Bis(9-ethylguaninium) and Bis(9-ethylguanine) Complexes of Pt(II): Preparation and Crystal Structures of *cis*-$[Cl_2Pt(9\text{-}EtGH_2)_2]Cl_2 \cdot 2H_2O$ and *cis*-$[(pra)_2Pt(9\text{-}EtGH)_2](NO_3)_2$ (pra = n-propylamine)

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Abstract

The structures of two Pt(II) complexes *cis*-$[Cl_2Pt(9\text{-}EtGH_2)_2]Cl_2 \cdot 2H_2O$ (2) and *cis*-$[(pra)_2Pt(9\text{-}EtGH)_2](NO_3)_2$ (3) with 9-$EtGH_2$ = 9-ethylguaninium cation, 9-EtGH = neutral 9-ethylguanine and pra = n-propylamine, are reported. Pt binding in both compounds is through N7 of the purine rings which in the case of 2 are protonated at N3. The guanines adopt head–tail orientations both in 2 and 3. The compounds crystallize in the space group $P2_1/c$ with the following cell dimensions: a = 14.214(3) (2), 7.990(4) (3), b = 12.197(3) (2), 38.292(6) (3), c = 15.525(3) (2), 10.271(4) (3) Å, β = 114.59(3) (2), 103.67(5)° (3), Z = 4.

Introduction

Among the adducts of the antitumor agent *cis*-$(NH_3)_2PtCl_2$ (*cis*-DDP, cisplatin) with DNA, the intrastrand cross-link between two guanines is the most frequent one, both *in vitro* and *in vivo* [1]. Based on structural studies of models of this cross-link [2–6] and in particular of those having the two purine bases in the proper head-to-head arrangement [3–6], it is believed that the major consequence of this cross-link for the DNA structure is a kink. Molecular mechanics calculations support this view [7].

Bis(guanine) complexes of *cis*-DDP analogs, containing amine ligands other than NH_3, have occasionally been studied, primarily with regard to the effect of bulky amine substituents on the rate of rotation of the purine bases about the Pt–N(7) bond [8–10] and isomer (head–tail versus head–head) stability [11]. In some cases crystal structure analyses of such compounds are available [12–14], all of which show the two bases arranged head-to-tail. The same is true for related complexes of Pt(IV) [15]. Considering the possible relationship between the bulk of the amine ligands, hence DNA binding properties of the Pt compound, and antitumor activity [16], both additional DNA binding studies with *cis*-DDP analogs and model studies of the expected adducts seem desirable.

We herewith report on the preparation and crystal structure analyses of two complexes of 9-ethylguanine (9-EtGH) and 9-ethylguaninium (9-$EtGH_2$), respectively, *cis*-$[(pra)_2Pt(9\text{-}EtGH)_2](NO_3)_2$ (pra = n-propylamine) and *cis*-$[Cl_2Pt(9\text{-}EtGH_2)_2]Cl_2 \cdot 2H_2O$. The latter compound was prepared with the aim of having a suitable starting material for the preparation of any bis(amine) complex *cis*-$[a_2Pt(9\text{-}EtGH)_2]^{2+}$ without prior preparation of *cis*-a_2PtCl_2.

Experimental

Preparations

K_2PtCl_4 (Degussa) and 9-ethylguanine (Chemogen, Konstanz) were obtained commercially, *cis*-$(pra)_2PtCl_2$ (pra = propan-1-amine) was prepared as described [17].

Crude $PtCl_2(9\text{-}EtGH)_2$ aq (1) was obtained as a white to slightly yellow powder by stirring a suspension of K_2PtCl_4 and 9-EtGH (1:1 or 1:2) in water

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(40 °C, 1 day or 75 °C, 1.5 h). A total of 100 mg of **1** was treated with 9 ml of 2.5 N HCl, filtered from undissolved residue, and the yellow solution allowed to slowly evaporate at room temperature. After 6 days, 48 mg of yellow, transparent cubes of *cis*-$[Cl_2Pt(9\text{-}EtGH_2)_2]Cl_2 \cdot 2H_2O$ (**2**) were filtered off and dried in air. Crystallization of **2** occasionally proved difficult, leading to glassy materials which, however, were identical with crystalline **2** based on the IR spectra. *Anal.* Calc. for $C_{14}H_{24}N_{10}O_4Cl_4Pt$: C, 22.93; H, 3.31; N, 19.10. Found: C, 22.78; H, 3.18; N, 18.90%.

