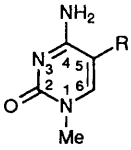
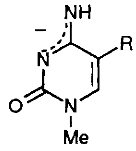
Cytosine Nucleobase as a Tridentate Ligand: Metal Binding to N(3), N(4) and O(2) in *trans*-$[(NH_2Me)_2Pt(dmcyt)_2Ag_2][NO_3]_2$ (dmcyt = 1,5-dimethylcytosinate)†

Dagmar Holthenrich,[a] Michael Krumm,[a] Ennio Zangrando,[b] Fabio Pichierri,[b] Lucio Randaccio*,[b] and Bernhard Lippert*,[a]
[a] *Fachbereich Chemie, Universität Dortmund, 44221 Dortmund, Germany*
[b] *Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy*

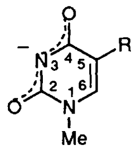
1,5-Dimethylcytosine (Hdmcyt), which is a model of the naturally occurring 5-methylcytidine nucleobase, has been demonstrated to be capable of binding three metal ions simultaneously, *via* N(3), monodeprotonated N(4) and O(2). The compound *trans*-$[(NH_2Me)_2Pt(dmcyt)_2Ag_2][NO_3]_2$ **1** was prepared from *trans*-$[Pt(NH_2Me)_2(Hdmyct\text{-}N^3)_2][NO_3]_2$ and $AgNO_3$ at alkaline pH, and its crystal structure determined. The Pt···Ag distances within the trinuclear cation are 2.892(1) and 3.040(1) Å. The compound is compared with related mixed Pt–Ag nucleobase complexes as well as other trinuclear d^{10}–d^8–d^{10} systems. Despite the problem of differentiation of the nucleobase arrangement (head-to-head or head-to-tail) due to the pseudo-two-fold symmetry of the 1,5-dimethylcytosine ligand, the head-to-head orientation has unambiguously been established by use of ^1H NMR spectroscopy following precipitation of AgCl.

Despite their structural simplicity, N^1-substituted cytosines and their biologically relevant analogues, the cytosine nucleosides and nucleotides, are rather versatile ligands for metal ions. Established binding patterns at the heterocyclic pyrimidine ring include monodentate binding through N^3, O^2 and the deprotonated N^4 and C^5 positions as well as bidentate binding through N^3, N^4 as well as N^3, O^2.[1] Here we report the first example of a cytosine nucleobase acting as a tridentate ligand, binding three metal ions simultaneously *via* N^3 (Pt^{II}), N^4 (Ag^I) and O^2 (Ag^I). We prepared this trinuclear compound following previous findings that *trans*-$[Pt(amine)_2L_2]^{2+}$ [L = 1-methylcytosine (Hmcyt) or 1,5-dimethylcytosine (Hdmcyt)] readily reacts with additional transition-metal ions M such as Pd^{II},[2] Hg^{II}[3] and Cu^{II}[4] with deprotonation of the exocyclic amine groups of the two L ligands and formation of heteronuclear complexes containing Pt→M dative bonds.[5] In all these compounds the O^2 oxygens of the cytosinate ligands are in stereochemically favourable positions for additional metal binding, yet such a binding pattern had not been observed in any of these compounds. With related, isoelectronic ligand systems (mura = 1-methyluracilate instead of mcyt; mthy = 1-methylthyminate instead of dmcyt) we[6,7] and others[8] occasionally had observed metal binding at N^3, O^4 and O^2. Specifically, the existence of a mixed $PtAg_2$ complex of mura, *trans*-$[(NH_3)_2Pt(mura)_2Ag_2][NO_3]_2\cdot 2H_2O$,[7] prompted us to attempt to synthesize the compound *trans*-$[(NH_2Me)_2Pt(dmcyt)_2Ag_2][NO_3]_2$.





