

Diplatinum(III) Complexes with Four Bridging 1-Methylcytosinato Nucleobases Derived from a Mononuclear *trans*-(NH₃)₂Pt^{II} Complex and Cu^{II}

Jens Müller,* Eva Freisinger, Pablo J. Sanz Miguel, and Bernhard Lippert*

Fachbereich Chemie, Universität Dortmund, D-44221 Dortmund, Germany

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A heteronuclear complex of composition *trans*-[(NH₃)₂Pt(N4-1-MeC⁻-N3)Cu(H₂O)₂](ClO₄)₂ (**1a**), with 1-MeC⁻ = 1-methylcytosinate, has been prepared and characterized by X-ray crystallography. **1a** (Cu,Pt) is a linkage isomer of a previously described compound with the two metals inverted (Pt,Cu). The intermetallic distances are significantly different in the two types of compounds, 2.6109(9) Å in **1a**, yet 2.49–2.56 Å in several forms of the linkage isomer. When heated in water in the presence of air, **1a** is converted in low yield into diplatinum(III) compounds [(H₃N)-Pt(1-MeC⁻-N3,N4)₄Pt(NH₃)₂]²⁺ (**2a**) and [(H₂O)Pt(1-MeC⁻-N3,N4)₄Pt(NH₃)₂]²⁺ (**2b**), which were crystallized as ClO₄⁻ salts. In a modified procedure a third representative of this group of diplatinum(III) compounds, [(O₂N)Pt(1-MeC⁻-N3,N4)₄Pt]⁺ (**2c**) was isolated. All three compounds contain the four bridging 1-MeC ligands in a *head,tail,head,tail* arrangement with Pt–Pt distances (2.4516(7)–2.4976(9) Å) that are the shortest ones among diplatinum(III) compounds containing nucleobases.

Introduction

Diplatinum(III) complexes containing a metal–metal single bond exist in several variations, with four or two bridging ligands or even unsupported by any bridge.^{1–3} Without exception, the orientation of the ligands about the Pt atom in two-fold-bridged compounds is *cis* (*head,tail* or *head,head* if the ligands are unsymmetrical). In fact, complexes derived from *cis*-(NH₃)₂Pt^{II} or enPt^{II} have contributed much to the development of the chemistry of diplatinum(III) species.^{4–6} As to examples for four-fold-bridged diplatinum(III) compounds, both simple anions such as sulfate,^{7,8} acetate,⁹ hydrogen phosphate,^{10,11} pyrophosphate,¹² acetamidate,^{1,13} or substituted formamidinate¹⁴ and S-contain-

ing heterocyclic pyrimidine^{15,16} or pyridine¹⁷ ligands have been applied. Here we report on diplatinum(III) complexes containing four bridging 1-methylcytosinato anions which display the shortest Pt–Pt bonds hitherto observed among diplatinum(III) nucleobase complexes. The compounds described are derivatives of *trans*-[Pt(NH₃)₂(1-MeC-N4)₂]²⁺ (1-MeC = 1-methylcytosine), a species containing the model nucleobase in its rare iminooxo tautomer structure. Apart from its way of formation, which involves a redox-assisted metal migration and is a textbook example for such a process,^{18–20} this complex (as well as the methylamine

* Authors to whom correspondence should be addressed. E-mail: jens.mueller@uni-dortmund.de (J.M.); bernhard.lippert@uni-dortmund.de (B.L.).

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analogue of the ammine species) is of interest for several additional reasons, which have been reported before. First, the metal-assisted nucleobase tautomerization (shift of proton from exocyclic to endocyclic N atom) may be relevant to the topic of base mispairing and metal-induced mutagenicity.^{20,21} Second, the acid/base equilibria of this compound (N3 position protonated or deprotonated) makes it a stereochemical pH switch.²² Third, interesting heteronuclear derivatives with and without intermetallic contacts can be derived from the parent compound.²³ As will be reported in this paper, there is a fourth feature of interest, which refers to an unexpected dimerization reaction of two mononuclear species in combination with ligand exchange and redox chemistry catalyzed by Cu^{II}.

Experimental Section

trans-[Pt(NH₃)₂(1-MeC-*N4*)₂](NO₃)₂²³ and [Pt(1-MeC-*N3*)₃Cl](NO₃)·1.5H₂O²⁴ were prepared as reported before. *Caution*: Perchlorate salts of metal complexes with organic ligands are potentially explosive!

trans-[(H₃N)₂Pt(*N4*-1-MeC-*N3*)₂Cu(OH)₂](ClO₄)₂ (**1a**). In 65 mL of H₂O at 50 °C are dissolved 244 mg (0.404 mmol) of *trans*-[Pt(NH₃)₂(1-MeC-*N4*)₂](NO₃)₂. After addition of 300 mg (0.808 mmol, 2 equiv) of Cu(ClO₄)₂·6H₂O in H₂O (3 mL), the solution turns pale blue. Successive addition of 8 × 100 μL of 1 M NaOH solution leads to a green solution, with the pH rising from 5.4 to 6.0. The reaction is stirred at 50 °C overnight for completion. Slow evaporation of the solvent in a stream of nitrogen yields green sticks of **1a** (268 mg, 0.345 mmol, 86%), which are isolated by filtration, washed with H₂O (1 mL), and dried (24 h, 40 °C). Anal. Calcd for C₁₀H₂₂O₁₂N₈Cl₂CuPt: C, 15.5; H, 2.9; N, 14.4. Found: C, 15.5; H, 2.8; N, 14.7. IR ($\tilde{\nu}$, cm⁻¹): 3359, 3315, 1651, 1552, 1442, 1311, 1109, 1042, 794, 779, 620.

head,tail,head,tail-[(H₃N)Pt(1-MeC-*N3,N4*)₄Pt(NH₃)](ClO₄)₂·2H₂O (**2a**). When heating a solution of 500 mg (0.644 mmol) of **1a** in H₂O (30 mL) under reflux for 5 h, its color changes from pale green to deep purple, and a black precipitate is formed. According to an electron probe X-ray microanalysis (EPXMA) this solid consists of Cu and O only. During the reaction, the pH drops from 6.1 to 5.4. Five days after removal of the precipitate by way of filtration, pale yellow cubes of **2a** (28 mg, 0.024 mmol, 8%) appear, which are isolated by filtration, washed with H₂O (1 mL) and dried (24 h, 40 °C). Anal. Calcd for C₂₀H₃₄O₁₄N₁₄Cl₂Pt₂: C, 20.8; H, 3.0; N, 17.0. Found: C, 20.6; H, 2.9; N, 17.0. IR ($\tilde{\nu}$, cm⁻¹): 3534, 3310, 3259, 1646, 1556, 1285, 1102, 763, 622. ¹⁹⁵Pt NMR (DMSO-*d*₆, δ , ppm): -574. ¹H NMR (DMSO-*d*₆, δ , ppm): 7.78 (s, N(4)H), 7.34 (d, ³J = 7.5 Hz, H6), 5.64 (d, ³J = 7.5 Hz, H5), 5.17 (s, NH₃), 3.23 (s, CH₃).