cis-$[(pra)_2Pt(9\text{-}EtGH)_2](NO_3)_2$ (**3**) was prepared via *cis*-$[(pra)_2Pt(H_2O)_2](NO_3)_2$ in analogy to the corresponding diamine complex [6] and recrystallized from water. *Anal.* Calc. for $C_{20}H_{36}N_{14}O_8Pt$: C, 30.18; H, 4.57; N, 24.65. Found: C, 30.08; H, 4.59; N, 24.79%.

Instruments

IR spectra were recorded on Perkin-Elmer 577 and 580 spectrometers, ^1H NMR spectra (D_2O, DMF-d_7) on Bruker AM 300 and Jeol JNM-GX 270 spectrometers as previously described [18].

Crystallography

The X-ray measurements were carried out on a Philips PW-100 single-crystal diffractometer (room temperature, Mo Kα radiation, λ = 0.71069 Å). Crystal and structure determination data are summarized in Table 1. Lp and in a later stage an empirical absorption correction [19] were applied. The positions of Pt were obtained from three-dimensional Patterson maps. Subsequent ΔF syntheses gave the positions of the non-hydrogen atoms. H atoms were ignored. Atoms were refined with anisotropic thermal parameters. Final atomic coordinates are given in Tables 2 and 3. For the anisotropic thermal parameters see 'Supplementary Material'. The highest peaks in the final difference maps were 2.0 (**2**, 1.5 Å away from Pt) and 2.1 (**3**, 0.9 Å away from Pt) $Å^{-3}$. Complex scattering factors for neutral atoms were taken from ref. 20. For the calculations the SHELX program package was used [21].

Results and Discussion

Formation and IR Spectra

Reactions of K_2PtCl_4 with purine nucleosides have previously been described [22]. Among others, compounds of composition *cis*- and *trans*-$PtCl_2(pu)_2$ (pu = inosine and/or guanosine) have been isolated. For the product **1**, which was obtained on reaction of K_2PtCl_4 with 9-ethylguanine in moderately acidic solution and which analyzed approximately as $Pt(9\text{-}EtGH)_2Cl_2 \cdot (H_2O)_x$, we assumed a *cis* geometry, as later verified for the HCl adduct **2**. The IR spectrum of **1** indicated the presence of N7 platinated 9-EtGH (e.g. strong bands at 1695, 1635 and 1590 cm^{-1}) and a Pt–Cl entity (ν Pt–Cl at 330 cm^{-1}). **1** dissolves in 2–5 N HCl to form a yellow solution from which, upon slow evaporation, yellow crystals of *cis*-$[Cl_2Pt(9\text{-}EtGH_2)_2]Cl_2$ (**2**) are isolated. The most prominent differences in the IR spectra of **1** and **2** are in the double bond stretching region (**2**:

TABLE 1. Crystallographic data

	2	3
Formula	$C_{14}H_{24}N_{10}O_4Cl_4Pt$	$C_{20}H_{36}N_{14}O_8Pt$
Formula weight	733.37	795.79
Space group	$P2_1/c$	$P2_1/c$
a (Å)	14.214(3)	7.990(4)
b (Å)	12.197(3)	38.292(6)
c (Å)	15.525(3)	10.271(4)
β (°)	114.59(3)	103.67(5)
V ($Å^3$)	2447.4	3050.4
Z	4	4
D_{calc} (g cm^{-3})	1.990	1.733
Crystal size (mm)	0.2, 0.2, 0.3	0.1, 0.1, 0.2
μ (cm^{-1})	59	45
θ range (°)	2–25	2–25
No. unique reflections	4317	5383
No. reflections used in calculations	4041 $F_o > 2\sigma F_o$	4625 $F_o > 3\sigma F_o$
No. parameters	289	388
R	0.060	0.086
$R_w(F)$	0.063	0.080
	$w^{-1} = \sigma^2(F) + 0.0007F^2$	$w^{-1} = \sigma^2(F) + 0.0003F^2$

