In search of an O6,N7 interaction of Pt^{IV} with guanine: X-ray structure and solution behaviour of *mer,trans*-[(dien)Pt(OH)$_2$(9-MeGH-*N7*)](ClO$_4$)$_2$·2H$_2$O

Gudrun Frommer, Hans Preut and Bernhard Lippert*

Fachbereich Chemie, Universität Dortmund, D-4600 Dortmund (FRG)

Abstract

A 9-methylguanine (9-MeGH) complex of composition *mer,trans*-[(dien)Pt(OH)$_2$(9-MeGH)](ClO$_4$)$_2$·2H$_2$O has been prepared and X-ray structurally and spectroscopically characterized. Pt coordination is via N7 of the guanine. The guanine O6 atom is involved in a hydrogen bond of 2.744(7) Å with one of the two axial OH ligands of the metal. This interaction affects the position of the ν(CO) band in the IR at 1650 cm^{-1}. The solution behaviour of the title compound is characterized by the following features: (i) reduction to [(dien)Pt(9-MeGH)]$^{2+}$, (ii) *mer*→*fac* isomerization of the dien ligand, (iii) slow substitution reaction of axial OH$^-$ by Cl$^-$. In two instances, novel Pt^{IV} 9-MeGH complexes of yet unknown composition were observed in the ^{1}H NMR, with guanine H8 resonances downfield (*c.* 8.50 ppm in D$_2$O and MeOD) from those of the title compound. It is not clear as yet, whether they represent O6,N7 chelates.

Introduction

Reports on structurally characterized Pt^{IV} complexes of guanine nucleobase complexes are scarce and essentially restricted to examples from the group of Bau [1]. The at most moderate interest in Pt^{IV} nucleobase chemistry relates to the generally assumed bioreduction of Pt^{IV} to Pt^{II} inside cells [2] and/or findings on the spontaneous reduction of Pt^{IV} nucleobase compounds in model studies [1, 3]. Nevertheless it should be pointed out that the bioreduction hypothesis is not undisputed [4]. With the recent introduction of orally applicable Pt^{IV} antitumor compounds [5] this question may turn out to be of high interest. Our interest in Pt^{IV} guanine compounds goes back to the question of the possible existence of a N7/O6 chelate of a guanine nucleobase with Pt(IV). While no hard evidence seems to exist for such a chelate in the case of Pt(II) [6], several lines of evidence suggest that it might be possible to prepare such a chelate with a Pt^{IV} species: (i) formation of a corresponding chelate of (CH$_3$)$_3$Pt^{IV} with theophylline [7], (ii) existence of five-membered chelates with Pt^{IV} and 8-hydroxychinolines [8], (iii) unusual four-membered rings in chelates of Pt^{IV} with the model nucleobase 1-methylcytosine [9]. We therefore decided

to prepare and study the solution behaviour of a 9-methylguanine compound of Pt^{IV}.

Experimental

Preparations

The starting compound [(dien)Pt(9-MeGH)](ClO$_4$)$_2$ was prepared as previously described [10], 9-MeGH was obtained from Chemogen (Konstanz, FRG). 1.855 g (2.8 mmol) of [(dien)Pt(9-MeGH)](ClO$_4$)$_2$ were dissolved in 100 ml of 20% aqueous H$_2$O$_2$ and stirred for 5 h at 50 °C. The solution was brought by rotary evaporation almost to dryness, redissolved in 20 ml of water and allowed to evaporate slowly at 30 °C. Colorless columns of *mer,trans*-[(dien)Pt(OH)$_2$(9-MeGH)]-(ClO$_4$)$_2$·2H$_2$O were isolated in 73% yield. *Anal.* Calc. for C$_{10}$H$_{26}$N$_8$O$_{13}$Cl$_2$Pt: C, 16.40; H, 3.58; N, 15.30; Cl, 9.80. Found: C, 16.8; H, 3.7; N, 15.0; Cl, 9.59%.

Oxidation of [(dien)Pt(9-MeGH)](ClO$_4$)$_2$ with Cl$_2$/water was performed as follows. 66 mg (0.1 mmol) of [(dien)Pt(9-MeGH)](ClO$_4$)$_2$ were dissolved in 10 ml of dilute chlorine water and the solution kept for 90 min at 22 °C. After rotary evaporation to dryness, the residue was dissolved in 15 ml of MeOH. From the now yellow solution, dicroitic crystals (red along long axis, pale yellow across other axes) are obtained in 30% yield besides a colorless powder of unknown composition.

