Taking Advantage of Right Angles in *N1,N7*-Diplatinated Purine Nucleobases: Toward Molecular Squares, Rectangles, and Meanders

Marc Sven Lüth, Eva Freisinger, Frank Glahé, Jens Müller, and Bernhard Lippert*

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

Received January 23, 1998

Di- and trinuclear complexes of *trans*-a_2Pt^{II} (a = NH_3 or NH_2CH_3) and the purine model nucleobases 9-methyladenine (9-MeA), 9-ethyladenine (9-EtA), 9-methylguanine (9-MeGH), and 9-ethylguanine (9-EtGH) have been prepared and characterized. The following five compounds have been studied using X-ray crystallography: *trans*-[$(NH_3)_2$Pt(9-EtA-*N7*)(9-MeGH-*N7*)]$(NO_3)_2$·1.4H_2O (**1b**), *trans,trans*-{[$Cl(NH_2CH_3)_2Pt]_2$-(9-EtA-*N1,N7*)}$(ClO_4)_2$ (**2**), *trans,trans*-{[Cla_2Pt](*N1*-9-MeA-*N7*)Pt$(NH_3)_2$(9-MeGH-*N7*)}$(ClO_4)_3$·*n*H_2O (a = NH_2-CH_3, *n* = 1 (**3a**); a = NH_3, *n* = 1.8 (**3b**)), and *trans,trans,trans*-{[$Cl(NH_3)_2Pt]_2$(*N1*-9-MeA-*N7*)$_2$Pt$(NH_3)_2$}-$(ClO_4)_4$·H_2O (**5**). In all diplatinated adenine species (**2**, **3a**, **3b**, and **5**) the Pt−N(1) and Pt−N(7) vectors are approximately at right angles, therefore making these complexes potential building blocks for molecular squares, rectangles, and meanders. Two open nucleobase quartets, **4** and **6**, consisting of three *trans*-diamineplatinum(II) entities and four purine nucleobases (two bridging 9-MeA′s and two terminal 9-MeGH (**4**) and 9-EtGH (**6**), respectively) have been isolated and characterized by elemental analysis and ^1H and ^{195}Pt NMR spectroscopy.

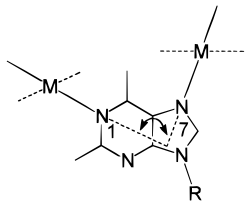
Introduction

Molecular squares are formed upon combining square-planar *cis*-(ligand)M^{II} (M = Pt or Pd) entities and a suitable second ligand, with the metal ions forming the corners and the second ligand, frequently 4,4′-bipyridine, representing the sides.[1−4] As has been pointed out,[5,6] the resulting species may better be described as open boxes, considering the fact that the sides of the squares are usually more or less perpendicular to the Pt coordination planes.

A while ago we have proposed that *N1,N7*-dimetalated purine nucleobases might be ideally suited to make true "squares" in combination with linear metal entities, with four coplanar organic ligands representing the corners of the square.[7] This is a consequence of the right angle formed by the two M−N(nucleobase) vectors at the purines (Chart 1). Apart from two cyclic arrays which, depending on the way of cross-linking the two donor sites lead either to a closed square or to a closed rectangle (Chart 2), there is also the possibility of the formation of meanders or, with the loss of coplanarity of all four bases, helices (Chart 3).

Here we report on the syntheses and crystal structures of several di- and trinuclear complexes containing *trans*-a_2Pt^{II} entities (a = NH_3 or CH_3NH_2) which can be considered fragments of these larger aggregates.

Chart 1



Experimental Section

Starting Compounds.[8] 9-MeA[9] and 9-EtA[10] were prepared as previously described. 9-MeGH and 9-EtGH were purchased from Chemogen, Konstanz, Germany, and used without further purification. *trans*-$Pt(NH_3)_2Cl_2$ was prepared according to the method of Kauffman and Cowan,[11] and *trans*-$Pt(NH_2CH_3)_2Cl_2$[12] was prepared as described in the literature. The preparation and isolation of *trans*-[$(NH_3)_2$Pt(9-MeGH-*N7*)Cl]Cl,[13] *trans*-[$(NH_3)_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)]$(NO_3)_2$·H_2O,[14] and *trans*-[$(NH_3)_2$Pt(9-MeA-*N7*)$_2$]$(NO_3)_2$·H_2O[14] was performed according to published methods. *Caution:* Perchlorate salts of metal complexes with organic ligands are potentially explosive!

(1) (a) Fujita, M.; Yazaki J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645. (b) Fujita, M. *J. Synth. Org. Chem., Jpn.* **1996**, *54*, 79. (c) Fujita, M.; Ogura, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471.
(2) (a) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273. (b) Manna, J.; Whiteford, J. A.; Stang, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 8731 and references cited therein. (c) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.
(3) (a) Rauter, H.; Hillgeris, E. C.; Lippert, B. *J. Chem. Soc., Chem. Commun.* **1992**, 1385. (b) Rauter, H.; Hillgeris, E. C.; Erxleben, A.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 616.
(4) Lehn, J. M. Supramolecular Chemistry, VCH: Weinheim, **1995.**
(5) (a) Hunter, C. A. *Angew. Chem.* **1995**, *107*, 1181. (b) Philp, D.; Stoddart, J. F. *Angew. Chem.* **1996**, *108*, 1243.
(6) Rauter, H.; Mutikainen, I.; Blomberg, M.; Lock, C. J. L.; Amo-Ochoa, P.; Freisinger, E.; Randaccio, L.; Zangrando, E.; Chiarparin, E.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1296.
(7) Schreiber, A.; Hillgeris, E. C.; Erxleben, A.; Lippert, B. *Z. Naturforsch.* **1993**, *48b*, 1603.
(8) Abbreviations used: 9-MeA = 9-methyladenine, 9-MeGH = 9-methylguanine, 9-EtGH = 9-ethylguanine, 9-EtA = 9-ethyladenine, 9-EtAH = 9-ethyladeninium cation, 9-MeG = 9-methylguanine anion, 1-MeC = 1-methylcytosine. Occasionaly, A and G are used for the nucleobases adenine and guanine. Coordination sites are indicated, e.g., 9-MeA-*N7*.
(9) Krüger, G. *Z. Physiol. Chem.* **1893**, *118*, 153.
(10) Nowick, J. S.; Chen, J. S.; Noronha, G. *J. Am. Chem. Soc.* **1993**, *115*, 7636.
(11) Kauffman, G. B.; Cowan, D. O.; *Inorg. Synth.* **1963**, *7*, 239.
(12) Arpalathi, J.; Schöllhorn, H.; Thewalt, U.; Lippert, B. *Inorg. Chim. Acta* **1988**, *153*, 51.
(13) (a) Raudaschl, G.; Lippert, B. *Inorg. Chim. Acta* **1983**, *80*, L49. (b) Aletras, V.; Hadjiliadis, N.; Lippert, B. *Polyhedron* **1992**, *11*, 1259.
(14) Schreiber, A.; Lüth, M. S.; Erxleben, A.; Fusch, E. C.; Lippert, B. *J. Am. Chem. Soc.* **1996**, *118*, 4124.

