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FULL PAPER

Crystal structures of a protonated form of *trans*-[Pt(NH$_3$)$_2$(mura)$_2$] and of a derivative containing three different metal ions, Pt^{2+}, Ag$^+$, and Na$^+$ (mura = 1-methyluracilate). Major difference in packing between heteronuclear pyrimidine nucleobase complexes of *cis*- and *trans*-(NH$_3$)$_2$Pt^{II}

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The complex *trans*-[Pt(NH$_3$)$_2$(mura)$_2$] **1** (mura = 1-methyluracilate), a compound of very low water solubility, is markedly solubilised in the presence of acid or suitable metal salts due to protonation and metal binding to the exocyclic oxygen atoms, respectively. The perchlorate salt *trans*-[Pt(NH$_3$)$_2$(Hmura)$_2$][ClO$_4$]$_2$·2H$_2$O **2** has been characterised by X-ray analysis. With Ag$^+$, **1** formed heteronuclear species of varying stoichiometries, *e.g.* Pt$_2$Ag$_3$ **3**, the composition of which can be further varied by the presence of alkali metal salts. The complex *trans*-[{Pt(NH$_3$)$_2$(mura)$_2$}$_2$AgNa(H$_2$O)$_4$][ClO$_4$]$_2$·6.5H$_2$O **4** appears to be the first structurally characterised example of a nucleobase complex containing three different metal ions. Tetranuclear cations of **4** are arranged in the crystal in such a way as to permit both intermolecular hydrogen bonding between NH$_3$ ligands and O^2 sites of mura nucleobases *and* π stacking between adjacent *trans*-[Pt(NH$_3$)$_2$(mura)$_2$] entities. This feature is radically different from that observed in related di- and tri-nuclear complexes derived from *cis*-(am)$_2$Pt^{II}. With mercury(II) salts initially binding to exocyclic oxygen atoms of the mura ligand takes place, followed by metal binding to the C^5 atoms of both uracil ligands of **1**.

Metal binding properties of *cis*-[Pt(am)$_2$L$_2$] [am = NH$_3$ or (am)$_2$ = diamine, L = mura = 1-methyluracilate or mthy = 1-methylthyminate] have been studied by us in detail,[1] as has protonation,[2] which produces metal-stabilised forms of the rare pyrimidine nucleobase tautomers. The extremely low solubility of *trans*-[Pt(NH$_3$)$_2$(mura)$_2$] **1** in any common solvent thus far has prevented a similar detailed study. Only with a large excess of Ag$^+$, a solubilisation of this compound in water has been achieved as well as the isolation and crystal structure determination of a polymeric complex of PtAg$_2$ stoichiometry.[3] In contrast, with the structurally related complex *trans*-[Pt(am)$_2$(Hmcyt)$_2$]$^{2+}$ (Hmcyt = 1-methylcytosine) a rich chemistry has been developed.[4] It has been realised that as a consequence of different metal orbitals interacting in dinuclear complexes of the two systems *cis*- and *trans*-(am)$_2$Pt^{II} the types of metal–metal bonds utilised are also different.[5] This fact has pronounced consequences for Pt–M distances. For example, while Pt^{II}–Pd^{II} separations in the *cis*-(am)$_2$Pt^{II} system are typically in the 2.8–2.9 Å range, they are around 2.5 Å in the case of compounds derived from *trans*-(am)$_2$Pt^{II}.

Here we report the crystal structure determinations of a protonated form of complex **1**, *trans*-[Pt(NH$_3$)$_2$(Hmura)$_2$][ClO$_4$]$_2$ **2**, as well as of a heteronuclear derivative of **1**, *trans*-[{Pt(NH$_3$)$_2$(mura)$_2$}$_2$AgNa(H$_2$O)$_4$][ClO$_4$]$_2$·6.5H$_2$O which contains three *different* metal ions in a nucleobase complex and which represents the first example of its kind. In addition, limited solution studies with other metal ions leading to a solubilisation of **1** have been carried out.

Experimental

Preparation of compounds

***trans*-[Pt(NH$_3$)$_2$(mura)$_2$] 1.** This complex was prepared by reaction of *trans*-[Pt(NH$_3$)$_2$Cl$_2$][6] (2 mmol in 20 cm^3 water) with AgNO$_3$ (3.98 mmol), filtration of AgCl, and addition of Hmura[7] (4 mmol) and NaOH (20 cm^3, 0.2 mol dm^{-3}), and stirring the mixture for 2 h at 60 °C and for 3 d at 40 °C. The white precipitate formed was filtered off, washed with water and dried. The solid (940 mg) was subsequently stirred in MeOH (500 cm^3) for 1 d to dissolve unchanged Hmura, filtered off, washed with more MeOH and dried at 100 °C. The yield of **1** was 94% (Found: C, 24.5; H, 3.5; N, 17.4. Calc. for C$_{10}$H$_{16}$N$_6$O$_4$Pt : C, 25.05; H, 3.37; N, 17.53%). IR: 3349s (sp), 3204s, 3138s, 1640vs, 1620 (sh), 1580vs, 1550s, 1475m, 1450s, 1420m, 1365s, 1340s, 1305s, 1230m, 1200w, 1150s, 955w, 885w, 845m, 830w, 810w, 775s, 725s, 645m, 595m, 490s, 445s, 370w and 310w cm^{-1}.

Partially (>50%) deuteriated complex **1** was obtained by keeping a sample of **1** (0.25 mmol) in D$_2$O–NaOD (10 cm^3, pD 9.9) for 24 h at 95 °C, filtering off the precipitate and drying the sample for 2 h at 50 °C. Deuteriation of the ammine ligands was evident from the IR spectrum, which revealed characteristic shifts of the *ν*(ND) modes (2495s, 2406s, 2297s cm^{-1}).

***trans*-[Pt(NH$_3$)$_2$(Hmura)$_2$][ClO$_4$]$_2$·2H$_2$O 2.** Complex **1** (0.2 mmol) was dissolved in aqueous HClO$_4$ (8 cm^3, 1 mol dm^{-3}), the solution filtered and kept for 1 week at 4 °C. Colourless crystals were filtered off, washed with a small amount of ice–water and dried in air. The yield was 48% (Found: C, 16.5; H, 2.9; N, 11.8. Calc. for C$_{10}$H$_{22}$Cl$_2$N$_6$O$_{14}$Pt: C, 16.77; H, 3.10; N, 11.73%). IR: 1639s, 1562s, 1481m, 1447s, 1371s, 1331s, 1094s, 806s, 775s, 625s, 482s, 443s and 365w cm^{-1}.

