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Synthesis, Characterization, and Structure of [{$PtMe_3$(9-MeA)}$_3$] (9-MeAH = 9-Methyladenine): A Cyclic Trimeric Platinum(IV) Complex with a Nucleobase

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Reaction of [{$PtMe_3I$}$_4$] with AgOAc in acetone results in formation of trimethylplatinum(IV) acetate (**1**) that reacts with 9-methyladenine (9-MeAH) in ratio 1:1 with its deprotonation yielding a trimethyl(9-methyladeninato)platinum-(IV) complex (**2**) that was obtained from acetone/diethyl ether as [{$PtMe_3$(9-MeA)}$_3$]·Me_2CO (**2a**) and from chloroform/diethyl ether as [{$PtMe_3$(9-MeA)}$_3$]·1.5Et_2O·2H_2O (**2b**). Single-crystal X-ray investigations revealed that **2a** and **2b** in the solid state form cyclic trimeric molecules in which three $PtMe_3$ moieties are bridged by deprotonated 9-methyladenine ligands in μ-κN^1:$\kappa^2 N^6$,N^7 coordination mode. The methyladeninato ligands include angles with the plane defined by the Pt_3 unit between 55.9(3)° and 66.6(3)°. Thus, the structures of the cyclic trimers resemble hollow truncated cones. Crystals of the acetone solvate **2a** consist of stacks of unidirectional trimeric molecules; the solvate acetone molecules lie between the trimers. In the crystals of complex **2b**, the trimeric molecules are arranged head-to-head, and the cavity between is filled with four water molecules. Complex **2** was also fully characterized by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopies. The existence of the cyclic trimeric structure of complex **2** in acetone solution was confirmed by ESI mass spectrometry exhibiting the protonated trimeric complex [{$PtMe_3$-(9-MeA)}$_3$H]$^+$ [**2** + H]$^+$ (*m*/*z* 1165) as base peak. CID experiments of that parent ion showed as main fragmentation processes loss of two methyl ligands (probably as ethane) and cleavage of a methyladenine ligand.

Introduction

Nucleobases exert a wide range of functions in living organisms, and metal binding to nucleobases is a key for understanding bioinorganic chemistry.[1] The discovery of carcinostatic properties of cisplatin (*cis*-[$PtCl_2(NH_3)_2$]) and that it exerts its biological influence by binding to nucleobases of DNA led to increased research activities in the coordination chemistry of platinum with nucleobases. Anticancer activity was found not only at numerous Pt^{II} complexes but also at Pt^{IV} complexes.[2] The ongoing debate whether the platinum(IV) complexes are reduced to "classical" platinum(II) complexes that subsequently coordinate to DNA or interact directly with DNA resulted in a growing interest in nucleobase−platinum(IV) complexes.[3]

There are two principal pathways to synthesize model complexes of platinum(IV) with bioligands, namely (i) by oxidation of preformed Pt^{II} complexes or (ii) via ligand substitution reactions which may be hampered by oxidative degradations of bioligands and the kinetic inertness of Pt^{IV} complexes (low-spin d^6), respectively. This may be the reason that only a limited number of platinum(IV) complexes with

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cytosine,[4] uracil,[5] and purine (theophylline[6] and 9-methylxanthine[7]) nucleobase ligands could be isolated and well characterized.

fac-$[PtMe_3(Me_2CO)_3]BF_4$ proved to be a suitable starting complex for ligand substitution reactions, and even with the weakly coordinating carbohydrates (L), a great number of trimethyl(carbohydrate)platinum(IV) complexes *fac*-$[PtMe_3L]BF_4$ could be obtained.[8] These investigations were the starting point for analogous reactions with nucleobases. Here, we report the reaction of trimethylplatinum(IV) acetate with 9-methyladenine (9-MeAH). Because of the blockade of N9 for metal binding, 9-methyladenine is the most simple model compound to mimic the coordination pattern of adenine in nucleotides.