S0020-1669(98)00081-0 CCC: $15.00
Published on Web 06/05/1998

Chart 2

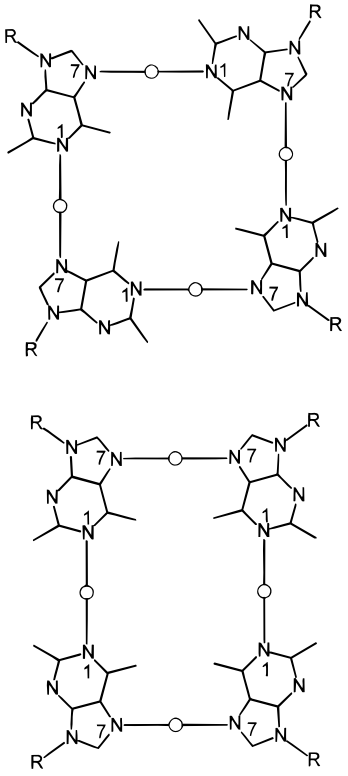
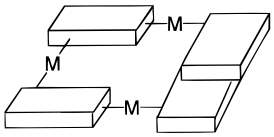


Chart 3



Synthesis of *trans*-[(NH$_3$)$_2$Pt(9-EtAH-*N7*)(9-MeGH-*N7*)](NO$_3$)$_3$ (1a). A 1500-mg sample of *trans*-[(NH$_3$)$_2$Pt(9-MeGH-*N7*)Cl]Cl·1.5H$_2$O (3 mmol) was suspended in 150 mL of water, and the pH was adjusted to 1.4 by means of 1 N HNO$_3$. A solution of 9-EtA (1468 mg, 9 mmol) in water (120 mL) was likewise brought to pH 1.4 and added to the suspension, and AgNO$_3$ (1008 mg, 5.94 mmol), dissolved in H$_2$O (40 mL), was slowly added over an 8-h period. The mixture was stirred for 6 days at 40 °C in the dark and cooled to 4 °C, and the precipitated AgCl was removed by filtration. Slow evaporation of the clear yellowish solution gave crystalline **1a**, which was washed several times with water to remove excess 9-EtA and dried in air (yield 48%). Anal. Calcd for C$_{13}$H$_{23}$N$_{15}$PtO$_{10}$: C, 20.9; H, 3.1; N, 28.2. Found: C, 21.2; H, 3.3; N, 28.0. ^{195}Pt NMR (D$_2$O, δ, ppm): −2458.

Synthesis of *trans*-[(NH$_3$)$_2$Pt(9-EtA-*N7*)(9-MeGH-*N7*)](NO$_3$)$_2$·1.4H$_2$O (1b). A 130-mg sample (0.18 mmol) of **1a** was dissolved in water (20 mL) at 45 °C, and 0.1 N NaOH was added until the pH was 4.5. Slow evaporation of the solvent at room temperature gave crystalline **1b**, which was filtered off, washed with water, and dried at 40 °C. The yield was 79%. Anal. Calcd for C$_{13}$H$_{24}$N$_{14}$PtO$_8$ (monohydrate): C, 22.3; H, 3.5; N, 28.0. Found: C, 22.3; H, 3.5; N, 27.9. Crystals suitable for X-ray crystallography were obtained upon recrystallization from D$_2$O. X-ray crystallography revealed the presence of 1.4D$_2$O per cation.

Synthesis of *trans*-[(NH$_3$)$_2$Pt(9-EtAH-*N7*)(9-MeGH-*N7*)]Cl$_3$·0.5H$_2$O (1d). Compound **1d** was obtained upon anion exchange (Merck, type II) from **1a**. A 158-mg sample (0.21 mmol) of **1a** was dissolved in water (20 mL), and the solution was loaded on the column. Elution of **1d** was carried out with water (100 mL). Slow evaporation of the solvent of the resulting solution to dryness was performed at room temperature. The yellowish-white residue was suspended in ice water (2 mL), filtered off, washed with acetone (10 mL), and dried in air (yield 71%). Anal. Calcd for C$_{13}$H$_{24}$N$_{12}$PtO$_{1.5}$Cl$_3$: C, 23.2; H, 3.6; N, 25.0. Found: C, 23.3; H, 3.6; N, 25.2.

Synthesis of *trans,trans*-{[Cl(NH$_2$CH$_3$)$_2$Pt]$_2$(9-EtA-*N1,N7*)}(ClO$_4$)$_2$ (2). A 500-mg sample (1.52 mmol) of *trans*-(NH$_2$CH$_3$)$_2$PtCl$_2$ was suspended in water (20 mL) and stirred along with 9-EtA (62 mg, 0.38 mmol) for 36 h at 45 °C. After the suspension was cooled to room temperature, unreacted *trans*-(NH$_2$CH$_3$)$_2$PtCl$_2$ was removed. An excess of solid NaClO$_4$ (122 mg, 1 mmol) was added to the clear solution. Crystalline **2** which precipitated immediately was filtered off, washed several times with water, and dried at 40 °C. The compound was isolated in 78% yield. Anal. Calcd for C$_{11}$H$_{29}$N$_9$Pt$_2$O$_8$Cl$_4$: C, 13.9; H, 3.1; N, 13.3. Found: C, 13.9; H, 2.9; N, 13.4. IR (cm^{-1}): 1095 (ν_3(ClO$_4$)), 349 (ν(Pt−Cl)). ^{195}Pt NMR (DMF-d_7, δ, ppm): −2421, −2481.

Synthesis of *trans,trans*-{[Cl(NH$_2$CH$_3$)$_2$Pt](*N1*-9-MeA-*N7*)Pt(NH$_3$)$_2$(9-MeGH-*N7*)}(ClO$_4$)$_3$·H$_2$O (3a). A 300-mg sample (0.44 mmol) of *trans*-[(NH$_3$)$_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)](NO$_3$)$_2$·H$_2$O was dissolved in water (40 mL) and stirred with an excess of *trans*-(NH$_2$CH$_3$)$_2$PtCl$_2$ (538 mg, 1.64 mmol) for 4 d at 40 °C. Then the mixture was cooled to 4 °C, and the unreacted *trans*-(NH$_2$CH$_3$)$_2$PtCl$_2$ was removed. The yellowish filtrate was concentrated to a 15-mL volume. An excess of solid NaClO$_4$ (195 mg, 1.6 mmol) was added, and **3a** precipitated as a white powder. It was filtered off, washed with ice water, and dried at 40 °C (yield 82%). Elemental analysis showed the presence of 2.5H$_2$O. Anal. Calcd for C$_{14}$H$_{35}$N$_{14}$Pt$_2$O$_{15.5}$Cl$_4$: C, 14.3; H, 3.0; N, 16.6. Found: C, 14.4; H, 2.9; N, 16.5. IR (cm^{-1}): 1093 (ν_3(ClO$_4$)), 351 (ν(Pt−Cl)). ^{195}Pt NMR (DMF-d_7, δ, ppm): −2471, −2502. Crystals suitable for X-ray crystallography were obtained by recrystallization from D$_2$O. X-ray crystallography revealed the presence of a single molecule of water of crystallization only.

Synthesis of *trans,trans*-{[Cl(NH$_3$)$_2$Pt](*N1*-9-MeA-*N7*)Pt(NH$_3$)$_2$(9-MeGH-*N7*)}(ClO$_4$)$_3$·1.8H$_2$O (3b). Preparation of **3b** was performed according to the method previously published by us.[14] The water content was established by X-ray crystallography.

Synthesis of *trans,trans,trans*-{(NH$_2$CH$_3$)$_2$Pt(*N1*-9-MeA-*N7*)$_2$[(NH$_3$)$_2$Pt(9-MeGH-*N7*)]$_2$}(ClO$_4$)$_6$·4H$_2$O·NaClO$_4$ (4). *trans*-(NH$_2$CH$_3$)$_2$PtCl$_2$ (67 mg, 0.21 mmol) was suspended in H$_2$O (10 mL) and stirred with AgNO$_3$ (69 mg, 0.4 mmol) for 36 h at 30 °C with daylight excluded. After the mixture was cooled to room temperature, AgCl was removed, and *trans*-[(NH$_3$)$_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)](NO$_3$)$_2$·H$_2$O (288 mg, 0.42 mmol), dissolved in water (30 mL), was added. The solution was stirred for 4 d at 40 °C. After filtration from an unidentified dark precipitate the filtrate was concentrated to a 20-mL volume. Unreacted *trans*-[(NH$_3$)$_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)](NO$_3$)$_2$·H$_2$O, which precipitated during evaporation, was removed, and an excess of NaClO$_4$ (171 mg, 1.4 mmol) was added to the yellowish solution. Crystalline **4** was isolated by filtration after 24 h at 4 °C and dried in air. The yield was 11%. Anal. Calcd for C$_{26}$H$_{58}$N$_{26}$Pt$_3$O$_{34}$Cl$_7$Na: C, 14.7; H, 2.8; N, 17.2. Found: C, 14.8; H, 2.7; N, 16.8. IR (cm^{-1}): 1092 (ν_3(ClO$_4$)). ^{195}Pt NMR (D$_2$O, d, ppm): −2466, −2591, −2624 (with relative intensities of 2:0.2:0.8). Scanning electron microscopy was consistent with the presence of Na.

