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Preparation and Characterization of (9-Methyladenine)triammineplatinum(II) and *trans*-Dihydroxo(9-methyladenine)triammineplatinum(IV) Complexes

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Abstract

The preparation is reported of $[(NH_3)_3Pt(9\text{-}MeA)]X_2$ (9-MeA = 9-methyladenine) with X = Cl (**1a**) and X = ClO_4 (**1b**) and of *trans*-$[(OH)_2Pt(NH_3)_3(9\text{-}MeA)]X_2$ with X = Cl (**2a**) and X = ClO_4 (**2b**), and the crystal structure of **1b**. $[(NH_3)_3Pt(C_6H_7N_5)](ClO_4)_2$ crystallizes in space group $P2_1/n$ with a = 20.810(7) Å, b = 7.697(3) Å, c = 10.567(4) Å, β = 91.57(6)°, Z = 4. The structure was refined to R = 0.054, R_w = 0.063. In all four compounds Pt coordination is through N7 of 9-MeA, as is evident from ^3J coupling between H8 of the adenine ring and ^{195}Pt. Pt(II) and Pt(IV) complexes can be differentiated on the basis of different ^3J values, larger for Pt(II) than for Pt(IV) by a factor of 1.57 (av). In $Me_2SO\text{-}d_6$, hydrogen bonding occurs between Cl^- and C(8)H of 9-MeA as well as between Cl^- and the NH_3 groups in the case of the Pt(II) complex **1a**. Protonation of the 9-MeA ligands was followed using ^1H NMR spectroscopy and pK_a values for the N1 protonated 9-MeA ligands were determined in D_2O. They are 1.9 for **1a** and 1.8 for **2a**, which compares with 4.5 for the non-platinated 9-MeA. Possible consequences for hydrogen bonding with the complementary bases thymine or uracil are discussed briefly. Protonation of the OH groups in the Pt(IV) complexes has been shown not to occur above pH 1.

Introduction

Nucleobase complexes of triammineplatinum(II), $(NH_3)_3Pt(II)$, are models of interactions between DNA and a monofunctional metal electrophile. Though triammineplatinum(II), like the corresponding (diethylenetriamine)platinum(II), (dien)Pt(II), does not show antitumor activity, it reacts readily with DNA and nucleotides [1]. Similar biological effects as those observed with (dien)Pt(II) [2] may be expected in the case of $(NH_3)_3Pt(II)$. As has recently been shown [3], triammineplatinum(II) complexes can be generated on DNA by treating monofunctionally bound *cis*-$(NH_3)_2Pt(II)$ with NH_4HCO_3, thus preventing formation of a cross-link. Using a similar approach we have in the past prepared triammineplatinum(II) complexes on a preparative scale by reacting (nucleobase)diammineplatinum(II) complexes with an excess of ammonia, according to:

$$[(\text{nucleobase})(NH_3)_2PtCl] + NH_3 \xrightarrow{-Cl^-} [(\text{nucleobase})(NH_3)_3Pt]$$

with nucleobase = thymine [4], uracil [5], and 9-ethylguanine [6] alternatively to the direct reaction of $(NH_3)_3Pt(II)$ and nucleobase.

In continuation of our recent work on the interaction of $(NH_3)_3Pt(II)$ with 9-ethylguanine (which, for example, proved a stepwise coordination at N7, then at N1, and finally at N3 [7]) we report here the preparation and crystal structure of (9-methyladenine)triammineplatinum(II) diperchlorate and its oxidation to the *trans*-dihydroxo platinum(IV) derivative.

Experimental

Preparation

$[(NH_3)_3Pt(9\text{-}MeA)]X_2$ Complexes

120 mg of $Cl_3Pt(9\text{-}MeAH)$, prepared as described in the literature [8], was dissolved in 10 ml of aqueous NH_3 (25%) and stirred for 2 h in a stoppered flask. The solution was then brought to dryness by rotary evaporation, the material re-dissolved in 5 ml

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H_2O, the solution brought to pH 4 by means of 0.4 N HNO_3, and allowed to evaporate slowly at 2 °C. The crystalline precipitate was collected and recrystallized from H_2O (70 °C). Yield 100 mg. *Anal.* Calcd. for $[(NH_3)_3Pt(C_6H_7N_5)]Cl_2 \cdot 2H_2O$, **1a**: C, 14.3; H, 4.0; N, 22.3; Pt, 38.9. Found: C, 14.3; H, 4.1; N, 22.7; Pt, 39.1.

