **1** with excess chloride.[29] With higher concentrations of Cl_2, oxidation of the diplatinum(II) complex took place, with the symmetrical, chloro-capped complex **12** being the first product to be isolated. **12** redissolved with continued Cl_2 treatment to give a deep red solution, from which

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[28] Humphreys, D.; Staples, P. J. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1185.

[29] Neugebauer, D.; Lippert, B. *Inorg. Chim. Acta* **1982**, *67*, 151.

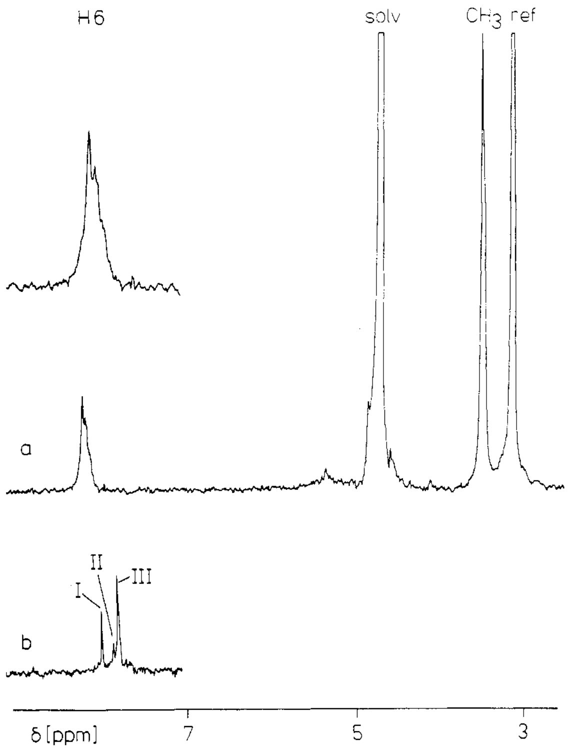

Figure 5. ^1H NMR spectrum of oxidation product of **1** with Cl_2 containing 5-chloro-1-methyluracilato ligands: (a) immediately after dissolving in D_2O (pD 1.9) and with H6 resonance expanded (insert); (b) 5 d after adding DCl (pD ~0). The spectrum then indicates the presence of free 5-Cl-1-MeUH (I), *mer*-$Cl_3Pt(NH_3)_2$(5-Cl-1-MeU) (II), and an unidentified Pt complex containing 5-Cl-1-MeU (III); the sample contains a crystalline precipitate of II. Addition of NaCl instead of DCl has qualitatively the same effect.

products crystallized with a composition of close to $[Cl(NH_3)_2Pt(C_5H_4N_2O_2Cl)]_2Cl_2{\cdot}H_2O$ (cf. Experimental Section). ^1H NMR spectroscopy unambiguously established that in these products, as with mononuclear platinum complexes previously reported,[15] substitution of H5 of the 1-MeU ligands by Cl had taken place (Figure 5a). The NMR spectra indicated the presence of at least two nonequivalent 5-chloro-1-methyluracilato ligands (with $^5J(^{195}Pt-^1H6) \simeq 6$ Hz each). Whether this was due to partial solvolysis of the axial Cl ligands (slow exchange), to partial substitution of NH_3 ligands as observed in the corresponding head–head diplatinum(III) complex,[11a] or to some other reason is unclear at present. Attempts to possibly shift a solvolysis equilibrium by addition of NaCl or HCl and, at the same time, recrystallization of the products were unsuccessful since they resulted in complex decomposition. Two decomposition products were identified by ^1H NMR (Figure 5b) and IR spectroscopy, namely *mer*-$Cl_3Pt(NH_3)_2(C_5H_4N_2O_2Cl)$[15] and 5-chloro-1-methyluracil. This finding suggested that degradation of the diplatinum(III) complex involves a disproportionation into Pt^{IV} and Pt^{II} species.

Acidity of Aqua Ligands in Diplatinum(III) Complexes. Potentiometric titration of $[(ONO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}3H_2O$ (**4**) in water showed two endpoints around pH 5 and 8.3 after addition of 1 and 2 equiv of NaOH (Figure 6a). The titration curve indicated a stepwise titration of two aqua ligands according to

$$[(OH_2)(NH_3)_2Pt(1\text{-}MeU)]_2^{4+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [(OH_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH)]^{3+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [(OH)(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}$$

The pK_a values estimated from the titration curve were ca. 3.5 for the first step and ca. 6.7 for the second step. These values are between those of aqua complexes of Pt^{II} and Pt^{IV} but closer to the former, e.g. 5.56 and 7.32 for *cis*-$[(NH_3)_2Pt(OH_2)_2]^{2+}$[30] yet ≪0 and <1 for *trans,trans,trans*-$[Pt(NH_3)_2(OH_2)_2(1\text{-}MeC)_2]^{4+}$ (with 1-MeC = 1-methylcytosine).[31] We suspect that the relatively weak bond between the axial aqua ligands and the platinum atoms in the diplatinum(III) complex is responsible for the rather small increase in acidity when going from Pt^{II} to Pt^{III}.