Synthesis of *trans,trans,trans*-{[Cl(NH$_3$)$_2$Pt]$_2$(*N1*-9-MeA-*N7*)$_2$Pt(NH$_3$)$_2$}(ClO$_4$)$_4$·H$_2$O (5). Complex **5** was prepared according to the published method.[14] X-ray crystallography showed the presence of one water molecule in contrast to earlier results based on elemental analysis.[14]

Synthesis of *trans,trans,trans*-{[(9-EtGH-*N7*)(NH$_3$)$_2$Pt]$_2$(*N1*-9-MeA-*N7*)$_2$Pt(NH$_3$)$_2$}(ClO$_4$)$_6$·6H$_2$O (6). A 300-mg sample (0.21 mmol) of *trans,trans,trans*-{[Cl(NH$_3$)$_2$Pt]$_2$(*N1*-9-MeA-*N7*)$_2$Pt(NH$_3$)$_2$}(ClO$_4$)$_4$ was suspended in water (40 mL) and stirred with AgNO$_3$ (69 mg, 0.41 mmol) for 24 h at 35 °C with daylight excluded. After the suspension was cooled to 4 °C, AgCl was filtered off, and 9-EtGH (74 mg, 0.42 mmol) was added. The mixture was kept at 35 °C for 7 d in the dark and filtered from some unidentified gray precipitate, and an excess of NaClO$_4$ (171 mg, 1.4 mmol) was added. **6** precipitated as a white powder. The suspension was cooled to 4 °C and the powder was filtered off, washed with ice water, and dried in air. The compound was isolated in 40% yield. Anal. Calcd for C$_{26}$H$_{62}$N$_{26}$Pt$_3$O$_{32}$Cl$_6$: C, 15.2; H, 3.1; N, 17.8. Found: C, 15.1; H, 2.8; N, 17.5. IR (cm^{-1}):

Table 1. Crystallographic Data for Compounds **1b**, **2**, **3a**, **3b**, and **5**

	1b	**2**	**3a**	**3b**	**5**
empirical formula	$C_{13}H_{21.8}N_{14}O_{8.4}Pt$	$C_{11}H_{29}N_9O_8Pt_2Cl_4$	$C_{14}H_{32}N_{14}O_{14}Pt_2Cl_4$	$C_{12}H_{29.6}N_{14}O_{14.8}Pt_2Cl_4$	$C_6H_{17}N_8O_{8.5}Pt_{1.5}Cl_3$
formula weight (g mol^{-1})	703.73	947.41	1152.52	1138.88	736.26
crystal size (mm)	0.44 × 0.25 × 0.13	0.73 × 0.60 × 0.44	0.50 × 0.44 × 0.13	0.50 × 0.13 × 0.13	1.05 × 0.43 × 0.39
temperature (K)	293	293	293	293	293
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	8.622(2)	14.005(3)	8.616(2)	8.370(2)	25.933(5)
b (Å)	11.292(2)	11.464(2)	11.437(2)	11.390(2)	8.496(2)
c (Å)	13.173(3)	17.813(4)	18.410(4)	18.064(4)	21.577(4)
α (deg)	109.83(3)		92.64(3)	91.79(3)	
β (deg)	93.06(3)	106.82(3)	93.23(3)	95.55(3)	125.04(3)
γ (deg)	92.62(3)		98.51(3)	100.03(3)	
V (Å^3)	1202.0(4)	2737.6(10)	1788.6(6)	1685.8(6)	3892.3(14)
Z	2	4	2	2	8
D_{calc} (g cm^{-3})	1.944	2.299	2.140	2.244	2.513
μ (Mo Kα) (mm^{-1})	5.909	10.651	8.188	8.687	11.252
F(000)	686	1784	1100	1084	2760
dist detector−crystal (mm)	26.768	26.773	25.948	26.828	26.870
oscillationstep (ω, deg)	1	1	1	1	1
no. of frames	360	360	360	360	360
scan time per frame (s)	60	10	20	45	8
2θ range (deg)	9.3−51.2	9.1−51.4	9.1−51.4	9.0−51.5	9.2−51.5
reflections collected	34631	67207	51565	48448	55775
reflections observed	3496 ($I \geq 2\sigma(I)$)	3118 ($I \geq 2\sigma(I)$)	4348 ($I \geq 2\sigma(I)$)	2513 ($I \geq 2\sigma(I)$)	2625 ($I \geq 2\sigma(I)$)
parameters refined	338	344	476	432	306
extinction coefficient		6.4(14) × 10^{-4}			
R_{int}	0.036	0.071	0.063	0.067	0.043
R_1 (obs data)[a]	0.029	0.0476	0.0487	0.0408	0.0361
wR_2 (obs data)[b]	0.065	0.1086	0.1193	0.0807	0.0855
goodness of fit, S	1.04	1.071	1.107	1.060	0.954
residual ρ_{max}, ρ_{min} (e Å^{-3})	0.71, −1.29	2.434, −2.647	1.986, −2.531	0.718, −0.927	1.804, −0.989

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

1089 ($\nu_3(ClO_4)$). ^{195}Pt NMR (DMSO-d_6, δ, ppm): −2443, −2526 (with relative intensities of 1:2).

Instrumentation. The ^{1}H NMR measurements were carried out at ambient temperature on a Bruker AC 200, a Bruker DPX 300, and a Bruker DRX 400 spectrometer using D_2O (with TSP as internal reference), DMSO-d_6 (using the signal of nondeuterated DMSO as internal reference, $\delta = 2.53$ ppm relative to TMS), and DMF-d_7 (using TMS or the signal of nondeuterated DMF as internal reference, $\delta =$ 8.01 ppm relative to TMS) as solvents. For aqueous solutions, pD values were determined by use of a glass electrode and addition of 0.4 to the pH meter reading. Uncorrected values (pH*) were used for the determination of pK_a values. The 43.02-MHz ^{195}Pt NMR spectra were recorded on the AC 200 spectrometer with Na_2PtCl_6 being the external reference. The NOESY experiments were acquired on the DPX 300 instrument with mixing times of 450 ms (**6**), 500 ms (**2, 3a**), and 1 s (**6**); the pulse repetition time was 1 s (**6**) and 2 s (**2, 3a**). A total of 256 FIDs of 1K size (**2, 3a**) and 2K size (**6**) with 16 scans (**3a**: 48 scans) each were collected. Squared cosine-bell multiplication, zero-filling (F2 dimension, only for **2** and **3a**), and linear prediction (F1 dimension) were applied before Fourier transformation. The NOESY experiments were carried out either in D_2O (**2, 3a**) or in DMF-d_7 (**6**). In both cases, the signal of residual water was suppressed via presaturation. H bonding between **3a** and 1-MeC in solution was proven by ^{1}H NMR spectroscopy in DMF-d_7. Resonances of the involved protons showed significant downfield shifts at different concentrations of a 1:1 mixture (0.02 M to 0.07 M).

Elemental analyses were performed on an elemental analyzer (model CHNS-932) of Leco Co. IR spectra were recorded on a Bruker FT-IR spectrometer (model IFS 28) with a He−Ne laser (wavelength $\lambda =$ 633 nm). Scanning electron microscopy was performed on a Stereoscan 360 of Cambridge Instruments Co.

X-ray Crystallography. Intensity data for **1b**, **2**, **3a**, **3b**, and **5** were collected on an Enraf-Nonius-KappaCCD diffractometer[15] with graphite-monochromated Mo K_δ radiation ($\lambda = 0.710\,69$ Å). It covered the whole sphere of reciprocal space by measurement of 360 frames rotating about ω in steps of 1° with different scantimes per frame for each compound (see Table 1). Unit cell parameters were obtained from the peaks of the first 10 frames and refined using the whole data set. Data reduction and cell refinement were carried out using the programs DENZO and SCALEPACK.[16] Reflections, which were partly measured on the previous and following frames, were used to scale these frames on each other. This procedure in part eliminated absorption effects and also considered a crystal decay if present. No empirical absorption correction was applied.