Treatment of **1a** (0.5 mmol, dissolved in 8 ml H_2O) with $AgClO_4 \cdot H_2O$ (0.96 mmol), filtration of AgCl after 3 h and slow evaporation of the colorless filtrate gave transparent cubes of $[(NH_3)_3Pt(9\text{-}MeA)](ClO_4)_2$, **1b**, in 60% yield. The compound was characterized by X-ray analysis.

trans-[(OH)$_2$(NH$_3$)$_3$Pt(9-MeA)]X$_2$ Complexes

To a solution of **1a** (0.4 mmol in 5 ml H_2O), 9 ml of an aqueous solution of H_2O_2 (10%) was added in small portions. The solution, which changed from colorless to slightly yellow, was concentrated in a stream of nitrogen to 4 ml and then allowed to evaporate at 3 °C. Within several days, 100 mg of a slightly-yellow precipitate was collected, washed with a small amount of cold water and dried in air. Yield 45%. *Anal.* Calcd. for $[(OH)_2(NH_3)_3Pt(C_6H_7N_5)]Cl_2$, **2a**: C, 13.0; H, 4.4; N, 20.2; Pt, 35.2. Found: C, 12.7; H, 4.2; N, 20.0; Pt, 34.7.

A slightly modified procedure (H_2O_2 treatment for 15 min at 60 °C) converted **1b** into a pale yellow material which, on recrystallization from H_2O (evaporation at 3 °C), was obtained as a microcrystalline material in 58% yield. *Anal.* Calcd. for $[(OH)_2(NH_3)_3Pt(C_6H_7N_5)](ClO_4)_2$, **2b**: C, 11.4; H, 2.9; N, 17.8. Found: C, 11.2; H, 2.9; N, 18.3.

Spectra

^1H NMR spectra were recorded on a Jeol JNM-FX 60 fourier-transform spectrometer at 30 °C in D_2O, with $[N(CH_3)_4]BF_4$ as internal reference, and in $Me_2SO\text{-}d_6$ using TMS as internal standard. Reported shifts with D_2O as solvent were calculated relative to TSP (sodium 3-(trimethylsilyl)propansulfonate), which absorbs 3.187 ppm upfield from the reference.

pD values were obtained by adding 0.4 to the pH meter reading. Reported pK_a values were not corrected for D_2O since they are identical with those determined in H_2O [9]. The potentiometric titration of **2a** was performed on a Metrohm E 536 potentiograph using 0.1 N HNO_3.

Crystallography of 1b

All X-ray measurements were carried out on a PHILIPS PW 1100 diffractometer with a crystal of dimensions 0.2 × 0.3 × 0.3 mm using graphite-monochromatized Mo-Kα radiation (λ = 0.71069 Å). Crystal data: Mr = 582.23, monoclinic, $P2_1/n$, a = 20.810(7), b = 7.697(3), c = 10.567(4) Å, β = 91.57(6)°, $Z = 4$, $D_c = 2.286$, $D_m = 2.32$ g/cm^3.

Intensity data were collected by the $\theta/2\theta$ technique, $\theta_{max} = 25°$. A total of 3407 reflections were scanned. Lp corrections and (in a later stage) an absorption correction (by the method of Walker and Stuart [10]; $\mu = 83.3$ cm^{-1}) were applied. The 2762 reflections having $F_0 \geqslant 2.0\sigma(F_0)$ were used in the following calculations.

The position of the Pt atom was determined from a Patterson synthesis. Subsequent ΔF syntheses revealed the positions of the other non-hydrogen atoms. Least-squares refinement with anisotropic temperature parameters led to $R = 0.054$ and $R_w(F) = 0.063$ ($R_w(F) = \Sigma w^{1/2} \| F_o| - |F_c \| / \Sigma w^{1/2} |F_o|$; $w = (\sigma^2(F_o) + 0.004\, F_o{}^2)^{-1}$). Hydrogen atoms were ignored at all stages. Scattering factors for neutral atoms were taken from Cromer and Mann [11]. Corrections for anomalous dispersion [12] were applied. Calculations were performed on a VAX 11/780 computer using the SHELX76 program system [13].