TABLE 2. Atomic coordinates and equivalent isotropic temperature factors ($Å^2$) for **2**

Atom	*x*	*y*	*z*	*U*
Pt1	0.2640(1)	0.3236(1)	0.7444(1)	0.040(1)
Cl1	0.1452(2)	0.3815(2)	0.5994(2)	0.067(1)
Cl2	0.3781(2)	0.2769(3)	0.6830(2)	0.072(1)
N1a	0.2366(5)	0.4306(6)	1.0524(5)	0.038(3)
C2a	0.1462(7)	0.4100(7)	1.0561(6)	0.039(3)
N2a′	0.1325(6)	0.4272(7)	1.1362(5)	0.048(3)
N3a	0.0666(5)	0.3717(6)	0.9792(5)	0.035(2)
C4a	0.0845(7)	0.3557(8)	0.9022(6)	0.040(3)
C5a	0.1739(7)	0.3757(8)	0.8939(6)	0.042(3)
C6a	0.2592(7)	0.4254(7)	0.9735(6)	0.039(3)
O6a′	0.3424(5)	0.4568(6)	0.9782(5)	0.054(3)
N7a	0.1620(6)	0.3526(7)	0.8019(5)	0.046(3)
C8a	0.0638(8)	0.3136(8)	0.7567(5)	0.050(4)
N9a	0.0135(6)	0.3189(7)	0.8161(5)	0.046(3)
C9a′	−0.0911(8)	0.2750(11)	0.7924(8)	0.062(4)
C9a″	−0.0819(13)	0.1514(15)	0.8177(13)	0.102(9)
N1b	0.3075(6)	0.0236(6)	0.9779(5)	0.044(3)
C2b	0.3984(7)	0.0190(8)	1.0555(6)	0.040(3)
N2b′	0.4160(7)	−0.0586(6)	1.1198(5)	0.049(3)
N3b	0.4740(5)	0.0917(6)	1.0666(5)	0.037(3)
C4b	0.4518(7)	0.1729(7)	1.0003(7)	0.040(3)
C5b	0.3616(7)	0.1787(7)	0.9207(6)	0.034(3)
C6b	0.2791(7)	0.1027(8)	0.9050(6)	0.041(4)
O6b′	0.1934(5)	0.0983(6)	0.8390(4)	0.051(2)
N7b	0.3679(6)	0.2677(6)	0.8693(5)	0.041(3)
C8b	0.4613(8)	0.3119(8)	0.9179(7)	0.048(4)
N9b	0.5140(6)	0.2564(6)	0.9984(6)	0.045(3)
C9b′	0.6167(9)	0.2854(11)	1.0745(8)	0.062(5)
C9b″	0.5986(11)	0.3581(12)	1.1468(9)	0.078(6)
Cl3	0.3495(2)	0.9488(2)	0.7488(2)	0.070(1)
Cl4	0.1017(2)	0.6580(2)	0.9477(2)	0.050(1)
O10	0.3117(8)	0.7453(8)	0.1088(6)	0.098(4)
O11	0.1386(7)	0.5886(7)	0.4622(9)	0.099(6)

TABLE 3. Atomic coordinates and equivalent isotropic temperature factors ($Å^2$) for **3**