All structures were solved by standard Patterson methods[17] and refined with difference Fourier syntheses, using the SHELXTL-PLUS[18] and SHELXL-93 programs.[19] The scattering factors for the atoms were those given in the SHELXTL-PLUS program. Hydrogen atoms were placed in geometrical calculated positions and refined with a common isotropic temperature factor, except those for C(92′) in **1b** because of its large anisotropic displacement factor. All non-hydrogen atoms were refined anisotropically with the following exceptions: the disordered nitrate oxygens O(13) and O(13a) in **1b**; the non fully occupied water molecules O(2w) (**1b**), O(1w) and O(2w) (**3a**), and O(1w) and O(1wa) (**3b**); the disordered methylamine carbon atoms C(21) and C(21a) in **2** (occupancy factors 0.5); and a part of the disordered perchlorate oxygens in **2**, **3a**, **3b**, and **5**.

Crystal data and data collection parameters are summarized in Table 1.

Results and Discussion

Synthesis and Solid-State Structure of a Metalated A−G Base Pair: *trans*-[(NH$_3$)$_2$Pt(9-EtA-*N7*)(9-MeGH-*N7*)](NO$_3$)$_2$·

(15) NONIUS BV, KappaCCD package, Röntgenweg 1, P. O. Box 811, 2600 AV Delft, Netherlands.

(16) Otwinowsky, Z.; Minor, W. DENZO and SCALEPACK. In *Methods in Enzymology*; Academic Press: New York, 1997; Vol. 276, p 307.
(17) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *A46*, 467.
(18) G. M. Sheldrick; SHELXTL-PLUS (VMS); Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.
(19) G. M. Sheldrick, SHELXL-93, Program for crystal structure refinement; University of Göttingen: Germany, 1993.

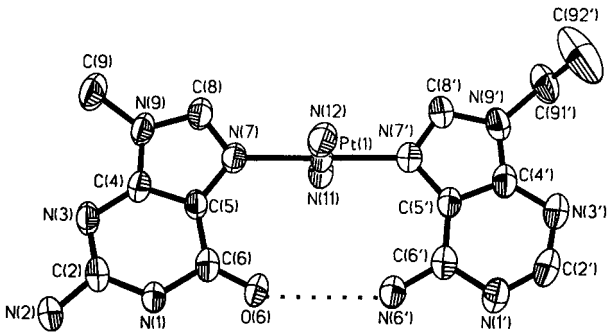


Figure 1. Cation of **1b** with atom-numbering scheme.

1.4H_2O (1b). In Figure 1, the cation of **1b** with the atom-numbering scheme is shown. The coordination geometry of Pt is square-planar, with angles about Pt and Pt−N bond lengths in the normal range (Pt(1)−N(7) = 1.999(4) Å, Pt(1)−N(7′) = 2.008(4) Å). Additional relevant angles and bond distances are given in the Supporting Information. Guanine and adenine are almost coplanar, and the best weighted planes through the two nucleobases form an angle of 0.4(2)°. The heterocycles adopt a *head*−*head* orientation (as far as *N9*-substituents are concerned), which is stabilized by an intramolecular hydrogen bond of 3.042(6) Å between N(6′) of adenine and O(6) of guanine.

As expected, the structure of the cation of **1b** is closely similar to that of the related complex *trans*-[$(NH_3)_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)]$(NO_3)_2\cdot H_2O$ with 9-MeA instead of 9-EtA.[14] We have prepared **1b** and its precursor **1a** for the following reasons: First, applying 9-EtA gave a higher yield of the desired compound and provided a better possibility for separating unreacted 9-EtA from **1a**. Both 9-EtA and 9-EtAH are more water soluble than the methyl analogues. Second, the solution of the solid-state structure of *trans*-[$(NH_3)_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)]$(NO_3)_2\cdot H_2O$ was hampered by a severe disorder of the cations.[14] In **1b** we observe no such disorder of the cations. Our interest in the relative orientation of the cations of **1b** and that of the previously reported 9-MeA analogue as well as in possible H-bonding interactions relates to the fact that these cations are, in principle, self-complementary and might give rise to dimerization via H bonds.[14] We note that with a related compound, *trans*-[$(NH_3)_2$Pt(1-MeC-*N3*)(9-EtG-*N7*)]$^+$, we have recently shown that association to a diplatinated nucleobase quartet indeed takes place, in both solution[20] and the solid state.[21]

The solution structure of **1b** has been explored by ^{1}H NMR spectroscopy. The simplicity of the spectrum (D_2O, DMSO-d_6) at ambient temperature (single sets of resonances) and the chemical shift of the adenine NH_2 resonance (δ, 8.57 ppm, DMSO-d_6) are consistent with a single rotamer form present, stabilized by an intramolecular H bond between O(6) of guanine and N(6′) of adenine, very much as in the solid state (Figure 1). Tables 2 and 3 give an overview of the ^{1}H NMR chemical shifts of all the compounds prepared, with Table 3 focusing on the adenine NH_2 resonances in the aprotic solvents DMSO-d_6 and DMF-d_7. As we have previously pointed out,[14] the chemical shift of the exocyclic NH_2 group of adenine is particularly sensitive and permits insight into the state of platination/protonation of the base *and* into the involvement of NH_2 in intramolecular H bonding. As far as the question of H bond formation between self-complementary cations is concerned, there is no concentration dependence of resonances of **1b** observed in any of the solvents applied, thus ruling out any measurable self-association in solution. Very much as in the solid-state structure of the corresponding 9-MeA complex,[14] where quartet formation is prevented by hydrogen bonding between a nitrate oxygen and the N(1′)H of guanine, the solid-state structure of **1b** reveals no cation association. Preliminary attempts to realize cation association in the presence of other anions, e.g., starting out from the chloride salt (c.f. Experimental Section), have been unsuccessful as yet since single crystals could not be obtained. It is also feasible that charge repulsion of the dipositive cations is not favorable for dimerization.

Table 2. ^{1}H NMR Chemical Shifts (D_2O, 25 °C)

	adenine				guanine			
compd	H8	H2	CH_2	CH_3	H8	CH_2	CH_3	pD
1b	8.84	8.38	4.39	1.54	8.36		3.78	3.6
1d	8.89	8.41	4.41	1.55	8.38		3.79	2.7
2	9.16	9.10	4.44	1.56				3.7
3a	8.92	9.10		4.00	8.37		3.79	3.8
4	9.01	9.34, 9.30		4.06	8.39		3.81	7.0
6	9.23	9.01		4.09	8.44	4.24	1.51	4.7

Table 3. Chemical Shifts of Exocyclic NH_2 Resonances of Adenine Ligands[a]

compd	solvent	Pt per A	δ(NH2)
1a	DMSO-d_6	1	8.67
1b	DMSO-d_6	1	8.57
2	DMF-d_7	2	9.70
3a	DMSO-d_6	2	9.54
	DMF-d_7	2	9.98
4	DMSO-d_6	1.5	9.72
	DMF-d_7	1.5	10.30
5	DMF-d_7	1.5	9.45
6	DMSO-d_6	1.5	9.36
	DMF-d_7	1.5	9.66

[a] Ambient temperature, in ppm.

