DALTON
FULL PAPER

Mono- and di-nuclear complexes of (trpy)M^{II} (M = Pd, Pt) with the model nucleobase 1-methylcytosine. Crystal structure and NMR solution studies †

Sultan Coşar,[a] Matthias B. L. Janik,[a] Matthias Flock,[a] Eva Freisinger,[a] Etelka Farkas[b] and Bernhard Lippert*[a]

[a] *Fachbereich Chemie, University of Dortmund, D-44221 Dortmund, Germany*
[b] *Department of Inorganic and Analytical Chemistry, L. Kossuth University, Debrecen, Hungary*

Received 12th April 1999, Accepted 2nd June 1999

Reactions of (trpy)M^{II} (M = Pd and Pt; trpy = 2,2′:6′,2″-terpyridine) with the model nucleobase 1-methylcytosine (Hmcyt) have been performed in water and studied by ^{1}H and ^{195}Pt NMR spectroscopy. Mononuclear [(trpy)M(Hmcyt-N^3)]$^{2+}$ **1** (M = Pd) and **3** (M = Pt) and dinuclear [{(trpy)M}$_2$(mcyt-N^3,N^4)]$^{3+}$ **2** (M = Pd) and **4** (M = Pt) complexes are formed. The two (trpy)M entities in the dinuclear species **2** and **4** are arranged *syn* to each other in the solid state. X-Ray crystal structures have been performed for [(trpy)Pd(Hmcyt-N^3)][NO_3]$_2$·5H_2O **1**, [{(trpy)Pd}$_2$(mcyt-N^3,N^4)][ClO_4]$_3$·H_2O **2b**, [(trpy)Pt(Hmcyt-N^3)][NO_3]$_2$·5H_2O **3** and [{(trpy)Pt}$_2$(mcyt-N^3,N^4)][ClO_4]$_3$·H_2O **4b**. The effect of the M–trpy entity on the resonances of the Hmcyt nucleobase in **1** and **3** (large downfield shifts of H^5 and H^6) is possibly related to the π-acceptor capacity of the trpy ligand.

Mono- and di-nuclear 2,2′:6′,2″-terpyridine (trpy) complexes of Pd^{II} and Pt^{II} have been the subject of numerous studies, *e.g.* with regard to photophysical[1,2] and electrochemical[3] properties as well as substitution-mechanistic aspects.[4] The mononuclear compounds have also been applied in biochemical and biochemistry-related studies as DNA intercalators[5,6] or metal probes for the imidazole moieties of histidine[7,8] and arginine residues.[9] Reactions of [(trpy)PtCl]$^+$ with thiols[10] and the unexpected easy cleavage of the Pt–S bond by Cu^{II} and Zn^{II} in phosphate buffers[11] have likewise been investigated. More recently, supramolecular aggregation of [(trpy)Pt(Me)]$^+$ to the α-helix of poly(L-glutamic acid) has been reported.[12] [(trpy)PtCl]$^+$,[13] [(trpy)Pt(OH)]$^+$,[14] and [{(trpy)Pt}$_2$L]$^{4+}$ (L = 4,4′-vinylenedipyridine[15a] or 4-picoline[15b]) have been found to initially intercalate into DNA before forming covalent adducts with bases, apparently preferentially with guanine.

We have recently carried out a solution study on the interaction of [(trpy)PdCl]$^+$ with model nucleobases such as 1-methylcytosine (Hmcyt).[16] Formation of mononuclear [(trpy)Pd(Hmcyt-N^3)]$^{2+}$ as well as dinuclear [{(trpy)Pd}$_2$(mcyt-N^3,N^4)]$^{3+}$ was clearly evident from potentiometric and proton NMR studies, but there was conflicting evidence as to the spatial orientation of the two metal entities in the dinuclear complex. The ambiguity was the result of rather unusual downfield shifts of the aromatic protons of the cytosine nucleobase, and in particular of H^5, which previously had been observed only in cases where a metal ion was attached to the exocyclic 4-position and oriented *anti* with respect to N^3. Lowe and Vilaivan,[15b] on the other hand, have assigned for a dinuclear cytidine complex of (trpy)Pt^{II} a stacked conformation on the basis of NMR and UV-vis spectra. We therefore decided to isolate and characterise the above complexes and to also study the Pt^{II} analogues.

† *Supplementary data available*: structures of cations **3** and **4b**; ^{1}H NMR and 2D DQF COSY spectra of **2** and **4**; chemical shifts and coupling constants of **1**–**4**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/2329/, otherwise available from BLDSC (No. SUP 57571, 8 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

Experimental

Synthesis of complexes

[(trpy)PdCl]Cl·2H_2O,[17] [(trpy)PtCl]Cl·2H_2O[18] and Hmcyt[19] were prepared as described in the literature.

[(trpy)Pd(Hmcyt-N^3)][NO_3]$_2$·5H_2O 1. To an aqueous solution of Hmcyt (0.025 g, 0.2 mmol) and $AgNO_3$ (0.068 g, 0.4 mmol) was added [Pd(trpy)Cl]Cl·2H_2O (0.089 g, 0.2 mmol). The reaction mixture was stirred in the dark at 40 °C for 1 d. After filtration of AgCl the pH of the yellow solution (3.0) was adjusted to 4.0 by addition of 0.1 M NaOH. The solution was concentrated at 35 °C to about half of the original volume (5–7 ml), and then left for crystallisation for 7 d. The product was filtered off and air-dried. Yield: 89.50 mg (67%) of yellow cubic crystals of **1**. A suitable crystal was characterised by X-ray crystallography (Found: C, 35.3; H, 3.9; N, 16.6. Calc. for $C_{20}H_{28}N_8O_{12}Pd$: C, 35.4; H, 4.2; N, 16.5%). IR (KBr, $\tilde{\nu}_{max}$/cm^{-1}): 1674s, 1628s (CO), 1374s (NO_3^-).

[{(trpy)Pd}$_2$(mcyt-N^3,N^4)][NO_3]$_3$·7.5H_2O 2a. [Pd(trpy)Cl]Cl·2H_2O (0.179 g, 0.4 mmol) was added to a solution of Hmcyt (0.025 g, 0.2 mmol) and $AgNO_3$ (0.136 g, 0.8 mmol) in water (15 ml). The resultant mixture was stirred in the dark at 40 °C for 1 d. The formed AgCl was filtered off and the pH of the resulting yellow solution (1.9) was adjusted to 7.9 by addition of 0.1 M NaOH solution. The volume was reduced at 30–35 °C to 5–6 ml and after several days at room temperature orange needles of **2a** formed. The yield of the product was 184.60 mg (41%) (Found: C, 37.3; H, 3.3; N, 15.0. Calc. for $C_{35}H_{43}N_{12}O_{17.5}Pd_2$: C, 37.4; H, 3.8; N, 15.0%). IR (KBr, $\tilde{\nu}_{max}$/cm^{-1}): 1629s, 1655s (CO), 1383s (NO_3^-). UV-vis (H_2O): ν/cm^{-1} (ε/l mol^{-1} cm^{-1}) 263 (25030), 332 (8900), 347 (12270), 364 (9330).

[{(trpy)Pd}$_2$(mcyt-N^3,N^4)][ClO_4]$_3$·H_2O 2b. To a solution of [{(trpy)Pd}$_2$(mcyt-N^3,N^4)][NO_3]$_3$ **2a** (0.067 g, 0.07 mmol) in water (8 ml) was added a $NaClO_4$ solution (0.35 M, 2 ml). A yellow amorphous precipitate was filtered off and recrystallised from acetonitrile (6 ml) to give orange-brownish crystals suit-

able for X-ray crystallography. Yield: 43.80 mg (58%) (Found: C, 37.6; H, 2.7; N, 11.4. Calc. for $C_{35}H_{30}N_9O_{14}Cl_3Pd_2$: C, 37.5; H, 2.7; N, 11.3%). IR (KBr, $\tilde{\nu}_{max}/cm^{-1}$): 1628s, 1653s (CO), 1089s (ClO_4^-), 624s (ClO_4^-).