***trans*-[{Pt(NH$_3$)$_2$(mura)$_2$}$_2$Ag$_3$][ClO$_4$]$_3$ 3.** To a suspension of complex **1** (0.23 mmol) in water (10 cm^3) was added NaClO$_4$·H$_2$O (1 mmol) and subsequently an aqueous solution of $AgNO_3$ (10^{-3} mol dm^{-3}) until all solid had dissolved (0.69 mmol). After heating to 60 °C and filtration from a very little unidentified gray precipitate, the resulting solution was brought to room temperature and then allowed to evaporate at 4 °C. Microcrystalline **3** was isolated in 22% yield. Electron probe X-ray microanalysis (EPXMA) gave a Pt : Ag ratio of 2 : 3 (Found: C, 14.9; H, 2.0; N, 10.6. Calc. for $C_{20}H_{32}Ag_3Cl_3N_{12}O_{20}Pt_2$: C, 15.23; H, 2.05; N, 10.66%). Alternatively: to a suspension of **1** (0.21 mmol) in water (15 cm^3) was added $AgClO_4$ (0.69 mmol), the mixture warmed to 60 °C to prevent immediate formation of a precipitate, filtered, and the solution (pH 5.3) allowed to stand at 4 °C for a day. Microcrystalline **3** was then filtered off (48% yield). IR: 3448vs (br), 3300 (sh), 3200 (sh), 1638vs, 1569s, 1525s, 1476m, 1447s, 1370s, 1329s, 1148s, 1120–1091vs, 810m, 774m, 723w, 627m, 493w and 451w cm^{-1}.

***trans*-$[\{Pt(NH_3)_2(mura)_2\}_2AgNa(H_2O)_4][ClO_4]_2\cdot 6.5H_2O$ 4.** This compound was obtained accidentally in the course of work concerned with the mixed mura/gly (gly = glycine anion) complex *trans*-$[Pt(NH_3)_2(mura\text{-}N^3)(gly\text{-}N)]$. A sample of the crude product, obtained from *trans*-$[Pt(NH_3)_2(mura)Cl]$, $AgNO_3$ and Hgly,[8] had been kept at 60 °C for 6 h in the presence of an excess of $NaClO_4$ and $HClO_4$ at pH 3. Following filtration of some unidentified grayish precipitate, and slow evaporation at 4 °C, single crystals of **4** were obtained in low yield (<5%) besides other products. Compound **4** was characterised by X-ray analysis only. Its formation was rationalised by means of ^1H NMR spectroscopy (see below).

***trans*-$[\{Pt(NH_3)_2(mura-H)_2\}Hg_3(CF_3CO_2)_4]\cdot 2H_2O$ 5.** To a suspension of complex **1** (0.2 mmol) in water (1 cm^3) was added solid $Hg(CF_3CO_2)_2$ (0.8 mmol). Within a few minutes a clear, yellow solution formed, which was stirred at room temperature for 24 h. Then a colourless precipate of **5** was filtered off, washed with water and dried in air. The yield was 88% (Found: C, 13.6; H, 1.2; N, 5.2. Calc. for $C_{18}H_{18}F_{12}Hg_3N_6O_{14}Pt$: C, 13.79; H, 1.16; N, 5.36%); EPXMA confirmed a Pt : Hg ratio of 3 : 1. Complex **5** is sparingly soluble in D_2O, giving a strongly acidic reaction (pD 1.9). Only resonances due to H^6 singlets are observed, at δ 7.58, 7.39 and 7.34 (*ca.* 1 : 4 : 3), and four CH_3 resonances (δ 3.47, 3.42, 3.37, 3.30, *ca.* 1 : 15 : 2 : 4), showing that both uracil ligands are mercurated at C^5. IR: 1663s, 1617s, 1558s, 1539s, 1209s, 1138s and 692m cm^{-1}.

Spectroscopic studies

The IR spectra (KBr pellets) were recorded on a Perkin-Elmer 580B and a Bruker IFS 28 spectrometer, ^1H, ^{195}Pt, and ^{199}Hg NMR spectra (200.13, 42.95, 35.79 MHz) on a Bruker AC200 instrument. Chemical shifts are given in ppm and referenced to internal $(Me_3Si)CH_2CH_2CH_2SO_3Na$ (TSP) (D_2O), tetramethylammonium tetrafluoroborate (D_2O, δ 3.1776 relative to TSP), external Na_2PtCl_6 (^{195}Pt), and external $HgCl_2$ in D_2O (^{199}Hg; to recalculate data referred to $HgMe_2$ add +1228 ppm), respectively. For the ^1H NMR spectra taken during the reaction of complex **1** with 5 equivalents Hg^{II}, a Gaussian window function (line broadening parameter = −4.5, Gaussian broadening parameter = 0.25) was applied prior to the Fourier transformation. The pD values (in D_2O) were obtained by adding 0.4 to the pH meter reading.

Crystallography

The crystal structure of complex **2** was determined on a CAD4 diffractometer at 190 K. Unit cell dimensions were obtained by a least-squares fit of the 2θ values of 25 high order reflections ($9.5 \le \theta \le 16.7°$). Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystals and of the experimental conditions, and measured every hour. The collected intensities were corrected for Lorentz-polarisation factors[9] and empirically for absorption[10] by using the azimuthal (ψ) scans of 2 "high-χ" ($\chi > 87°$) reflections. The standard deviations on intensities were calculated in terms of statistics alone. The structures were solved by a combination of Patterson and Fourier methods and refined by full matrix least squares[9] (the function minimised being $\Sigma[w(F_o - k^{-1}F_c^{-1})^2]$), using anisotropic displacement parameters for all atoms except for those of a counter ion (see below). No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[11] The oxygen atoms of the two water molecules were refined anisotropically, however, it was not possible to locate the positions of the hydrogen atoms bonded to them. One of the two perchlorate counter ions is strongly disordered, even at low temperature. Therefore a model was constructed using the strongest peaks of a Fourier difference map. During the refinement, the positional parameters of the oxygen atoms were kept fixed and only their isotropic displacement parameters were allowed to vary, while the chlorine was refined anisotropically without constraints. The hydrogen atom bonded to atom O^4 was located on a Fourier difference map, while the remaining hydrogen atoms were put in calculated positions, [C–H 0.95 Å, $B(H) = 1.3B(C_{bonded})$ Å^2]; their contribution was taken into account but not refined. Upon convergence no significant features were found in the final Fourier difference map. All calculations were carried out using the Enraf-Nonius MOLEN package.[9]

Intensity data for complex **4** were collected on an Enraf-Nonius-KappaCCD diffractometer[12] with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) at room temperature. It covered the whole sphere of reciprocal space by measurement of 360 frames rotating about ω in steps of 1° with 45 s scan time per frame. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames and refined using the whole data set. Frames were integrated and corrected for Lorentz-polarisation effects using DENZO.[13] The scaling as well as the global refinement of crystal parameters was performed by SCALEPACK.[13] Reflections, which were partly measured on previous and following frames, were used to scale these frames on each other. This empirical procedure in part eliminates absorption effects and also considers a crystal decay if present.