Deprotonation of **1a** gives, in a first step, compound **1b**. The pK_a value for this acid/base equilibrium of the 9-EtAH ligand was determined by pH dependent ^{1}H NMR spectroscopy in D_2O as 1.9(0.1). Deprotonation of the guanine ligand (pH brought to 8) did not lead to *trans*-[$(NH_3)_2$Pt(9-EtA-*N7*)(9-MeG-*N7*)](NO_3) (**1c**), but rather yielded a poorly soluble species of what appears to be a 1:1 adduct between **1b** and **1c**.

$$\underset{\textbf{1a}}{\textit{trans}\text{-}[(NH_3)_2\text{Pt}(9\text{-EtAH-}N7)(9\text{-MeGH-}N7)]^{3+}} \overset{-H^+}{\underset{+H^+}{\rightleftharpoons}} \underset{\textbf{1b}}{\textit{trans}\text{-}[(NH_3)_2\text{Pt}(9\text{-EtA-}N7)(9\text{-MeGH-}N7)]^{2+}} \overset{-H^+}{\underset{+H^+}{\rightleftharpoons}} \underset{\textbf{1c}}{\textit{trans}\text{-}[(NH_3)_2\text{Pt}(9\text{-EtA-}N7)(9\text{-MeG-}N7)]^{+}} \quad (1)$$

We assume that this species contains the guanine−guanine base-pairing pattern previously reported by us.[22]

Synthesis and Solid-State Structure of a *N1,N7*-Dimetalated Adenine Model Nucleobase: *trans,trans*-{[Cl(NH_2CH_3)$_4$Pt]$_2$(9-EtA-*N1,N7*)}(ClO_4)$_2$ (2). Reaction of 9-EtA with an excess of *trans*-$(NH_2CH_3)_2PtCl_2$ leads to the *N1,N7*-diplatinated adenine complex **2**. Figure 2 shows the cation structure with the atom-numbering scheme. Each Pt has a square-planar coordination geometry. Bond lengths and angles about the heavy metals are not unusual and compare well with those found in the corresponding 9-MeA compound[7] (see Supporting

(20) Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1996**, *118*, 12467.
(21) Sigel, R. K. O.; Freisinger, E.; Lippert, B., submitted for publication.
(22) (a) Faggiani, R.; Lock, C. J. L.; Lippert, B. *J. Am. Chem. Soc.* **1980**, *102*, 5418. (b) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1982**, *21*, 3216.

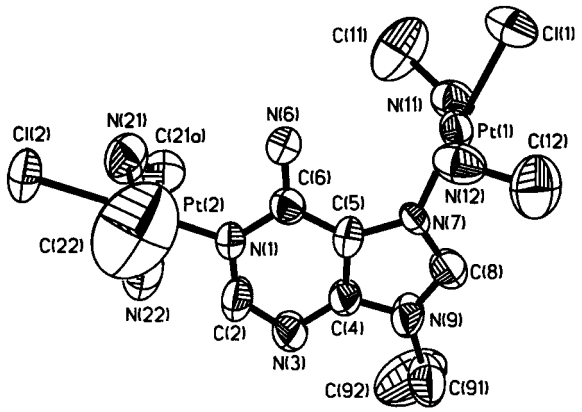


Figure 2. View of the cation of *trans,trans*-{[Cl(NH_2CH_3)$_2$Pt]$_2$(9-EtA-*N1,N7*)}(ClO_4)$_2$ (**2**) with atom-numbering scheme.

Information). The most important detail of the cation structure, relevant to the formation of metalated-purine quartets, represents the angle formed between the two vectors Cl(1), Pt(1), N(7) and Cl(2), Pt(2), N(1), which is 87.9(4)°. This value confirms one of the three main features previous work on platinated purine nucleobases containing *trans*-a$_2$Pt^{II} entities (a = NH_3 or NH_2CH_3) has revealed, namely the orthogonality of Pt-*N1* and Pt-*N7* vectors.[7,14]

The assignment of the signals of **2** in the ^{1}H NMR spectrum in D_2O and DMF-d_7 is given in Tables 2 and 3. A NOESY experiment was performed to differentiate between the two singlets at 9.16 and 9.10 ppm. The cross peak between the singlet at 9.16 and the CH_2 quartet around 4.44 ppm clearly identifies the former as being due to H8 of 9-EtA. As expected, two equally intense ^{195}Pt signals are observed at −2421 (Pt(1)−N(7)) and −2481 ppm (Pt(2)−N(1)) (DMF-d_7). The chemical shifts of these resonances are consistent with those found in other Pt complexes having ClN_3Pt coordination spheres.[14,23] Basicity considerations (N(1) > N(7)) suggest that the upfield resonance should be assigned to Pt(2) bonded to N(1).

Syntheses and X-ray Structures of Diplatinated A−G Base Pairs: *trans,trans*-{[Cl(NH_2CH_3)$_2$Pt](*N1*-9-MeA-*N7*)Pt(NH_3)$_2$(9-MeGH-*N7*)}(ClO_4)$_3$·H_2O (3a) and *trans,trans*-{[Cl(NH_3)$_2$Pt](*N1*-9-MeA-*N7*)Pt(NH_3)$_2$(9-MeGH-*N7*)}(ClO_4)$_3$·1.8H_2O (3b). Possible Starting Compounds for Rectangles. There are two ways which seem to be promising in generating rectangles built up of four purine nucleobases and four metal entities coordinating in a linear fashion. Figure 3 displays these routes with *trans*-[(NH_3)$_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)](NO_3)$_2$·H_2O representing the starting compound. In both cases, a two-step reaction should lead to rectangular aggregates. On one hand, there is the possibility to generate the diplatinated A−G base pair **3a** or **3b** which, upon loss of HCl, could undergo condensation reactions to form either a closed rectangle or an open meander (not shown). On the other hand, cross-linking of two platinated A−G base pairs with a third and finally a fourth *trans*-[a$_2$Pt(H_2O)$_2$]$^{2+}$ entity could lead to a closed rectangle or alternatively to open meanders (not shown). The triplatinated "open" metal-modified nucleobase quartet **4**, which has in fact been isolated, is an intermediate on this way.

Starting with the mononuclear bis(purine) complex *trans*-[(NH_3)$_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)](NO_3)$_2$·H_2O, reaction with an excess of *trans*-a$_2$PtCl_2 (a = NH_2CH_3 for **3a** and a = NH_3 for **3b**) gives the dinuclear complexes **3a** and **3b**, respectively. As for compound **1b**, suitable crystals for X-ray structure analyses were obtained upon recrystallization of **3a** and **3b** from D_2O. Figure 4a gives a view of the cation of the diplatinated A−G base pair **3a**. Each Pt has a square-planar coordination geometry. No unusual bond lengths and distances are observed (see Supporting Information). Selected structural features of **3a**,**3b** as well as of related compounds containing di- and triplatinated purine bases are put together in Table 4. In **3a**, the heterocycles adopt a *head−head* orientation (as far as *N9*-substituents are concerned), which is stabilized by an intramolecular H bond of 3.03(1) Å between the exocyclic NH_2 group of adenine and O(6′) of guanine. This feature, intramolecular hydrogen bond formation, confirms previous findings in related mixed nucleobase complexes of *trans*-a$_2$Pt(II).[14] Pt-*N1* and Pt-*N7* vectors are also almost orthogonal (86.7(3)°). Only the third feature, coplanarity of nucleobases as forced by the presence of two amine ligands, is violated. We find a remarkable high propeller-twist angle of 26.8(3)° between the purine bases. It appears to be caused by base stacking of the guanine ligands and by intermolecular contacts. The G−G stacking distance amounts to ca. 3.4 Å, a value comparable to natural B-DNA base stacking. Figure 4b provides salient features of the crystal packing. First, intermolecular contacts of 3.564(3) Å between Cl(1) of Pt(2) and Pt(1), make Pt(1) in a sense "five-coordinate".[7] Second, Pt(2) is weakly interacting with a fifth ligand, namely, the perchlorate oxygen O(33) (3.6-(1) Å). However, compared to truly five-coordinate Pt^{II}, both axial interactions of Pt atoms are too weak to be considered bonds.[24] Third, a water molecule O(1w) bridges N(1′) of 9-MeGH with O(6′) of a second 9-MeGH, with H-bonding distances of 2.893(9) and 2.830(8) Å, respectively.