head,tail,head,tail-[(H₂O)Pt(1-MeC-*N3,N4*)₄Pt(NH₃)](ClO₄)₂·1.625H₂O (**2b**). A solution of 10.3 mg (13.3 μmol) of **1a** in H₂O (10 mL) is heated to 80 °C for 7 d without stirring. After 24 h, the

solution turns from pale green to pale pink, and the color intensifies within the next days. The black precipitate formed is removed and discarded. After 14 d at ambient temperature, brown-yellow sticks of **2b** (0.3 mg, 0.26 μmol, 4%) crystallize, which are isolated by filtration, washed with H₂O (1 mL), and dried (24 h, 40 °C). ¹H NMR (DMSO-*d*₆, δ , ppm): 8.94, 7.71 (s, N(4)H), 7.41, 7.38 (d, ³J = 7.4 Hz, H6), 5.90, 5.75 (d, ³J = 7.4 Hz, H5), 5.17 (s, NH₃), 3.24, 3.23 (s, CH₃).

head,tail,head,tail-[(O₂N)Pt(1-MeC-*N3,N4*)₄Pt](ClO₄)·6-H₂O (**2c**). A solution of 60 mg (99 μmol) of *trans*-[Pt(NH₃)₂(1-MeC-*N4*)₂](NO₃)₂ and 45 mg (0.12 mmol, 1.2 equiv) of Cu(ClO₄)₂·6H₂O in H₂O (30 mL, pH 6.2) is heated for 30 h under reflux and vigorous stirring. After 4 h, the solution turns purple. The black precipitate formed is removed and discarded. After addition of 5 mL of a saturated solution of NaClO₄, an amorphous pink solid precipitates which is recrystallized from H₂O (15 mL). After 20 d at ambient temperature, deeply red cubes of **2c** (0.4 mg, 0.35 μmol, 1%) crystallize, which are isolated by filtration and dried (24 h, 40 °C).

trans-Pt(1-MeC-*N3*)₂I₂ (**3**). *trans*-Pt(1-MeC-*N3*)₂I₂ (**3**) was obtained according to a slightly modified version of Hegmans²⁵ by converting [Pt(1-MeC-*N3*)₃Cl](NO₃)·1.5H₂O²⁴ to the corresponding chloride salt via anion exchange and by subsequent treatment of [Pt(1-MeC-*N3*)₃Cl]Cl with KI (2.25 equiv) at pH 2 (HClO₄) for 3 d at 80 °C.

Instrumentation. ¹H NMR measurements were carried out at ambient temperature on Bruker AC 200 and Bruker DRX 400 spectrometers. ¹⁹⁵Pt NMR and ¹H,¹⁹⁵Pt HMQC spectra were recorded at 43 MHz on the AC 200 instrument. Chemical shifts are referenced to internal tetramethylsilane (¹H) and external Na₂PtCl₆ (¹⁹⁵Pt). pD values were obtained by adding 0.4 to the pH meter reading.²⁶ Elemental analyses were carried out on a LECO Elemental Analyzer CHNS-932 and a Carlo Strumentazione 1106 instrument. IR spectra were recorded on a Bruker FT-IR spectrometer (model IFS 28) with a He-Ne laser (λ = 633 nm). UV/vis spectra were recorded on a Lambda 15 spectrometer (Perkin-Elmer).

X-ray Crystallography. Intensity data of **1a**, **2a**, **2b** and **2c** were collected on an Enraf-Nonius KappaCCD²⁷ (Mo K α , λ = 0.71069 Å, graphite-monochromator). Structures were solved by standard Patterson methods²⁸ and refined by full-matrix least-squares based on *F*² using the SHELXTL-PLUS²⁹ and SHELXL-93 programs.³⁰ The positions of all non-hydrogen atoms were deduced from difference Fourier maps and refined anisotropically. Exceptions are the disordered oxygen atoms of one perchlorate anion in **2a** and **2b** as well as the positions of the water molecules and part of the 1-MeC ring atoms (to save parameters to compensate for the poor observed reflections-to-parameter ratio) in **2b**, all of which were refined isotropically. Hydrogen atoms were included in calculated positions and refined with isotropic displacement parameters according to the riding model. Crystal data and data collection parameters are summarized in Table 1.

Results and Discussion

Formation of Cu,Pt (**1a**) and X-ray Structure Analysis.

The synthesis of *trans*-[(H₃N)₂Pt(*N4*-1-MeC-*N3*)₂Cu(OH)₂]-

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Table 1. Crystallographic Data for Compounds **1a**, **2a**, **2b**, and **2c**

	1a	2a	2b	2c
formula	C ₁₀ H ₂₂ N ₈ O ₁₂ PtCuCl ₂	C ₂₀ H ₃₄ N ₁₄ O ₁₄ Pt ₂ Cl ₂	C ₂₀ H _{32.75} N ₁₃ O _{14.88} Pt ₂ Cl ₂	C ₂₀ H ₃₆ N ₁₃ O ₁₆ Pt ₂ Cl
fw	775.88	1155.69	1154.42	1140.25
space group	<i>Pnma</i> (No. 62)	<i>P2₁/n</i> (No. 14)	<i>P4₂/n</i> (No. 86)	<i>P1</i> (No. 2)
unit cell dimensions				
<i>a</i> , Å	9.327(2)	12.753(3)	22.756(3)	11.241(2)
<i>b</i> , Å	22.674(5)	20.758(4)	22.756(3)	12.370(2)
<i>c</i> , Å	10.317(2)	13.302(3)	13.686(3)	13.158(3)
α , deg				91.69(3)
β , deg		90.29(3)		112.23(3)
γ , deg				93.36(3)
<i>V</i> , Å ³	2181.8(8)	3521.4(13)	7087.1(20)	1688.1(6)
<i>Z</i>	4	4	8	2
<i>T</i> , K	133	293	293	293
$\lambda_{\text{MoK}\alpha}$, Å	0.71069	0.71069	0.71069	0.71069
ρ_{calcd} , g cm ⁻³	2.362	2.180	2.164	2.243
μ , mm ⁻¹	7.702	8.171	8.121	8.448
ind reflns	8131	6985	4985	5662
obsd reflns	1949	3973	2753	4251
[<i>I</i> > 2 σ (<i>I</i>)]				
R1 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0299	0.0425	0.0366	0.0339
wR2 [<i>I</i> > 2 σ (<i>I</i>)] ^b	0.0700	0.0896	0.0699	0.0774