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*Author to whom correspondence should be addressed.

Anal. Calc. for $C_{30}H_{60}N_{24}O_{27}Cl_8Pt_3$ (dicroitic crystals): C, 17.51; H, 2.94; N, 16.33; Cl, 13.78. Found: C, 17.5; H, 2.85; N, 16.1; Cl, 13.38%.

Spectroscopy

^1H NMR spectra were recorded on Bruker AM 300 and Bruker AC 200 instruments. TSP ($\delta = 0.0$ ppm relative to TMS) was used as internal standard in D_2O, $N(CH_3)_4BF_4$ ($\delta = 3.189$ ppm relative to TMS) as internal standard in CD_3OD. The pK_a values determined graphically ($\Delta\delta$ versus pH*) were obtained by using uncorrected pH* values (Metrohm 6321 and standardized glass electrode). IR spectra (KBr pellets) were taken at a Perkin-Elmer 580 B instrument, and UV spectra on a Perkin-Elmer Lambda 15.

X-ray analysis

The X-ray measurements of the title compound were carried out on a Nicolet R3m/V diffractometer at 291(1) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The compound crystallizes in the orthorhombic system, $Pna2_1$, with $a = 14.103(4)$, $b = 9.412(4)$, $c = 18.020(9)$ Å, $V = 2392(2)\ Å^3$, $Z = 4$, D_{calc} (g cm^{-3}) $= 2.034$. The structure was refined to $R = 0.031$, $R_w = 0.037$ on the basis of 4012 unique observed diffractometer data of $F \geqslant 3.0\sigma(F)$. Positional parameters and the equivalent values of the anisotropic displacement parameters for the non-H atoms are given in Table 1. See also 'Supplementary material'.

Results and discussion

Crystal structure

Figure 1 gives a view of *mer,trans*-[Pt(dien)(OH)$_2$(9-MeGH-*N7*)](ClO$_4$)$_2$·2H$_2$O and Table 2 lists distances and angles. In the cation, the Pt^{IV} has a N$_4$O$_2$ coordination sphere, built by three nitrogens of the dien ligand, N7 of 9-methylguanine and two oxygens of hydroxo ligands. The coordination sphere deviates markedly from ideal octahedral geometry. While deviations due to the bite of the dien ligand are expected, e.g. 84–85° angles for N14–Pt–N17(11) angles and corresponding larger angles of 95–96° for N7–Pt–N17(11), deviations of the hydroxyl ligands (e.g. O1–Pt–O2 angle of 174.3(2)°) are remarkable. Pt–N and Pt–O distances are normal [9], as are geometries of the guanine nucleobase [11], the dien ligand [12] and the ClO$_4^-$ anions [13]. The dien ligand adopts a 'sting-ray' configuration [12]. The two halves of the purine ring form a slight angle (4.0(2)°) and the purine plane is at a 57° (av.) angle relative to the PtN$_4$ plane (Fig. 2). Hydrogen bonding interactions (Table 3 and Fig. 3) can be differentiated into four categories: (i) within the cation or between cations, (ii) between the cation and water

TABLE 1. Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^4$)