The structure was solved by standard Patterson methods[14] and refined by full matrix least squares based on F^2 using the SHELXTL-PLUS[15] and SHELXL 93 programs.[16a] The scattering factors for the atoms were those given in the SHELXTL-PLUS program. Transmission factors were calculated with SHELXL 97.[16b] Hydrogen atoms were placed in geometrical calculated positions and refined with a common isotropic thermal parameter, except for the ammine hydrogens and those of the methyl group C^1 [$U(H) = 1.5U(N_{bonded})/U(C_{bonded})$ Å^2]. A part of the mura non-hydrogen ring atoms were only refined isotropically in order to save parameters as well as the partly disordered perchlorate anions and water molecules (except O^{1w}) and the Na^+. Thermal parameters for O atoms of ClO_4^- were applied to H_2O molecules bound to Na^+ and gave the occupation scheme.

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

CCDC reference number 186/1251.

See http://www.rsc.org/suppdata/dt/1999/175/ for crystallographic files in .cif format.

Results and discussion

Starting compound 1 and protonated form 2

Unlike *cis*-$[Pt(NH_3)_2(mura)_2]\cdot 2H_2O$,[17] which is well soluble in water, *trans*-$[Pt(NH_3)_2(mura)_2]$ **1** represents an extremely poorly

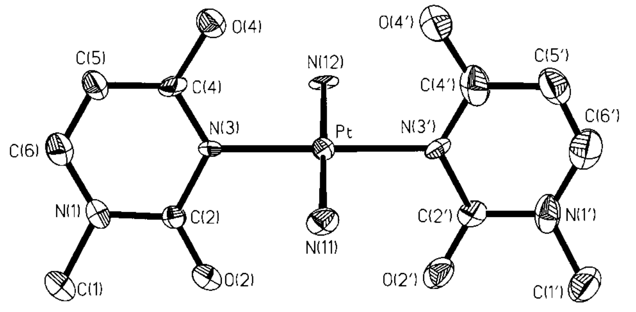

Fig. 1 View of *trans*-$[Pt(NH_3)_2(Hmura)_2][ClO_4]_2$ **2** with atom numbering scheme.

soluble microcrystalline material. The IR spectrum of **1** in the 3000–3500 cm^{-1} range is, unlike that of the *cis* isomer, very characteristic, however, with three prominent and sharp absorptions at 3349, 3204, and 3138 cm^{-1}. Upon deuteriation, these bands are shifted to 2495, 2406, and 2297 cm^{-1}, respectively, identifying them as ν(NH) modes. The isotope shifts are 1.342, 1.332, and 1.366. Taken together, these values suggest involvement of the NH_3 protons in weak hydrogen bonding.[18] With *trans*-$[Pt(NH_3)_2Cl_2]$, the ν(NH) modes occur at 3300 and 3220 cm^{-1}, the ν(ND) modes at 2465 and 2341cm^{-1}, with wavenumber shifts of 1.339 and 1.375.[19] We note that in the heteronuclear derivatives **3** and **4** this characteristic pattern of NH_3 modes is lost and rather ill structured bands occur between 3500 and 3200 cm^{-1}.

The ^1H NMR resonances of complex **1** in D_2O, pD 7.4 occur at δ 7.46 (d, ^3J 7.4 Hz) for H^6, 5.72 (d) for H^5, and 3.38 (s) for CH_3. These resonances are downfield relative to those of the *cis* isomer (δ 7.30; 5.52; 3.26), and reflect the situation that no intracomplex nucleobase stacking is possible in the case of the *trans* compound. Addition of acid to a suspension of **1** in D_2O leads to formation of a clear solution, with ^1H NMR resonances of the uracil ligands downfield from those of **1**, *e.g.* at δ 7.89 (H^6), 6.15 (H^5), and 3.52 (CH_3) at pD 0 (1 mol dm^{-3} DNO_3). The ^{195}Pt NMR shift (−2458 ppm) is consistent with a PtN_4 environment. As with neutral uracil and thymine ligands bound to *cis*-$(am)_2Pt^{II}$,[2] the Hmura ligands of **2** are susceptible to Pt–N^3 bond cleavage, leading to complex decomposition and release of Hmura. The half-life of **2** at pD $\approx$ 0, 22 °C is approximately 25 h.

Cation structure of complex 2 and packing pattern

The cation structure of complex **2** is given in Fig. 1. Platinum is bound to the N^3 positions of the two 1-methyluracil nucleobases, which are oriented *head-head* and are close to coplanar [dihedral angle 8(2)°]. Selected interatomic distances and angles of compound **2** are reported in Table 2. The two uracil rings in **2** do not display any significant differences in bond lengths and internal ring angles. Comparison of C–O bond lengths shows a lengthening of C^4–O^4 [1.326(16) Å] as compared to C^2–O^2 [1.237(18) Å] in the same base, which corresponds to 3.7 σ [with e.s.d. calculated according to $\sigma = (\sigma_1{}^2 + \sigma_2{}^2)^{\frac{1}{2}}$ and σ_1 and σ_2 being the standard deviations of the two bonds] and suggests that O^4 is protonated. In the second uracil ligand this difference [1.331(22) *vs.* 1.258(17) Å] corresponds to 2.6σ only. Both O^4 and $O^{4'}$ are involved in short hydrogen bonds to water molecules, distances being 2.56(2) Å for $O^4 \cdots O^{w1}$ and 2.48(2) Å for $O^{4'} \cdots O^{w2}$. This feature does not permit an unambiguous differentiation between the three possible forms $[Pt(NH_3)_2(Hmura)_2][ClO_4]_2 \cdot 2H_2O$, $[H_3O][Pt(NH_3)_2(Hmura)(mura)][ClO_4]_2 \cdot H_2O$, and $[H_3O]_2[Pt(NH_3)_2(mura)_2][ClO_4]_2$, as discussed in similar cases,[3a] but we tentatively favor the first possibility, hence the presence of the rare 4-hydroxo, 2-oxo tautomeric form for the following reason: the IR spectrum of **2** gives no hint for the presence of two different uracil ligands (Hmura, mura), but displays a pronounced shift of the intense 1580 cm^{-1} band of **1** to 1562 cm^{-1} for **2**, consistent with a loss in double-bond character of one of the CO groups. Moreover, the ^1H NMR spectrum of **2** clearly indicates protonation of the mura ligands in solution.