[(trpy)Pt(Hmcyt-N^3)][NO_3]$_2$·5H_2O 3. To a solution of Hmcyt (0.025 g, 0.2 mmol) and $AgNO_3$ (0.068 g, 0.4 mmol) in water was added [Pt(trpy)Cl]Cl·2H_2O (0.107 g, 0.2 mmol). The reaction mixture was stirred in the dark at 65 °C for 3 d. The red suspension was cooled to room temperature and the pH was raised from 3.8 to 4.0 by addition of 0.1 M NaOH solution. The reaction mixture was stirred for a further 2 d at 65 °C. After cooling to room temperature the AgCl was filtered off, and the volume was reduced to 5–6 ml on a rotavapor. After several days yellow cubic crystals of compound **3** had formed. The crystals were filtered off and air-dried. The product was identified by X-ray crystallography. Yield: 25.10 mg (17%) (Found: C, 31.4; H, 3.4; N, 14.9. Calc. for $C_{20}H_{28}N_8O_{12}Pt$: C, 31.3; H, 3.7; N, 14.6%). IR (KBr, $_{max}/cm^{-1}$): 1671s, 1628s (CO), 1381s (NO_3^-).

[{(trpy)Pt}$_2$(mcyt-N^3,N^4)][NO_3]$_3$·4H_2O 4a. [Pt(trpy)Cl]Cl·2H_2O (0.200 g, 0.4 mmol) was added to a solution of Hmcyt (0.023 g, 0.2 mmol) and $AgNO_3$ (0.127 g, 0.7 mmol) in water (15 ml) and stirred at 40 °C for 1 d. The orange-red suspension was heated to 90 °C and stirred for 1 d. Then the red reaction mixture was cooled to room temperature, the pH brought from 1.8 to 8.7 with 0.1 M NaOH solution, and the suspension stirred at 70 °C for another 2 d. After cooling to room temperature AgCl was filtered off and the pH of 6.3 was adjusted to 9.3. Following reduction of the volume to 4 ml, **4a** crystallised as dark red crystals after a few days. The product was filtered off and air-dried. Yield: 192.20 mg (43%) (Found: C, 33.6; H, 3.1; N, 13.4. Calc. for $C_{35}H_{36}N_{12}O_{14}Pt_2$: C, 33.9; H, 3.1; N, 13.6%). IR (KBr, $\tilde{\nu}_{max}/cm^{-1}$): 1636s, 1658s (CO), 1384s (NO_3^-). UV-vis (H_2O): ν/cm^{-1} (ε/l mol^{-1} cm^{-1}) 280 (25450), 340 (13940), 432 (1710), 462 (2380), 492 (2870).

[{(trpy)Pt}$_2$(mcyt-N^3,N^4)][ClO_4]$_3$·H_2O 4b. To an aqueous solution (20 ml) of Hmcyt (0.025 g, 0.2 mmol) and $AgClO_4$·H_2O (0.1803 g, 0.8 mmol) was added [Pt(trpy)Cl]Cl·2H_2O (0.214 g, 0.4 mmol). The red suspension was stirred in the dark at 65 °C for 1 d, the pH was raised from 2.5 to 8.9 by addition of 0.1 M NaOH and stirred for another 2 d. After cooling to room temperature AgCl was filtered off and the pH was again adjusted to 9.2. From this orange solution, X-ray quality crystals of **4b** (37.50 mg, 7%) precipitated over several days at −4 °C (Found: C, 32.1; H, 2.3; N, 9.7. Calc. for $C_{35}H_{30}O_{14}N_9Cl_3Pt_2$: C, 32.4; H, 2.3; N, 9.7%). IR (KBr, ν_{max}/cm^{-1}): 1685s, 1656s (CO), 1087s, 622s (ClO_4^-).

Physical measurements

Fourier-transform infrared spectra (KBr pellets) were recorded on a Bruker IFS 113 v FTIR instrument. A Hitachi U-2000 spectrophotometer was used to record UV-vis spectra. Proton NMR spectra were recorded on Bruker AC 200, DPX 300 and DRX 400 spectrometers at ambient temperature. Sodium 3-(trimethylsilyl)propanesulfonate, TSP (^{1}H, D_2O) or tetramethylsilane, TMS (^{1}H, DMSO[D_6], DMF[D_7]) were used as internal references. 2D DQF COSY, NOESY (t_m 1.5 s) and TOCSY (t_m 150 ms) spectra were recorded with 1k or 2k data points in f_2 and 256 or 512 experiments in f_1 and apodized with 90° phase-shifted squared sine bell functions in both dimensions. For ^{195}Pt{^{1}H} NMR spectra, the ^{195}Pt edited ^{1}H NMR spectrum and the ^{195}Pt, ^{1}H HMQC spectrum were recorded on the AC 200 spectrometer operating at 42.9 MHz at 323 K. ^{195}Pt chemical shifts were referenced against external Na_2PtCl_6. For the HMQC 64 experiments with 128 transitions were collected in f_1 with 2k data points in f_2. A 90° shifted squared sine bell function in f_2 and an exponential multiplication in f_1 were applied prior to Fourier transformation. t_1 Noise was removed by background subtraction. The sequence was optimized for a J value of 25 Hz.

pD values were obtained by adding 0.4 to the pH meter reading (Metrohm 6321; combination glass electrode). pH* Values represent uncorrected pH meter readings in D_2O solutions.

Crystallography

Intensity data for **1**, **2b**, **3** and **4b** were collected on an Enraf-Nonius Kappa CCD[20] (Mo-Kα, λ = 0.71069 Å, graphite monochromator) with sample-to-detector distances of 28.7 (**1**, **2b**) and 30.2 mm (**3**, **4b**). They covered the whole sphere of reciprocal space by measurement of 360 frames rotating about ω in steps of 1° with scan times of 60 (**1**, **3**), 22 (**2b**), and 20 s (**4b**) per frame. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames, respectively, and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO.[21] The scaling and the global refinement of crystal parameters were performed by SCALEPACK.[21] Reflections, which were partly measured on previous and following frames, were used to scale these frames on each other. This procedure in part eliminates absorption effects and also considers crystal decay if present.

The structures were solved by standard Patterson methods[22] and refined by full-matrix least-squares based on F^2 using the SHELXTL-PLUS[23] and SHELXL-93 programs.[24] The scattering factors for the atoms were those given in the SHELXTL-PLUS program. Transmission factors were calculated with SHELXL-97.[25] Hydrogen atoms were placed at calculated positions and refined with a common isotropic temperature factor, except for those in **4b**, which could be localised with difference Fourier syntheses and were not further refined. None of the structures show any disorder besides **2b**, where the oxygens of two perchlorate anions were spread over eight and seven positions, respectively. All non-hydrogen atoms were refined anisotropically with the following exceptions in order to save parameters: the atoms of the Hmcyt ring, some of the atoms of the trpy ligand, the disordered perchlorate oxygens and the water molecule O(1w) in **2b** as well as some of the trpy atoms in **4b**.

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

CCDC 186/1486.

See http://www.rsc.org/suppdata/dt/1999/2329/ for crystallographic files in .cif format.