	R	
Hmcyt	H	$mcyt^-$
Hdmcyt	Me	$dmcyt^-$



	R
$mura^-$	H
$mthy^-$	Me

Experimental

Preparation.—The complex *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2][NO_3]_2$ was prepared as described[3] from *trans*-$[PtCl_2(NH_2Me)_2]$[9] and Hdmcyt (Chemogen, Konstanz). Compound **1** was obtained by reaction of *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2][NO_3]_2$ (0.018 mmol) with $AgNO_3$ (0.045 mmol) in water (50 cm^3). The colourless solution was brought to pH 12 by addition of 1 mol dm^{-3} NaOH, which resulted in the formation of a brown precipitate of silver hydroxide. After stirring at 22 °C for 24 h, the brown precipitate was filtered off, the colourless solution was concentrated to 5 cm^3 by rotary evaporation and allowed to evaporate. After 32 d colourless crystals of *trans*-$[(NH_2Me)_2Pt(dmcyt)_2Ag_2][NO_3]_2$ **1** had formed in 30% yield, which were filtered off and dried in air (Found: C, 19.3; H, 3.1; N, 16.4. Calc. for $C_{14}H_{26}Ag_2N_{10}O_8Pt$: C, 19.3; H, 3.0; N, 16.0%). IR (cm^{-1}): 1380vs, 1520s, 1610s and 1670s. Raman (cm^{-1}, solid state): 552s, 807s, 1130vs, 1256s and 1263s.

Spectroscopy.—Proton NMR spectra were recorded on a Bruker AC 200 spectrometer (200 MHz) in D_2O solutions containing sodium 3-trimethylsilylpropanesulfonate as internal reference, ^{195}Pt NMR spectra on the same spectrometer (42.95 MHz) in $(CD_3)_2SO$ in order to reach a sufficiently high concentration. Values of pD (D_2O solutions) were determined by use of a glass electrode and addition of 0.4 to the meter reading;[10] DCl was used to precipitate AgCl. The IR spectra were recorded as KBr discs on a Perkin-Elmer 580 B

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

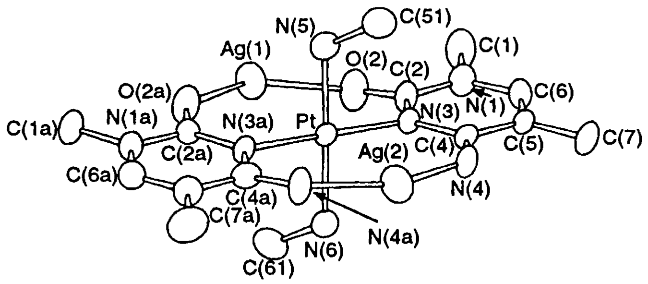


Fig. 1 An ORTEP drawing and atom numbering scheme of compound **1** (50% probability thermal ellipsoids)

Table 1 Crystallographic data and details of refinements for $[(NH_2Me)_2Pt(dmcyt)_2Ag_2][NO_3]_2$

Formula	$C_{14}H_{26}Ag_2N_{10}O_8Pt$
M	873.3
Crystal dimensions/mm	0.20 × 0.25 × 0.40
Crystal system	Monoclinic
Space group	$P2_1/n$ (alternative setting of no. 14)
a/Å	7.115(4)
b/Å	21.363(5)
c/Å	14.867(8)
β/°	94.71(3)
U/Å^3	2252(2)
D_c/g cm^{-3}	2.57
Z	4
μ(Mo-Kα)/cm^{-1}	80.3
F(000)	1664
Secondary extinction	$5.3(2) \times 10^{-8}$
% Transmission, maximum, minimum	99.5, 60.7
$2\theta_{max}$/°	56
No. reflections measured	5779
No. independent reflections [$I > 3\sigma(I)$]	3851
No. parameters refined	317
Weighting scheme	Unit
R (F_o)	0.044
R' (F_o)	0.044
Goodness of fit	4.18
Maximum, minimum in ΔF map/e Å^{-3}	2.82 [close to Ag(2)], −2.76

spectrometer, Raman spectra on a Codberg T800 spectrometer (exciting radiation 514.5 nm from an argon-ion laser and 647.1 nm from a krypton-ion laser).