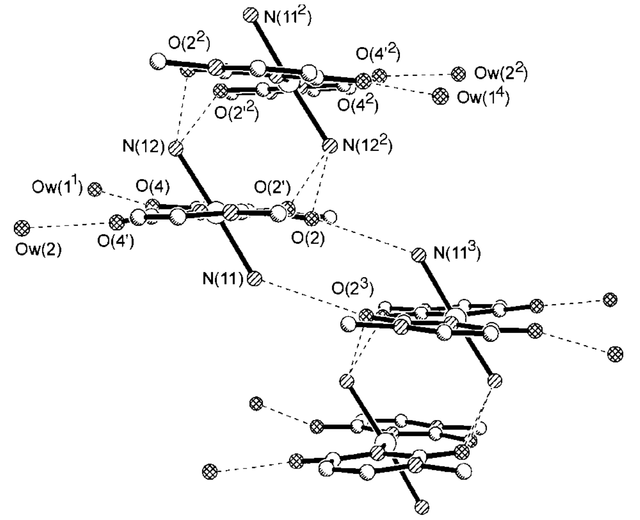

Fig. 2 Detail of stacking pattern of cations of complex **2** with hydrogen bonds indicated.

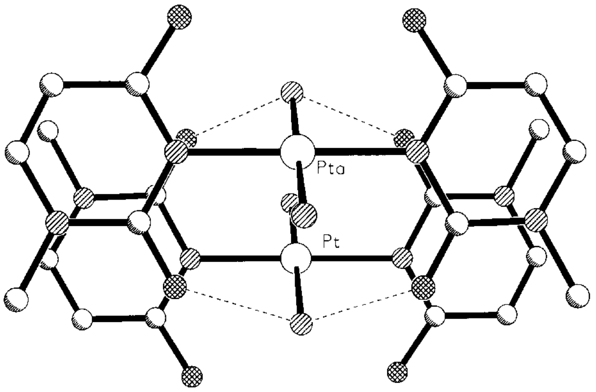

Fig. 3 Detail of stacking pattern of complex **2** with view perpendicular to the uracil rings to demonstrate the base overlap.

A section of the packing of the cation of complex **2** and the water molecules is presented in Fig. 2. As can be seen cations are arranged in pairs with stacking (*ca.* 3.5 Å) between the four bases and four hydrogen bonds involving the O^2 oxygen atoms of the two bases and the N^{12} ammine groups. Distances and angles are included in Table 2. As a consequence of this packing, N^{11}–Pt–N^{12} vectors are parallel, forming a 58° angle with the mean plane of the two uracil bases. The Pt $\cdots$ Pt separation within the stacked pair is 4.046(1) Å. Pairs of stacked cations are interconnected by longer hydrogen bonds between N^{11} and O^2. In addition there is hydrogen bonding between water molecules and the O^4 sites, as mentioned above.

The extent of base stacking between cations of complex **2** deserves some comment. As seen in a view perpendicular to the planes of the uracil ligands (Fig. 3), stacking is quite substantial and, as mentioned above, the stacking distance is only slightly longer than in unperturbed DNA (3.4 Å). With regard to cross-linking adducts of *trans*-$(NH_3)_2Pt^{II}$ with two complementary bases in double-stranded DNA,[20] this implies that the NH_3 groups of a *trans*-$(NH_3)_2Pt^{II}$ entity within the center of a DNA helix do *not automatically* disrupt base stacking by increasing the separation between the platinated base pair and the adjacent pairs. If the NH_3 groups are not perpendicular to the mean plane of the two bases but held through hydrogen bonds in a position similar to that seen in **2**, base stacking is expected strongly to depend on the flanking sequences. A model of a DNA dodecamer duplex containing a central guanine, cytosine

Table 1 Crystallographic data for compounds **2** and **4**

	2	**4**
Chemical formula	$C_{10}H_{22}Cl_2N_6O_{14}Pt$	$C_{10}H_{26.5}Ag_{0.5}ClN_6Na_{0.5}O_{13.25}Pt$
M	716.31	738.84
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	8.210(2)	17.379(3)
b/Å	17.582(5)	20.590(4)
c/Å	15.511(5)	14.925(3)
β/°	98.88(2)	108.52(3)
V/Å^3	2212(1)	5064.1(17)
T/K	190	293(2)
Z	4	8
μ(Mo-Kα)/mm^{-1}	6.728	6.085
2θ Range/°	5–50	6.3–46.4
No. reflections collected	3886	55374[a]
No. independent reflections [$F_o^2 > 4\sigma(F^2)$]	2873	1760
T_{max}/T_{min}	1.097/0.7535	0.700/0.115
R_{int}		0.085
$R/R1$ (obs. data)	0.052[b]	0.0440[c]
$R'/wR2$ (obs. data)	0.075[b]	0.0922[c]

[a] Number of reflections after merging of the redundant data: 6765. [b] $R = \Sigma\|F_o| - (1/k)|F_c\|/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - k^{-1}|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [c] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

Table 2 Selected distances (Å) and angles (°) for *trans*-$[Pt(NH_3)_2(Hmura)_2][ClO_4]_2\cdot 2H_2O$ **2**[a]

Pt–N(11)	2.06(1)	C(4)–O(4)	1.33(2)
Pt–N(12)	2.06(1)	C(2)–O(2)	1.24(2)
Pt–N(3)	2.05(1)	C(4′)–O(4′)	1.33(2)
Pt–N(3′)	2.07(1)	C(2′)–O(2′)	1.26(2)
N(11)–Pt–N(12)	177.7(5)	N(12)–Pt–N(3)	90.4(4)
N(11)–Pt–N(3)	89.6(5)	N(12)–Pt–N(3′)	88.8(5)
N(11)–Pt–N(3′)	91.2(5)	N(3)–Pt–N(3′)	179.2(5)
O(4)–Ow(1^1)	2.56(2)	N(12)–O(2^2)	2.90(2)
O(4′)–Ow(2)	2.48(2)	N(12)–O($2'^2$)	2.92(2)
N(11)–O(2^3)	3.20(1)		

[a] Symmetry operations: 1 1 + *x*, 0.5 − *y*, 0.5 + *z*; 2 − *x*, − *y*, 1 − *z*; 3 1 − *x*, − *y*, 1 − *z*.

cross-link and two different pairs at either side and obtained by molecular mechanics, gives a mixed result, namely retention of base stacking on one side and a rise of base residues to 5 Å on the other.[21] The packing pattern found in **2** is very similar to that of **4** (see below) and analogous to that in *trans*-$[Pt(NH_3)_2(Hmcyt\text{-}N^3)(dmgua\text{-}N^1)]^{2+}$ (Hmcyt = 1-methylcytosine, dmgua = 7,9-dimethylguanine),[22] although in the latter case the base overlap is more reduced.