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

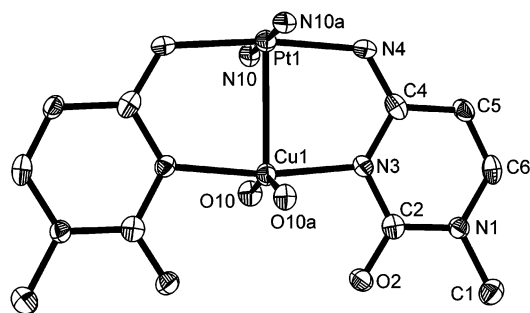


Figure 1. View of cation of *trans*-[(NH₃)₂Pt(*N4*-1-MeC⁻-*N3*)₂Cu(H₂O)₂](ClO₄)₂ (**1a**) with atom numbering scheme. The ellipsoids are drawn at 50% probability.

(ClO₄)₂ (**1a**), Cu,Pt,³¹ proceeds smoothly if *trans*-[Pt(NH₃)₂-(1-MeC-*N4*)₂](NO₃)₂ is cautiously titrated with NaOH in the presence of Cu(ClO₄)₂. Any excess of base (pH > 9) has to be avoided to prevent precipitation of the poorly soluble *trans*-Pt(NH₃)₂(1-MeC⁻-*N4*)₂. Formation of **1a** is evident from the development of a green color ($\lambda_{\text{abs}} < 460$ nm and $\lambda_{\text{abs}} > 620$ nm) and eventually from crystallization of dark green sticks of **1a**. Under slightly modified conditions, a second heteronuclear species (**1b**) was isolated in low yield. It is a dimer of **1a** with either a Cu–OH–Cu or Cu–O–Cu bridge between the two halves. The poor crystal quality of **1b** had thus far prevented us from obtaining a complete structure determination.

Figure 1 provides a view of the cation of **1a**. Selected interatomic distances and angles are listed in Table 2. In **1a**, Pt^{II} is coordinated via the *N4* positions to the 1-methylcytosinato ligands, which are arranged in *trans* fashion, adopt a *head,head* orientation, and are close to coplanar (dihedral angle 2.6(3)°). Cu^{II} binds to the endocyclic *N3* positions of the nucleobases. The intracationic metal–metal distance is 2.6109(9) Å. The coordination spheres of Pt^{II} and Cu^{II} are completed by two *trans*-positioned ammine ligands and two

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1a** (Cu,Pt)

Pt1–N4	2.005(4)	Cu1–N3	1.972(4)
Pt1–N10	2.053(5)	Cu1–O10	2.071(5)
Pt1–N10a	2.028(5)	Cu1–O10a	2.044(4)
Pt1–Cu1	2.6109(9)		
N4–Pt1–N4'	172.9(2)	N3–Cu1–N3'	169.9(2)
N10–Pt1–N10a	178.9(2)	O10–Cu1–O10a	157.4(2)

aqua ligands, respectively. Thus, the coordination geometry of Pt^{II} is square-pyramidal (with Cu^{II} in the apical position), whereas that of Cu^{II} is, according to a conformational analysis using the method of Holmes et al.³² as well as that of Sheldrick et al.,³³ between a square pyramid (with Pt^{II} in the apical position) and a trigonal bipyramid with *N3* and *N3'* representing the axial ligands (Supporting Information). Pt–N bond lengths are not unusual. Cu–N (1.972(4) Å) and Cu–O (2.044(4), 2.071(5) Å) distances are in the range typically observed in Cu^{II} salts having four (reasonably) strong bonds to N and O donors in a plane.³⁴ The *N4*–Pt1–*N4'* angle of 172.9(2)° deviates from the ideal 180° in such a way that the Pt appears to be pushed away from the Cu center. Intracationic N10⋯O10 and N10a⋯O10a separations are 2.947(7) Å and 3.120(7) Å. The highly significant difference in these two distances (17 σ) suggests that there exists a weak intramolecular H bond between *N10* and *O10*, while there is none between the other sites. The position of a proton of the *N*(10)H₃ group (as calculated) indeed makes such a H bond likely (*N10*–H⋯*O10*, 142(3)°; Cu–*O10*⋯H, 87.6(2)°). If true, the arrangement of cations of **1a** (Figure 2) could be rationalized in terms of *O10a* acting as an intermolecular H bond acceptor both for *O10* (3.270(7) Å) and *N10a* (3.120(7) Å).

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(31) In this shortform, the metal bonded to *N3* is mentioned first. Cu,Pt corresponds to **1a** whereas Pt,Cu corresponds to its linkage isomer with Pt bonded to *N3* and Cu to *N4*.

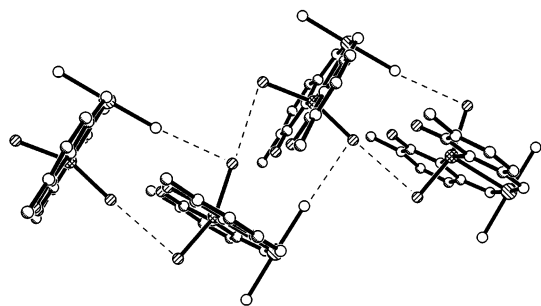
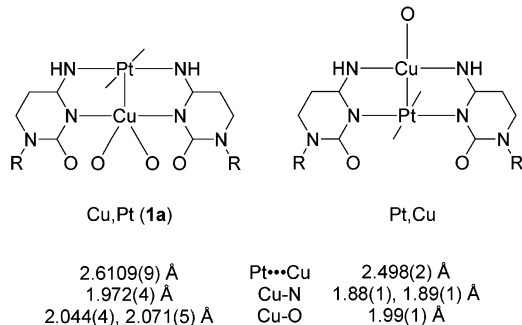


Figure 2. Crystal packing of cations of **1a**. The orientation is along the *x*-axis. Possible intermolecular H bonds are indicated.