X-Ray Crystal Structure Analysis.—The unit-cell dimensions of compound **1**, determined from Weissenberg and precession photographs, were refined using 25 reflections in the range $13 < \theta < 19°$ on a CAD-4 Enraf-Nonius single-crystal diffractometer equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.7107 Å). Data were collected at room temperature. Three standard reflections measured at regular intervals did not show any intensity decay.

Intensities having $I > 3\sigma(I)$ were corrected for Lorentz-polarization effects, and for secondary extinction. An empirical absorption correction *via* ψ scans was applied. The structure was solved by conventional Patterson and Fourier methods, refined through full-matrix least-squares calculations with $\Sigma w(|F_o| - |F_c|)^2$ being minimized, and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were placed at calculated positions (bond distance 0.95 Å) with isotropic $B = 1.3B_{eq}$ of the corresponding C or N atom to which they are bonded. Final R and R' factors and crystallographic data are reported in Table 1.

Owing to pseudo-two-fold symmetry of the 1,5-dimethylcytosinate ligand, an alternative model, where atoms O(2) and N(1) were interchanged with N(4) and C(5), respectively, was refined. The final B_{eq} (Å^2) of N(1), C(5), O(2) and N(4) were 3.1(2), 2.1(2), 4.7(2) and 2.8(2) for one dmcyt$^-$ ligand and 4.0(3), 1.8(2), 4.4(2) and 2.8(2) for the other. Since these thermal parameters have less uniform values than those of the previous model this model was rejected, although the refinement gave the same R value.

Table 2 Positional parameters of $[(NH_2Me)_2Pt(dmcyt)_2Ag_2][NO_3]_2$

Atom	x	y	z
Pt	0.497 12(6)	0.494 75(1)	0.249 80(3)
Ag(1)	0.703 2(2)	0.471 83(4)	0.434 19(6)
Ag(2)	0.308 3(2)	0.516 99(4)	0.072 94(6)
O(2)	0.555(1)	0.565 3(4)	0.434 2(5)
N(1)	0.464(1)	0.664 6(4)	0.395 5(6)
N(3)	0.432(1)	0.583 3(4)	0.287 7(5)
N(4)	0.274(1)	0.602 1(4)	0.149 8(6)
C(1)	0.536(2)	0.687 8(6)	0.485 4(8)
C(2)	0.488(1)	0.602 7(4)	0.374 2(6)
C(4)	0.331(1)	0.622 2(4)	0.227 4(7)
C(5)	0.301(1)	0.685 4(4)	0.254 1(6)
C(6)	0.369(2)	0.704 6(5)	0.335 7(7)
C(7)	0.192(2)	0.727 9(5)	0.190 3(8)
O(2a)	0.730(1)	0.388 7(4)	0.342 3(5)
N(1a)	0.695(1)	0.307 3(4)	0.243 5(6)
N(3a)	0.559(1)	0.406 3(4)	0.208 7(5)
N(4a)	0.419(1)	0.423 8(4)	0.064 3(5)
C(1a)	0.807(2)	0.267 7(5)	0.306 8(8)
C(2a)	0.664(1)	0.369 3(4)	0.267 1(6)
C(4a)	0.499(1)	0.386 0(5)	0.122 9(6)
C(5a)	0.528(2)	0.322 8(5)	0.101 2(7)
C(6a)	0.627(2)	0.285 6(5)	0.162 3(7)
C(7a)	0.451(2)	0.297 3(7)	0.013 7(8)
N(5)	0.761(1)	0.522 6(4)	0.220 4(5)
C(51)	0.776(2)	0.572 4(6)	0.154 8(8)
N(6)	0.238(1)	0.465 5(4)	0.280 8(6)
C(61)	0.231(2)	0.417 5(6)	0.350 4(8)
N(7)	0.990(1)	0.401 1(5)	0.585 6(6)
O(71)	1.080(2)	0.375 5(5)	0.649 3(7)
O(72)	0.939(2)	0.369 8(6)	0.520 3(7)
O(73)	0.960(2)	0.458 3(5)	0.589 8(8)
N(8)	0.020(1)	0.611 3(5)	−0.081 5(6)
O(81)	0.033(2)	0.646 9(5)	−0.016 9(6)
O(82)	−0.052(2)	0.630 9(5)	−0.155 0(6)
O(83)	0.067(2)	0.556 1(5)	−0.075 8(8)