	x	y	z	U_{eq}[a]
Pt(1)	0.87333(1)	0.90160(2)	1.0(0)	283
Cl(1)	1.0042(2)	0.4164(2)	1.0324(2)	632
O(11)	1.0620(5)	0.5146(9)	1.008(1)	1725
O(12)	0.9159(7)	0.468(2)	1.0424(9)	1745
O(13)	1.0397(7)	0.307(2)	1.071(1)	2269
O(14)	0.980(2)	0.338(2)	0.968(1)	2658
Cl(2)	0.7508(4)	0.8435(4)	0.7459(2)	1278
O(21)	0.751(2)	0.702(1)	0.7387(7)	2165
O(22)	0.714(2)	0.902(2)	0.6847(8)	2854
O(23)	0.717(1)	0.912(2)	0.8074(7)	1844
O(24)	0.855(2)	0.855(4)	0.756(2)	2423
O(1)	0.9647(3)	0.9944(6)	0.9304(3)	382
O(2)	0.7884(4)	0.8206(5)	1.0773(3)	441
O(3)	0.8831(5)	1.158(1)	0.8141(5)	875
O(4)	0.8635(6)	0.6799(9)	1.1910(5)	961
N(11)	0.9810(4)	0.8258(7)	1.0633(3)	393
C(12)	1.0120(6)	0.943(1)	1.1148(5)	604
C(13)	0.9274(6)	1.0293(8)	1.1367(4)	510
N(14)	0.8845(5)	1.0774(8)	1.0633(5)	427
C(15)	0.7912(6)	1.1480(9)	1.0657(5)	468
C(16)	0.7593(5)	1.1519(8)	0.9847(4)	464
N(17)	0.7583(4)	1.0042(7)	0.9547(3)	378
N(1)	0.6508(4)	0.5151(7)	0.9070(4)	426
C(2)	0.6880(5)	0.4220(7)	0.8562(4)	388
N(2)	0.6296(4)	0.3232(9)	0.8298(5)	596
N(3)	0.7770(5)	0.4274(6)	0.8345(4)	410
C(4)	0.8253(5)	0.5351(7)	0.8653(4)	358
C(5)	0.7924(5)	0.6317(8)	0.9164(4)	344
C(6)	0.6971(5)	0.6259(8)	0.9399(4)	372
O(6)	0.6563(3)	0.7075(5)	0.9824(3)	482
N(7)	0.8670(3)	0.7266(6)	0.9324(4)	336
C(8)	0.9375(5)	0.6873(7)	0.8894(4)	425
N(9)	0.9156(4)	0.5732(7)	0.8473(4)	414
C(9)	0.9762(6)	0.511(1)	0.7911(6)	686

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i \cdot \mathbf{a}_j$.

of crystallization, (iii) between the cation and anions, (iv) between the anions and water. The three shortest ones, which belong to types (i) and (ii) are of particular interest: OH(2) forms a H bond with guanine–O(6) of 2.744(7) Å, thus giving rise to what has been termed an 'indirect chelate' [14] and at the same time forms a short (2.66(1) Å) H bond to the water molecule H$_2$O(4). Another short H bond of 2.660(7) Å is between N(1)H of guanine and an OH(1) group of a symmetry-related ($+x-\frac{1}{2}$, $-y+\frac{1}{2}+1$, $+z$) cation.

The hydrogen bonding network provides, in theory, the basis for the formation of several tautomeric structures of the title compound, two of which are depicted in Fig. 4. I: a tautomer with a guanine deprotonated at N(1) and the hydroxo group OH(1) converted to an aqua group. The internal ring angle C(2)–N(1)–C(6) of 126.5(6)°, which is close to that observed in neutral guanines [11], rules against any substantial contribution of this form to the overall structure, however. II: a second possibility, generated in a simultaneous H trans-
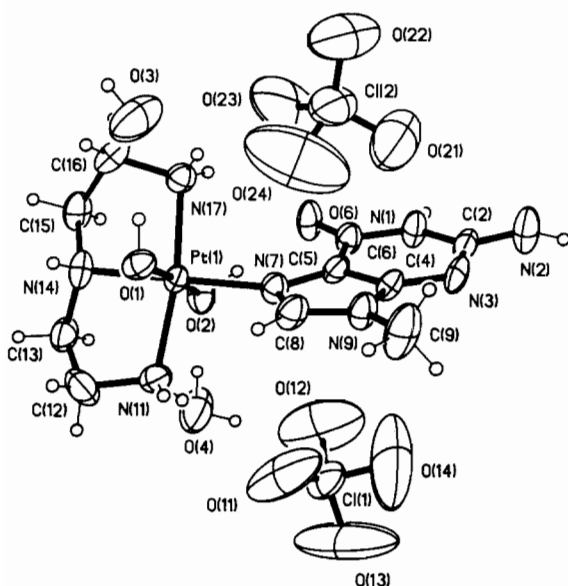
Fig. 1. General view (SHELXTL PLUS graphics) of the compound and atom numbering schemes. Protons were placed in geometrically calculated positions.
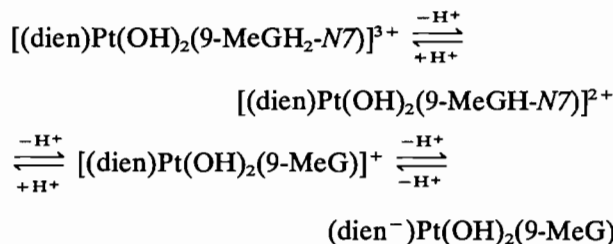
fer from OH(2) to O(6) and from $H_2O(4)$ to OH(2), would lead to a rare iminol tautomer of guanine. This possibility is considered less likely since it formally would generate a OH^- counterion.