Chart 1. Structural Features of Cu,Pt (**1a**) and Pt,Cu



Comparison of Cu,Pt (1a**) with Related Linkage Isomers Pt,Cu.** We have previously described heteronuclear complexes Pt,Cu prepared from *trans*-[a₂Pt(1-MeC-N3)]²⁺ (*a* = NH₃ or CH₃NH₂) with Cu^{II}, in which Cu^{II} is bonded through the deprotonated exocyclic N4 groups.³⁵ These compounds represent linkage isomers of **1a** with the two metal ions inverted. The metal–metal interaction (2.49–2.56 Å) is to be considered a Pt→Cu donor bond of bond order 0.5,³⁶ and Pt represents a ligand of Cu. The coordination number of Cu is 4 or 5, depending on other ligands present. A comparison of a few salient structural features of Cu,Pt (**1a**) and its linkage isomer Pt,Cu (with an oxygen donor at Cu *trans* to Pt) is given in Chart 1. The comparison reveals that in Pt,Cu both the metal–metal and the Cu–N bond distances are significantly shorter than in Cu,Pt (**1a**). There is also a trend to shorter Cu–O distances in Pt,Cu.³⁷ In this context it is noteworthy that the situation in a trinuclear Cu,Pt,Cu complex derived from [Pt(1-MeC-N3)₄]²⁺, [Pt(N3-1-MeC⁻-N4,O2)₄Cu₂X₂]ⁿ⁺ is rather similar to that of Pt,Cu, with short Pt–Cu (2.519(2)–2.531(2) Å) and short Cu–N4 bonds (1.89(2)–1.927(6) Å).³⁸ Consistent with theoretical considerations, the situation in both Pt,Cu and Cu,Pt,Cu has been viewed in terms of an interaction of the half-filled d_{x²-y²} orbital of Cu^{II} with the four ligands Pt^{II}, (N4)₂ and the ligand *trans* to Pt→Cu.^{36,38}

Although the Cu geometry as seen in Cu,Pt (**1a**) is without precedence among heteronuclear complexes containing Pt

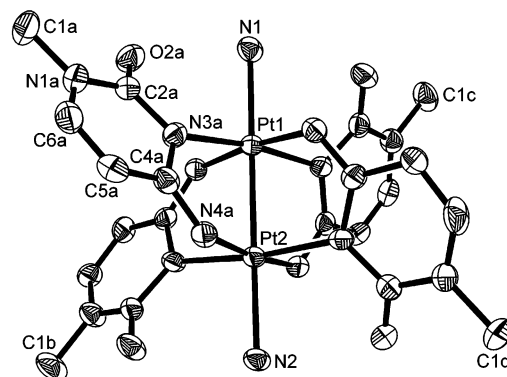


Figure 3. View of cation of [(NH₃)Pt(1-MeC⁻)₄Pt(NH₃)](ClO₄)₂·2H₂O (**2a**). The orientation of the four bridging 1-methylcytosinato ligands is *head,tail,head,tail*. The ellipsoids are drawn at 30% probability.

and nucleobases (or other heterocycles)^{35,38–43} because of the particular *trans*-N₂CuO₂ donor set, there is no doubt that any Pt→Cu interaction in **1a** is considerably reduced as compared to Pt,Cu and Cu,Pt,Cu.

Diplatinum(III) Species Derived from Cu,Pt (**1a**).

Prolonged heating of an aqueous solution of **1a** is accompanied by a color change from green to intense purple ($\lambda_{\text{max}} \approx 533$ and 700 nm) and formation of a black precipitate which, according to electron probe X-ray microanalysis (EPXMA), consists exclusively of Cu and O (black CuO). Within several days at 20 °C, yellow cubes precipitate in low yield from the purple solution. Elemental analysis data, NMR spectroscopy, and X-ray analysis show this compound to be [(H₃N)Pt(1-MeC⁻-N3,N4)₄Pt(NH₃)](ClO₄)₂·2H₂O (**2a**). Slight modifications of this procedure yield two closely related compounds, [(H₂O)Pt(1-MeC⁻-N3,N4)₄Pt(NH₃)](ClO₄)₂·1.625H₂O (**2b**) and [(O₂N)Pt(1-MeC⁻-N3,N4)₄Pt](ClO₄)·6H₂O (**2c**), again in low yield. All attempts to improve the yields of **2a–2c** have been unsuccessful as yet.

Description of X-ray Crystal Structures of **2a–2c**.

Figure 3 shows the cation of the diplatinum(III) complex *head,tail,head,tail*-[(H₃N)Pt(1-MeC⁻-N3,N4)₄Pt(NH₃)](ClO₄)₂·2H₂O (**2a**). It consists of two Pt ions which are bridged by four 1-methylcytosinato ligands through the endocyclic N3 and the exocyclic N4 sites and capped by an ammine ligand each. The regular orientation of the four bridges, *head,tail,head,tail*, which leads to a N3,N4,N3,N4 sequence of donor atoms about each Pt, contrasts the situation in diplatinum(III) complexes containing heterocyclic N,S ligands,^{15–17} where *head,head,tail,tail* as well as *head,head,head,tail* arrangements have been observed. The differences are, at least as far as *head,tail,head,tail* and *head,head,tail,tail* orientations are concerned, rationalized on the basis of the starting materials applied for the generation of these diplati-

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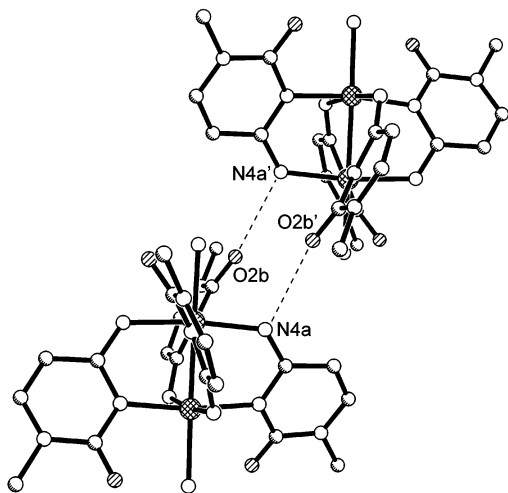
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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **2a–2c**

	2a	2b	2c
Pt1–Pt2	2.465(1)	2.451(1)	2.498(1)
Pt1–X	2.175(7) ^a	2.259(6) ^c	2.044(1) ^e
Pt1–N3a	2.068(6)	2.054(8)	2.063(6)
Pt1–N4b	1.993(7)	2.003(8)	2.019(6)
Pt1–N3c	2.060(6)	2.032(8)	2.067(6)
Pt1–N4d	1.990(7)	1.983(9)	2.027(6)
Pt2–Y	2.181(6) ^b	2.112(7) ^d	
Pt2–N4a	2.005(7)	1.998(9)	2.008(6)
Pt2–N3b	2.066(6)	2.053(8)	2.025(6)
Pt2–N4c	1.999(7)	2.008(8)	2.004(6)
Pt2–N3d	2.063(7)	2.055(8)	2.031(6)
N3a–Pt1–N3c	171.9(3)	173.3(3)	173.4(2)
N4b–Pt1–N4d	172.7(3)	173.2(3)	173.4(2)
X–Pt1–Pt2	178.8(2) ^a	176.6(2) ^c	179.2(3) ^e
N4a–Pt2–N4c	173.4(3)	173.1(3)	174.5(2)
N3b–Pt2–N3d	172.6(3)	172.6(3)	174.5(2)
Y–Pt2–Pt1	178.7(2) ^b	179.4(3) ^d	
1-MeC _a /1-MeC _c	53.4(3)	49.7(4)	34.4(3)
1-MeC _b /1-MeC _d	48.5(3)	55.3(4)	20.3(4)
Pt1N ₄ /Pt2N ₄	0.54(4)	0.8(3)	0.2(3)