Results and Discussion

$[(NH_3)_3Pt(9\text{-}MeA)]^{2+}$ was prepared by treating trichloro(9-methyladeninium)platinum(II), $Cl_3Pt(9\text{-}MeAH)$ [8], with an excess of NH_3 according to:

$$Cl_3Pt(9\text{-}MeAH) + 4NH_3 \longrightarrow [(NH_3)_3Pt(9\text{-}MeA)]^{2+} + 3Cl^- + NH_4{}^+$$

The compound formed was characterized by ^1H NMR spectroscopy, elemental analysis and, with the corresponding perchlorate salt, by X-ray analysis. Oxidation with H_2O_2 gave the respective Pt(IV) complexes according to:

$$[(NH_3)_3Pt(9\text{-}MeA)]^{2+} + H_2O_2 \longrightarrow trans\text{-}[(OH)_2Pt(NH_3)_3Pt(9\text{-}MeA)]^{2+}$$

which were characterized using elemental analysis and ^1H NMR spectroscopy.

On the NMR scale, the reaction between $[(NH_3)_3Pt(D_2O)]^{2+}$ and 9-MeA (1:1) was studied. As with the related complexes *cis*- and *trans*-$[(NH_3)_2Pt(1\text{-}MeC)D_2O]^{2+}$ (1-MeC = 1-methylcytosine) [14], three products were formed, the complex with N7 coordination at the 9-MeA, the compound with 9-MeA platinated at N1, and the N1, N7 bridged complex. The compounds were identified by the use of C8-deuterated 9-MeA [15] and $^{195}Pt-^1H$ coupling, and by comparison with the N7 complex prepared as outlined above. The distribution of the three species formed was (1:1, pD 5, 30 °C) 50% N7 coordination, 20% N1 coordination, and 20% N1, N7 bridging. Thus $(NH_3)_3Pt(II)$ favors N7 coordination to a similar degree as do *cis*-$[(NH_3)_2Pt(1\text{-}MeU)(D_2O)]^+$

TABLE I. ^{1}H NMR Resonances of 9-MeA Complexes.[a]

(a) in D_2O ($c_{Pt} \simeq 0.05$ M)

	H8[b]	H2	N–CH_3	pD
1a	8.690 $^3J = 23.7$ Hz	8.360	3.922	6
1b	8.674 $^3J = 23.6$ Hz	8.347	3.922	6
2a	9.058 $^3J = 15.6$ Hz	8.372	3.988	5
2b	9.042 $^3J = 14.7$ Hz	8.372	4.000	4.6

(b) in Me_2SO-d_6 ($c_{Pt} = 0.1$ M)

	H8[b]	H2	NH_2	NH_3[c]	N–CH_3
1b	8.691 $^3J = 24.1$ Hz	8.372	8.037	4.40; 4.22 $^2J \simeq 50$ Hz	3.853
1a	8.826 $^3J = 23.4$ Hz	8.330	8.037	4.96; 4.51[d] $^2J \simeq 50$ Hz	3.828
1b + 0.3 M LiCl	8.903 $^3J = 23.5$ Hz	8.331	8.037	5.06; 4.59[d] $^2J \simeq 50$ Hz	3.845

[a] Shifts in ppm. [b] ^3J values refer to coupling between ^{195}Pt and H8. [c] ^2J values refer to coupling between ^{195}Pt and NH_3 (both sets). [d] Relative intensities of low field signal to high field signal is *ca.* 1:2.

and *cis*-$[(NH_3)_2Pt(1\text{-}MeT)D_2O]^+$ (1-MeU = 1-methyluracil anion, 1-MeT = 1-methylthymine anion) [16].