Atom	*x*	*y*	*z*	*U*
Pt1	0.0886(1)	0.3909(1)	0.9327(1)	0.048(1)
N10	−0.0409(19)	0.3689(3)	1.0628(13)	0.066(6)
C10	−0.2379(28)	0.3700(6)	1.0123(22)	0.093(10)
C11	−0.3197(42)	0.3525(10)	1.1149(28)	0.156(18)
C12	−0.2827(52)	0.3165(12)	1.1340(34)	0.219(25)
N11	0.1282(17)	0.4358(3)	1.0409(12)	0.053(5)
C13	0.3216(26)	0.4413(5)	1.1100(22)	0.086(9)
C14	0.3508(34)	0.4760(6)	1.1828(27)	0.117(12)
C15	0.3151(35)	0.5087(5)	1.0882(31)	0.120(14)
N1A	0.1527(16)	0.4980(3)	0.6571(11)	0.049(4)
C2A	0.2785(19)	0.4960(4)	0.5864(15)	0.047(5)
N2A′	0.2954(18)	0.5245(3)	0.5142(13)	0.060(5)
N3A	0.3752(16)	0.4674(3)	0.5867(11)	0.048(4)
C4A	0.3388(19)	0.4423(4)	0.6652(14)	0.051(5)
C5A	0.2190(18)	0.4414(3)	0.7420(12)	0.039(4)
C6A	0.1179(18)	0.4734(4)	0.7453(14)	0.044(5)
O6A′	0.0100(16)	0.4779(3)	0.8102(13)	0.081(5)
N7A	0.2265(16)	0.4096(3)	0.8050(11)	0.045(4)
C8A	0.3433(21)	0.3894(5)	0.7642(15)	0.061(6)
N9A	0.4168(16)	0.4089(4)	0.6794(11)	0.055(5)
C9A′	0.5586(23)	0.3973(4)	0.6233(18)	0.069(7)
C9A″	0.4870(32)	0.3902(6)	0.4657(21)	0.106(11)
N1B	0.2513(18)	0.2658(4)	0.9718(13)	0.065(5)
C2B	0.2115(22)	0.2459(3)	0.8528(14)	0.050(5)
N2B′	0.2739(19)	0.2134(3)	0.8574(14)	0.065(6)
N3B	0.1187(17)	0.2589(3)	0.7393(12)	0.059(5)
C4B	0.0733(19)	0.2930(3)	0.7474(14)	0.044(5)
C5B	0.1062(20)	0.3133(5)	0.8574(13)	0.060(6)
C6B	0.1985(22)	0.3000(4)	0.9842(16)	0.055(6)
O6B′	0.2331(18)	0.3150(2)	1.0928(11)	0.075(5)
N7B	0.0466(16)	0.3470(3)	0.8229(11)	0.050(4)
C8B	−0.0267(21)	0.3458(4)	0.6880(15)	0.058(6)
N9B	−0.0127(17)	0.3132(3)	0.6426(12)	0.049(4)
C9B′	−0.0767(24)	0.3023(4)	0.4966(14)	0.061(6)
C9B″	−0.2442(39)	0.2846(10)	0.4804(24)	0.182(20)
N20	0.0187(19)	0.9111(4)	0.1201(15)	0.066(6)
O20	0.0676(18)	0.9166(4)	0.0159(12)	0.096(6)
O21	−0.0447(22)	0.8820(3)	0.1379(15)	0.097(7)
O22	0.0323(20)	0.9343(3)	0.2078(13)	0.091(6)
N30	0.4936(27)	0.2992(4)	0.7046(18)	0.083(8)
O30	0.3884(22)	0.3167(4)	0.6199(16)	0.101(7)
O31	0.4994(19)	0.2680(3)	0.6918(14)	0.091(6)
O32	0.5648(32)	0.3144(4)	0.8018(19)	0.178(12)

1740s, 1690vs cm^{-1}), and in the 2500–3000 cm^{-1} range. The presence of a broad, intense band centered at 2700 cm^{-1} in the spectrum of **2** is the result of strong hydrogen bonding [23].

X-ray Structures of 2 and 3

Figure 1 depicts the molecular cation of *cis*-$[Cl_2Pt(9\text{-}EtGH_2)_2]Cl_2\cdot 2H_2O$ (**2**) and Table 4 lists selected distances and angles of the cation. Pt binding is through N7 of the protonated guanine ligands, which are arranged head–tail. Dihedral angles of the guaninium rings with the Pt coordination plane are rather small, 43° and 63°, respectively. The angle between the two nucleobase planes (58°) is of similar magnitude as in other bis(guanine) compounds of *cis*-$a_2Pt(II)$ with head–tail arranged bases [2, 12, 13] except in compounds containing the bulky *N,N,N′,N*-tetramethylethylenediamine chelate [14]. There, base/base angles of 81–88° are observed as a consequence of the roughly perpendicular orientation of the bases with respect to the Pt plane. These angles are actually bigger than in *cis*-$a_2Pt(II)$ complexes with the two bases in head–head orientation (cf. 68–78° for base/base angles in *cis*-$[(NH_3)_2Pt(9\text{-}EtGH)_2]^{2+}$ [6] or 76–87° in *cis*-$\{(NH_3)_2Pt[d(pGpG)]\}$ [5]). Thus, despite the cationic nature of the two ligands and the absence of intracomplexes hydrogen bonding involvement of O(6) of 9-$EtGH_2$, believed to be crucial in rotamer preference of bis(amine)bis(purine) Pt(II) complexes [11], intramolecular base stacking is surprisingly efficient in **2**. The quite substantial deviation of Pt from one of the