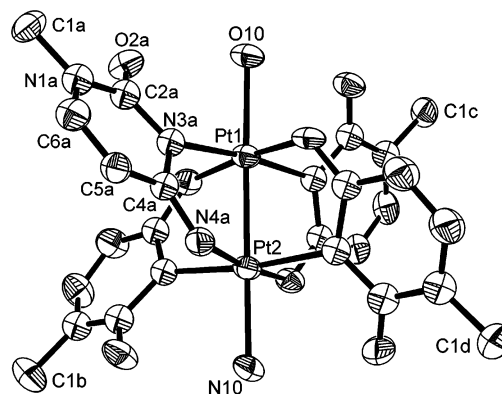
^a X = N1. ^b Y = N2. ^c X = O10. ^d Y = N10. ^e X = N1n.

**Figure 4.** Pairs of enantiomeric cations of **2a** with intermolecular H bonds of 2.857(9) Å indicated.

num(III) compounds. The Pt–Pt distance in **2a** is 2.4651(6) Å.

Table 3 gives selected interatomic distances and angles for the cation of **2a**. Among these data the relatively long Pt–NH₃ distances (2.181(6), 2.175(7) Å) are to be mentioned, as well as the substantial torsional angles between the bridging bases (48.5(3)–53.4(3)°), which appear to be influenced by both the ligand bite distance and the possibilities of H-bonding interactions between the axial NH₃ ligands and the exocyclic O2 oxygen atoms of the 1-methylcytosinato bridges (2.672(9)–2.703(9) Å). The cation of **2a** is chiral. Via intercationic H bonds (N4a···O2b', 2.857(9) Å) it is connected to its enantiomer (Figure 4). No unusual contacts between ClO₄[−] counterions or water of crystallization and the cations are observed.

The structure of *head,tail,head,tail*-[(H₂O)Pt(1-MeC[−]-N3,N4)₄Pt(NH₃)](ClO₄)₂·1.625H₂O (**2b**) is very similar to that of **2a** (Figure 5 and Table 3). The major difference to **2a** is the substitution of one of the axial ammine ligands by

**Figure 5.** View of cation of [(H₂O)Pt(1-MeC[−])₄Pt(NH₃)](ClO₄)₂·1.625H₂O (**2b**). As with **2a**, the four 1-methylcytosinato ligands are arranged *head,tail,head,tail*. The ellipsoids are drawn at 30% probability.

an aqua ligand and the resulting shorter Pt–Pt bond of 2.4516(7) Å. In fact, this distance is the shortest one in any diplatinum(III) complex with bridging nucleobases reported so far. It needs to be emphasized, however, that in all these other compounds⁴⁴ only two bridging nucleobases are present and that the two bases are oriented *cis*, which allows for some tilting of the Pt coordination planes and hence for a lengthening of the Pt–Pt bond. The Pt–OH₂ bond length (2.259(6) Å) is significantly longer than the Pt–NH₃ bond in **2b** (2.112(7) Å). Although OH₂ and NH₃ cannot rigorously be differentiated by X-ray crystallography, the assignment is supported by NMR spectroscopy (*vide infra*) and a comparison with bond lengths in **2a**.

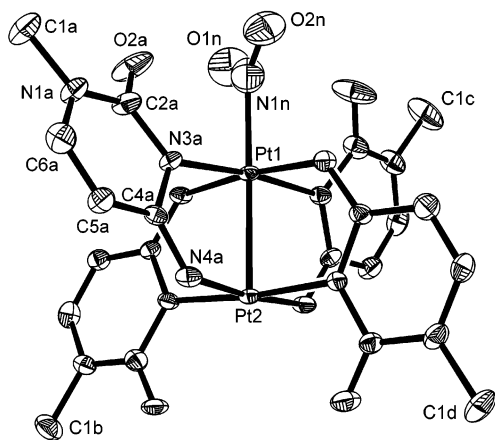
Head,tail,head,tail-[(O₂N)Pt(1-MeC[−]-N3,N4)₄Pt](ClO₄)·6H₂O (**2c**) differs from **2a** and **2b** in that only one of the two Pt atoms is six-coordinate, whereas the second Pt atom is five-coordinate only (Figure 6, Table 3). The axial ligand is a nitro group that, due to its substantial *trans* influence, not only causes a lengthening of the Pt–Pt bond (2.4976(9) Å) but also the loss of the *trans*-axial ligand.⁶ The orientation of the NO₂[−] group is such that its oxygen atoms escape any clash with the exocyclic O2 atoms of the two 1-MeC[−] rings. The propeller twists between mutually *trans*-oriented bases are reduced in **2c** to 34.4(3)° between rings **a** and **c** and even to 20.3(4)° between rings **b** and **d**. The latter clearly is a consequence of the missing axial ligand of one of the two Pt atoms. Again, pairs of enantiomeric cations interact through intermolecular H bonds between N(4)H and O2 groups. The closest intermolecular Pt···Pt separation (between five-coordinate Pt2 atoms) is 5.685(2) Å, considerably shorter than in **2a** (6.475(1) Å) and **2b** (6.537(1) Å), even though in **2b** there is also a short intermolecular Pt1···Pt1 distance of 5.752(1) Å.

Solution Behavior of 2a. Despite the fact that most diplatinum(III) compounds exhibit a fast exchange of axial ligands with solvent molecules, **2a** is stable in DMSO-*d*₆ solution for several days. Both ¹H and ¹⁹⁵Pt NMR spectra show only a minimum of signals (one signal only for H5, H6, and Pt) and thus reveal the high symmetry of the molecule (Table 4). The ¹⁹⁵Pt NMR chemical shift (−574

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Table 4. Assignment of the ^1H and ^{195}Pt NMR Spectra of **2a** and **2a'** ($\text{DMSO-}d_6$, δ/ppm and J/Hz)