Spectroscopic characterization

The position of the $\nu(CO)$ vibration of the guanine has occasionally been considered as being indicative of the coordination state of the nucleobase [15]. Specifically, any shift of this band to lower energy has been interpreted in terms of N7,O6 chelate formation. The IR spectrum of the title compound rules against such an interpretation. The highest absorption in the double-bond stretching region occurs at 1650(vs) cm^{-1} which is lower compared to both the free, neutral 9-MeGH (1690 cm^{-1}) and the [(dien)Pt^{II}(9-MeGH-N7)]$^{2+}$ precursor (1715; 1695 cm^{-1} [10]). Quite clearly, hydrogen bonding of O6 as observed in the crystal structure is sufficient to cause this shift which overrides the expected shift in opposite direction on coordination of the polarizing Pt^{IV} electrophile at N7.

In the ^{1}H NMR spectrum (D$_2$O, pD 5), the CH$_3$ resonance is observed at 3.80 ppm and H8 at 8.39 ppm with both resonances downfield from those of the dienPt^{II} precursor (3.70 and 8.12 ppm). $^3J(^{195}$Pt–^{1}H(8)) satellites of 12 Hz are clearly to be seen even at 200 MHz, in agreement with expectations [16] and are smaller in magnitude [17] as compared to the [(dien)Pt^{II}(9-MeGH-N7)]$^{2+}$ (19 Hz). Proton resonances due to the dien ligand form complicated multiplets centered around 2.8, 3.45 and 3.6 ppm [18]. On the basis of pD dependent spectra, pK_a values for the

following equilibria have been determined:

$$[(dien)Pt(OH)_2(9\text{-}MeGH_2\text{-}N7)]^{3+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}$$

$$[(dien)Pt(OH)_2(9\text{-}MeGH\text{-}N7)]^{2+}$$

$$\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [(dien)Pt(OH)_2(9\text{-}MeG)]^+ \underset{-H^+}{\overset{-H^+}{\rightleftharpoons}}$$

$$(dien^-)Pt(OH)_2(9\text{-}MeG)$$

They are p$K_{a1} \leqslant 1$, p$K_{a2} = 7.1$ and p$K_{a3} \simeq 9$. Protonation of the OH groups is expected to occur in strongly acidic medium but was not detected by our methods. The acid/base equilibrium involving protonation/deprotonation at the guanine N1 position was also studied by UV spectroscopy and confirmed the value determined by ^{1}H NMR. Expectedly, coordination of Pt^{IV} at N7 acidifies the N1 proton to a larger extent than does a Pt^{II} electrophile (pK_a c. 8–8.5 [19]).

Solution behaviour

mer,trans-[(dien)Pt(OH)$_2$(9-MeGH)]$^{2+}$ undergoes a spontaneous reduction to [(dien)Pt(9-MeGH)]$^{2+}$ when dissolved in H_2O or D_2O. Interestingly, reduction occurs considerable more slowly in D_2O as compared to deionized water. At 22 °C in D_2O, 10% is reduced within 70 days, but 30% in 3 days at 22 °C in H_2O. We assume that a catalytic impurity in H_2O is responsible for the observed difference.

Upon heating (D_2O, 80 °C), a second process takes place which is a *mer→fac* isomerization of the dien ligand (Fig. 5). This interpretation is based on the observed NMR changes of the dien resonances (and those of 9-MeGH) which, in the case of the related [(dien)Pt(OH)$_2$(1-MeC-N3)]$^{2+}$ system (1-MeC = 1-methylcytosine) unambiguously have been confirmed by X-ray analysis [20]. Thus the three dien multiplets of *mer,trans*-[(dien)Pt(OH)$_2$(9-MeGH)]$^{2+}$ are characteristically shifted to c. 2.9, 3.2 and 3.4 ppm upon isomerization. The isomerization process is slow, the half life being 7 days at 80 °C. Unlike *mer,trans*-[(dien)Pt(OH)$_2$(1-MeC-N3)]$^{2+}$, which on heating also undergoes dehydrogenation of the dien ligand to the tridentate Schiff base NH_2–CH_2–CH=N–CH_2–CH_2–NH_2 [20a], the methylguanine analogue does not seem to react in an analogous way.