Neutral-atom scattering factors were taken from ref. 11. Calculations were carried out on a Micro VAX 2000 computer, by using the MOLEN system of programs.[12] Positional parameters are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Structure of Compound **1**.—An ORTEP[13] drawing of the cation of **1**, *trans*-$[(NH_2Me)_2Pt(dmcyt)_2Ag_2]^{2+}$, is depicted in Fig. 1. The cation possesses approximately a mirror plane passing throughout the metals and N(5) and N(6) atoms, when the amine groups are excluded. Selected distances and bond angles are given in Table 3. The three metal centres, nearly collinear [Ag(1)–Pt–Ag(2) 178.85(3)°] are bridged by two 1,5-dimethylcytosinate ligands arranged head-to-head, in such a way that Pt is *trans*-co-ordinated by endocyclic N(3) and N(3a) [Pt–N(3) 2.039(7), Pt–N(3a) 2.045(8) Å, N(3)–Pt–N(3a) 178.6(3)°] whereas Ag(1) is co-ordinated by O(2) and O(2a) [Ag(1)–O(2) = Ag(1)–O(2a) 2.259(8) Å, O(2)–Ag(1)–O(2a) 139.3(3)°] and Ag(2) by the deprotonated N(4) and N(4a) [Ag(2)–N(4) 2.172(9), Ag(2)–N(4a) 2.149(9) Å, N(4)–Ag(2)–N(4a) 149.9(3)°].

The different angles in the two X-Ag-X fragments correspond to Ag(1)···Pt and Ag(2)···Pt distances of 3.040(1) and 2.892(1) Å, respectively.

Table 3 Selected co-ordination bond lengths (Å) and angles (°) for compound **1**

Pt···Ag(1)	3.040(1)	Pt–N(6)	2.036(9)
Pt···Ag(2)	2.892(1)	Ag(1)–O(2)	2.259(8)
Pt–N(3)	2.039(7)	Ag(1)–O(2a)	2.259(8)
Pt–N(3a)	2.045(8)	Ag(2)–N(4)	2.172(9)
Pt–N(5)	2.052(9)	Ag(2)–N(4a)	2.149(9)
Ag(1)–Pt–Ag(2)	178.85(3)	N(3a)–Pt–N(5)	88.9(3)
Ag(1)–Pt–N(3)	90.2(2)	N(3a)–Pt–N(6)	90.4(3)
Ag(1)–Pt–N(3a)	91.2(2)	N(5)–Pt–N(6)	178.7(3)
Ag(1)–Pt–N(5)	81.8(2)	Pt–Ag(1)–O(2)	70.6(2)
Ag(1)–Pt–N(6)	97.2(2)	Pt–Ag(1)–O(2a)	68.9(2)
Ag(2)–Pt–N(3)	90.0(2)	O(2)–Ag(1)–O(2a)	139.3(3)
Ag(2)–Pt–N(3a)	88.6(2)	Pt–Ag(2)–N(4)	73.9(2)
Ag(2)–Pt–N(5)	97.1(2)	Pt–Ag(2)–N(4a)	75.9(2)
Ag(2)–Pt–N(6)	83.9(2)	N(4)–Ag(2)–N(4a)	149.9(3)
N(3)–Pt–N(3a)	178.6(3)	Ag(1)–O(2)–C(2)	135.2(7)
N(3)–Pt–N(5)	91.3(3)	Ag(1)–O(2a)–C(2a)	139.3(7)
N(3)–Pt–N(6)	89.4(3)		

Mean values for 44 Ag–O distances, ranging from 2.149 to 2.301 Å, in the fragment Ag–O=C and for 63 Ag–N distances, ranging from 2.087 to 2.249 Å, in the fragment Ag–N=C derived from the Cambridge Structural Database[14] are 2.235(5) and 2.168(6) Å, respectively. The Ag(1)–O and Ag(2)–N(4) distances in our compound are close to these mean values. This observation gives further support to the choice of the model described in the Experimental section.