	{(CD ₃) ₂ SO}Pt _A (1-MeC ⁻ -N4) ₂ system of 2a'		(NH ₃)Pt _B (1-MeC ⁻ -N4) ₂ system of 2a'		2a
Pt	-1021	$^1J(^{195}\text{Pt}_A, ^{195}\text{Pt}_B) = 7149$	-551	$^1J(^{195}\text{Pt}_A, ^{195}\text{Pt}_B) = 7149$	-574
N(4)H	8.83	$^2J(^1\text{H}_A, ^{195}\text{Pt}_A) = 13$	7.72	Not observed	7.78
NH ₃	—	—	7.23	$^2J(^1\text{H}_B, ^{195}\text{Pt}_B) = 40$	5.17
H6	7.38	$^5J(^1\text{H}_{6A}, ^{195}\text{Pt}_A) = 12$	7.41	$^5J(^1\text{H}_{6B}, ^{195}\text{Pt}_B) = 12$	7.34
H5	5.75	$^4J(^1\text{H}_{5A}, ^{195}\text{Pt}_B) = 20$	5.88	$^4J(^1\text{H}_{5B}, ^{195}\text{Pt}_A) = 20$	5.64
CH ₃	3.24	—	3.31	—	3.23

**Figure 6.** View of cation of $[(\text{O}_2\text{N})\text{Pt}(1\text{-MeC}^-)_4\text{Pt}](\text{ClO}_4)\cdot 6\text{H}_2\text{O}$ (**2c**). The orientation of the four nucleobases is as in **2a** and **2b**. The ellipsoids are drawn at 30% probability.

ppm) clearly provides proof for the +III oxidation state of the metal atoms. Acidification of a solution of **2a** by means of DNO_3 leads to the rapid formation of *head,tail,head,tail*- $[(\text{H}_3\text{N})\text{Pt}(1\text{-MeC}^- \text{-}N3, N4)_4\text{Pt}\{\text{SO}(\text{CD}_3)_2\}]$ **2a'**. The accompanied decrease in symmetry can easily be followed by NMR spectroscopy. As can be seen from Figure 7, two sets of signals are detected, one for the $\text{Pt}(1\text{-MeC-}N4)_2$ system with axially bound $\text{DMSO-}d_6$ (labeled Pt_A) and one for the $\text{Pt}(1\text{-MeC-}N4)_2$ system with axially bound NH_3 (labeled Pt_B). On the basis of the assumption that the chemical shift of one platinum atom of **2a** does not depend on the substitution of the other platinum atom, a ^1H , ^{195}Pt HMQC spectrum of **2a'** helps assign the resonances. The chemical shift of Pt_A (-1021 ppm) suggests a coordination of the $\text{DMSO-}d_6$ ligand via oxygen. The two metal atoms show a strong 1J coupling of 7149 Hz, which is in the range of quadruply bridged diplatinum(III) species (between 10500 Hz in $[\text{ClPt}(\text{CH}_2\text{-}\{\text{P}(\text{O})\text{OH}\}_2)_4\text{PtCl}]^{4-}$ and 3464 Hz in $[(\text{H}_2\text{O})\text{Pt}(\text{SO}_4)_4\text{-PtCl}]^{3-}$).^{45,46} Although there is no linear relation between the size of a 1J coupling and the strength of the metal–metal bond, a large value like the one found in **2a'** is a typical characteristic of a strong metal–metal bond.⁴⁷ The complete assignment of the NMR spectra of **2a** and **2a'** is given in Table 4. A ROESY spectrum of a mixture of **2a** and **2a'** reveals fast exchange of coordinated $\text{DMSO-}d_6$ and NH_3 (Supporting Information). The formation of a doubly $\text{DMSO-}d_6$ coordinating species cannot be detected.

The difference in axially coordinating ligands in **2a** and **2b** can be seen not only by X-ray crystallography but also

by NMR spectroscopy. The ^1H NMR spectrum of **2b** shows two sets for both aromatic protons and hence indicates a substitution pattern with different axial ligands (Table 5). The similarity of the ^1H NMR spectra of **2b** and **2a'** leads to the conclusion that in **2b** one Pt is coordinated to an NH_3 group whereas the other Pt binds to an oxygen donor. The large difference in the chemical shifts of the ammine ligand can be explained by the much higher concentration of acid in the solution of **2a'**. Hence, the NMR spectroscopic data of **2b** are in good agreement with its X-ray structure, which shows axial binding of one NH_3 and one H_2O ligand.

Conversion of Cu,Pt (1a) to $[\text{Pt}^{\text{III}}]_2$. To understand the formation of **2a–2c** from **1a**, a series of experiments has been carried out. (i) Treatment of *trans*- $[\text{Pt}(\text{NH}_3)_2(1\text{-MeC-}N4)_2](\text{NO}_3)_2$ with oxidizing agents: we have applied KMnO_4 , $\text{Ce}(\text{SO}_4)_2$, KIO_3 , HNO_3 , and $\text{Fe}(\text{NO}_3)_3$ at both room temperature and under reflux and found that either no oxidation or oxidation to Pt^{IV} species took place, according to NMR spectroscopy (^1H , ^{195}Pt). These observations suggest that Cu^{II} is required for the formation of diplatinum(III) species. (ii) Oxidation of *trans*- $[(\text{H}_3\text{N})_2\text{Pt}(N4\text{-}1\text{-MeC-}N3)_2\text{Hg}](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$: the previously described Hg^{II} analogue of **1a**²³ has been applied to probe the idea that Cu^{II} might have a template effect, hence having the function of properly orienting the two bases in the monomeric precursors of $[\text{Pt}^{\text{III}}]_2$. Treatment of Hg,Pt with KIO_4 leads, however, to *trans*- $[\text{Pt}(\text{NH}_3)_2(1\text{-MeC-}N4)_2]^{2+}$ and a series of unidentified decomposition or condensation products, as judged by ^1H NMR spectroscopy, yet not to $[\text{Pt}^{\text{III}}]_2$ species. This experiment therefore points to a direct involvement of Cu^{II} in the redox process. (iii) Variation of pH: it turns out that the rate of color change from green to purple is faster at pH 6 than at pH 3. (iv) Role of oxygen: access of air (through rapid stirring of the solution of **1a**) markedly accelerates formation of the purple color.