Experimental Section

General Considerations. Syntheses were performed under Ar using standard Schlenk techniques. Diethyl ether and acetone were dried over Na/benzophenone and B_2O_3 followed by 4 Å molecular sieves, respectively, and distilled prior to use. NMR spectra were obtained with Varian UNITY 500, Gemini 2000, and Gemini 200 spectrometers using solvent signals (^1H and ^{13}C) as internal references and $Na_2[PtCl_6]$ ($\delta(^{195}Pt) = +4520$ ppm) as an external reference. Mass spectra were obtained on an ESI mass spectrometer LCQ (Finnigan Mat) using $\approx 10^{-3}$ M solution of the complex in acetone under the following conditions: flow 8 μL/min; ESI spray voltage 3.3 kV; capillary temperature 120 °C; capillary voltage 34 V; sheath gas N_2; mass resolution 1 unit. The CID experiments were performed in the MS detector mass analyzer (mass analyzer CID) applying a resonance excitation RF voltage (0−5 V peak-to-peak), using helium as the collision gas. $[\{PtMe_3I\}_4]$[9] and 9-methyladenine (9-MeAH)[10] were prepared according to literature methods. All other materials were purchased commercially.

Synthesis of [{PtMe$_3$(9-MeA)}$_3$] (2). AgOAc (60.0 mg, 0.36 mmol) and $[\{PtMe_3I\}_4]$ (132.1 mg, 0.09 mmol) were suspended in acetone (10 mL) and stirred vigorously overnight at room temperature in the absence of light. AgI precipitation was filtered off to afford a clear filtrate, to which 9-methyladenine (53.6 mg, 0.36 mmol) was added. After stirring for 30 min, unreacted 9-methyladenine was removed by filtration. The filtrate was concentrated to ≈1 mL under reduced pressure, and product **2** was precipitated by addition of ether (5−10 mL), filtered, washed with ether and water, and dried in vacuo. Yield: 103 mg (70%). Crystals of $[\{PtMe_3(9\text{-MeA})\}_3]\cdot Me_2CO$ (**2a**) and $[\{PtMe_3(9\text{-MeA})\}_3]\cdot 1.5Et_2O\cdot 2H_2O$ (**2b**) suitable for X-ray diffraction measurements were obtained by slow vapor evaporation of diethyl ether at room temperature into an acetone and chloroform solution of **2**, respectively.

Table 1. Crystal Data Collection and Processing Parameters for Complexes **2a** and **2b**

	2a	**2b**
empirical formula	$C_{30}H_{51}N_{15}OPt_3$	$C_{33}H_{64}N_{15}O_{3.5}Pt_3$
fw	1223.13	1312.26
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	9.583(2)	22.955(4)
b, Å	18.980(4)	20.820(4)
c, Å	21.417(4)	19.973(3)
β, °	96.36(3)	108.79(2)
V, Å^3	3872(1)	9037(3)
Z	4	8
ρ_{calcd}, g cm^{-3}	2.098	1.929
μ, mm^{-1}	10.859	9.315
θ limits, °	2.14−26.01	2.15−25.95
no. of reflns colld	28694	32869
no. of unique reflns	7220	8232
no. of obsd reflns [$I > 2\sigma(I)$]	5427	6339
R(int)	0.1470	0.1105
no. of data	442	482
R1/wR2 [$I > 2\sigma(I)$]	0.0716/0.1546	0.0430/0.1047
R1/wR2 (all data)	0.0943/0.1783	0.0606/0.1226
GOF	0.991	0.981
largest peak/hole, e A^{-3}	2.77/−3.07	1.84/−1.36

X-ray Crystallography. Intensity data of complexes **2a** and **2b** were collected on a STOE IPDS diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 203(2) K. A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 1. The structures were solved with direct methods (SHELXS-97).[11] Subsequent Fourier-difference syntheses revealed the positions of all non-hydrogen atoms which were refined with anisotropic displacement parameters by full-matrix least-squares routines against F^2 (SHELXL-93).[12] The water molecules in **2b** are highly disordered in large cavities and were refined isotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with fixed displacement parameters (riding model).

Results and Discussion

Synthesis. Reaction of tetrameric trimethylplatinum(IV) iodide with silver acetate in acetone results in precipitation of AgI and trimethylplatinum(IV) acetate **1** being soluble in acetone (Scheme 1). It can be assumed that the complex is monomeric in acetone solutions as it was shown for aqueous solutions.[13] Complex **1** reacts with 9-methyladenine (9-MeAH) in ratio 1:1 in acetone with deprotonation of 9-methyladenine yielding a trimethyl(9-methyladeninato)-platinum(IV) complex, **2**, that was isolated by addition of diethyl ether to the acetone solution as a colorless microcrystalline substance (**2**·Me_2CO) in 70% yield. The solvent molecules included vary with the workup procedure.