Table 4. Features of Novel Compounds Derived from Solid-State Structures

compd	Pt-*N1*/Pt-*N7* vectors (deg)	purine/purine planes (deg)	N(6)A−O(6′)G (Å)
1b		0.4(2)	3.04(1)
2	87.9(4)		
3a	86.7(3)	26.8(3)	3.03(1)
3b	87.4(4)	21.8(3)	3.01(1)
5	88.4(3)	0	

For comparison, the solid-state structure of the related diammine complex **3b** was also determined by X-ray crystallography. The preparation and solution behavior of **3b** were reported by us earlier.[14] Figure 5 shows the cation with the atom-numbering scheme, and Table 4 lists selected geometrical parameters. The best weighted planes through the nucleobases in **3b** form an angle of 21.8(3)°, slightly lower than that found in compound **3a**. The purine bases again adopt a *head−head* orientation, and there is also an intramolecular H bond of 3.01-(1) Å between N(6) of adenine and O(6′) of guanine. As for complex **3a**, stacking of guanine bases of adjacent cations is observed, and there also exists a contact of 3.404(4) Å between Cl(2) at Pt(2) and Pt(1) and another one of 3.728(1) Å between Pt(2) and a perchlorate oxygen O(44). Again, a water molecule O(1w) bridges N(1′) and O(6′) of two 9-MeGH with distances of 2.98(1) and 2.97(1) Å, respectively.

The simplicity of the ^{1}H NMR spectra of **3a** both in D_2O and DMF-d_7, namely, single sets of 9-MeA and 9-MeGH resonances (see Tables 2 and 3, assignment of H(8) and H(2) of 9-MeA by NOESY), suggests a single fixed structure for **3a**

(23) (a) Pregosin, P. S. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 285. (b) Appleton, T. G.; Bailey, A. J.; Barnham, K. J.; Hall, J. R. *Inorg. Chem.* **1992**, *31*, 3077.

(24) van Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010.

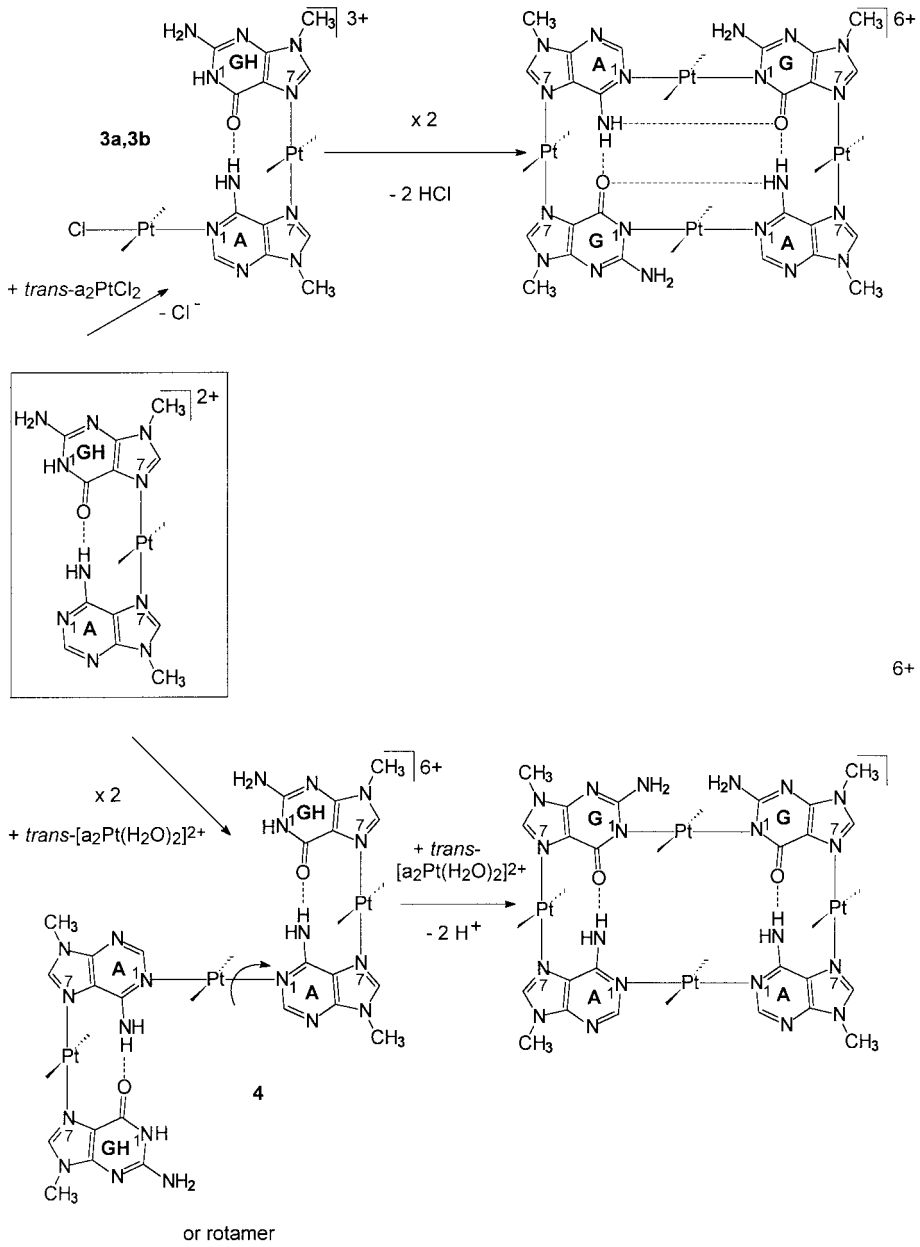


Figure 3. Possible reaction pathways toward molecular rectangles via a diplatinated A−G base pair (top) or a metal-modified purine nucleobase quartet (bottom).

in solution with preservation of the *head*−*head* orientation of the two nucleobases, as found in the solid-state structure. This assumption is supported by the extreme downfield shift of the NH_2 protons of the 9-MeA ligand in DMF-d_7 (9.98 ppm, Table 3).[14] As expected, two equally intense ^{195}Pt signals are observed, at −2471 and −2502 ppm (D_2O). Unfortunately, an exact assignment of the Pt signals on the basis of an HMQC experiment was impossible, due to an unfavorable Pt relaxation behavior at room temperature. Heating of the sample caused decomposition of **3a**. The pK_a values for the possible deprotonation reactions of **3a**, determined by ^{1}H NMR spectroscopy, were found to be ca. 8.0(0.6) for pK_{a1}(G−N(1)H) and 11.8(0.3) for pK_{a2}(A−N(6)H_2).

In view of our ultimate goal of preparing rectangular species (Figure 3, top), the *head*−*head* orientation of the two bases in **3a** and **3b** even in solution appears to be definitely favorable.

Synthesis of an "Open" Metal-Modified Nucleobase Quartet: *trans,trans,trans*-{(NH$_2$CH$_3$)$_2$Pt(*N1*-9-MeA-*N7*)$_2$[(NH$_3$)$_2$Pt-(9-MeGH-*N7*)]$_2$}(ClO$_4$)$_6$·4H$_2$O·NaClO$_4$ (4). Realizing the Other Route toward Rectangles. As shown in Figure 3 (bottom), **4** was prepared by reaction of *trans*-[(NH$_2$CH$_3$)$_2$Pt-(H$_2$O)$_2$]$^{2+}$ with 2 equiv of *trans*-[(NH$_3$)$_2$Pt(9-MeA-*N7*)(9-MeGH-*N7*)](NO$_3$)$_2$·H$_2$O at pH 4−5. The ^{1}H NMR spectrum in D_2O is consistent with 2-fold Pt coordination at N(1) and N(7) of 9-MeA ligands (A−H2, A−H8 shifted downfield by 0.9 and 0.2 ppm as compared to the starting compound) and indicates the presence of two species (A−H2 resonance split, see Table 2), due to rotamers in a ratio of 4:1. This view is supported by the ^{195}Pt NMR spectrum (D_2O, ambient temperature). We observe three resonances at −2466, −2591, and −2624 ppm with relative intensities of 2:0.2:0.8. The major signal is assigned to the two Pt atoms coordinated by 9-MeGH-*N7* and 9-MeA-*N7*, while the two minor resonances are due to the Pt bound to the two 9-MeA-*N1* sites. ^{1}H NMR spectra recorded in DMSO-d_6 and DMF-d_7 unambiguously provide evidence for a *head*−*head* arrangement of the two N(7)-bound purine bases (δ NH_2 (9-MeA), 9.72−10.30 ppm; cf. Table 3), while A−H2 and G−N(1)H resonances are split in a 4:1 ratio