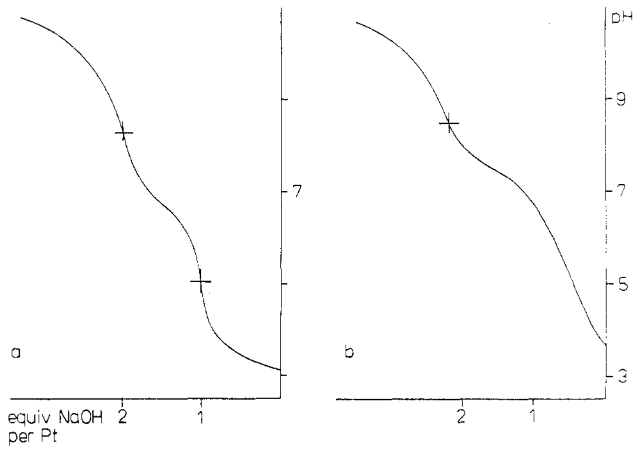

Figure 6. Titration of (a) 0.01 mmol of **4**, dissolved in 4 mL of H_2O, with 0.02 N NaOH, and (b) 0.01 mmol of **3**, dissolved in 4 mL of H_2O, with 0.02 N NaOH.

Table V. Bond Distances (Å) and Angles (deg) in $[(NO_3)(NH_3)_2Pt(C_5H_5N_2O_2)Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}2H_2O$ (**5**)

(a) Distances and Angles in Pt Coordination Sphere			
Pt1–Pt2	2.560 (1)	Pt2–N21	2.03 (1)
Pt1–N10	2.06 (1)	Pt2–O20	2.12 (1)
Pt1–N11	2.05 (1)	Pt2–N3b	2.02 (1)
Pt1–O10	2.17 (1)	Pt2–O4a′	2.04 (1)
Pt1–N3a	2.05 (1)	N22–O20	1.35 (2)
Pt1–O4b′	2.04 (1)	N22–O21	1.19 (2)
Pt2–N20	2.02 (1)	N22–O22	1.20 (2)
Pt2–Pt1–N10	100.3 (3)	Pt1–Pt2–N20	99.3 (4)
Pt2–Pt1–N11	96.9 (4)	Pt1–Pt2–N21	101.0 (4)
Pt2–Pt1–O10	168.1 (3)	Pt1–Pt2–O20	175.2 (3)
Pt2–Pt1–N3a	83.7 (4)	Pt1–Pt2–N3b	82.5 (4)
Pt2–Pt1–O4b′	83.1 (3)	Pt1–Pt2–O4a′	83.3 (3)
N10–Pt1–N11	91.4 (5)	N20–Pt2–N21	90.2 (5)
N10–Pt1–O10	91.6 (5)	N20–Pt2–O20	77.1 (5)
N10–Pt1–N3a	92.5 (5)	N20–Pt2–N3b	176.5 (5)
N10–Pt1–O4b′	176.4 (5)	N20–Pt2–O4a′	88.2 (5)
N11–Pt1–O10	82.4 (5)	N21–Pt2–O20	82.4 (5)
N11–Pt1–N3a	175.8 (6)	N21–Pt2–N3b	92.5 (5)
N11–Pt1–O4b′	89.5 (5)	N21–Pt2–O4a′	175.6 (4)
O10–Pt1–N3a	96.2 (5)	O20–Pt2–N3b	100.9 (5)
O10–Pt1–O4b′	85.1 (4)	O20–Pt2–O4a′	93.3 (4)
N3a–Pt1–O4b′	86.4 (5)	N3b–Pt2–O4a′	88.9 (5)
(b) Distances in 1-MeU			
N1a–C1a′	1.51 (3)	N1b–C1b′	1.49 (3)
N1a–C2a	1.36 (2)	N1b–C2b	1.41 (2)
C2a–O2a′	1.23 (2)	C2b–O2b′	1.19 (2)
C2a–N3a	1.35 (2)	C2b–N3b	1.41 (2)
N3a–C4a	1.31 (2)	N3b–C4b	1.40 (2)
C4a–O4a′	1.28 (2)	C4b–O4b′	1.27 (2)
C4a–C5a	1.45 (2)	C4b–C5b	1.41 (3)
C5a–C6a	1.37 (3)	C5b–C6b	1.40 (3)
C6a–N1a	1.38 (2)	C6b–N1b	1.33 (2)

The titration curve of $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Pt(OH_2)](NO_3)_3{\cdot}5H_2O$ (**3**) is given in Figure 6b. An endpoint (pH ≃8.5) was reached after addition of ca. 2 equiv of NaOH, very similar as with **4**. The apparent differences in curve shapes of **3** and **4** presumably were a consequence of the fact that

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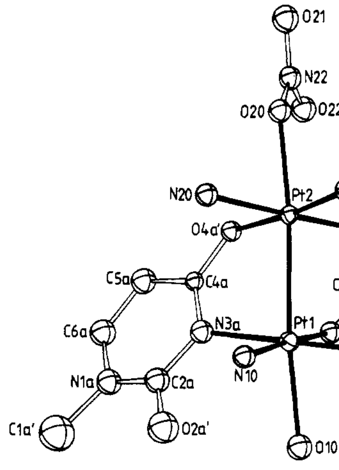

Figure 7. Molecular cation of $[(NO_3)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3\cdot 2H_2O$ (**5**) with atom numbering.

the nitro ligand was substituted by an aqua (hydroxo) group during titration.