Our working hypothesis is that the purple species, which is remarkably stable over days at 20 °C, is an intermediate in the formation of $[\text{Pt}^{\text{III}}]_2$ rather than a species formed in a parallel way. This view stems from the observation that **2a–2c** are obtained from such solutions only. Although it is felt that the species giving rise to the purple color might be a mixed-valence Pt compound, e.g. a $\text{Pt}^{\text{III}}\text{Pt}^{\text{II}}$ compound, the EPR spectrum of a frozen purple solution does not display the typical characteristics of such compounds, namely a spectrum of approximately axial symmetry with $g_{\perp} \approx 2.4\text{--}2.5$ and $g_{\parallel} \approx 2$.^{48,49} Rather, its spectrum with two g values

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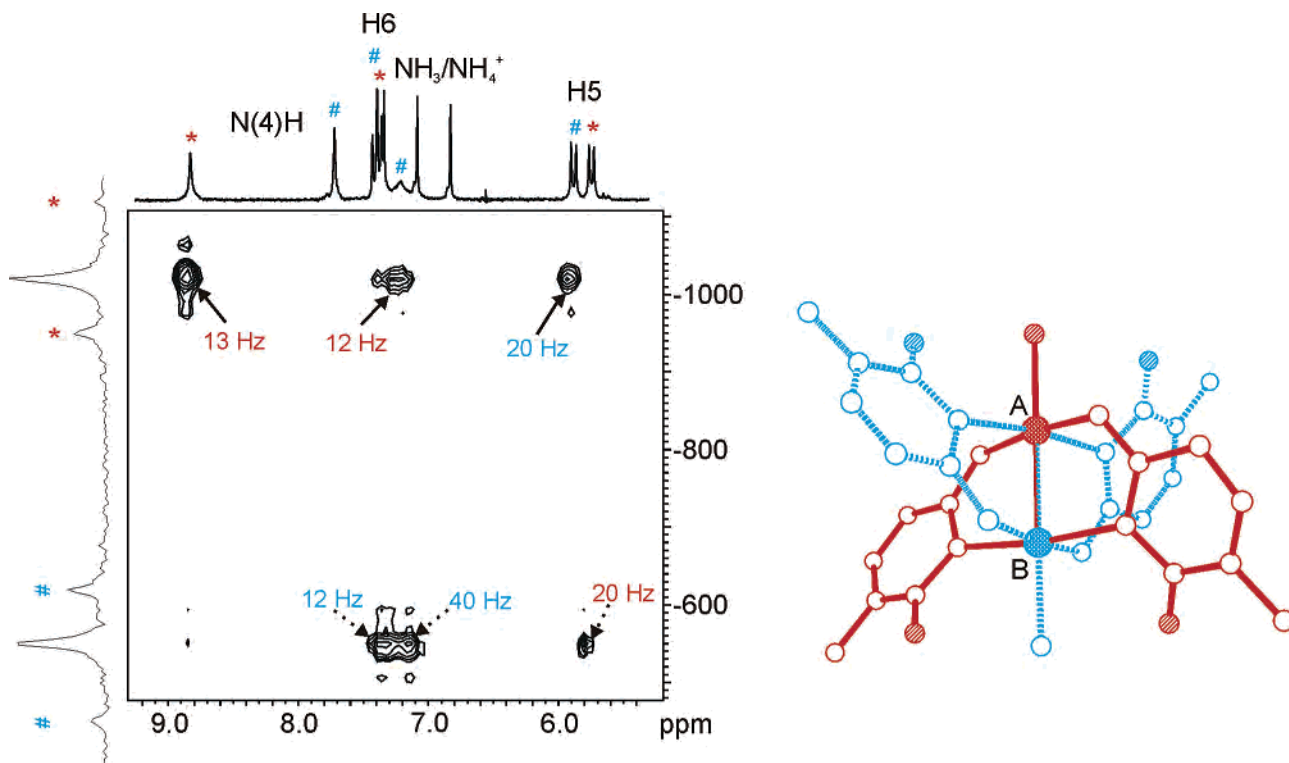


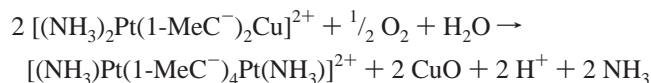
Figure 7. ^1H , ^{195}Pt HMQC spectrum of **2a'** (* and straight lines = signals belonging to the $\text{Pt}_\text{A}(\text{1-MeC-}N_4)_2$ system with axially bound $\text{DMSO-}d_6$; # and dotted lines = signals belonging to the $\text{Pt}_\text{B}(\text{1-MeC-}N_4)_2$ system with axially bound NH_3).

Table 5. Comparison of the ^1H NMR Data of **2a'** and **2b** ($\text{DMSO-}d_6$, δ/ppm)

	N(4)H		H6		H5		NH ₃	CH ₃	
2a'	8.83	7.72	7.41	7.38	5.88	5.75	7.23	3.31	3.24
2b	8.94	7.71	7.41	7.38	5.90	5.75	5.17	3.24	3.23

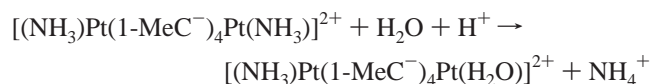
($g_1 \approx 2.26$; $g_2 \approx 2.1$) is reminiscent of a Cu^{II} species as seen in Pt,Cu,Pt compounds,⁴⁰ even though the typical splitting of g_1 into four components is not seen.

A feasible reaction equation rationalizing the formation of the diplatinum(III) complex **2a** from the Cu,Pt complex **1a**, which is consistent with the experimental observations (requirement of Cu^{II} and O_2 ; formation of CuO ; slower reaction at lower pH), would be the following one:



The above equation does not provide a rationale for the way of formation of $[\text{Pt}^{\text{III}}]_2$, however, nor does it explain the role of Cu^{II} nor the structural reorganization at the Pt center when one of the original NH_3 ligands of the starting compound is lost.

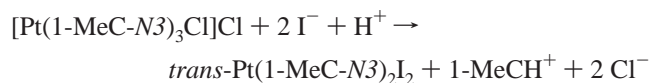
Formation of **2b** involves a simple substitution of one of the axial NH_3 ligands by H_2O under slightly acidic conditions, further supported by the higher reaction temperature and longer reaction time:



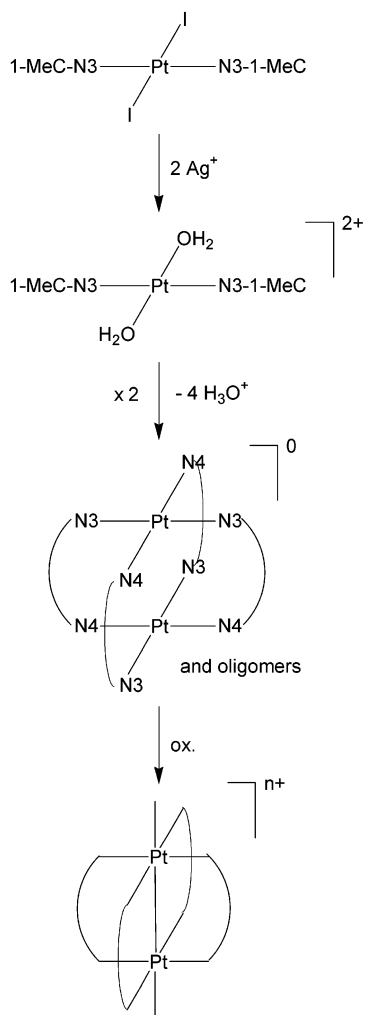
Substitution reactions in the axial positions of diplatinum(III) complexes are quite common.^{1–5,50} Even NH_3 ligands in the equatorial positions have been shown to be subject to facile displacement once the Pt atom has reached the +III oxidation state.⁵¹

Formation of **2c** can be attributed to the fact that during its synthesis **1a** as the starting material for the oxidation had not been isolated by crystallization as a perchlorate salt but used without further purification. Apparently, the nitrate present during the reaction served as an oxidizing agent, leaving a nitrite anion as axial ligand in **2c**. It is not unlikely that in an initial step **2a** is being formed, followed by a substitution reaction of one axial NH_3 by NO_2^- and the subsequent dissociation of the other NH_3 because of the larger trans influence of NO_2^- . This larger trans influence also explains the increased Pt–Pt bond length in **2c** as compared to those in **2a** and **2b**.