Solubilisation of complex 1 by metal ions

Heterometal ion (Ag^+, Hg^{2+}, Cu^{2+}, Zn^{2+}, Tl^+) binding to complex **1** in aqueous solution is immediately evident from the fact that **1** dissolves in part or fully and, with diamagnetic ions, leads to a significant improvement of the signal : noise ratio of the mura resonances in the ^1H NMR spectra. With increasing amounts of the metal salt added, slight downfield shifts of the aromatic protons of the mura ligands of **1** are observed, with no indication of the formation of kinetically inert heterometallic species with Ag^+, Zn^{2+} and Tl^+, however. Considering the rather modest effects in the ^1H NMR spectra, low formation constants seem likely. For example, with an excess of Ag^+ (>5 equivalents) downfield shifts of H^5 and H^6 are *ca.* 0.05 ppm only ($c_{Pt} \approx 0.075$ mol dm^{-3}, D_2O). Likewise, the ^{195}Pt NMR resonance (δ −2405 of **3**) is hardly affected by an excess of Ag^+.

Mixed-metal complexes Pt_2Ag_3 3 and Pt_2AgNa 4

The isolation and crystal structure analysis of a polymeric mixed $PtAg_2$ complex of composition *trans*-$[Pt(NH_3)_2(mura)_2Ag_2(NO_3)_2(H_2O)]\cdot H_2O$ has previously been reported by us.[3] Applying only a slight modification, *viz.* addition of an excess of $NaClO_4$ to a mixture of **1** and $AgNO_3$, gave a compound of different stoichiometry, $[\{Pt(NH_3)_2(mura)_2\}_2Ag_3][ClO_4]_3$ **3**. It appears to be a member of a similar group of compounds of general composition $Pt_xAg_y(mura)_z$ previously reported for the *cis*-$Pt(NH_3)_2(mura)_2/Ag^+$ system.[23] As in the former system, and by no means restricted to Ag,[17] it is not possible to predict complex stoichiometry in a rational way. Considering the large structural variety of mixed platinum–silver complexes found in the *cis*-$[Pt(NH_3)_2L_2]$ system (L = mura or mthy),[24–28] it is not possible to assign a specific structure to **3**.

We had hoped that addition of $NaClO_4$ to a mixture of complex **1** and $AgNO_3$, rather than producing **3**, would give in higher yield and in a rational way *trans*-$[\{Pt(NH_3)_2(mura)_2\}AgNa(H_2O)_4][ClO_4]_2\cdot 6.5H_2O$ **4**, a compound which we had accidentally obtained in crystalline form but low yield in a rather different way (*cf.* Experimental section). As we have clarified by ^1H NMR spectroscopy,[8] upon addition of $HClO_4$ to *trans*-$[Pt(NH_3)_2(mura\text{-}N^3)(gly\text{-}N)]$ (and in the absence of Ag^+ and Na^+) a complicated rearrangement takes place, following initial protonation of the glycinate and the mura ligand. This situation parallels that seen for *cis*-$[Pt(NH_3)_2(mura)(gly)]$.[29] As a consequence, both Hgly and Hmura are partially displaced, but within 30 h at 40 °C, pH 3, there is clear evidence for formation of **1**, both from ^1H NMR spectroscopy and precipitation of **1**. Considering the relatively low pH, formation of **1** from the mono(nucleobase) complex and free Hmura is remarkable.

The tetranuclear cation of *trans*-$[\{Pt(NH_3)_2(mura)_2\}_2AgNa(H_2O)_4][ClO_4]_2\cdot 6.5H_2O$ **4** (Fig. 4, Table 3) consists of two Pt^{2+}, a Ag^+, and a Na^+ ion, arranged in the form of a Y, with an angle of 146.9(1)° between the two Pt–Ag bars. The Pt–Ag distances are 2.847(1) Å, in the normal range for mixed platinum–silver complexes of uracil and thymine, regardless if derived from *cis*- or *trans*-$(am)_2Pt^{II}$,[3,24–28] or different systems.[30,31] The Ag^+ and Na^+ are 3.57(1) Å apart. All four mura nucleobases are arranged *head-head* and use their O^4 oxygen atoms as heterometal (Ag, Na) binding sites. The cation has a C_2 symmetry axis which passes through Ag and Na.

Ignoring Pt^{2+} and Na^+ ions, Ag^+ is bound to four oxygen atoms of four mura ligands, which form a distorted tetrahedron (Table 3). Distances to the bridging $O^{4'}$ oxygen atoms [2.462(9) Å] are slightly longer than those to the O^4 oxygen atoms [2.411(9) Å], which bind in a monodentate fashion, yet are in the normal range.[3,32] The Ag^+ is markedly out of the

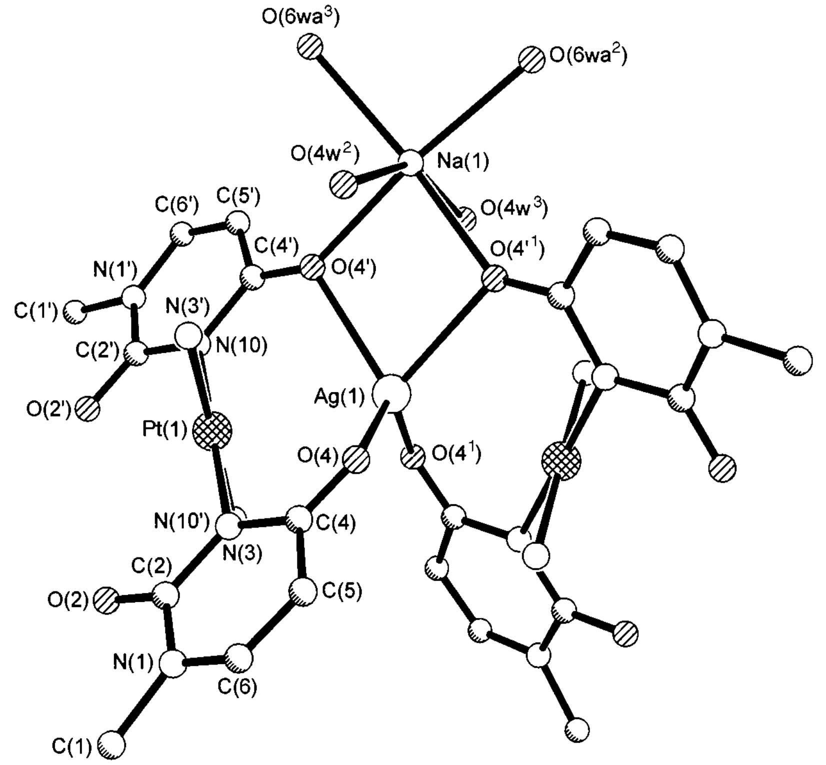

Fig. 4 View of the cation of *trans*-[{Pt(NH$_3$)$_2$(mura)$_2$}$_2$AgNa(H$_2$O)$_4$][ClO$_4$]$_2$·6.5H$_2$O **4** with atom numbering scheme.