Results and discussion

Solid state structures of [(trpy)M(Hmcyt-N^3)][NO_3]$_2$·5H_2O (M = Pd (1), Pt (3))

The two compounds **1** and **3** are isostructural. As an example, the cation of **1** and the atom numbering scheme is given in Fig. 1. The cation of **3** is depicted in the Supplementary Material (SUP 57571). Selected interatomic distances and angles of the two compounds are listed in Table 2. Metal binding is through the N^3 position of the neutral Hmcyt nucleobase. The metal coordination sphere is square planar, with the expected deviations from right angles about the heavy metal. The M–N bond length to the central N atom of the trpy ligand is well below 2 Å and significantly shorter than any of the three other M–N bonds. The trpy ring and the Hmcyt base are almost perpendicular to each other (dihedral angle 84.2(2)°, av. of **1** and **3**). There are no unusual structural features of the (trpy)M^{II} entity when compared with other [(trpy)MX]$^{n+}$ species.[26,27] Comparison of **1** and **3** with the Hmcyt complexes *trans*-[M(NH_3)$_2$(Hmcyt-N^3)$_2$][NO_3]$_2$ (M = Pd,[28] Pt[29]) and *trans*-[$PdCl_2$(Hmcyt-N^3)$_2$][30] reveals differences only in the cases of the Pd

Table 1 Crystallographic data for compounds **1**, **2b**, **3** and **4b**

	1	**2b**	**3**	**4b**
Chemical formula	$C_{20}H_{28}N_8O_{12}Pd$	$C_{35}H_{30}N_9O_{14}Cl_3Pd_2$	$C_{20}H_{28}N_8O_{12}Pt$	$C_{35}H_{30}N_9O_{14}Cl_3Pt_2$
Formula weight	678.90	1119.83	767.59	1297.21
T/K	293(2)	293(2)	126(2)	163(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Cc	$P2_1/c$	Cc	$P2_1/c$
a/Å	11.104(2)	14.309(3)	11.061(2)	14.066(3)
b/Å	10.193(2)	10.961(2)	9.993(2)	10.988(2)
c/Å	24.365(5)	25.975(5)	24.211(5)	25.783(5)
β/°	99.34(3)	100.95(3)	98.70(3)	101.70(3)
V/Å^3	2721.1(9)	3999.8(14)	2645.3(9)	3902.2(13)
Z	4	4	4	4
μ(Mo-Kα)/mm^{-1}	0.758	1.181	5.382	7.451
No. reflections measured	7866	11271	8522	10867
No. reflections observed	3427 $I > 2\sigma(I)$	2980 $I > 2\sigma(I)$	4699 $I > 2\sigma(I)$	3277 $I > 2\sigma(I)$
R_1 (obs. data)	0.0366	0.0439	0.0238	0.0409
wR_2 (obs. data)	0.0641[a]	0.0954[b]	0.0579[c]	0.0747[d]

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [a] $w = 1/[\sigma^2(F_o^2) + 0.0239P^2 + 0.00P]$. $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. [b] $w = 1/[\sigma^2(F_o^2) + 0.0553P^2 + 0.00P]$. $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. [c] $w = 1/[\sigma(F_o^2) + 0.0351P^2 + 0.00P]$. $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. [d] $w = 1/[\sigma^2(F_o^2) + 0.0327P^2 + 0.00P]$. $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.

Table 2 Selected distances (Å) and angles (°) for **1** and **3**

	1	**3**
M–N(3)	2.028(7)	2.056(8)
M–N(1a)	2.013(4)	2.014(4)
M–N(1b)	1.932(7)	1.941(8)
M–N(1c)	2.011(4)	2.025(4)
N(1a)–M–N(3)	96.8(2)	96.6(3)
N(1c)–M–N(3)	100.8(2)	101.0(3)
N(1a)–M–N(1b)	82.0(3)	81.9(3)
N(1c)–M–N(1b)	80.5(3)	80.7(3)
C(2)–N(3)–C(4)	119.0(7)	120.8(7)
C(4)–N(4)	1.328(8)	1.327(7)
C(2)–O(2)	1.234(6)	1.229(6)
trpyM/Hmcyt	84.0(2)	84.4(2)

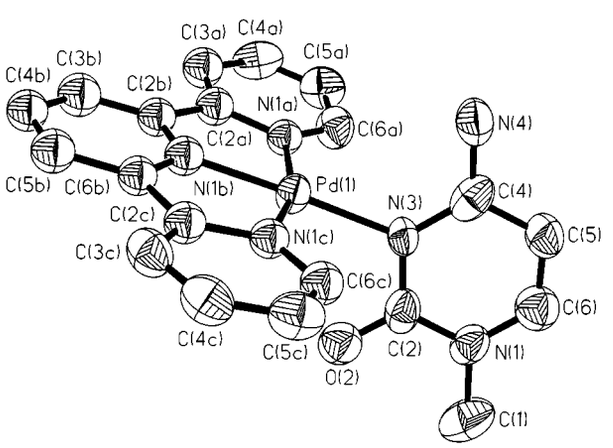


Fig. 1 Molecular cation of [(trpy)Pd(Hmcyt-N^3)][NO_3]$_2$·5H_2O **1** with atom numbering scheme. The Pt analogue **3** is similar and not shown.

complexes: thus in **1** the internal ring angle at N(3) (119.0(7)°) is somewhat smaller (3.8σ, with $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$) than that found in the two other Pd compounds, whereas the internal ring angle at C(2) (120.5(6)°) is larger (4.8–5.7σ) in **1**. The angle at N(3) is therefore comparable to that of free Hmcyt (120.0(1)°)[31] and much smaller than that of N^3-protonated cytosine, H_2mcyt$^+$ (124.7(3)°,[32] 8.5σ). There are no statistically significant differences in bond lengths between any of the Pd^{II} or Pd^{II} compounds discussed here and Hmcyt or H_2mcyt$^+$. This applies in particular for bond lengths involving the C(5) atom (see below).

The packing patterns of **1** and **3** are dominated by the following motifs: cations are arranged like tiles of a roof with pyridine

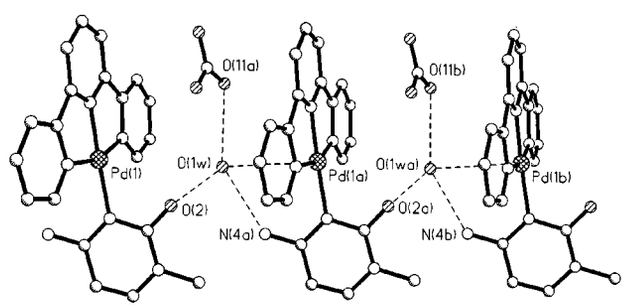


Fig. 2 Section of crystal packing of **1** with H_2O molecules connecting the nucleobases *via* H bond formation indicated (O(2)–O(1w), 2.772(5) Å; O(1w)–N(4a), 2.933(6) Å). O(1w) also forms a short contact (3.305(4) Å) with Pd(1a). Pd···Pd distances are 7.537(1) Å. Each trpy ring is part of a tile-like arrangement of (trpy)Pd running approximately perpendicular to the plane of the paper. Differentiation of light atoms: C, shaded; N, empty; O, hatched.

rings a and c of each trpy ligand stacking with their respective neighbours. Cytosine rings, which are approximately perpendicular to the trpy ligands, are likewise parallel, but 7.0 Å apart. In between two adjacent cytosine rings a NO_3^- anion is sandwiched. Individual rows of tiles are interconnected by a hydrogen bonding pattern (Fig. 2, compound **1**) which involves a water molecule, O^2 of one nucleobase and N^4 of another, as well as a NO_3^- anion which is sandwiched between trpy ligands. Interestingly there is also a relatively short contact of 3.305(4) Å between the water molecule (O(1w) in Fig. 2) and one of the Pd ions (Pd(1a)). In the case of the Pt complex **3** this distance is 3.339(4) Å. The other water molecules form an ordered spine of hydration which occasionally involves oxygen atoms of nitrate anions and, with the exception of N(4) (O(3w)–N(4a), 3.12(1) Å), no other atoms of the cations.