In an attempt to substitute the *trans*-positioned hydroxo ligands by Cl$^-$ and H_2O, the title compound was treated with 2 equivalents of (i) DCl, (ii) NaCl and (iii) DNO$_3$ in D_2O at 22 °C. Solutions (ii) and (iii) are virtually unchanged after 24 days, whereas in solution (i) a new product has been formed (60%; H(8), 8.37 ppm; CH$_3$, 3.79 ppm) in this period (in addition to 5% of reduced Pt^{II} species) which, according to ^{1}H NMR (^{195}Pt satellites; dien pattern) is a Pt^{IV} complex

TABLE 2. Bond distances (Å), bond angles (°), least-squares planes and dihedral angles (°)

Pt(1)–O(1)	1.999(5)	N(14)–C(15)	1.48(1)
Pt(1)–O(2)	1.989(5)	C(15)–C(16)	1.53(1)
Pt(1)–N(11)	2.029(6)	C(16)–N(17)	1.49(1)
Pt(1)–N(14)	2.016(8)	N(1)–C(2)	1.37(1)
Pt(1)–N(17)	2.057(6)	N(1)–C(6)	1.366(9)
Pt(1)–N(7)	2.050(6)	C(2)–N(2)	1.33(1)
Cl(1)–O(11)	1.31(1)	C(2)–N(3)	1.32(1)
Cl(1)–O(12)	1.35(1)	N(3)–C(4)	1.341(9)
Cl(1)–O(13)	1.34(2)	C(4)–C(5)	1.38(1)
Cl(1)–O(14)	1.41(2)	C(4)–N(9)	1.362(9)
Cl(2)–O(21)	1.34(1)	C(5)–C(6)	1.410(9)
Cl(2)–O(22)	1.34(2)	C(5)–N(7)	1.410(9)
Cl(2)–O(23)	1.37(1)	C(6)–O(6)	1.227(9)
Cl(2)–O(24)	1.48(3)	N(7)–C(8)	1.314(9)
N(11)–C(12)	1.51(1)	C(8)–N(9)	1.35(1)
C(12)–C(13)	1.50(1)	N(9)–C(9)	1.45(1)
C(13)–N(14)	1.52(1)		

N(17)–Pt(1)–N(7)	96.1(2)	N(11)–C(12)–C(13)	109.2(7)
N(14)–Pt(1)–N(7)	177.3(3)	C(12)–C(13)–N(14)	104.4(7)
N(14)–Pt(1)–N(17)	84.3(3)	Pt(1)–N(14)–C(13)	106.2(5)
N(11)–Pt(1)–N(7)	94.8(2)	C(13)–N(14)–C(15)	117.6(7)
N(11)–Pt(1)–N(17)	168.1(3)	Pt(1)–N(14)–C(15)	108.4(5)
N(11)–Pt(1)–N(14)	84.9(3)	N(14)–C(15)–C(16)	104.2(7)
O(2)–Pt(1)–N(7)	94.7(2)	C(15)–C(16)–N(17)	109.0(6)
O(2)–Pt(1)–N(17)	89.0(2)	Pt(1)–N(17)–C(16)	106.7(4)
O(2)–Pt(1)–N(14)	88.0(3)	C(2)–N(1)–C(6)	126.5(6)
O(2)–Pt(1)–N(11)	85.5(2)	N(1)–C(2)–N(3)	122.6(7)
O(1)–Pt(1)–N(7)	90.4(2)	N(1)–C(2)–N(2)	116.7(7)
O(1)–Pt(1)–N(17)	93.1(2)	N(2)–C(2)–N(3)	120.8(7)
O(1)–Pt(1)–N(14)	86.9(3)	C(2)–N(3)–C(4)	113.0(6)
O(1)–Pt(1)–N(11)	91.3(2)	N(3)–C(4)–N(9)	125.1(6)
O(1)–Pt(1)–O(2)	174.3(2)	N(3)–C(4)–C(5)	127.3(7)
O(13)–Cl(1)–O(14)	96(1)	C(5)–C(4)–N(9)	107.5(6)
O(12)–Cl(1)–O(14)	94(1)	C(4)–C(5)–N(7)	107.7(6)
O(12)–Cl(1)–O(13)	123.8(9)	C(4)–C(5)–C(6)	119.8(7)
O(11)–Cl(1)–O(14)	104(1)	C(6)–C(5)–N(7)	132.4(7)
O(11)–Cl(1)–O(13)	119.0(6)	N(1)–C(6)–C(5)	110.8(6)
O(11)–Cl(1)–O(12)	111.4(7)	C(5)–C(6)–O(6)	127.6(6)
O(23)–Cl(2)–O(24)	102(1)	N(1)–C(6)–O(6)	121.6(6)
O(22)–Cl(2)–O(24)	118(1)	Pt(1)–N(7)–C(5)	131.5(4)
O(22)–Cl(2)–O(23)	110(1)	C(5)–N(7)–C(8)	105.4(6)
O(21)–Cl(2)–O(24)	94(1)	Pt(1)–N(7)–C(8)	122.9(5)
O(21)–Cl(2)–O(23)	123.4(8)	N(7)–C(8)–N(9)	112.5(6)
O(21)–Cl(2)–O(22)	109.5(9)	C(4)–N(9)–C(8)	106.8(6)
Pt(1)–H(2a)–O(2)	59.9(4)	C(8)–N(9)–C(9)	125.5(6)
Pt(1)–N(11)–C(12)	107.8(5)	C(4)–N(9)–C(9)	127.6(7)