plane of the chelating mura pairs (see below) because the two oxygens bridging Ag$^+$ and Na$^+$ are pulled together by Na$^+$ [O$^{4'}$···O$^{4'a}$ 3.20(1) Å]. In *trans*-[(NH$_2$Me)$_2$Pt(dmcyt)$_2$Ag$_2$][NO$_3$]$_2$ (dmcyt = 1,5-dimethylcytosinate), which represents a good structural model of a hypothetical *trans*-[(NH$_3$)$_2$Pt(mura)$_2$Ag]$^+$ cation, the two Ag$^+$ ions are essentially coplanar with the two bases.[4f]

The Na$^+$ ion is surrounded by two oxygens (O$^{4'}$) of the mura ligands and by four water molecules (O^{4w}, O^{6wa}) (Table 3). The Na–O distances are somewhat variable but not unusual.[33] The quadrilateral formed by Na, Ag, and the two oxygen atoms O$^{4'}$ and O$^{4'a}$ can be considered a mix of two similar quadrilaterals seen in the solid state structures of *trans*-[Pt(NH$_3$)$_2$(mura)$_2$Ag$_2$(NO$_3$)$_2$(H$_2$O)]·H$_2$O [3] (Ag$_2$,O$_2$) and *cis*-[Pd(en)(mthy)$_2$Na$_2$][NO$_3$]$_2$·H$_2$O [34] (Na$_2$,O$_2$), respectively. In all three cases the motif is identical, *viz.* exocyclic oxygen atoms of the pyrimidine bases function as bridges between the metal ions.

The two mura bases within one half of the cation are close to planar [dihedral angle 4.9(8)°] and inclined by 63° (average) with respect to the PtN$_4$ plane. As compared to other bis(nucleobase) complexes of *trans*-(am)$_2$Pt^{II}, where frequently almost perpendicular orientations are observed,[22,35] this value is relatively low. It is the consequence of both intra- and intermolecular hydrogen bonding (see below). The Ag$^+$ is markedly out of the planes of the mura ligands, by 1.05(2) Å from the ring containing N^3, and by 1.38(2) Å from the ring containing N$^{3'}$.

Packing pattern of complex 4. Cations of complex **4** form infinite zigzag arrays with repetitive Pt–Ag–Pt···Pt–Ag–Pt units (Fig. 5) and intercationic Pt···Pt separations of 4.271(2) Å. A detail of the packing is shown in Fig. 6. It demonstrates that adjacent cations interact both through stacking (3.5 Å) of four mura ligands and intermolecular hydrogen bonding between NH$_3$ ligands and O^2 oxygen atoms of the mura rings very much as in **2**: N^{10}···O^{2a} 2.87(1); N^{10}···O$^{2'a}$ 2.95(1) Å; Pt^1–N^{10}–O^{2a} 117.6(5); Pt^1–N^{10}–O$^{2a'}$ 116.8(5)°. This situation is reminiscent of that realised in related mixed nucleobase complexes ("metal-modified base pairs") of *trans*-(am)$_2$Pt^{II}.[22,36]

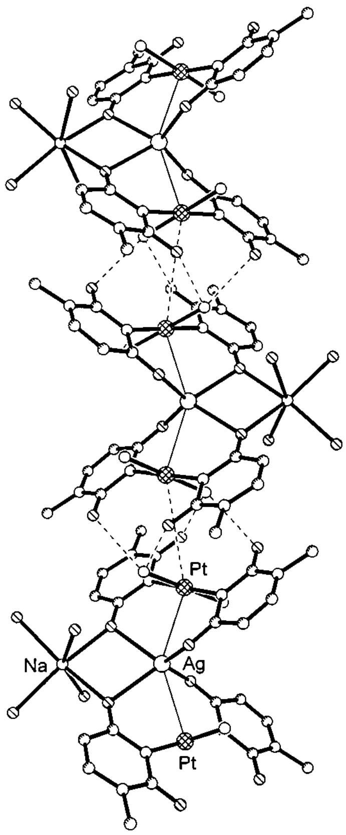

Fig. 5 Packing pattern of cations of complex **4**.

The packing pattern seen in complex **4** is completely different from those of dinuclear Pt$_2$ or multinuclear mixed Pt$_x$M$_y$ complexes of mura or mthy with *cis*-(am)$_2$Pt^{II}.[37] While in both systems strings of metal ions form, with intermolecular hydrogen bonding between the am(m)ine ligands of Pt and carbonyl oxygen atoms of the pyrimidine nucleobases, only in the *trans*-(am)$_2$Pt^{II} complex **4** there is π stacking between the nucleobases. If intermolecular π stacking is observed in *cis*-(am)$_2$Pt^{II} complexes, it either involves aromatic amine ligands of the Pt^{II}, *e.g.* 2,2′-bipyridine, yet not nucleobases,[38] or it is intramolecular as a consequence of a stereoactive electron lone pair at a heterometal ion (Tl^{I}) bound to *cis*-$(NH_3)_2Pt(mthy)_2$.[39] As far as intercationic Pt···Pt separations are concerned, they are rather variable with *cis*-$(am)_2Pt^{II}$ compounds, depending on relative nucleobase orientation (*head-head* or *head-tail*) and packing of the cationic units.[37b] They may be as low as 3.25 Å [25] and as long as 5.66 Å.[37b] The intermolecular distance seen in **4** [4.271(2) Å] is in between these two extremes and considerably shorter than in mononuclear complexes of *trans*-$(am)_2Pt^{II}$ displaying a similar stacking pattern.[22,36]

Reactions of complex 1 with HgX_2 (X = NO_3 or CF_3CO_2)

Reactions of complex **1** with $Hg(NO_3)_2$ and $Hg(CF_3CO_2)_2$ were carried out in D_2O and followed by ^1H NMR spectroscopy. Addition of either salt to a suspension of **1** in D_2O ($1 \le pD \le 2$) instantaneously leads to solubilisation of **1** and gives rise to new sets of resonances of mura, all of which are downfield with respect to those of **1**. For example, at a 1 : 1 ratio *r* of Hg^{II} and **1**, two sets of resonances of relative intensities of 3 : 1 are observed, *viz.* at δ 7.57, 5.83, 3.45 (major species, A) and at 7.55, 5.88, 3.39 (minor species, B). Within hours, a new H^6 singlet of low intensity at *ca.* δ 7.45 grows in (C). The latter resonance forms more quickly and in higher yield as the ratio *r* is increased. With *r* = 5 (Fig. 7) this resonance represents the only one in the aromatic region after 2–3 h (pD 1, 22 °C). Application of a Gaussian window function to the FID of the spectra clearly