The same reaction took place with an excess of 9-methyladenine (9-MeAH/**1** = 2/1). Reaction of 9-MeAH with

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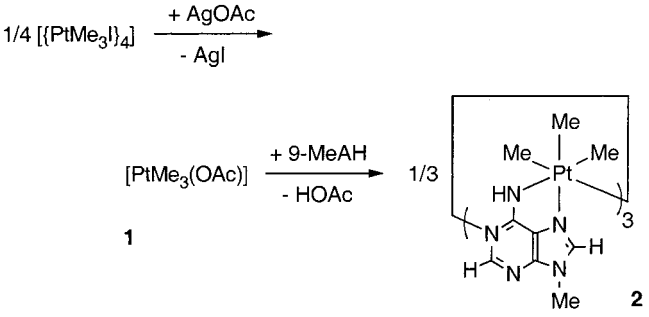
Scheme 1



$[PtMe_3(Me_2CO)_3]BF_4$[14] did not result in formation of complex **2**, but a mixture of complexes with nondeprotonated adenine ligands was obtained which was not further identified. Thus, the acetate anion is decisive for proton abstraction of 9-MeAH.

The trimethyl(9-methyladeninato)platinum(IV) complex **2** is thermally stable (T_{dec} 180 °C) and stable in air. Complex **2** is well soluble in solvents such as acetone, methanol, methylene chloride, and chloroform. Its constitution was unambiguously confirmed by X-ray crystallography, ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy, and electrospray ionization (ESI) mass spectrometry.

Solid-State Structure of Complex 2. Single crystals suitable for X-ray diffraction measurements of complex **2** could be obtained by slow vapor evaporation of diethyl ether into a solution of **2** in acetone and chloroform, respectively. In both cases, solvated cyclic trimeric complexes with composition $[\{PtMe_3(9\text{-}MeA)\}_3]\cdot Me_2CO$ (**2a**) and $[\{PtMe_3(9\text{-}MeA)\}_3]\cdot 1.5Et_2O\cdot 2H_2O$ (**2b**), respectively, were obtained. The molecular structure of the cyclic trimer $[\{PtMe_3(9\text{-}MeA)\}_3]$ in complex **2a** is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The cyclic trimer in complex **2b** is very similar to that in complex **2a** (cf. Table 2). The deprotonated 9-methyladenine ligands act as bridging ligands bound bidentately to one platinum center via N6 and N7 and monodentately via N1 to another platinum center (coordination mode: μ-κN^1:$\kappa^2 N^6,N^7$). Thus, platinum centers are octahedrally coordinated by three methyl ligands and three nitrogen donors. The restricted bite of the N6,N7 chelate results in a remarkable deviation from the 90° angle (mean values N6−Pt−N7: 78.9°, **2a**; 79.5°, **2b**). The other N−Pt−N angles and the C−Pt−C angles are close to 90°.

The 9-methyladeninato ligands are essentially planar; atom deviations from the least-squares planes do not exceed 0.06(2) Å (**2a**) and 0.09(1) Å (**2b**), respectively. Maximal deviations of the two platinum atoms coordinated to these planes amount for **2a** to 0.511(1) Å (Pt2 from N1a → C9a) and for **2b** to 0.170(1) Å (Pt3 from N1b → C9b). In good approximation, the three platinum atoms define an equilateral triangle. With that plane, the methyladeninato ligands include angles of 58.6(3)°, 66.6(3)°, and 55.9(3)° (**2a**) and 60.4(1)°, 57.9(2)°, and 60.0(2)° (**2b**), respectively. Thus, the structures of the cyclic trimers resemble hollow truncated cones (tori) and exhibit approximate C_3 symmetry.