Solid state structures of [{(trpy)M}$_2$(mcyt-N^3,N^4)][ClO_4]$_3$·H_2O (M = Pd (2b), Pt (4b))

The dinuclear complexes [{(trpy)M}$_2$(mcyt-N^3,N^4)]$^{3+}$ (M = Pd (**2**), Pt (**4**)) were prepared from [(trpy)M(H_2O)]$^{2+}$/[(trpy)-M(OH)]$^+$ and Hmcyt in slightly alkaline solution (pH 8–9). Previous work[16] had shown (in the case of M = Pd) that formation of **2** under these conditions is quantitative. **2** and **4** were isolated as nitrate and perchlorate salts, but only crystals of the ClO_4^- salts **2b** and **4b** proved suitable for X-ray analysis.

Fig. 3 gives a view of the dinuclear cation of **2b**. The Pt_2 complex **4b** is very similar to that of **2b** and therefore is not

Table 3 Selected distances (Å) and angles (°) for **2b** and **4b**

	2b	**4b**
M(1)–N(3)	2.059(5)	2.050(8)
M(1)–N(11)	2.033(5)	2.028(7)
M(1)–M(12)	1.951(5)	1.936(8)
M(1)–N(13)	2.024(5)	2.023(7)
N(3)–M(1)–N(11)	101.2(2)	101.3(3)
N(3)–M(1)–N(13)	98.0(2)	97.7(3)
N(11)–M(1)–N(12)	80.7(2)	80.3(3)
N(13)–M(1)–N(12)	80.3(2)	81.0(3)
M(2)–N(4)	1.996(6)	1.980(9)
M(2)–N(21)	2.014(6)	2.019(8)
M(2)–N(22)	1.928(6)	1.935(9)
M(2)–N(23)	2.005(7)	2.040(8)
N(4)–M(2)–N(21)	97.8(3)	98.2(3)
N(4)–M(2)–N(23)	100.6(3)	100.1(4)
N(21)–M(2)–N(22)	80.9(3)	80.5(3)
N(23)–M(2)–N(22)	80.7(3)	81.2(3)
C(2)–N(3)–C(4)	123.4(6)	121.3(9)
C(4)–N(4)	1.308(8)	1.341(12)
C(2)–O(2)	1.225(7)	1.220(12)
M(1)–M(2)	3.0431(11)	3.0350(10)
ω [a]	18	18
trpy/trpy	17.5(3)	17.1(4)
trpy/M(1)–mcyt	89.8(2)	87.7(2)
trpy/M(2)–mcyt	90.0(2)	87.6(2)
M(1)–M(1a)	5.996(2) [b]	5.834(2) [c]

[a] Torsional angle about M(1)–M(2) vector. [b] Symmetry operation $-x+1; -y+1; -z+1$. [c] Symmetry operation $-x; -y+2; -z$.

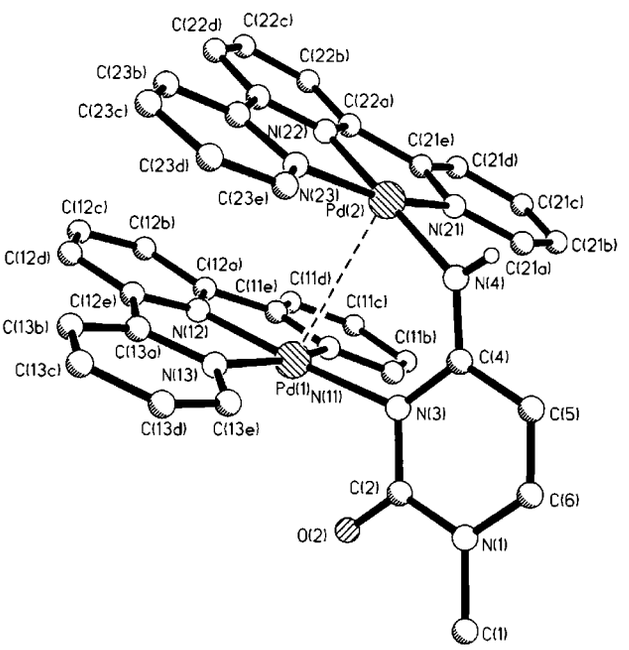


Fig. 3 Dinuclear cation of $[\{(trpy)Pd\}_2(mcyt\text{-}N^3,N^4)][ClO_4]_3\cdot H_2O$ **2b**. The Pt compound has an analogous structure and is not shown. The numbering scheme of the trpy ligands is different from that used for **1**. Differentiation of light atoms as in Fig. 2.

discussed in detail. Selected interatomic distances and angles of **2b** and **4b** are listed in Table 3. As can be seen, the two (trpy)Pd^{II} entities in **2b** adopt a *syn* orientation when binding to N^3 and the deprotonated N^4 position of the cytosine base. Both (trpy)Pd entities are again close to perpendicular to the cytosine plane. The two (trpy)Pd^{II} planes are not exactly parallel (dihedral angle 17.5°) and are also slightly twisted (18°) with respect to each other. Pd–N distances are in the expected range, with the Pd–N(4) bond being significantly (8.5σ) shorter than the Pd–N(3) bond. Again, of the M–N bonds those involving N atoms of the trpy ligands (*trans* to N(3) and *trans* to N(4)) are significantly shorter than any of the six other M–N bonds. The Pd–Pd distance within the cation of **2b** is 3.0431(11) Å. This

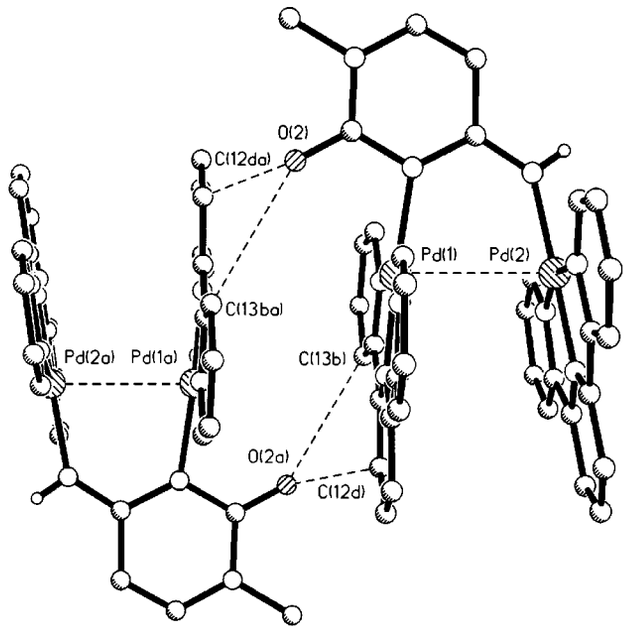


Fig. 4 Centrosymmetric dimer-of-dimers arrangement of **2b**. Short contacts between O(2) of mcyt and heteroaromatic trpy C atoms are indicated. Differentiation of light atoms as in Fig. 2.

value is shorter than twice the van der Waals radius of Pd (3.2 Å),[33] but much longer than Pd–Pd separations observed in dinuclear Pd^{II} complexes containing two bridging mcyt nucleobases (2.948(1) Å [28]) or two bridging 1-methylthyminato ligands (2.848(1) Å [34]).

The imido proton at the N^4 position of mcyt in **2b** was located in the structure determination (N(4)–H, 0.81(6) Å; C(4)–N(4)–H, 111(5)°). Its position is consistent with sp^2 hybridization of N(4). The distance between this proton and H(5) of mcyt is 2.34(7) Å (*c.f.* NMR section below).

Dinuclear cations of **2b** are stacked to give centrosymmetric pairs, as shown in Fig. 4. The stacking distance between the trpy rings of Pd(1) and Pd(1a) (symmetry operation $-x+1; -y+1; -z+1$) is ≅ 3.4 Å. Each O(2) oxygen atom of the bridging cytosinato ligands forms two short intercationic contacts with the opposite trpy, *e.g.* O(2)–C(12d), 3.258(9) Å, and O(2)–C(13b), 3.187(9) Å. The intercationic Pd(1)–Pd(1a) separation is 5.996(2) Å.