The cation of compound **1** (Fig. 1) is very similar to that found in *trans*-$[(NH_3)_2Pt(mura)_2Ag_2][NO_3]_2\cdot 2H_2O$ **2**[7] where both silver ions are co-ordinated only by oxygen atoms, with approximately the same geometry characterized by O–Ag–O angles 136.6(7) and 121.4(8)° and Ag–O distances ranging from 2.24(2) to 2.45(3) Å (Fig. 3). However, in the latter case, the two mura ligands are arranged head-to-tail with very similar Pt···Ag distances [2.896(3) and 2.863(3) Å] close to the Pt···Ag(2) but shorter than the Pt···Ag(1) distance [3.040(1) Å] found in our compound. Furthermore, the Ag(1) and Ag(2) atoms in the mura complex **2** are significantly out of the mean plane passing through the two mura ligands by +0.6 and −1.1 Å, respectively, while in the dmcyt$^-$ complex they are essentially in the plane passing through the two dmcyt$^-$ ligands, being displaced by 0.05 and 0.01 Å, respectively.

Table 4 summarizes all the structurally characterized heterotrinuclear complexes, with different M–M′–M backbones, having a d^{10}–d^8–d^{10} electronic configuration. In all the complexes, excluding the present one, the ligands are arranged in such a way that the co-ordination around the M metals is chemically equivalent and the two intermetallic distances are very similar (see Δ, Table 4). In our complex, where the co-ordination around the silver centres is different, the Δ value is significantly larger.

The Pt···Ag distances found in both compounds are close to those reported for other nucleobase-bridged Pt–Ag complexes. In *cis*-$[(NH_3)_2Pt(mura)(Hmcyt)Ag(OH_2)_2][NO_3]_2\cdot AgNO_3\cdot 2.5H_2O$[21] containing the neutral Hmcyt and anionic mura nucleobases bridging in a *cis* arrangement, the intermetallic distance is 2.906(1) Å. Analogously, it is 2.853(1) and 2.860(3) Å in *cis*-$[(NH_3)_2Pt(mura)Ag]_2[NO_3]_4\cdot 2H_2O$[6b] and in *cis*-$[\{(NH_3)_2Pt(mura)\}_2Ag][NO_3]_3\cdot AgNO_3\cdot 0.5H_2O$[6c] respectively, whereas the shortest contact of 2.787(1) Å was reported for $[\{(NH_3)_2Pt(mura)\}_4Ag][NO_3]_5\cdot 4H_2O$.[6a] However, these distances are longer than those reported for complexes[22,23] where a direct Pt–Ag bond of substantial strength is suggested [range 2.637(1)–2.692(2) Å].

The platinum co-ordination is completed by two NH_2Me molecules in *trans* positions [Pt–N(5) 2.052(9) and Pt–N(6) 2.036(9) Å] oriented in opposite directions with respect to the $Ag_2Pt(dmcyt)_2$ moiety of the cation, with atoms C(51) and C(61) pointing approximately towards N(4) and O(2a), respectively (Fig. 1). This arrangement is similar to those found in dinuclear cations of type $[(NH_2Me)PtL_2Hg]^{2+}$ where L = mcyt or dmcyt.[3]

Table 4 Heterotrinuclear M–M′–M complexes with d^{10}–d^8–d^{10} electronic configuration

	d/Å			
Metallic core	M···M′	M′···M	Δ/Å	Ref.
Ag^I–Pt^{II}–Ag^I	2.896(3)	2.863(3)	0.033	7
Ag^I–Pt^{II}–Ag^I	3.040(1)	2.892(1)	0.148	This work
Au^I–Pt^{II}–Au^I	3.034(1)	3.034(1)	—	15
Hg^{II}–Pt^{II}–Hg^{II}	3.138(1)	3.138(1)	—	16
Au^I–Au^{III}–Au^I	3.052(1)	3.049(1)	0.003	17
Au^I–Rh^I–Au^I	3.028(2)	3.006(2)	0.022	18
	3.034(2)	3.074(2)	0.040	
Au^I–Ir^I–Au^I	3.013(2)	2.985(2)	0.028	19
	3.014(2)	3.025(2)	0.011	
Au^I–Ir^I–Au^I	2.835(1)	2.835(1)	—	20