No.	Plane through atoms	Equation of the plane (x along a; y in the plane ab; z along c*)	χ^2
1	N(1), C(2), N(3), C(4), C(5), C(6)	−0.270x + 0.605y − 0.749z = −11.78 Å	5.97
2	C(4), C(5), N(7), C(8), N(9)	−0.335x + 0.600y − 0.726z = −12.18 Å	14.57
3	Pt(1), N(11), C(12), C(13), N(14)	0.656x + 0.483y − 0.580z = 1.72 Å	3677.8
4	Pt(1), N(14), C(15), C(16), N(17)	0.633x + 0.477y − 0.610z = 0.84 Å	3898.4
5	Pt(1), N(7), N(11), N(14), N(17)	0.631x + 0.439y − 0.646z = 0.23 Å	498.1

Dihedral angles
1.2: 4.0(2)°; 1.3: 56.6(2)°; 1.4: 54.9(2)°; 1.5: 55.0(2)°; 2.3: 60.5(2)°; 2.4: 58.8(2)°; 2.5: 58.9(2)°; 3.4: 2.2(1)°; 3.5: 5.1(2)°; 4.5: 3.4(2)°.
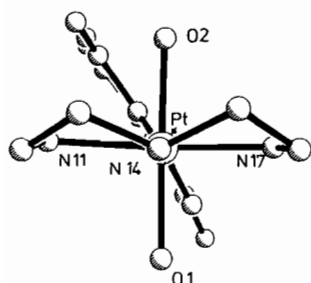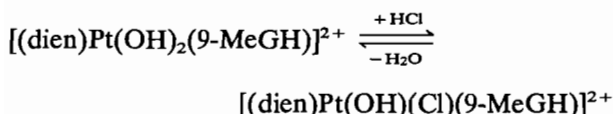
Fig. 2. Cation viewed along the N14–Pt–N7 vector indicating the orientation of the guanine nucleobase relative to the PtN$_4$ plane.

with dien in a *mer* orientation. We tentatively assign the new product to *mer*-[(dien)Pt(OH)(Cl)(9-MeGH-*N7*)]$^{2+}$, formed according to

$$[(dien)Pt(OH)_2(9\text{-MeGH})]^{2+} \xrightleftharpoons[-H_2O]{+HCl}$$

$$[(dien)Pt(OH)(Cl)(9\text{-MeGH})]^{2+}$$

and consistent with the slight rise in pD observed with time. Upon subsequent heating (12 days, 50 °C), a solution of (i) shows the formation of two additional guanine H8 resonances (8.50 and 8.54 ppm) of equal intensities and signs of ^{195}Pt coupling (Fig. 6). We can safely exclude the possibility that the two new resonances actually are a doublet. In the spectrum, no corresponding second doublet is detected and any ligand change, e.g. demethylation at N9, should not lead to a H8 doublet either because of rapid H→D exchange at N9. There are no indications for any *mer*→*fac* isomerization of

the dien ligand. We cannot, at present, safely assign the two new resonances. However, it appears that they are Pt^{IV} species containing neutral 9-MeGH ligands which, on the basis of their chemical shifts, should be binding in a bidentate fashion rather than via N7 alone. Whether the new resonances are due to a dinuclear, singly 9-MeGH bridged species as reported for *cis*-[(NH$_3$)$_2$Pt^{II}(9-EtGH)(H$_2$O)]$^{2+}$ [21], or due to two N7,O6 chelates differing in the sixth ligand (Cl or OH), is unclear. Alternatively, a cyclic structure as observed in a Cu inosine compound [22], appears possible as well.