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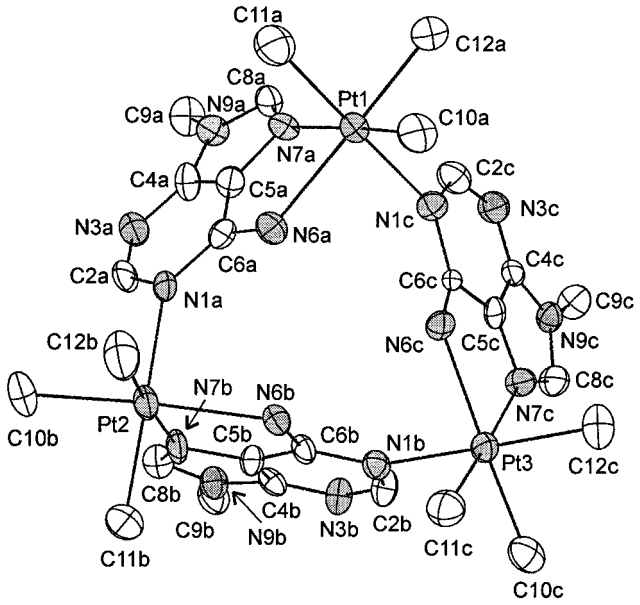

Figure 1. Molecular structure of $[\{PtMe_3(9\text{-}MeA)\}_3]\cdot Me_2CO$ (**2a**). Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (in Å) and Angles (in deg) of Complexes **2a** and **2b**

	2a	**2b**		**2a**	**2b**
Pt1−C10a	2.04(2)	2.03(1)	Pt1−N6a	2.19(1)	2.201(7)
Pt1−C11a	2.02(2)	2.071(9)	Pt1−N7a	2.25(1)	2.194(8)
Pt1−C12a	2.06(2)	2.061(9)	Pt1−N1c	2.19(1)	2.221(7)
Pt2−C10b	2.06(2)	2.080(9)	Pt2−N6b	2.19(1)	2.180(7)
Pt2−C11b	2.05(2)	2.05(1)	Pt2−N7b	2.19(1)	2.226(7)
Pt2−C12b	2.03(2)	2.056(8)	Pt2−N1a	2.23(1)	2.197(7)
Pt3−C10c	2.04(2)	2.05(1)	Pt3−N6c	2.18(1)	2.183(7)
Pt3−C11c	2.03(2)	2.03(1)	Pt3−N7c	2.25(1)	2.204(8)
Pt3−C12c	2.05(2)	2.04(1)	Pt3−N1b	2.20(1)	2.211(7)
C10a−Pt1−N7a	173.2(6)	175.1(3)	C11c−Pt3−N7c	176.2(6)	174.1(3)
C11a−Pt1−N1c	177.9(7)	177.7(4)	C12c−Pt3−N1b	177.9(6)	177.4(4)
C12a−Pt1−N6a	178.8(6)	177.1(4)	N6a−Pt1−N7a	78.6(5)	79.2(3)
C10b−Pt2−N6b	176.3(7)	176.2(3)	N6b−Pt2−N7b	79.7(5)	79.3(3)
C11b−Pt2−N1a	176.5(7)	177.1(3)	N6c−Pt3−N7c	78.7(5)	80.1(3)
C12b−Pt2−N7b	175.4(6)	173.8(3)	N1−Pt−N6/N7	88.7[a]	88.3[a]
C10c−Pt3−N6c	176.0(6)	176.3(4)	C−Pt−C	87.4[a]	87.9[a]

[a] Mean value.

The most noticeable feature of the crystal structures of complexes **2a** and **2b** is the different packing of the cyclic trimers (Figure 2). In the acetone solvate **2a**, stacks of unidirectional trimeric molecules are built up; in these stacks, the trimers are related by the space group translation parallel to crystallographic axis *a*. The solvate acetone molecules lie between the trimers but do not penetrate into the broader side of the torus: The C112 atom of the acetone molecule lies 0.59(3) Å above a plane defined by the three N9 atoms. In crystals of complex **2b**, the trimeric molecules are arranged head-to-head forming "dimers" with closest intermolecular contact of 3.42(2) Å (C9b···N3a′) between nonhydrogen atoms. The two molecules of a "dimer" are related by the space group 2-fold screw axis; then, via an inversion center, stacks of these "dimers" are generated in direction parallel *xz*. The cavity built up by the "dimerization" is filled with four water molecules. Oxygen atom of water O3 lies only 0.154(9) Å above the plane defined by the three N9 atoms.