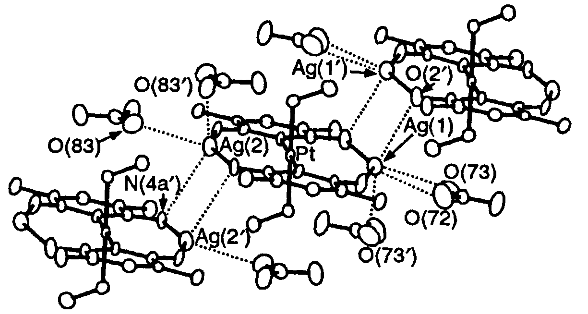


Fig. 2 Crystal arrangement of Ag–Pt–Ag cations in compound **1**. Spheres of arbitrary radius; dotted lines represent silver contacts longer than 2.4 Å

The two eight-membered rings, including Ag(1) and Ag(2), are planar within ±0.16(1) and ±0.07(1) Å, respectively, and their planes make a dihedral angle of 1.0(3)°. The two dmcyt$^-$ units are essentially coplanar [dihedral angle 2.0(2)°], and their planes form angles of 83.2(2) and 81.0(2)° with the platinum co-ordination mean plane.

The cations are arranged in the crystal as steps of a staircase, related to each other by crystallographic symmetry centres (Fig. 2). Since the two sides of the cation of **1** are not equivalent, the arrangement is Ag(1)–Pt–Ag(2)•Ag(2)–Pt–Ag(1)•Ag(1)–Pt–Ag(2), where • indicates a symmetry centre and the Ag(1)–Pt–Ag(2) unit the cation. Therefore, the Ag(2) ion of each unit loosely co-ordinates to N(4a′) of the preceding unit [Ag···N(4a′) 3.189(9) Å], whereas the Ag(1) ion co-ordinates to O(2′) of the next unit [Ag···O(2′) 2.902(9) Å]. The Ag(1)···Ag(1′) and Ag(2)···Ag(2′) distances are 3.817(1) and 3.694(1) Å, respectively. Nitrate anions are arranged in rows running along the staircase, completing the silver co-ordination through some of their oxygen atoms, at distances Ag(2)···O(83) and Ag(3)···O(83′) of 2.81(1) and 3.10(1) Å, respectively. The N(7) nitrate ions chelate each Ag(1) through O(72) [Ag(1)···O(72) 2.97(1) Å] and O(73)[Ag(1)···O(73) 2.84(1) Å] and the symmetry-related N(7′) nitrate ion through O(73′) [Ag(1)···O(73′) 2.87(1) Å] (Fig. 2). Assuming that the N(7) nitrate anion occupies one co-ordination position, the co-ordination spheres of Ag(1) and Ag(2) represent distorted trigonal bipyramids.

The cations of the $PtAg_2$ complex of 1-methyluracil (**2**) are arranged in zigzag-like chains, with the sequence Ag(1)–Pt–Ag(2)···Ag(1)–Pt–Ag(2)···Ag(2)–Pt–Ag(1), where the Ag(1) and O(4) of each unit co-ordinate O(4a′) and Ag(2′) of the adjacent unit, respectively (Fig. 3). The Ag(1)–O(4a′) and

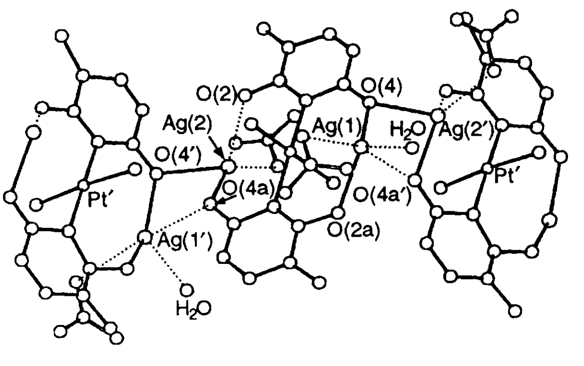


Fig. 3 Crystal arrangement of Ag–Pt–Ag in the related complex containing mura instead of dmcyt ligands, *trans*-$[(NH_3)_2Pt(mura)_2Ag_2][NO_3]_2{\cdot}2H_2O$ **2** (spheres of arbitrary radius; dotted lines represent silver contacts longer than 2.4 Å)