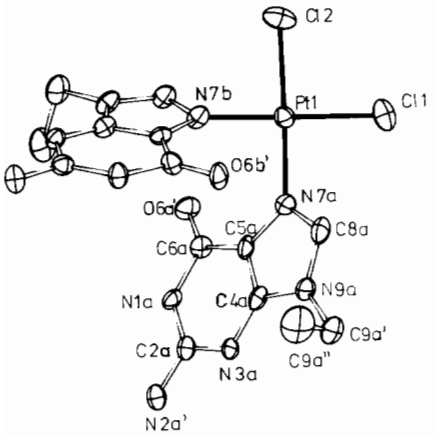

Fig. 1. Molecular cation *cis*-$[Cl_2Pt(9\text{-}EtGH_2)_2]^{2+}$ (**2**).

TABLE 4. Selected distances (Å) and angles (°) of **2**

(a) Pt coordination sphere			
Pt1–Cl1	2.29(1)	Cl1–Pt1–Cl2	91.6(1)
Pt1–Cl2	2.27(1)	Cl1–Pt1–N7a	90.5(2)
Pt1–N7a	2.03(1)	Cl1–Pt1–N7b	178.0(3)
Pt1–N7b	2.01(1)	Cl2–Pt1–N7a	175.4(3)
		Cl2–Pt1–N7b	87.3(3)
		N7a–Pt1–N7b	90.4(4)
(b) Guanine ligands			
N1a–C2a	1.33(2)	N1b–C2b	1.35(1)
C2a–N2a	1.35(2)	C2b–N2b	1.32(1)
C2a–N3a	1.34(2)	C2b–N3b	1.35(1)
N3a–C4a	1.34(2)	N3b–C4b	1.37(1)
C4a–C5a	1.35(2)	C4b–C5b	1.36(1)
C4a–N9a	1.37(1)	C4b–N9b	1.36(1)
C5a–C6a	1.46(1)	C5b–C6b	1.43(1)
C5a–N7a	1.40(1)	C5b–N7b	1.37(1)
C6a–O6a'	1.22(1)	C6b–O6b'	1.22(1)
C6a–N1a	1.39(2)	C6b–N1b	1.41(1)
N7a–C8a	1.36(1)	N7b–C8b	1.34(1)
C8a–N9a	1.38(2)	C8b–N9b	1.34(1)
N9a–C9a'	1.48(2)	N9b–C9b'	1.49(1)
C9a'–C9a''	1.55(2)	C9b'–C9b''	1.54(2)

two 9-$EtGH_2$ planes (0.48 Å from ring *a*) contributes to this phenomenon.

While the acidic proton of the 9-ethylguaninium cation has not been located crystallographically, we assume it to be N3. The arguments are as follows. (i) The internal C2–N3–C4 ring angles (*a*, 116.3°; *b*, 117.3°) are sufficiently large to assume that protonation has taken place at this site. In neutral 9-EtGH (111.5, 111.9°) [24] and N7 platinated neutral 9-EtGH (111.5–112.6°) [6b] this angle as expected [25] is smaller. (ii) Without a proton at the N3 position, the close proximity between N3 and ionic Cl^- (ring *a*, 3.07 Å; ring *b*, 2.96 Å) does not make sense. (iii) None of the short contacts of the water molecules (to N1 or N2, Table 5) can be