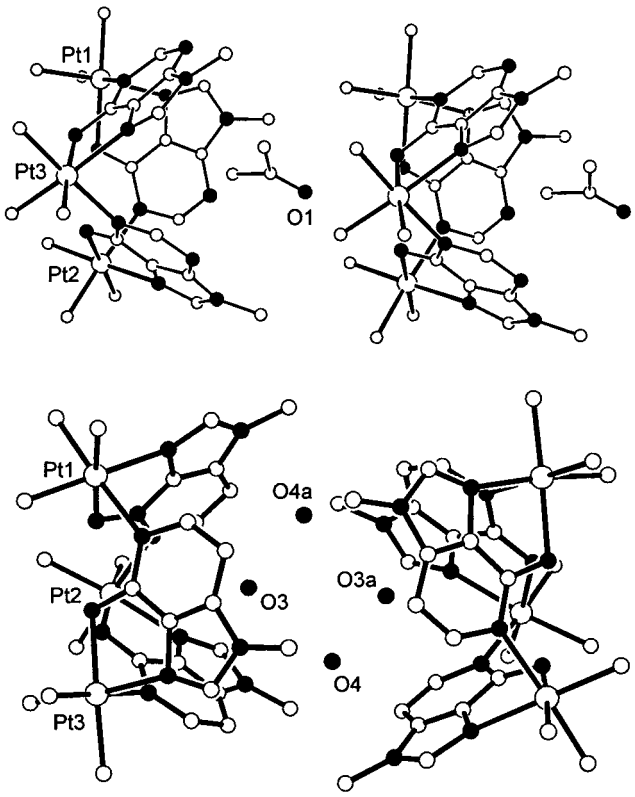

Figure 2. Fragment of molecular packing of $[\{PtMe_3(9\text{-MeA})\}_3]\cdot Me_2CO$ (**2a**) with translation along *a* axis (top) and of $[\{PtMe_3(9\text{-MeA})\}_3]\cdot 1.5Et_2O\cdot 2H_2O$ (**2b**) parallel *xz* direction (bottom). Diethyl ether molecules of **2b** have been omitted for clarity.

The same coordination mode (μ-κN^1:$\kappa^2 N^6$,N^7) as in complex **2** was observed in tricationic cyclic-trimeric rhodium(III) and ruthenium(II) complexes $[\{Rh(9\text{-MeA})(\eta^5\text{-}C_5Me_5)\}_3](OTf)_3$[15] and $[\{Ru(9\text{-EtA})L\}_3](OTf)_3$ ($L = \eta^6$-*p*-MeC_6H_4iPr, η^6-C_6H_6),[16] respectively, as well as in analogous complexes with nucleosides (adenosine) and nucleotides (adenosine 5′-monophosphate and its phosphate methyl ester, nicotinamide adenine dinucleotide). As in complex **2**, in all these complexes the exocyclic NH_2 group of adenine is deprotonated. Additional deprotonation of the phosphate group in adenosine 5′-monophosphate (H_2AMP) resulted in formation of neutral cyclic-trimeric complexes such as $[\{Rh(AMP)(\eta^5\text{-}C_5Me_5)\}_3]$ and $[\{Ru(AMP)L\}_3]$.[15,16]

NMR Spectroscopy. Complex **2** was fully characterized by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopies (Table 3). By means of HETCOR-NMR experiments, it was shown that the signal flanked with platinum satellites at 7.81 ppm has to be assigned to H2 and the signal without couplings to platinum at 8.21 ppm to H8. This assignment was also confirmed by intramolecular NOE experiments: Irradiation into the N9−CH_3 proton resonance resulted in enhancement of the intensity of the signal at 8.21 ppm, and thus, it has to be assigned to the neighboring proton H8. The signal intensity of the remote proton H2 (7.81 ppm) remains almost unchanged.