The ^{1}H NMR chemical shifts of **1a** and **1b** are listed in Table I. While the spectra of the two compounds recorded in D_2O are virtually identical, the H8 and NH_3 resonances exhibit a strong anion-dependence when Me_2SO is the solvent. In the presence of chloride, these resonances are shifted appreciably downfield, indicating hydrogen bonding between Cl^- and these groups. Interestingly, H2 and the exocyclic amino group of the 9-MeA ligand are not involved in such interactions, at least not in the presence of the moderate excess of Cl^- used in the experiment. From model building it appears that a particularly favorable hydrogen bond can be formed with Cl^- linking H8 and one of the ammonia hydrogens of the NH_3 group *cis* to the Pt–N7 bond. Hydrogen bonding interactions between chloride and nucleobases, both free [17] and platinated [18], have previously been observed in Me_2SO.

The Pt(IV) complexes **2a** and **2b** (spectra in D_2O only) have the H8 resonance of 9-MeA shifted downfield relative to H8 in the corresponding Pt(II) complexes (Table I). In addition, coupling between ^{195}Pt and H8 is smaller in the case of the Pt(IV) compounds, 23.7 Hz (**1a**, **1b**) *vs.* 15.6 Hz (**2a**), 14.7 Hz (**2b**). The ratios for $J_{Pt(II)}/J_{Pt(IV)}$ are thus 1.52–1.61, in good agreement with published data on diamine complexes of Pt(II) and Pt(IV) [19]. The reduction in ^3J when going from Pt(II) to Pt(IV) is due to the smaller s-contribution in d^2sp^3 hybridized Pt(IV) as compared to dsp^2 hybridized Pt(II) [20].

Addition of acid to aqueous solutions of either Pt(II) or Pt(IV) complex leads to protonation of the respective 9-MeA ligand at the N1 position, as evident from downfield shifts of all 9-MeA resonances and in particular of H2. The pK_a values determined ^{1}H NMR spectroscopically in D_2O were 1.9 for **1a** and 1.8 for **2a**. These values compare with 4.5 for the non-complexed adeninium cation [21] and values of close to 2 for a series of related Pt(II) complexes containing N7 bound adenines [14, 16, 22]. While the increase in N(1)H acidity of the adeninium (and the concomitant decrease in N1 basicity of neutral adenine) as a consequence of metal binding is not unexpected, the fact that it is similar for Pt(II) and Pt(IV) is somewhat surprising. One might have expected that, as with ammine complexes, Pt(IV) exerts a considerably higher polarizing effect than does Pt(II). As to the consequences of the decrease in N1 basicity with respect to base pairing with thymine or uracil, it is clear that Pt coordination at N7 results in a disturbance of the electronic complementarity of the two partners. It leads to a weakening of the hydrogen bond between N1 of adenine and N3 of thymine (uracil). On the other hand, the effect of Pt on the exocyclic NH_2 group of adenine probably is to increase its acidity and to strengthen the hydrogen bond with O4 of thymine (uracil). The net result on a base pair between thymine (uracil) and platinated adenine thus depends on the magnitudes of the two opposing effects.

With the Pt(IV) complex *trans*-$[(OH)_2(NH_3)_3Pt(9\text{-}MeA)]^{2+}$ protonation of the hydroxo groups to aqua groups is expected to also occur in acidic medium. Since such a process may not be detected in D_2O applying ^1H NMR spectroscopy, we used potentiometric titration to determine any protonation of OH ligands. As a result, no protonation has been found to occur before the adenine ring is being protonated. This means that the equilibrium:

$$[(OH)_2(NH_3)_3Pt(9\text{-}MeA)]^{3+} + H^+ \rightleftharpoons [(OH)(H_2O)(NH_3)_3Pt(9\text{-}MeAH)]^{4+}$$

is to the left and that the pK_a for this process must be smaller than 1–2. If one compares this value with pK_a values common to aqua complexes of Pt(II), which usually are between 5 and 7 [23], there is a remarkably strong polarizing effect of Pt(IV) on this group, which might account for the relatively small effect on the purine ring.

A view of the cation of $[(NH_3)_3Pt(9\text{-}MeA)](ClO_4)_2$, **1b**, is given in Fig. 1, atomic parameters are listed in Table II, and interatomic distances and angles in Table III. The general feature of the cation of **1b** is very similar to that of the $PtCl_3(9\text{-}MeAH)$ starting compound [8b, 8c], the differences being that the Cl ligands are replaced by NH_3 groups and that the N1 position is not protonated in **1b**. In both compounds Pt is coordinated to the 9-methyladenine ring through N7. There are slight deviations from an ideal square-planar coordination geometry about the Pt (Tables III and IV), differences however which are not uncommon in these types of complexes.