TABLE 5. Close contacts (<3.4 Å) in **2**

N2b'–O10[1]	2.78	C2b–N2b'–O10[1]	130
Cl4–O10[2]	3.18		
N2a'–Cl4[3]	3.20	C2a–N2a'–Cl4[3]	96
N3a–Cl4[3]	3.07	C2a–N3a–Cl4[3]	102
N2b'–Cl3[4]	3.38	C2b–N2b'–Cl3[4]	90
N3b–Cl3[4]	2.96	C2b–N3b–Cl3[4]	109
N1a–Cl2[5]	3.34	C2a–N1a–Cl2[5]	100
N2a'–O6b'[5]	2.92	C2a–N2a'–O6b'[5]	152
N1b–O11[5]	2.69	C2b–N1b–O11[5]	123
O10–O11[6]	3.27		
N1a–Cl3[7]	3.16	C2a–N1a–Cl3[7]	99
N2a'–Cl3[7]	3.22	C2a–N2a'–Cl3[7]	96
Cl3–O10[7]	3.11		
Cl4–O11[7]	3.13		

Symmetry operations: [1]: $x, -1+y, 1+z$; [2]: $x, y, 1+z$; [3]: $-x, 1-y, 2-z$; [4]: $1-x, 1-y, 2-z$; [5]: $x, 0.5-y, 0.5+z$; [6]: $x, 1.5-y, -0.5+z$; [7]: $x, 1.5-y, 0.5+z$.

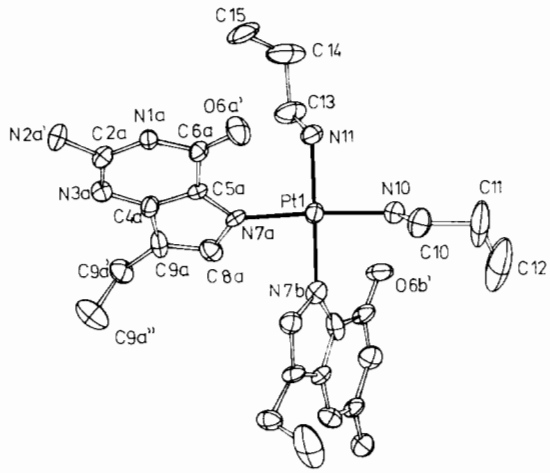

Fig. 2. Molecular cation *cis*-$[(pra)_2Pt(9\text{-}EtGH)_2]^{2+}$ (**3**).

water molecules (to N1 or N2, Table 5) can be attributed to a H_3O^+ entity. The only other reasonable site of protonation, O6, is also unlikely: C6–O6 distances are not indicative of protonation and the only intermolecular hydrogen bonding interaction of an O6 oxygen – with a NH_2(2) group – is not either. (iv) In a related complex described by Terzis and Mentzafos [26], $PtCl_3(9\text{-}MeGH_2)$, the protonation site appears to be N3 as well. There, the internal ring angle at N3 is 116°. (v) Finally, it also fits the picture that N7,N1 diplatinated guanine accepts a third metal electrophile – Pt(II) [18] or Ag(I) [27] – at N3 rather than O6.

In Fig. 2 the molecular cation of *cis*-$[(pra)_2Pt(9\text{-}EtGH)_2](NO_3)_2$ (**3**) is shown. Structural details are listed in Table 6 (selected distances, angles) and Table 7 (close contacts). As with **2**, Pt binding is through N7, but the heterocyclic rings are neutral.

TABLE 6. Selected distances (Å) and angles (°) of **3**

(a) Pt coordination sphere			
Pt1–N10	2.05(2)	N10–Pt1–N11	91.6(6)
Pt1–N11	2.03(1)	N10–Pt1–N7a	176.1(5)
Pt1–N7a	2.03(1)	N10–Pt1–N7b	88.9(6)
Pt1–N7b	2.01(1)	N11–Pt1–N7a	91.0(5)
		N11–Pt1–N7b	178.9(5)
		N7a–Pt1–N7b	88.6(5)
(b) Amine ligands			
N10–C10	1.54(3)		
C10–C11	1.52(4)		
C11–C12	1.41(6)		
N11–C13	1.56(2)		
C13–C14	1.52(3)		
C14–C15	1.57(4)		
(c) Guanine ligands			
N1a–C2a	1.37(2)	N1b–C2b	1.41(2)
C2a–N2a′	1.34(2)	C2b–N2b′	1.34(2)
C2a–N3a	1.34(2)	C2b–N3b	1.32(2)
N3a–C4a	1.33(2)	N3b–C4b	1.36(2)
C4a–C5a	1.38(2)	C4b–C5b	1.35(2)
C5a–C6a	1.47(2)	C5b–C6b	1.43(2)
C6a–O6a′	1.22(2)	C6b–O6b′	1.23(2)
C6a–N1a	1.38(2)	C6b–N1b	1.39(2)
C5a–N7a	1.37(2)	C5b–N7b	1.39(2)
N7a–C8a	1.35(2)	N7b–C8b	1.37(2)
C8a–N9a	1.38(2)	C8b–N9b	1.35(2)
N9a–C9a′	1.46(3)	N9b–C9b′	1.52(2)
C9a′–C9a″	1.61(3)	C9b′–C9b″	1.47(4)