2b and **4b** have a close structural similarity with other diplatinum(II) complexes containing two trpy ligands and a bridging NCN type ligand such as canavanine,[9] guanidine,[10] or formamidine.[35] Similarities include the nearly eclipsed arrangement of the two trpy ligands in the dinuclear complex, and to similar metal–metal distances. These distances in **2b** (3.0431(11) Å) and **4b** (3.0350(10) Å) are at the lower end of this series, the shortest ones being 2.9884(7) and 2.9872(8) Å for two crystallographically independent cations of the canavanine [9] complex of Pt^{II}. They are significantly shorter than those observed in dinuclear complexes containing different types of bridges (pyrazole [36] or azaindole [2b]) as well as within pairs of unbridged $[(trpy)PtX]^{n+}$ [1b,2a,5a] or $[(trpy)Ag(MeCN)]^+$ cations (3.1698(12) Å).[37] However, they are larger than the distance observed in a metal–metal bonded, acetato-bridged dirhodium(II) complex (2.6341(9) Å).[38]

Solution NMR spectra of mononuclear Pt compound 3

Fig. 5 gives the low field portion of the ^1H NMR spectrum of $[(trpy)Pt(Hmcyt\text{-}N^3)]^{2+}$ **3** in D_2O. Individual trpy resonances have been assigned by a 2D DQF COSY experiment. Chemical shifts and coupling constants are close to previously found values, except the upfield shifted resonance of $H^{6'}$ which is known to be strongly concentration dependent.[5a] What are unusual are the shifts of the H^5 and H^6 doublets of the Hmcyt

Table 4 Comparison of chemical shifts of protons of Hmcyt, H_2mcyt^+, and cytosine ligands in **1**–**4** in D_2O

	H^{6a}	H^{5a}	CH_3	pD	Ref.
Hmcyt	7.54	5.95	3.36	9	This work
[(dien)Pd(Hmcyt-N^3)]$^{2+}$	7.59	5.95	3.40	10.6	16
$[H_2mcyt]^+$	7.81	6.13	3.44	2	This work
1	7.87	6.26	3.54	3.7	This work
3	7.91	6.32	3.57	4.8	This work
2	7.50	6.38	3.49	6.2	This work
4	7.53	6.49	3.53	8.8	This work

[a] Doublet, $^3J \cong 7.5$ Hz.

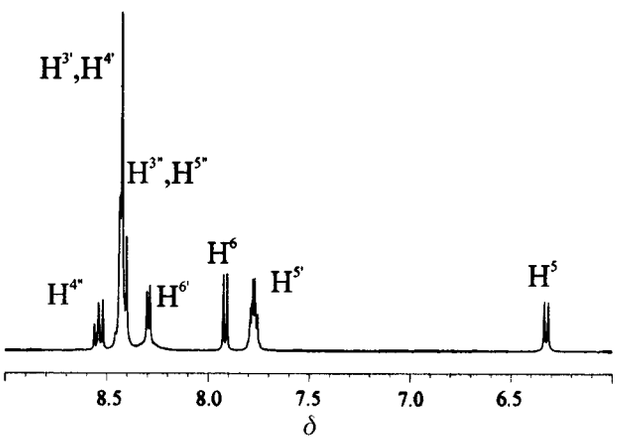


Fig. 5 ^{1}H NMR spectrum of **3** in D_2O, pD 4.8 ($c = 1.6 \times 10^{-2}$ M). H^5 and H^6 resonances are due to the Hmcyt ligand.

nucleobase (δ 6.32 and 7.91, ^3J 7.5 Hz). As with the Pd analogue **1** (see below), the downfield shifts of these resonances relative to the free nucleobase as a consequence of (trpy)M^{II} binding to N^3 exceed those of the N^3 protonated nucleobase (Table 4). This situation appears to be unique for the trpy ligand in that it violates the "rule of thumb" according to which the effect of a metal ion such as Pd^{II} or Pt^{II} carrying Cl, H_2O, NH_3, or aliphalic amine ligands is usually less than that of a proton sitting at the same donor atom. This rule holds up even for metal ions in a higher oxidation state, *e.g.* Pt^{IV}, having a coordination sphere of similar ligands (H_2O, OH, NH_3, or amine).[39] There are no changes in the ^{1}H NMR spectrum with time (days), indicating that **3** is kinetically inert.

In DMF[D_7] the N^4H_2 resonances of the Hmcyt ligand in **3** occur at δ 9.04 (NH *syn* to N^3) and δ 9.19 (NH *anti* to N^3) as two singlets, which compares with δ 6.85 and δ 7.10 for free Hmcyt in the same solvent. This dramatic downfield shift reflects a substantial increase in the acidity of this group due to (trpy)Pt^{II} binding at the N^3 site. An additional effect of the anion, as observed with protonated cytosine,[40] may also contribute to this downfield shift. Attempts to differentiate the two N^4 protons on the basis of NOE cross-peaks with H^5 of the Hmcyt ligand were at first sight not fully conclusive, in that cross-peaks between H^5 and both amino protons, albeit of different intensities, were observed. However, a differentiation of the two amino protons is possible by the following arguments. First, the NH *syn* to N^3 should resonate at higher field than the proton *anti* to N^3 as a consequence of the ring current of trpy. Second, the cross-peak of the *syn* proton with H^5 should be weaker than that of the *anti* proton because of the larger distance to H^5. Both criteria are fulfilled.

The ^{195}Pt NMR resonance of **3** at δ −2791 (D_2O, 25 °C) is in agreement with a N_4Pt coordination sphere.

Solution spectra of dinuclear Pt compound 4

The ^{1}H NMR spectrum of [{(trpy)Pt}$_2$(mcyt-N^3,N^4)]$^{3+}$ **4** in D_2O, pD 8.8 reveals in the low field region an additional downfield shift of the cytosine H^5 resonance (δ 6.49) relative to the free base, yet an upfield shift (as compared to **3**) of H^6 (δ 7.53, d, ^3J 7.5 Hz). The latter probably reflects deprotonation of the cytosine base at N^4. The trpy resonances are strongly superimposed and therefore not further distinguished, with the exception of individual resonances of the $H^{6'}$ protons. Overall, an upfield shift of 0.1–0.4 ppm of the trpy resonances as compared to **3** is observed, which points toward stacking interactions of the aromatic rings, hence suggesting a *syn* orientation of the two (trpy)Pt^{II} entities as seen in the solid state. More direct evidence—interligand NOE's between the two trpy entities—is not available due to extreme signal overlap and insignificant chemical shift dispersion. ^{1}H NMR spectra (2D NOESY, 2D DQF COSY; see also SUP 57571) permit the assignment of a number of individual resonances of **4** (Fig. 6). Cross-peaks of the proton of the exocyclic amino group N^4 (δ 8.22) with H^5 of mcyt and $H^{6'}$ of the trpy ligand bound to N^4 are observed. While not inconsistent with a *syn* orientation of the two trpy ligands, and hence a stacked conformation, the cross-peak between N^4H and H^5 of mcyt is no proof of such an arrangement (see above).