Alternative Routes to Fourfold Bridged 1-Methylcytosinato Diplatinum(III) Compounds. The unsatisfactory yields of **2a–2c** prompted us to search for alternative routes to tetrakis(1-methylcytosinato)diplatinum(III) compounds. To this end (Scheme 1), we have prepared *trans*- $\text{Pt}(\text{1-MeC-}N_3)_2\text{I}_2$ (**3**) from $[\text{Pt}(\text{1-MeC-}N_3)_3\text{Cl}]\text{Cl}$ upon reaction with KI at pH 2 (HClO_4) according to



and converted it to the diaqua species *trans*- $[\text{Pt}(\text{H}_2\text{O})_2(\text{1-MeC-}N_3)_2]^{2+}$ to study possible condensation reactions. It was the hope to obtain a $[\text{Pt}^{\text{II}}]_2$ precursor which, upon oxidation,

Scheme 1. Alternative Route to Fourfold Bridged 1-Methylcytosinato Diplatinum(III) Complexes

should have led to diplatinum(III) compounds with a *head,tail,head,tail* arrangement of the four bases as seen in **2a–2c**. Reactions were followed by ¹H NMR spectroscopy (D₂O, c_{Pt} = 24 mM) at 20, 40, 60, and 80 °C over a period of 3 days. In all cases the aging process of the diaqua species was associated with a marked drop in pD, usually to 2.3–2.2, and development of a reddish brown color at temperatures higher than room temperature. Only at 20 °C the sample kept a yellow color. Spectra turned out to become rather complicated with multiple cytosine/cytosinato resonances observed. With time, spectra simplify to H6 singlets as a consequence of isotopic exchange of the aromatic protons at C5. Typically, H6 singlets are dispersed over the range of 7.0–7.8 ppm. Some of these resonances are broad, suggesting the presence of a paramagnetic species or dynamic processes of some kind. None of these resonances corresponds to free 1-methylcytosine in its protonated form. Addition of NaCl to an aged solution (3 d, 80 °C) of *trans*-[Pt(D₂O)₂(1-MeC-N3)₂]²⁺, carried out to quench condensation processes, causes a general sharpening of H6 resonances.

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(51) Lippert, B.; Schöllhorn, H.; Thewalt, U. *Inorg. Chem.* **1986**, 25, 407.

At least seven H6 singlets (7.15, 7.17, 7.20, 7.47, 7.50, 7.54, 7.82 ppm) are then clearly discernible. In the ¹⁹⁵Pt NMR spectrum of an aged solution (3 d, 80 °C) of the diaqua species of **3** a single resonance is observed at –513 ppm. This resonance is assigned to a diplatinum(III) complex of high symmetry, with both Pt atoms having identical donor sets. Comparison with **2a** (–574 ppm) tentatively suggests that the observed resonance is due to a *head,tail,head,tail*-diplatinum(III) complex with axial aqua or hydroxo ligands. Nevertheless, such species can account for only one of the many H6 singlets, with the others and their ¹⁹⁵Pt counterparts unassigned and undetected, respectively. Formation of the diplatinum(III) compound occurs without any extra oxidant (but air, present in the NMR tube) added.

The ¹H NMR spectrum of an aged sample of a diaqua species of **3** lyophilized from D₂O and redissolved in DMSO-*d*₆ turned out not to be very instructive either. In the aromatic region (6.8–9.6 ppm) multiple resonances were observed (Supporting Information). However, much to our surprise a triplet at 7.14 ppm (¹J = 51 Hz) was identified that corresponds to NH₄⁺! It strongly suggests that platinated 1-MeC in **3** has undergone (partial) hydrolysis at the exocyclic amino group, most likely giving uracil species. The large number of H6 resonances thus could be, at least in part, due to a mixture of 1-methylcytosine/1-methylcytosinato and 1-methyluracilate ligands. As we have demonstrated in numerous cases,^{3,44} 1-methyluracilate itself is an excellent ligand for Pt in its various oxidation states.

Summary

We have reported for the first time the formation of a series of diplatinum(III) nucleobase complexes from a starting compound with *trans* geometry of the ligands. The reaction comprises not only an oxidation but also a rearrangement of the platinum coordination planes and the dissociation of two ammine ligands. Although the precise mechanism could not be unraveled yet, it appears that the oxidation takes place with a copper atom involved in the formation of the starting complex *trans*-[(NH₃)₂Pt(N4-1-MeC⁻-N3)₂Cu(H₂O)₂](ClO₄)₂ (**1a**) serving as a mediator for the electron transfer from platinum to molecular oxygen. Alternative routes to diplatinum(III) complexes with a *head,tail,head,tail* orientation of the 1-methylcytosinato ligands starting from a *trans*-[Pt-(H₂O)₂(1-MeC-N3)₂]²⁺ species have been devised but could not be turned into productive preparative routes so far. Nevertheless, ¹⁹⁵Pt NMR spectroscopy supports the presence of such species in aged solutions. Finally, we note that we have seen indication for an unexpected hydrolytic pathway of 1-MeC, leading to the liberation of NH₄⁺.

Acknowledgment. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged. We also thank the Land Nordrhein-Westfalen for a graduate fellowship (J.M.), C. Dalhoff and A. Richter for help with the syntheses, and F. Glahé for assistance in the X-ray work. This work is dedicated to Professor Heinrich Nöth at the occasion of his 75th birthday.

Diplatinum Complexes with Four Bridging Nucleobases

Supporting Information Available: Conformational analysis of **1a**, ROESY spectrum of a mixture of **2a** and **2a'**, ¹H NMR spectrum of an aged sample of *trans*-[Pt(D₂O)₂(1-MeC-N₃)₂](NO₃)₂, crystallographic data for the structures reported (CIF file).

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