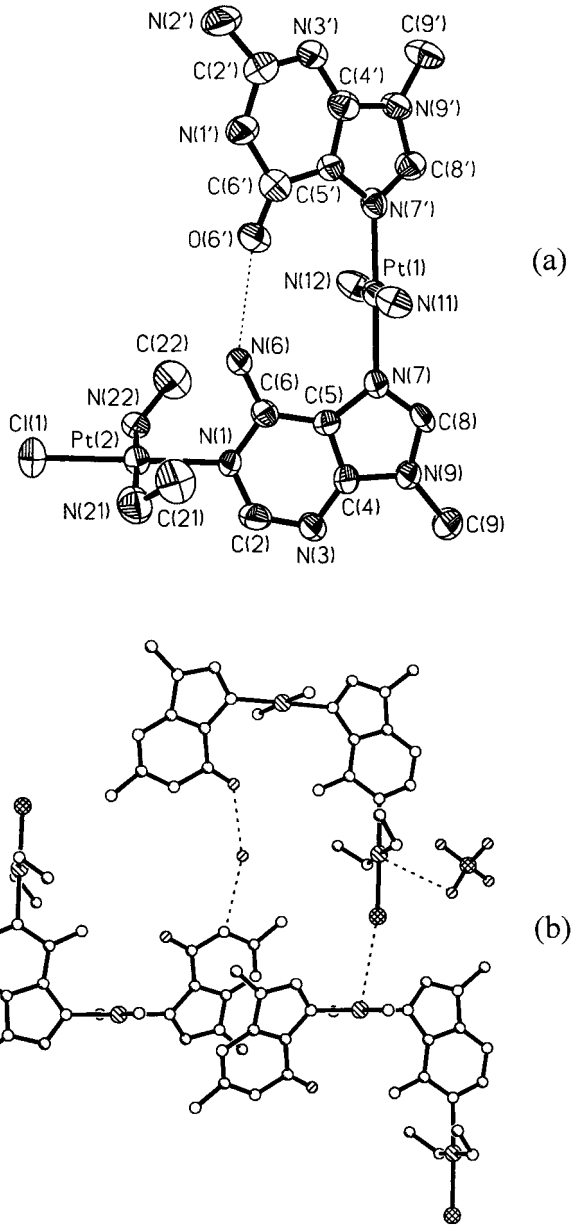


Figure 4. (a) Molecular cation of *trans*,*trans*-{[Cl(NH_2CH_3)$_2$Pt](*N1*-9-MeA-*N7*)Pt(NH_3)$_2$(9-MeGH-*N7*)}(ClO_4)$_3$·H_2O (**3a**) and (b) section of packing of the crystal with significant interatomic contacts indicated.

in DMSO-d_6 and DMF-d_7, indicative of two rotamers being present in these solvents. Figure 6 depicts the two possible structures. Rotamer (a) is expected to be favored at first glance, but stabilizing effects of solvent molecules can, in principle, reverse the situation.[25,26]

***trans,trans,trans*-{[Cl(NH_3)$_2$Pt]$_2$(*N1*-9-MeA-*N7*)$_2$Pt(NH_3)$_2$}-(ClO_4)$_4$·H_2O (5).** The preparation and characterization of the trinuclear complex **5** has earlier been reported by us.[14] In this work we are able to provide the solid-state structure determined by X-ray crystallography. Figure 7 gives a view of the cation with the atom-numbering scheme. The cation is centrosymmetric, with Pt(1) being on the inversion center. Consequently, the two bases are in a *head*−*tail* orientation and perfectly coplanar. Bond lengths and angles are in the normal range

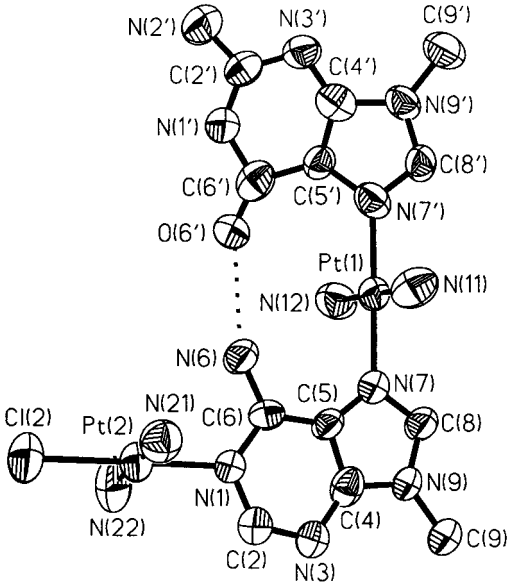


Figure 5. View of the cation of *trans*,*trans*-{[Cl(NH_3)$_2$Pt](*N1*-9-MeA-*N7*)Pt(NH_3)$_2$(9-MeGH-*N7*)}(ClO_4)$_3$·1.8H_2O (**3b**) with atom-numbering scheme.

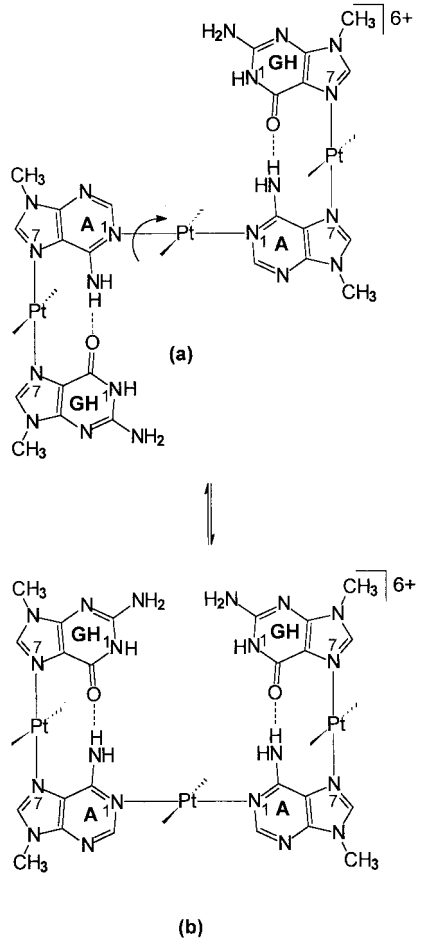


Figure 6. Possible rotamers of **4** in solution.

(Supporting Information). The adenine nucleobases are approximately perpendicular to the square planar coordinated Pt centers. Orthogonality of the Pt-*N1* and Pt-*N7* vectors is also fulfilled, the angle amounts to 88.4(3)°.

***trans, trans, trans*-{[(9-EtGH-*N7*)(NH_3)$_2$Pt]$_2$(*N1*-9-MeA-*N7*)$_2$Pt(NH_3)$_2$} (ClO_4)$_6$·6H_2O (6).** The triplatinated A−A base pair **5** was applied to prepare the mixed adenine−guanine

(25) Metzger, S.; Erxleben, A.; Lippert, B. *J. Biol. Inorg. Chem.* **1997**, *2*, 256.
(26) Holthenrich, D.; Sóvágó, I.; Fusch, G.; Erxleben, A.; Fusch, E. C.; Rombeck, I.; Lippert, B. *Z. Naturforsch.* **1995**, *50b*, 1767.