Crystal Structures of 4 and 5. The cation of compound **5** is shown in Figure 7; distances and angles are given in Table V (for **4**, see supplementary material). Cations of **5** and **4** (not shown) have rather similar geometries, consisting of dinuclear *cis*-$(NH_3)_2Pt$ units bridged by 1-MeU through N3 and O4′ in a head–tail orientation and capped by aqua (Pt1) and nitrato groups (Pt2). Pt–Pt distances are 2.556 (1) Å for **4** and 2.560 (1) Å for **5** and are thus shorter by ca. 0.4 Å than in the Pt^{II} starting compound.[32] Pt–NH_3, Pt–N3, and Pt–O4′ distances are in the range observed for related complexes,[10,14,20,33] but the distances between Pt atoms and the axial oxygen donors are substantially longer than in the case of Pt^{II} complexes: Pt–OH_2 (2.17 (1)–2.18 (1) Å) and Pt–ONO_2 (2.14 (1)–2.12 (1) Å) in **4** and **5** compare with 2.052 (8) Å in Pt^{II}–OH_2[34] and 1.99 (1)–2.03 (1) Å in Pt^{II}–ONO_2.[24,35] This marked lengthening of the metal–axial ligand bonds has been attributed to the strong trans influence of the Pt–Pt single bond,[9] very similar to the case of dirhodium(II) carboxylates.[36] A comparison of the Pt coordination geometries of the here discussed mixed aqua, nitrato complexes, **4** and **5**, with the previously described mixed aqua, nitro complex, **3**,[10] reveals another interesting aspect: It appears that the trans influence of the Pt–Pt bond and the trans influence of the axial ligand ($NO_2 > ONO_2$) are additive, making the Pt–OH_2 bond in the mixed aqua, nitro complex extremely long (2.253 (9) Å). Our recent findings in the related diplatinum(III) system with head–head-oriented 1-MeU ligands suggests that the additive effect can be high enough to prevent coordination of an axial ligand at the second Pt.[11b,38]

The Pt atoms in **4** and **5** are displaced from the planes defined by the two NH_3 groups, N3, and O4′ and directed toward each other, e.g. 0.056 Å (Pt1) and 0.050 Å (Pt2) in **4**. The equatorial Pt planes are tilted by 22.6° (**4**) and 22.7° (**5**), which compares with 35.8° in the Pt^{II} starting compound.

The Pt–Pt vectors in **4** and **5** are not collinear with the Pt–(axial donor) vectors (angles about Pt1 being 168–169° and about Pt2 being 175°), but this is not only a consequence of the tilting of the equatorial Pt planes but also of the fact that the capping square pyramids (as defined by $2NH_3$, N3, O4′, and axial O donor) are not regular but severely distorted (cf. Table V).

The heterocyclic rings are not ideally planar, with the exocyclic groups (CH_3, O2′, O4′) deviating most, e.g. 0.15 Å of O4b′ in **4** (cf. supplementary material). The Pt atoms are not coplanar with the 1-MeU rings either. While this is not unexpected for the respective Pt bound through O4′, it also applies for the N3-bound Pt, e.g. 0.55 Å of Pt1 from ring a and 0.63 Å of Pt2 from ring b in **4**. There are no major changes in bond lengths and angles in the platinated 1-MeU rings of **4** and **5** as compared to those of free 1-methyluracil.[37]

Possible hydrogen-bonding interactions in **4** and **5** are given in the supplementary material. They involve NH_3 groups, O2′, oxygens of NO_3^-, and coordinated and lattice water molecules. The coordinated water molecule O10 has in both compounds three contacts, to two nitrate oxygens and one lattice water molecule, one of these (to a NO_3^-) being rather short, 2.69 Å in **4** and 2.65 Å in **5**. It is noted that an even shorter hydrogen bond (2.58 Å) between the axial water molecule of a diplatinum(III) complex of α-pyridone and a lattice water molecule has been reported before.[9c]

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Note Added in Proof. While this paper was being written, two reports bearing some relevance to the results described here have appeared.[39,40]

Registry No. **1**, 103439-45-8; **1a**, 103530-12-7; **2**, 88665-50-3; **3**, 89040-98-2; **4**, 103439-48-1; **5**, 103530-13-8; **9b**, 103439-49-2; **10**, 103530-15-0; **11**, 103456-64-0; **12**, 103456-66-2; **13**, 103456-67-3; Pt, 7440-06-4; 1-methyluracil, 615-77-0.

Supplementary Material Available: Listings of positional parameters, distances and angles, planes and dihedral angles, and short contacts for **4** and **5** and UV–vis spectra (16 pages). Ordering information is given on any current masthead page.

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