When *mer,trans*-[(dien)Pt(OH)$_2$(9-MeGH)]$^{2+}$ is dissolved in CD$_3$OD (H8, 8.37 ppm; CH$_3$, 3.82 ppm) and kept at 22 °C, a new product is formed in 70% yield within 24 h with H8 downfield (8.50 ppm) and exhibiting ^{195}Pt satellites of 11.2 Hz, which indicates a Pt^{IV} oxidation state of the new species. The dien resonances are consistent with a *mer* orientation. It is tempting to speculate on the nature of this product as a N7,O6 chelate, but we have been unable as yet to isolate it.

Cl$_2$ oxidation of [dienPt^{II}(9-MeGH)]$^{2+}$

Treatment of [dienPt^{II}(9-MeGH-*N7*)]$^{2+}$ with chlorine water yielded an intensely yellow product which, from ^{1}H NMR spectroscopy (e.g. H8, 8.37 ppm with ^3J(^{195}Pt–^{1}H) = 13 Hz; CH$_3$, 3.79 ppm), proved to be a Pt^{IV} complex. The dien resonance pattern did neither correspond to *mer*- nor *fac*-arrangement and we suspect that partial chlorination of the dien ligand may have occurred as well. Attempts to recrystallize the product

TABLE 3. Possible hydrogen bonds

Donor…acceptor	H…acceptor	Donor–H…acceptor
O(1)…O(3)(0)	H(1a)…O(3)(0)	O(1)–H(1a)…O(3)(0)
2.85(1)	1.95(1)	178.5(6)
O(2)…O(6)(0)	H(2a)…O(6)(0)	O(2)–H(2a)…O(6)(0)
2.744(7)	1.845(7)	178.6(6)
O(4)…O(2)(0)	H(4a)…O(2)(0)	O(4)–H(4a)…O(2)(0)
2.66(1)	1.76(1)	179(1)
N(17)…O(23)(0)	H(17a)…O(23)(0)	N(17)–H(17a)…O(23)(0)
2.85(1)	2.08(1)	143.9(7)
O(3)…N(3)(1)	H(3a)…N(3)(1)	O(3)–H(3a)…N(3)(1)
2.97(1)	2.07(1)	178(1)
O(4)…O(22)(2)	H(4b)…O(22)(2)	O(4)–H(4b)…O(22)(2)
2.83(1)	1.93(1)	175(1)
N(11)…O(6)(3)	H(11b)…O(6)(3)	N(11)–H(11b)…O(6)(3)
2.886(7)	2.011(7)	163.9(6)
N(17)…O(11)(5)	H(17b)…O(11)(5)	N(17)–H(17b)…O(11)(5)
2.93(1)	2.15(1)	144.6(7)
N(1)…O(1)(5)	H(1b)…O(1)(5)	N(1)–H(1b)…O(1)(5)
2.660(7)	1.780(7)	165.1(7)
N(2)…O(4)(6)	H(2c)…O(4)(6)	N(2)–H(2c)…O(4)(6)
2.84(1)	2.05(1)	146.4(7)