In the ^{195}Pt NMR spectrum (DMSO[D_6], 50 °C) of **4** two signals at δ −2630 and −2540 are observed. Based on the ^{1}H–^{195}Pt coupling patterns (Fig. 7), the assignment of the N^3-bound Pt to the δ −2540 resonance and the N^4-bound Pt to the δ −2630 resonance is straightforward.[41,42] Thus Pt at N^3 couples strongly with H^5 of mcyt ($^4J \approx 20$ Hz), whereas Pt at N^4 couples with N^4H ($^2J \approx 15$ Hz) and weakly with H^6 of mcyt ($^5J \approx 7$ Hz). In addition, cross-peaks of both Pt signals with trpy resonances $H^{6'}$ ($^3J \approx 40$ Hz), $H^{5'}$ and $H^{3'}$ (both $^3J \approx 20$ Hz) are observed. As compared to the mononuclear Pt compound **3**, the ^{195}Pt NMR resonances of the diplatinum species **4** are shifted by some 200 ppm (see above). A similar trend has been reported in other complexes of dimetallated mcyt, especially in cases with metal–metal interactions occurring.[42–44] However, a ^1J coupling between the two Pt atoms in **3**, which would be the ultimate proof of a *syn* orientation of the two trpy ligands, is not seen, even at a very good signal to noise ratio. Similar observations have, however, also been made in other diplatinum(II) complexes having Pt–Pt distances as short as 2.9–2.95 Å and the two Pt $d_{x^2-y^2}$ orbitals parallel.[45]

Crystals of **4**, which are reddish-black in the solid state, dissolve to give an orange-red color in water. In the UV-vis spectrum, multiple absorptions occur between 246 and 492 nm. The absorption bands in the visible region, at 462 and 492 nm, are similar to those reported by Lowe *et al.* for the analogous complex of 2′-deoxycytidine,[15b] but relative intensities of these two bands are reversed in the case of **4**, *viz.* 492 nm (ε 2870 l mol^{-1} cm^{-1}) and 462 nm (ε 2380 l mol^{-1} cm^{-1}). The Lambert–Beer law is obeyed, proving that stacking association of dinuclear species **4** is not playing a major role in solution. Che and co-workers[1] have assigned a 480 nm band of comparable intensity in a guanidinate-bridged dinuclear Pt–trpy complex to a ^{1}[dσ*-(Pt_2) ⟶ σ(π*)(trpy)] transition, with dσ* representing an orbital formed by the antibonding interaction of the d_{z^2} orbitals of the two Pt atoms. If applicable to our system, this interpretation lends support to a *syn* orientation of the two Pt(trpy) entities in **4** since any interaction between Pt orbitals requires a stacked conformation within the cation.

Solution behaviour of mononuclear Pd (1) and dinuclear Pd (2) compounds

The ^{1}H NMR spectrum of redissolved crystals of [(trpy)-Pd(Hmcyt-N^3)]$^{2+}$ **1** in D_2O is more complicated than that of the Pt_1 species **3** in that three sets of cytosine resonances are observed, and are assigned to **1**, **2** and free Hmcyt (in equilibrium with H_2mcyt^+, depending on pH*).[16] Mononuclear **1** is the dominant component in weakly acidic solution, consistent

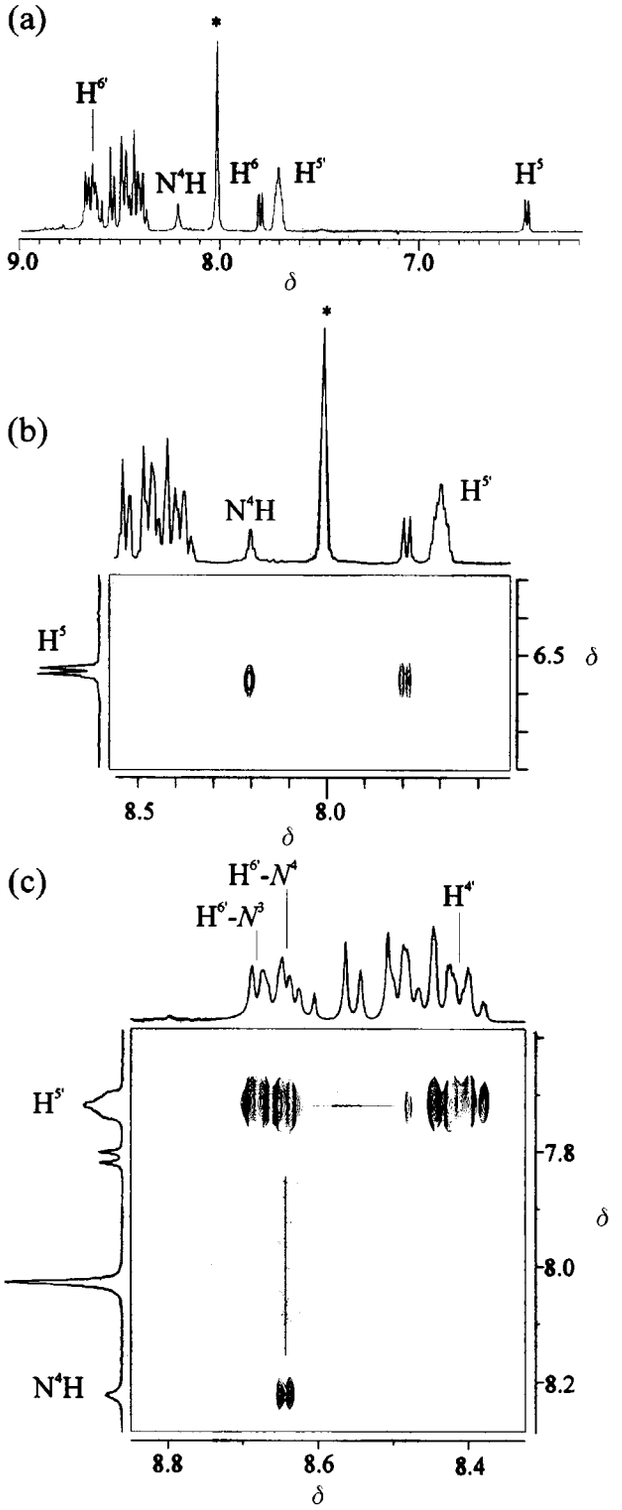


Fig. 6 Downfield regions of the ^{1}H NMR spectra of **4** recorded in DMF[D_7]: (a) 1D NMR spectrum, (b, c) portions of a 2D NOESY spectrum ($c = 1.5 \times 10^{-2}$ M, t_m 1.5 s). N^4H reveals cross-peaks to H^5 of mcyt and $H^{5'}$ of the N^4 coordinated trpy ligand.

with the species distribution established by potentiometry and ^{1}H NMR.[16] The following equilibria exist:

$$[(trpy)Pd(Hmcyt)]^{2+} + H_2O \rightleftharpoons [(trpy)Pd(H_2O)]^{2+} + Hmcyt$$

$$[(trpy)Pd(Hmcyt)]^{2+} + [(trpy)Pd(H_2O)]^{2+} \rightleftharpoons [\{(trpy)Pd\}_2(mcyt)]^{3+} + H_3O^+$$

As with **3**, it is striking that the H^5 and H^6 signals of the Hmcyt nucleobase of **1** are downfield as compared to the (dien)Pd^{II} complex containing Hmcyt-N^3 but no trpy ligands (Table 4).

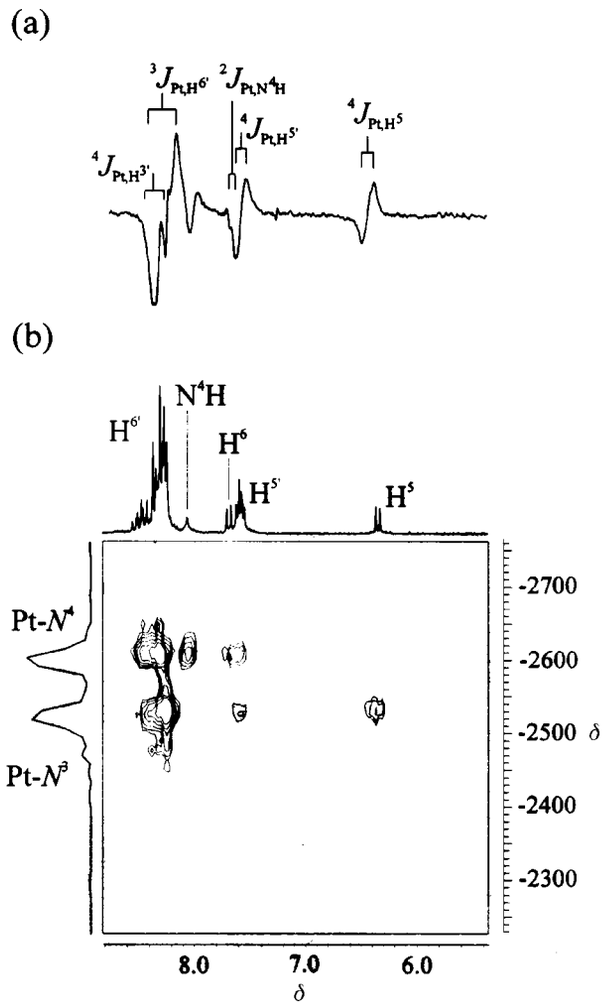


Fig. 7 ^{195}Pt edited ^{1}H NMR spectrum of **4** (a) and a 2D ^{1}H,^{195}Pt HMQC spectrum (b) (DMSO[D_6], $c = 5.3 \times 10^{-2}$ M, 50 °C). The N^4 coordinated Pt is identified by its coupling to N^4H ($^2J_{Pt,N^4H} \approx 15$ Hz) and H^6 ($^5J_{Pt,H^6} \approx 7$ Hz) of the mcyt ligand.