The Pt electrophile does not cause any significant structural changes in the 9-MeA ring, as can be seen from a comparison with a series of neutral adenine residues [24], in contrast to protonation which leads to structural changes at and in the vicinity of the N1 position [8a, 8b, 24]. The 9-MeA ring in **1b** is approximately planar (Table IV), including the exocyclic groups and the platinum atom. The

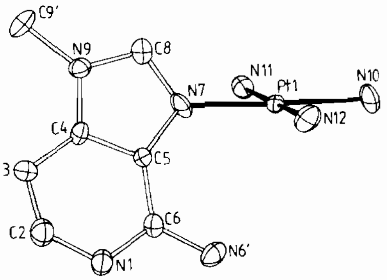

Fig. 1. View of the cation of $[(NH_3)_3Pt(9\text{-}MeA)](ClO_4)_2$, **1b**.

TABLE II. Atomic Parameters for $[(NH_3)_3Pt(9\text{-}MeA)](ClO_4)_2$.[a]

Atom	x	y	z	U_{eq}
Pt1	0.1119(1)	0.1934(1)	0.2717(1)	0.025(1)
N10	0.1017(6)	0.2087(12)	0.4611(9)	0.051(11)
N11	0.1342(4)	−0.0614(11)	0.2785(7)	0.039(7)
N12	0.0913(5)	0.4538(13)	0.2612(9)	0.050(9)
N1	−0.0141(4)	0.2284(14)	−0.1426(8)	0.051(9)
C2	0.0242(6)	0.2083(14)	−0.2429(11)	0.050(12)
N3	0.0855(4)	0.1856(11)	−0.2461(9)	0.046(9)
C4	0.1130(5)	0.1804(12)	−0.1262(9)	0.035(9)
C5	0.0803(4)	0.1985(10)	−0.0161(9)	0.029(8)
C6	0.0128(5)	0.2178(11)	−0.0253(9)	0.033(9)
N6′	−0.0250(4)	0.2371(13)	0.0772(9)	0.047(9)
N7	0.1248(5)	0.1820(10)	0.0850(8)	0.041(9)
C8	0.1829(5)	0.1643(12)	0.0313(9)	0.036(8)
N9	0.1764(3)	0.1587(10)	−0.0965(7)	0.033(6)
C9′	0.2281(5)	0.1356(19)	−0.1856(11)	0.057(12)
Cl1	0.2783(1)	0.1347(4)	0.4369(2)	0.046(2)
O10	0.3430(4)	0.1089(19)	0.4826(11)	0.095(13)
O11	0.2377(4)	0.0099(12)	0.4925(8)	0.067(9)
O12	0.2568(8)	0.3033(13)	0.4622(18)	0.117(21)
O13	0.2770(4)	0.1068(17)	0.3009(7)	0.082(11)
Cl2	−0.0855(1)	0.3004(3)	0.4068(2)	0.045(2)
O20	−0.0531(5)	0.1557(14)	0.4676(12)	0.085(12)
O21	−0.1287(5)	0.3700(17)	0.4914(10)	0.089(12)
O22	−0.0382(7)	0.4245(18)	0.3750(21)	0.167(29)
O23	−0.1180(6)	0.2491(22)	0.2946(11)	0.108(15)

[a] U_{eq} (in A^2) was calculated from the final U_{ij} values by the formula $U_{eq} = 1/3\Sigma_{ij}U_{ij}a_i^*a_j^*a_i \cdot a_j$

TABLE III. Interatomic Distances (A) and Angles (deg).