Signal intensities in the ^{1}H NMR spectrum gave evidence for the coordination of deprotonated 9-methyladenine to the trimethylplatinum(IV) moiety in 1:1 ratio. It is obvious from Table 3 that there are considerable shifts due to deprotonation of 9-MeAH and its coordination to the Me_3Pt^{IV} moiety. Especially, the pronounced downfield shift of H8 ($\Delta\delta = 0.27$ ppm) accompanied by an opposite shift for H2 ($\Delta\delta = 0.37$ ppm) is said to be diagnostic for the cyclic trimer formation.[15,16] Further indication for that gives the coupling of H2 with platinum ($^3J_{Pt,H} = 8.04$ Hz). Deprotonation of the NH_2 group and coordination results in a remarkable upfield shift of the NH proton (6.23 vs 7.51 ppm) and in its coupling to platinum ($^2J_{Pt,H} = 52.3$ Hz).

Table 3. ^{1}H and ^{13}C NMR Spectroscopical Data (δ in ppm, J in Hz) of 9-MeAH and $[\{PtMe_3(9\text{-MeA})\}_3]$ (**2**)

	9-MeAH		$[\{PtMe_3(9\text{-MeA})\}_3]$ (**2**)	
	δ_C/δ_H[a]	δ_H[b]	δ_C/δ_H[b]	$^1J_{Pt,C}/^2J_{Pt,H}$
Pt−CH_3			−8.8/0.78	674.6/70.9
			−8.5/1.06	689.1/67.9
			−13.3/1.32	729.7/77.4
C2−H	152.0/8.13	8.18	158.1/7.81	−/8.0[c]
C8−H	141.0/8.06	7.94	136.7/8.21	
N−CH_3	29.3/3.70	3.73	30.2/3.75	
NH	−/7.15	7.51	−/6.23	−/52.3
C4	149.5		146.8	
C5	118.4		126.9	
C6	155.5		161.0	

[a] In [D$_6$]dmso. [b] In [D$_6$]acetone. [c] $^3J_{Pt,H}$.

The three methyl ligands are chemically nonequivalent. All proton and carbon signals are well separated and flanked by platinum satellites. Corresponding methyl protons and carbon atoms were determined by means of gHMQC experiments (cf. Table 3). The methyl ligand with the largest $^1J_{Pt,C}$ coupling (729.7 Hz) exhibits, as expected, the largest $^2J_{Pt,H}$ coupling (77.4 Hz), too. Trans to that methyl ligand, the ligand with the weakest donor capability should be coordinated,[17] but an assignment remains speculative. The ^{195}Pt NMR signal of complex **2** is observed at 2231 ppm.

ESI-MS Analyses. The existence of the cyclic trimeric structure of complex **2** in acetone solution was confirmed by mass spectrometry (ESI; acetone solvent). By far, the most intense peak (base peak) is that of the protonated trimeric complex $[\{PtMe_3(9\text{-MeA})\}_3H]^+$ ($[\mathbf{2} + H]^+$, *m*/*z* 1165) (Figure 3). The observed isotopic pattern of that peak is in good agreement with the calculated values. Furthermore, peaks with much lower intensity such as $[PtMe_3(9\text{-MeA})H]^+$ (*m*/*z* 389: $[1/3\ \mathbf{2} + H]^+$), $[\{PtMe_3(9\text{-MeA})\}_2H]^+$ (*m*/*z* 778: $[2/3\ \mathbf{2} + H]^+$), and $[(PtMe_3)_3(9\text{-MeA})_2]^+$ (*m*/*z* 1016: $[\mathbf{2} + H - 9\text{-MeAH}]^+$) were detected. As the NMR data show, these species are not present in the original solution but formed mostly by thermal decomposition (proven by varying the capillary temperature from 120 to 200 °C).

Collision-induced dissociation (CID) experiments of the isolated parent ion $[\mathbf{2} + H]^+$ showed a series of fragmentation processes (Figure 3). To determine the *m*/*z* values of the fragmentation peaks with higher accuracy, a CID experiment was also performed with one isotopomer of the parent ion