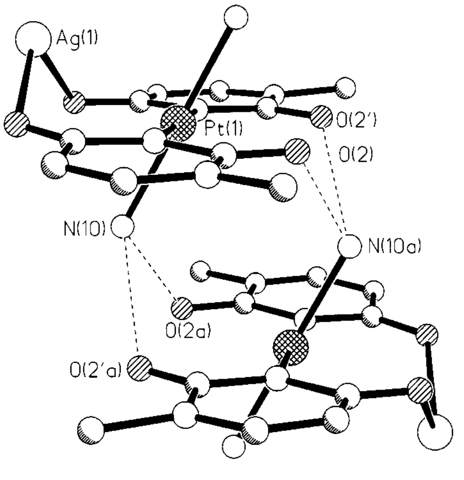

Fig. 6 Detail of packing pattern of cations of complex **4**, demonstrating hydrogen bonding and π-stacking interactions of platinum entities of adjacent cations.

Table 3 Selected bond lengths (Å) and angles (°) for the cation of complex **4**[a]

Pt(1)–N(3)	2.049(9)	Pt(1)–Ag(1)	2.8474(11)
Pt(1)–N(3′)	1.998(10)	Ag(1)–O(4)	2.411(9)
Pt(1)–N(10)	2.044(9)	Ag(1)–O(4′)	2.462(9)
Pt(1)–N(10′)	2.037(9)	Ag(1)···Na(1)	3.568(12)
Na(1)–O(4′)	2.318(13)	Na(1)–O(6wa^{2,3})	2.44(4)
Na(1)–O(4w^{2,3})	2.61(2)		
N(3)–Pt(1)–N(3′)	179.1(4)	O(4′)–Na(1)–O(6wa^3)	93.4(9)
N(3)–Pt(1)–N(10)	89.6(4)	O(4′)–Na(1)–O(4w^2)	82.9(6)
N(3)–Pt(1)–N(10′)	90.9(4)	O(4′)–Na(1)–O(4w^3)	77.1(6)
N(3′)–Pt(1)–N(10)	89.8(4)	O(6wa^2)–Na(1)–O(6wa^3)	90(2)
N(3′)–Pt(1)–N(10′)	89.7(4)	O(6wa^2)–Na(1)–O(4w^2)	109.7(12)
N(10)–Pt(1)–N(10′)	179.4(4)	O(6wa^2)–Na(1)–O(4w^3)	90.0(11)
O(4′)–Na(1)–O(4′^{1})	86.6(6)	O(4w^2)–Na(1)–O(4w^3)	152.5(11)
O(4′)–Na(1)–O(6wa^2)	167.0(10)		
O(4)–Ag(1)–O(4^1)	130.9(5)	O(4)–Ag(1)–O(4′)	118.1(3)
O(4)–Ag(1)–O(4′^{1})	99.4(3)	O(4′)–Ag(1)–O(4′^{1})	80.4(4)

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

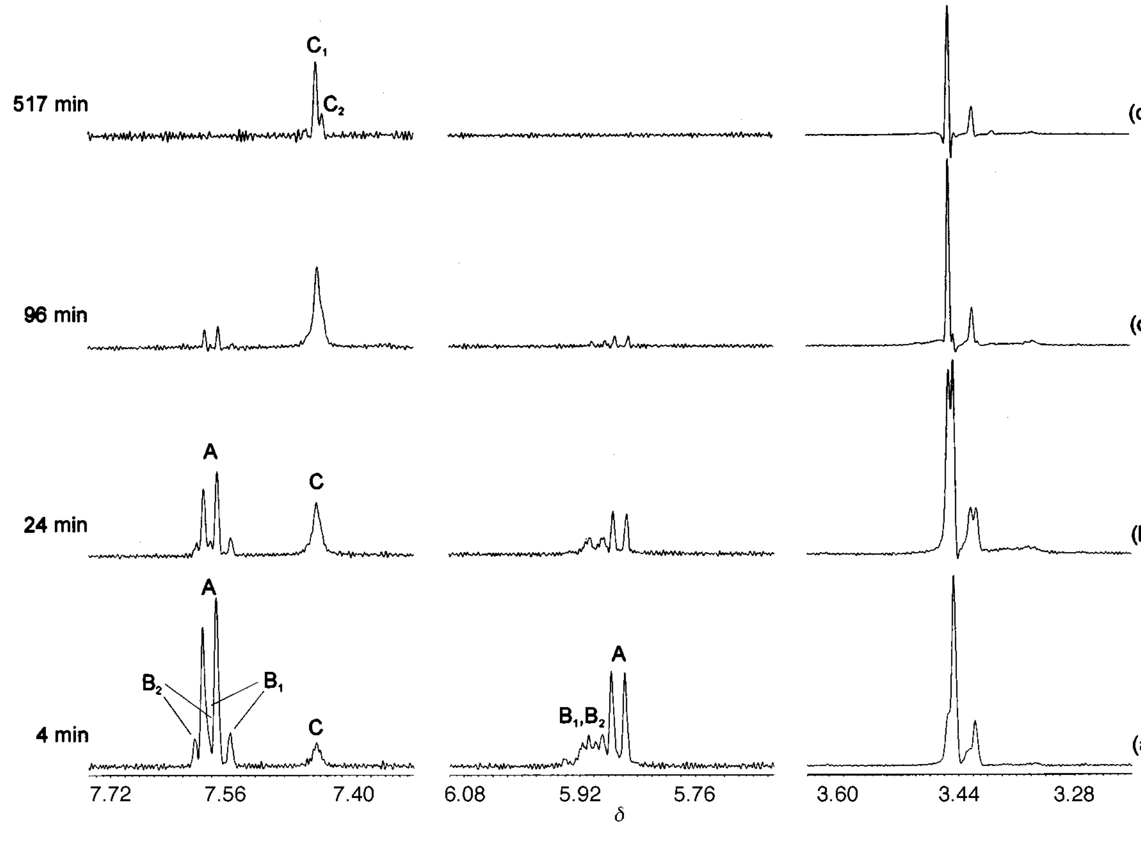

Fig. 7 Proton NMR spectra (H^6, H^5 and NCH_3 protons) of mixtures of $Hg(CF_3CO_2)_2$ and complex **1** (*r* = 5) at different reaction times, recorded in D_2O (pD 1–2).