Atoms	Distance	Atoms	Angle
Pt Coordination Sphere			
Pt1–N10	2.022(10)	N10–Pt1–N11	92.9(4)
Pt1–N11	2.016(9)	N10–Pt1–N12	88.3(4)
Pt1–N12	2.052(10)	N10–Pt1–N7	178.1(5)
Pt1–N7	2.000(9)	N11–Pt1–N12	178.3(4)
		N11–Pt1–N7	87.4(3)
		N12–Pt1–N7	91.3(4)
9-MeA Ligand			
N1–C2	1.352(16)	C6–N1–C2	118.4(10)
C2–N3	1.288(17)	N1–C2–N3	129.8(12)
N3–C4	1.377(14)	C2–N3–C4	111.5(10)
C4–C5	1.372(14)	N3–C4–C5	125.1(10)
C4–N9	1.358(13)	N3–C4–N9	126.4(9)
C5–C6	1.413(14)	C5–C4–N9	108.6(8)
C5–N7	1.400(14)	C4–C5–C6	117.9(9)
C6–N6′	1.363(14)	C4–C5–N7	107.7(9)
C6–N1	1.348(13)	C6–C5–N7	134.2(9)
N7–C8	1.357(16)	C5–C6–N6′	123.4(9)
C8–N9	1.355(13)	N1–C6–N6′	119.4(10)

(continued overleaf)

TABLE III. *(continued)*

Atoms	Distance	Atoms	Angle
N9–C9′	1.459(15)	C5–C6–N1	117.1(9)
		C5–N7–C8	105.6(9)
		N7–C8–N9	110.7(9)
		C8–N9–C9′	126.3(9)
		C4–N9–C9′	126.5(9)
		C8–N9–C4	107.2(8)
ClO_4^- Anions			
Cl1–O10	1.431(10)	O10–Cl1–O11	109.4(7)
Cl1–O11	1.418(10)	O10–Cl1–O12	111.5(9)
Cl1–O12	1.401(12)	O10–Cl1–O13	107.8(6)
Cl1–O13	1.452(9)	O11–Cl1–O12	110.5(8)
Cl2–O20	1.444(12)	O11–Cl1–O13	108.3(6)
Cl2–O21	1.393(12)	O12–Cl1–O13	109.1(10)
Cl2–O22	1.418(15)	O20–Cl2–O21	108.2(7)
Cl2–O23	1.406(13)	O20–Cl2–O22	107.9(8)
		O20–Cl2–O23	111.5(9)
		O21–Cl2–O22	111.0(9)
		O21–Cl2–O23	110.1(7)
		O22–Cl2–O23	108.1(11)

TABLE IV. Pt Coordination Plane and 9-MeA Plane in **1b**.[a]

(a) Pt plane:

$20.10520x + 1.70902y + 1.10937z = 2.908$ Å

Deviations of atoms from best plane (Å):

N10* 0.01; N11* −0.01; N12* −0.01; N7* 0.01; Pt −0.03

(b) 9-MeA plane

$2.71838x + 7.62921y - 0.26757z = 1.722$ Å

Deviations of atoms from best plane (Å):

N1* 0.02; C2* 0.00; N3* −0.01; C4* −0.01; C5* 0.02; C6* −0.02; N7* −0.02; C8* 0.02; N9* −0.01; N6′ 0.00; C9′ −0.02; Pt −0.02

(c) Dihedral angle

Pt plane/9-MeA plane 69.9°

[a] Atoms with an asterisk were used for the calculation of the plane.

dihedral angle between the purine ring and the Pt coordination plane is 69.9°.

Between the cation and the perchlorate anions are a number of close contacts (2.99–3.33 Å) which probably represent hydrogen bonding interactions, and which can be categorized as follows:

Interactions between (a) NH_3 groups and $OClO_3$ ions, (b), between the exocyclic amino group N6′ and $OClO_3$, and (c), between the aromatic protons at C2 and C8 and $OClO_3$. In addition, there are two intermolecular contacts between NH_3 groups and N1 of 9-MeA. The contacts between perchlorate oxygens and aromatic protons, C(2)H–O22 (symmetry transformation $-x$, $1-y$, $-z$) 3.17 Å, C(8)H–O11 (symmetry transformation $0.5-x$, $0.5+y$, $0.5-z$) 3.15 Å, and/or C(8)H–O12 (symmetry transformation $0.5-x$, $-0.5+y$, $0.5-z$) 3.05 Å, confirm observations that C–H groups adjacent to a nitrogen atom are likely to form hydrogen bonds with oxygens or halides [25].

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