Symmetry codes: (0) x, y, z; (1) $+x, +y+1, +z$; (2) $-x+\frac{1}{2}+1, +y-\frac{1}{2}, +z+\frac{1}{2}$; (3) $+x+\frac{1}{2}, -y+\frac{1}{2}+1, +z$; (4) $x+\frac{1}{2}+1, +y+\frac{1}{2}, +z+\frac{1}{2}$; (5) $+x-\frac{1}{2}, -y+\frac{1}{2}+1, +z$; (6) $-x+\frac{1}{2}+1, +y-\frac{1}{2}, +z-\frac{1}{2}$.
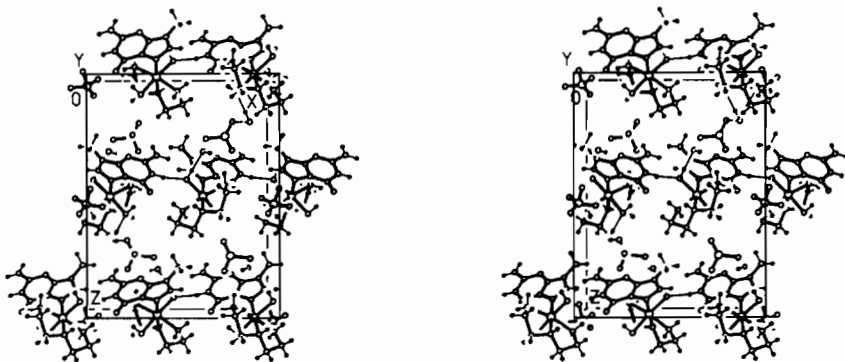
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Fig. 3. Spectroscopic view (SHELXTL PLUS graphics) of the unit cell.
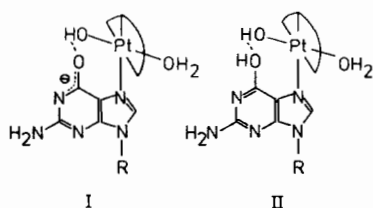

Fig. 4. Two feasible tautomers (I) and (II) of the title compound derived via H transfer along H bonds as observed in the solid state of the title compound.
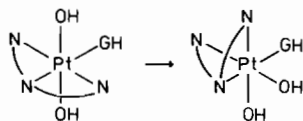

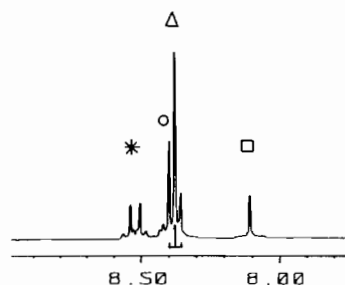Fig. 5. Schematic representation of $mer \rightarrow fac$ isomerization of the dien ligand upon heating.

Fig. 6. ^{1}H NMR spectrum (300 MHz, D$_2$O, H(8)-guanine region only) of the title compound plus 2 equiv. of DCl after 24 days at 22 °C and subsequently 12 days at 50 °C. Identified species are as follows: O, starting Pt^{IV} compound; △, mixed OH,Cl Pt^{IV} compound; □, reduced Pt^{II} compound. Unidentified new products (*) occur furthest downfield.

from water failed and resulted in reduction to the Pt^{II} starting material. Recrystallization from MeOH gave, among others, dicroitic crystals (deep red along long axis, pale yellow across short axes). The ^{1}H NMR spectrum and elemental analysis data are consistent with a mixed-valence state compound which contains Pt^{IV} and Pt^{II} in a 1:2 ratio. A feasible composition would be a μ-Cl bridged trinuclear complex with a

central, $mer,trans$-[(dien)PtCl$_2$(9-MeGH)]$^{2+}$ unit and two capping [(dien)Pt(9-MeGH)]$^{2+}$ entities.

Conclusions

Our attempts to unambiguously prove the formation of a guanine N7,O6 chelate with Pt^{IV} were not successful. The working hypothesis that, similar as in the case of $trans,trans,trans$-[Pt(NH$_3$)$_2$(OH)$_2$(1-MeC-$N3$)$_2$]$^{2+}$ [9], a condensation between an axial H$_2$O ligand of Pt and O6 of a cis-oriented guanine or between an axial OH and a 6-OH of guanine (either as reactive iminol tautomer or as a protonated guanine ligand) might result in chelation, failed. The obvious route, condensation of the deprotonated guanine ring with an axial H$_2$O ligand, which should lead to the chelate of the guanine anion, appears impossible based on pK_a considerations. We feel that our findings do not necessarily disprove our idea but that it may be necessary to extend the work to ligand systems other than dien and/or to apply strictly non-aqueous solvents. It is noteworthy in this respect that in a related system (Ir^{III}, 9-MeGH) strong indications for an involvement of N7 and O6 in metal binding of the neutral guanine exist, when CH$_2$Cl$_2$ is applied as the solvent [23].

Supplementary material

Details of the data collection, structure solution, atomic coordinates and equivalent isotropic or isotropic displacement parameters and a listing of observed and calculated structure factors can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, under CSD 55629 on request. Requests should be accompanied by the complete literature citation.

Acknowledgements

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