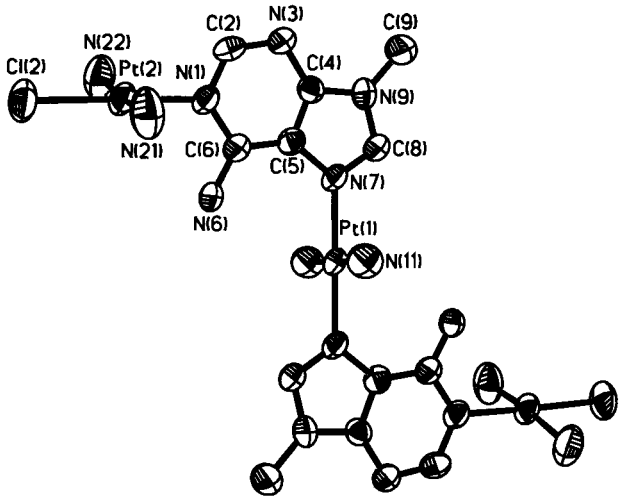


Figure 7. Cation of *trans,trans,trans*-{[Cl(NH$_3$)$_2$Pt]$_2$(*N1*-9-MeA-*N7*)$_2$Pt(NH$_3$)$_2$}(9-MeGH-*N7*)}(ClO$_4$)$_4$ with atom-numbering scheme.

complex **6** by substituting the two Cl ligands in **5** by two 9-EtGH nucleobases. Ignoring the differences in amine ligands at the two Pt centers bound to the adenine nucleobases and the difference in *N*9-substituents of the guanine nucleobases, **6** is a linkage isomer of **4**. As a consequence of Pt^{II} binding to N(7) of guanine, the guanine H(8) singlet is shifted downfield by 0.6 ppm relative to the free ligand. In contrast, the aromatic adenine resonances are very little affected (Table 2). We observe two resonances at −2443 and −2526 ppm in the ^{195}Pt NMR spectrum (DMSO-d_6) with relative intensities of 1:2. The minor signal is to be assigned to the Pt bound to the two adenine N(7) sites. Its position is consistent with the lower basicity of the N(7) site relative to N(1), while the major resonance arises from the two equivalent Pt atoms coordinated by guanine N(7) and adenine N(1).

Intramolecular hydrogen bonding between O(6) of guanine and N(6)H$_2$ of adenine is confirmed by the ^{1}H NMR spectra in DMF-d_7 and DMSO-d_6 (see Table 4). Therefore, only rotation about the central Pt−(9-MeA-*N7*) bonds seems possible. Figure 8 depicts the two feasible rotamer structures in solution. Unlike in **4**, the two guanine ligands in **6** cannot easily get past each other. Molecular models suggest that intramolecular base stacking of the two guanine ligands could stabilize a helical arrangement as shown in Figure 8, bottom. ^{1}H NMR spectra in different solvents reveal no signal splitting, suggesting the existence of single rotamers at room temperature (see Tables 2 and 3). Two NOESY spectra with different mixing times, recorded in DMF-d_7, do not display cross peaks between the NH$_3$ group of Pt bound to N(1) of 9-MeA and the N(1)H of a stacked 9-EtGH, as could have been expected from a helical arrangement. The repulsive interactions of the exocyclic groups of the purines also seem to favor the presence of the "open" rotameric form and may be responsible for preventing this interaction.

H Bonding between 3a and 1-MeC. Another point of interest of the here described complexes relates to their possibility to form H-bonded larger aggregates. For example, the metalated-guanine ligands in all compounds presented are, in principle, capable of either forming Watson−Crick pairs with cytosine nucleobases such as 1-MeC or, upon hemideprotonation, self-aggregating via guanine−guanine pairing or, upon deprotonation, associating with free guanine.[20,27−29] The question of the effect of a ligand (nucleobase or other ligand) at the

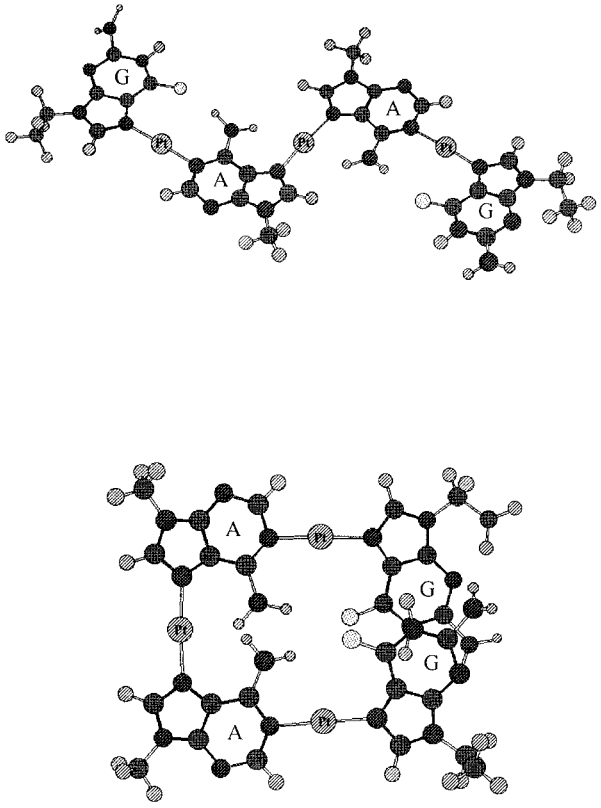
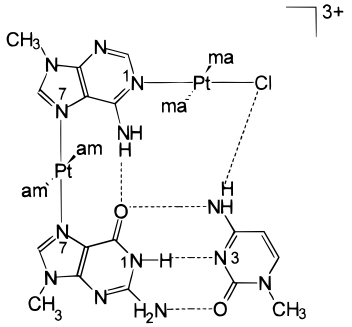


Figure 8. Possible rotamers of **6**. From model building, it is evident that the two guanine bases in the rotamer at the bottom cannot be coplanar due to steic interference.

Chart 4



periphery of the two interacting bases, e.g., guanine and cytosine, appears to be of interest. For this reason we have studied the interaction of **3a** with 1-MeC (1:1) in DMF-d_7 over a concentration range of 0.02−0.07 M. As expected for a Watson−Crick pattern, concentration-dependent downfield shifts of the G−NH$_2$, G−N(1)H, and C−NH$_2$ resonances are observed (Supporting Information), with no indication of any (rapid) binding of 1-MeC to the Pt moiety at *N1* of 9-MeA.[30] However, we note that the interaction shift of C−NH$_2$ is more pronounced than expected for a simple Watson−Crick scheme with one of the two amino protons (on average) involved in H bond formation only. We propose that this feature either is a consequence of the fact that the second amino proton is experiencing the effect of the chloro

(27) Lippert, B. *J. Am. Chem. Soc.* **1981**, *103*, 5691.

(28) Dieter-Wurm, I.; Sabat M.; Lippert, B. *J. Am. Chem. Soc.* **1992**, *114*, 357.

(29) Schröder, G.; Lippert, B.; Sabat, M.; Lock, C. J. L.; Faggiani, R.; Song, B.; Sigel, H. *J. Chem. Soc., Dalton Trans.* **1995**, 3767.

(30) With an excess of 1-MeC and upon heating (50 °C), substitution of Cl$^-$ by 1-MeC takes place, as evident from ^{1}H NMR spectroscopy.

ligand as well (Chart 4)[31] or reflects any additional H-bonding interaction of a second 1-MeC via its exocyclic amino group. Whether or not such ternary interactions involving the chloro ligand might be suitable to strengthen the Watson−Crick pair and/or advantageous for recognition purposes will be the subject of future work.

Conclusion and Outlook

Structural data on several complexes reported in this paper support the idea that taking advantage of the right angles formed by metal−N(1) and metal−N(7) purine vectors indeed leads to novel molecular architecture of nucleobases and metal entities. We are optimistic that in particular the "open" nucleobase quartet **4** can be closed to a rectangle and/or converted in a regular meander through cross-linking by appropriate metal entities.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. This work is dedicated to Prof. Achim Mueller, Bielefeld, at the occasion of his 60th birthday.

Supporting Information Available: Tables of X-ray structural data on compounds **1b**, **2**, **3a**, **3b**, and **5**; NOESY spectra of **2**, **3a**, and **6**; and ^{1}H NMR data of mixture of **3a** and 1-MeC (84 pages). Ordering information is given on any current masthead page.

IC980081O

(31) From model building, it appears that the separation between the N proton and the Cl atom is in the order of ≤ 3.5 Å. This distance certainly does not allow strong H bond formation but does not rule out any effect on NH in the NMR.