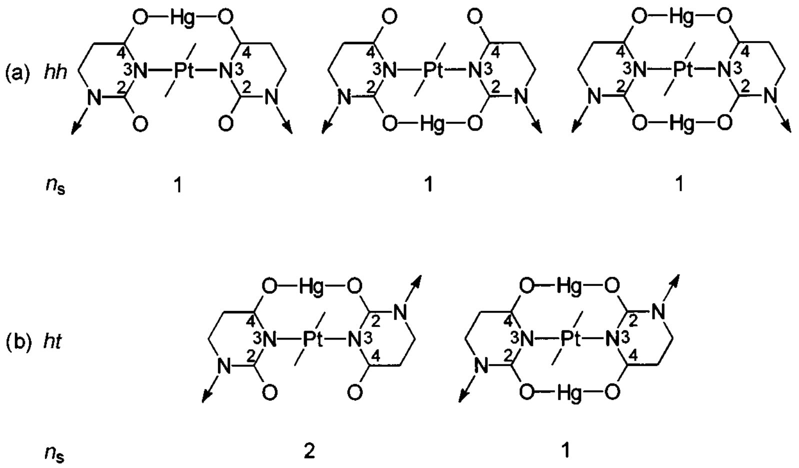

Fig. 8 Possible di- and tri-nuclear, mixed Pt, Hg_x ($x = 1$ or 2) complexes derived from *head-head* (*hh*) and *head-tail* (*ht*) rotamers of **1**. The expected number n_s of H^5 and H^6 doublets is given.

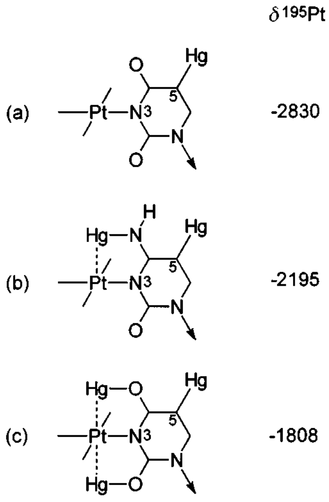

Fig. 9 Chemical shifts of ^{195}Pt NMR resonances for mixed Pt, Hg_x species (a,b) and proposed structure of the compound formed at $r = 5$ (Hg^{II} : **1**).

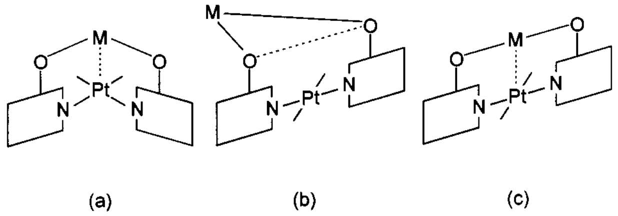

Fig. 10 Schematic representations of dinuclear Pt, M complexes derived from (a) *cis*-$[Pt(NH_3)_2(mura\text{-}N^3)_2]$, (b) *trans*-$[Pt(NH_3)_2(mura\text{-}N^3)_2]$ as observed in **4** and (c) *trans*-$[Pt(NH_3)_2(mura\text{-}N^3)_2]$ with M coplanar with Pt and the two nucleobases.

reveals that the apparent singlet C consists of two components (C_1, C_2), as does the NCH_3 resonance. In the initial state of the reaction, three H^6 and H^5 doublets of uneven intensities (A, B_1, B_2) are observed, unlike with $r = 1$ (two doublets).

We propose that the species formed in the early stage of the reaction (A, B) represent heteronuclear $PtHg_x$ ($x = 1$ or 2) species with Hg^{II} binding to exocyclic oxygen atoms (O^4, O^2) of the mura ligands. Chemical shifts of the H^6 and H^5 doublets are neither consistent with protonated **1** nor with free Hmura. We are unable to assign these species, considering the multiplicity of products feasible, depending on the relative orientations of the two bases (Fig. 8). All we can tell is that the species formed are not in fast exchange and apparently depend on *r*. Species C and C_1, C_2, respectively, represent C^5-mercurated species, since the disappearance of the H^5 doublets of mura during the reaction is not due to an isotope exchange (^{2}D *vs.* ^{1}H) as clearly seen from the behaviour of the H^6 doublets. The chemical shift of the H^6 singlet is in the range expected for this kind of species.[40–43] However, unlike in similar cases, we do not observe coupling between the ^{199}Hg isotope and H^6. Values of ^3J of 100–170 Hz could have been expected.[43] Likewise, a ^{199}Hg NMR resonance is not detected. The ^{195}Pt NMR resonance of the sample $r = 5$ containing only species C_1 and C_2 consists of an unusually broad (half width *ca.* 200 ppm) signal at an unexpected chemical shift (δ −1808). This value compares with δ −2830 for a complex of Hmura with a $(dien)Pt^{II}$ entity at N^3 and a Hg^{II} at C^5,[40] and δ −2195 for a cyclic complex of 1-methylcytosine containing Pt^{II} at N^3 and Hg^{II} both bound to N^4 and C^5 [Fig. 9(a), 9(b)].[4b] It suggests that in the present case Pt^{II} might be surrounded by two Hg^{II}, as schematically pointed out in Fig. 9(c). It is neither possible at present to assign a rotational state (*head-head* or *head-tail*) of the two uracil rings nor to determine the degree and kind of condensation (dimeric, polymeric, cyclic) *via* C^5–Hg–C^5 bonds. Attempts further to characterise complex **5**, which was obtained in a preparative scale with $r = 4$, were unsuccessful. However, mercuration of both uracil ligands at C^5 was clearly evident.

Conclusion

As shown in this work, *trans*-$[Pt(NH_3)_2(mura\text{-}N^3)_2]$ **1** behaves as a ligand toward other metal ions (Ag^+, Na^+, Hg^{2+}). In this respect, **1** is very similar to the corresponding *cis* isomer, *cis*-$[Pt(NH_3)_2(mura\text{-}N^3)_2]$.[1] What is different in the two systems, is essentially the relative orientations of the metal ions (Fig. 10) as well as the intercationic interactions. Thus, in dinuclear complexes derived from *cis*-$[Pt(NH_3)_2(mura\text{-}N^3)_2]$, Pt and the second metal in general are facing each other [Fig. 10(a)], unless severe bulk of other ligands prevents it.[44] If the second metal ion is likewise Pt^{II} in a *cis* geometry, this feature permits removal of electrons from the d_{z^2} orbitals directed toward each other, hence oxidation. In **4**, Pt^{II} and Ag^I are not at the closest possible distance [Fig. 10(b)], which they would be if Ag^I were linearly co-ordinated by two O^4 oxygen atoms and coplanar with the two uracil rings [Fig. 10(c)]. As to the differences in intermolecular interactions between cations of **4**, and likewise of **2**, from those seen in related compounds of *cis* geometry, nucleobase stacking in the *trans* compounds appears to be a recurring motif[22] as opposed to mainly hydrogen bonding in *cis* complexes, with the latter sometimes reinforced by metal–metal bond formation.[45]

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