In DMF[D_7], **1** also equilibrates with **2** and free Hmcyt. Resonances of the amino protons of the Hmcyt ligand in **1** are observed at δ 9.14 and 9.50. The assignment of the two N^4H_2 protons is similar to that of **3** (see above).

The ^{1}H NMR spectra of the dinuclear Pd species **2a** and **2b** in D_2O are identical, as expected. There is no indication from ^{1}H NMR spectroscopy that **2** undergoes any dissociation in water that leads to individual resonances.

The ^{1}H NMR spectrum of **2b** in DMF[D_7] (Fig. 8) differs from the D_2O spectrum and from that of **4** in DMF[D_7] in the following points. First, there is dissociation of **2b** in DMF[D_7] according to

$$[\{(trpy)Pd\}_2(mcyt)]^{3+} + H_2O + DMF \longrightarrow [(trpy)Pd(Hmcyt)]^{2+} + [(trpy)Pd(DMF)]^{2+} + OH^-$$

with H^+ for nucleobase protonation probably originating from water of crystallization. There is yet another minor species present containing cytosine, which will be discussed below. Second, the proton at N^4 (δ 7.40) occurs upfield in **2b** as compared to **4**. Third, the trpy proton pattern of **2b** is somewhat different from that of **4**. Fourth, trpy resonances of **1** are observed around δ 8.8.

The second minor species present in DMF solution has been identified by TOCSY as a species containing cytosine with H^5 and H^6 doublets at δ 6.99 and 7.89, respectively. The rather spectacular extra downfield shift of the H^5 doublet strongly points to an *anti* orientation of the (trpy)Pd^{II} entity at N^4.[42,46]

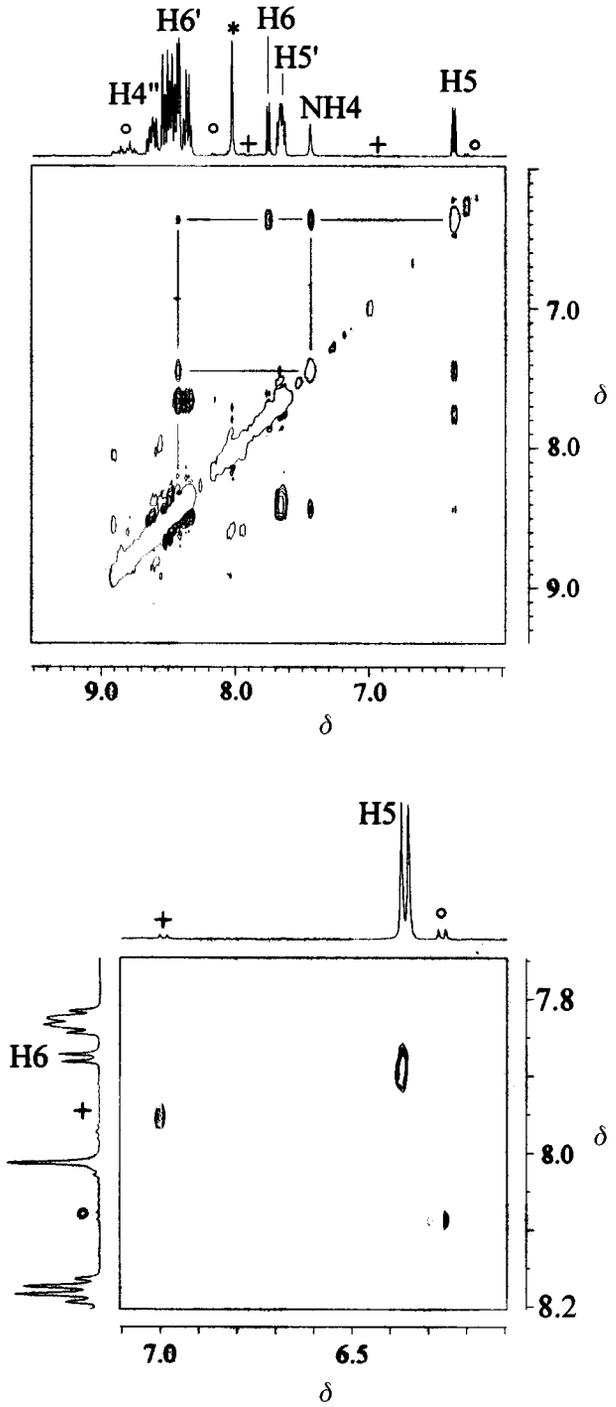
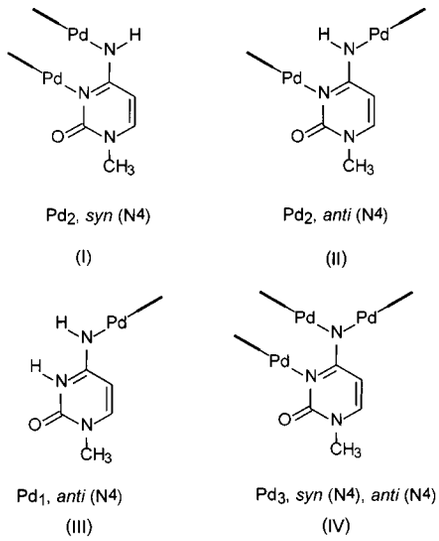


Fig. 8 Downfield region of the ^{1}H NMR spectrum of **2** (DMF[D_7], $c = 1.8 \times 10^{-2}$ M) (a) and H^5, H^6 cross-peak section of 2D TOCSY spectrum (○ = **1**, + = *anti* conformer of **2**) (b).

Whether the resonances are due to a dinuclear complex (II, Scheme 1) or a mononuclear species (III, Scheme 1) with the (trpy)Pd^{II} at N^4 in an *anti* orientation, is not clear at present. However, a trinuclear species (IV), which would be analogous to a CH_3Hg^{II} species previously reported,[47] can be ruled out, since addition of $[(trpy)Pd(DMF)]^{2+}$ to a solution of **2** in DMF[D_7] does not lead to an increase in the signal intensity of the resonances at δ 6.99 and 7.89.

Summary

Mono- and dinuclear (trpy)M^{II} (M = Pd, Pt) complexes containing the model nucleobase 1-methylcytosine have been prepared, X-ray structurally characterised and their solution behaviour studied by ^{1}H NMR spectroscopy. The ^{1}H NMR



Scheme 1

chemical shifts of the cytosine resonances H^5 and H^6 do not match expectations based on known findings of the effect of M entities carrying aliphatic amines or other nucleobases or simple ligands such as NH_3, H_2O, OH^-, Cl^-. Rather the effect of the (trpy)M entity bound to N^3 of Hmcyt in shifting the heteroaromatic protons of the nucleobases to lower field is more pronounced than that of a proton. This is obviously a consequence of the π-acceptor properties of the trpy ligand, which causes a significant deshielding of the H^5 and H^6 atoms.