TABLE 7. Close contacts (<3.4 Å) in **3**

N11–O6a′	2.84	Pt1–N11–O6a′	93
N2a′–N3a[1]	3.06	C2a–N2a′–N3a[1]	118
N10–O21[2]	3.03	Pt1–N10–O21[2]	124
N11–O22[2]	3.14	Pt1–N11–O22[2]	113
N2b′–O6b′[3]	2.87	C2b–N2b′–O6b′[3]	111
N1b–O31[4]	2.93	C2b–N1b–O31[4]	114
N2b′–O30[4]	3.33	C2b–N2b′–O30[4]	112
N1a–O22[5]	2.86	C2a–N1a–O22[5]	118
N2a′–O20[5]	2.90	C2a–N2a′–O20[5]	119

Symmetry operations: [1]: $1-x, 1-y, 1-z$; [2]: $-x, -0.5+y, 1.5-z$; [3]: $x, 0.5-y, -0.5+z$; [4]: $x, 0.5-y, 0.5+z$; [5]: $x, 1.5-y, 0.5+z$.

The two bases adopt a head–tail arrangement. Dihedral angles between the guanine planes and the Pt coordination planes are 47° (ring *a*) and 62° (ring *b*), that between the two nucleobase planes is 64°. Pt is coplanar with ring *a*, yet by 0.34 Å off from that of ring *b*. The propyl groups of the amine ligands are, like the guanines, pointing to different sides with respect to the Pt coordination planes. Unusual features are not observed.

^1H NMR Spectra

The ^1H NMR spectrum of **3** in D_2O is normal in that 9-EtGH rotation at 5, 30 and 70 °C is sufficiently rapid to produce only single sets of resonances for the two guanine rings. The individual protons display the following chemical shifts (δ [ppm], pD 5): 8.15 (H8, s), 4.05 (CH_2(9-EtGH), q), 1.33 (CH_3(9-EtGH), t); 2.47 (α-CH_2(cpa), t), 1.71 (β-CH_2 (cpa), m), 0.83 (γ-CH_3, t). ^{195}Pt coupling is not observed under the conditions of the experiment (270 MHz).

In dimethylformamide-d_7, **2** shows resonances at 10.93 (N(1)H, s, b) 8.31 (H8, s), 6.89 (NH_2, s, b) 4.12 (CH_2, q) and 1.38 (CH_3, t) ppm. The acidic protons exchange with H_2O (averaged signal at 3.6 ppm). Immediately after sample preparation and after 3 days at 22 °C, the ^1H NMR spectrum gives no indication of any chloride solvolysis (single DMF resonance at 8.03 ppm, single sets of guanine resonances).

Reaction with NH_3

Preliminary studies on the reaction of **1** and **2** with excess NH_3 suggest that these compounds indeed represent suitable starting material for the preparation of bis(amine) complexes according to

$$[Cl_2Pt(9\text{-}EtGH_2)_2]Cl_2 + 4a \longrightarrow [a_2Pt(9\text{-}EtGH)_2]Cl_2 + 2[aH]Cl$$

It appears that conversion of **1** into **2** is a useful step to avoid the formation of additional products such as $[a_3Pt(9\text{-}EtGH)]^{2+}$, for example.

Supplementary Material

Observed and calculated structure factors as well as anisotropic thermal factors can be obtained from the authors on request.

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