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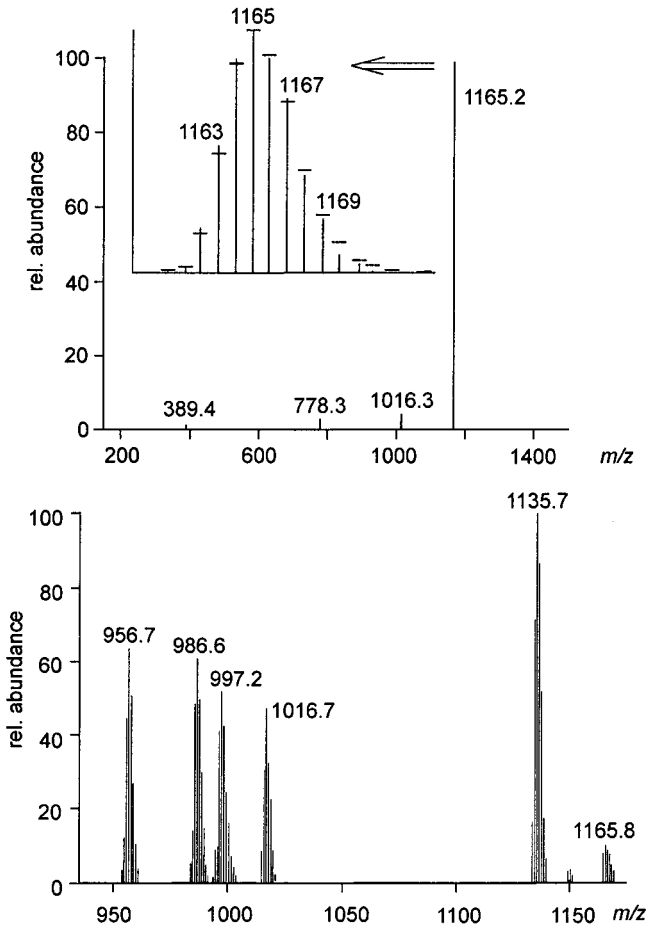

Figure 3. ESI mass spectrum (acetone solvent) of $[\{PtMe_3(9\text{-MeA})\}_3]\cdot Me_2CO$ (**2a**). Full scan mass spectrum showing the molecular mass of $[\{PtMe_3(9\text{-MeA})\}_3H]^+$ ($[\mathbf{2} + H]^+$, *m*/*z* 1165) and expanded spectrum showing the isotopic pattern of that ion (calculated intensities are shown by horizontal bars) (top). CID spectrum (dissociation of the isolated parent ion $[\mathbf{2} + H]^+$; isolation width, 15 amu) (bottom).

(*m*/*z* 1165.8). The spectra show the highest fragment ions at *m*/*z* 1016.7 and at *m*/*z* 1135.7 which correspond to the loss of 9-methyladenine ($\Delta m = 149$ amu) and two methyl ligands probably as ethane ($\Delta m = 30$ amu) of a $PtMe_3$ moiety, respectively. Such reductive elimination processes were also observed in ESI-MS experiments of trimethyl(carbohydrate)-platinum(IV) complexes $[PtMe_3L]BF_4$ (L = carbohydrate ligand). In these cases, it was proved by using a complex with perdeuterated methyl ligands that these were cleaved off and the reductive elimination proceeded with formation of a platinum(II) complex.[8,18]

9-Protected adenine ligands offer four different *N*-coordination sites.[19] The present investigation exhibits that, for the tridentately *facial* binding trimethylplatinum(IV) unit, as for other *facial* binding complex moieties ($Rh^{III}(\eta^5\text{-}C_5Me_5)$,[15] $Ru^{II}(\eta^6$-aromatic)[16]), 1:1 complex formation with bridging $\mu\text{-}\kappa N^1\text{:}\kappa^2N^6,N^7$ 9-methyladeninato ligands is the preferred coordination mode under the premise that the exo-amino group of purine is deprotonated. The cyclic hexamer $[\{PtMe_3(thp)\}_6]\cdot 12CHCl_3$,[6] where deprotonated theophylline ligands (Hthp = theophylline, 3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dion) exhibit an analogous coordination pattern ($\mu\text{-}\kappa N^9\text{:}\kappa^2O^6,N^7$), gives further evidence for the marked tendency of the $PtMe_3$ moiety to form cyclic oligonuclear complexes with deprotonated purine bases.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. This material has also been deposited at the Cambridge Crystallographic Data Center, CCDC, Nos. 778901 (**2a**) and 178902 (**2b**), respectively. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, U.K. (Fax: +44-1223-336033. E-mail: deposit@ccdc.cam.ac.uk. Web address: http://www.ccdc.cam.ac.uk.)

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