Binding of a second (trpy)M^{II} entity to [(trpy)M(Hmcyt-N^3)]$^{2+}$ does not require strongly alkaline conditions and starts even at acidic pH. It is accompanied by loss of a proton from the exocyclic amine group and a further downfield shift of H^5 of the cytosine nucleobase in the ^{1}H NMR spectrum. As pointed out there is circumstantial evidence only for a *syn* orientation of the two trpy ligands: neither Pt–Pt coupling nor clear-cut inter-residue NOE cross-peaks between the two trpy ligands in the dinuclear complexes are observed, and the NOE cross-peak between N^4H and H^5 of mcyt is ambiguous. On the other hand, the upfield shift of several of the trpy resonances in dinuclear **2** and **4** as compared to mononuclear **1** and **3** (at comparable concentrations) points to a stacked conformation rather than an *anti* orientation of the two (trpy)M entities, and the visible spectrum with its absorptions at 492 nm and 462 nm (sh) is likewise in agreement with such a structure. The solid state structures of **2b** and **4b** further confirm that a stacked conformation is possible, in principle.

Acknowledgements

This work has been supported by the Fonds der Chemischen Industrie (FCI) and the DAAD (fellowship for E. Farkas).

References

1 (*a*) H.-K. Yip, C.-M. Che, Z.-Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1992, 1369; (*b*) H.-K. Yip, L.-K. Cheng, K.-K. Cheung and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 2933.
2 (*a*) J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1995, **34**, 4591; (*b*) J. A. Bailey, V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, 1993, **32**, 369.
3 M. G. Hill, J. A. Bailey, V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, 1996, **35**, 4585 and refs. cited therein.
4 R. J. Mureinik and M. Bidani, *Inorg. Chim. Acta*, 1978, **29**, 37.
5 (*a*) K. W. Jennette, J. T. Gill, J. A. Sadownick and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 6159; (*b*) A. H.-J. Wang, J. Nathans,

G. A. van der Marel, J. H. van Boom and A. Rick, *Nature*, 1978, **276**, 471.
6 G. Arena, L. Monsú Scolaro, R. F. Pasternack and R. Romeo, *Inorg. Chem.*, 1995, **34**, 2994.
7 (*a*) H. M. Brothers II and N. M. Kostic, *Biochemistry*, 1990, **29**, 7468; (*b*) H. M. Brothers II and N. M. Kostic, *Inorg. Chem.*, 1988, **27**, 1761.
8 T. G. Appleton, F. J. Pesch, M. Wienken, S. Menzer and B. Lippert, *Inorg. Chem.*, 1992, **31**, 4410.
9 E. M. A. Ratilla, B. K. Scott, M. S. Moxness and N. M. Kostic, *Inorg. Chem.*, 1990, **29**, 918.
10 A. K. Fazlur-Rahman and J. G. Verkade, *Inorg. Chem.*, 1992, **31**, 2064.
11 C.-C. Cheng and Y.-K. Lu, *Chem. Commun.*, 1998, 253.
12 L. Monsú Scolaro, A. Romeo and A. Terracina, *Chem. Commun.*, 1997, 1451.
13 M. Howe-Grant, K. C. Wu, W. R. Bauer and S. J. Lippard, *Biochemistry*, 1976, **15**, 4339.
14 C. S. Peyratout, T. K. Aldridge, D. K. Crites and D. R. McMillin, *Inorg. Chem.*, 1995, **34**, 4484.
15 (*a*) G. Lowe, J. A. McCloskey, J. Ni and T. Vilaivan, *Bioorg. Med. Chem.*, 1996, **4**, 1007; (*b*) G. Lowe and T. Vilaivan, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1499.
16 A. Kiss, E. Farkas, I. Sóvágó, B. Thormann and B. Lippert, *J. Inorg. Biochem.*, 1997, **68**, 85.
17 G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1932, 20.
18 G. Annibale, M. Brandolisio and B. Pitteri, *Polyhedron*, 1995, **14**, 451.
19 T. J. Kistenmacher, M. Rossi, J. P. Caradonna and L. G. Marzilli, *Adv. Mol. Relax. Interact. Processes*, 1979, **15**, 119.
20 NONIUS BV, KappaCCD package, Röntgenweg 1, P.O. Box 811, 2600 AV Delft, Netherlands.
21 Z. Otwinowsky and W. Minor, DENZO and SCALEPACK, *Methods Enzymol.*, 1997, **276**, 307.
22 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
23 G. M. Sheldrick, SHELXTL-PLUS (VMS), Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.
24 G. M. Sheldrick, SHELXL-93, Program for crystal structure refinement, University of Göttingen, Germany, 1993.
25 G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
26 G. M. Intille, C. E. Pfluger and W. A. Baker, *J. Cryst. Mol. Struct.*, 1973, **3**, 47.
27 W. Zhang, C. Bensimon and R. J. Crutchley, *Inorg. Chem.*, 1993, **32**, 5808.
28 M. Krumm, I. Mutikainen and B. Lippert, *Inorg. Chem.*, 1991, **30**, 884.
29 B. Lippert, C. J. L. Lock and R. A. Speranzini, *Inorg. Chem.*, 1981, **20**, 808.
30 E. Sinn, C. M. Flynn, Jr. and R. B. Martin, *Inorg. Chem.*, 1977, **16**, 2403.
31 M. Rossi and T. J. Kistenmacher, *Acta Crystallogr., Sect. B*, 1977, **33**, 3962.
32 M. Rossi, J. P. Caradonna, L. G. Marzilli and T. J. Kistenmacher, *Adv. Mol. Relax. Interact. Processes*, 1979, **15**, 103.
33 A. Bondy, *J. Phys. Chem.*, 1964, **68**, 441.
34 W. Micklitz, W. S. Sheldrick and B. Lippert, *Inorg. Chem.*, 1990, **29**, 211.
35 J. A. Bailey, V. M. Miskowski and H. B. Gray, *Acta Crystallogr., Sect. C*, 1993, **49**, 793.
36 J. A. Bailey and H. B. Gray, *Acta Crystallogr., Sect. C*, 1992, **42**, 1420.
37 E. C. Constable, A. J. Edwards, G. R. Haire, M. J. Hannon and P. R. Raithby, *Polyhedron*, 1998, **17**, 243.
38 F. P. Pruchnik, F. Robert, Y. Jeannin and S. Jeannin, *Inorg. Chem.*, 1996, **35**, 4261.
39 H. Schöllhorn, R. Beyerle-Pfnür, U. Thewalt and B. Lippert, *J. Am. Chem. Soc.*, 1986, **108**, 3680.
40 L. G. Marzilli, C.-H. Chang, J. P. Caradonna and T. J. Kistenmacher, *Adv. Mol. Relax. Interact. Processes*, 1979, **15**, 85.
41 B. Lippert, *Gazz. Chim. Ital.*, 1988, **118**, 153.
42 J. Müller, E. Zangrando, N. Pahlke, E. Freisinger, L. Randaccio and B. Lippert, *Chem. Eur. J.*, 1998, **3**, 397.
43 C. Mealli, F. Pichierri, L. Randaccio, E. Zangrando, M. Krumm, D. Holthenrich and B. Lippert, *Inorg. Chem.*, 1995, **34**, 3418.
44 F. Pichierri, E. Chiarparin, E. Zangrando, L. Randaccio, D. Holthenrich and B. Lippert, *Inorg. Chim. Acta*, 1997, **264**, 109.
45 T. V. O'Halloran and S. J. Lippard, *Inorg. Chem.*, 1989, **28**, 1289.
46 F. Pichierri, D. Holthenrich, E. Zangrando, B. Lippert and L. Randaccio, *J. Biol. Inorg. Chem.*, 1996, **1**, 439.
47 J.-P. Charland, M. Simard and A. L. Beauchamp, *Inorg. Chim. Acta*, 1983, **80**, L57.

Paper 9/02862E