Ag(2′)–O(4) distances are 2.84(2) and 2.37(2) Å, with an intermolecular Ag(1) ··· Ag(2) separation of 3.597 Å. The co-ordination to Ag is completed by O atoms of water molecules and of nitrate anions, in such a way that the co-ordination sphere of Ag(1) is a strongly distorted bipyramid and that of Ag(2) is a tetrahedron. Comparison of the distances in the Ag(1)–O–Ag(2)–O ring of **2** with those in the four-membered rings Ag(1)–O–Ag(1)–O and Ag(2)–N–Ag(2)–N in **1** suggests that the cations in the latter chain are less strongly bonded. The significant difference between the chains of these two $PtAg_2$ complexes may be attributed to the presence of the additional methyl group bonded at C(5) in the $dmcyt^-$ ligands.

Solution Studies.—The ^1H NMR spectrum of compound **1** (D_2O, pD 9–10) consists of single sets of resonances for the cytosine protons H(6) (δ 6.99), $C(5)H_3$ (δ 1.88), $C(1)H_3$ (δ 3.28) and the CH_3 protons of the amine ligands [δ 2.26; $^3J(^{195}Pt-^1H)$ ≈40 Hz] in the expected intensity ratios. All nucleobase resonances have undergone upfield shifts as compared to the platinum starting compound as a consequence of nucleobase deprotonation and heterometal complexation. The upfield shift is most prominent for the H(6) proton (*ca.* 0.6 ppm). Unlike for the starting compound, ^4J coupling between $C(5)H_3$ and H(6) is not resolved at 200 MHz. No $^{107,109}Ag$ coupling with nucleobase protons is likewise observed. The ^{195}Pt NMR spectrum $[(CD_3)_2SO]$ displays a single resonance at δ −2223, a position similar to that seen for related $Pt-Hg^{II}$ complexes.[3] No $^{195}Pt-^{107,109}Ag$ coupling is seen, but this may be a consequence of the relatively large half-width of the ^{195}Pt signal (260 Hz at 18 °C) and/or a small coupling constant between ^{195}Pt and $^{107,109}Ag$. Representative ^1J coupling constants of other heteronuclear Pt–Ag complexes are *ca.* 170–200 Hz[24–26] and only occasionally larger.[27] Upon standing, the $PtAg_2$ compound is altered in Me_2SO, presumably decomposed.

Addition of HCl (pH 2–3) to an aqueous solution of compound **1** causes rapid precipitation of AgCl and formation of *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2]^{2+}$. In the ^1H NMR spectrum the H(6) resonance at δ 6.99 disappears at once and reappears at δ 7.55 (Fig. 4). Within minutes, a second H(6) resonance slightly downfield from the former (δ 7.57 ppm) grows in, which increases at the expense of the original resonance. Within 24 h, the resonance at δ 7.57 dominates that resonance at δ 7.55 by a ratio of *ca.* 4:1. The spectrum is then identical with that of the original starting compound *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2]^{2+}$ at the same pD. For this compound we had assumed a rotamer equilibrium with a preferential head-to-tail orientation of the two nucleobases in aqueous solution.[3] Consequently, the behaviour of the $PtAg_2$ compound in the presence of HCl (DCl) suggests initial formation of the head-to-head rotamer of *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2]^{2+}$ which converts into the thermodynamically preferred head-to-tail rotamer until a 1:4 ratio of the two species is reached. This interpretation is in agreement with results obtained with the two rotamers of the corresponding mcyt complex which has now been crystallized in both rotameric forms.[28] When dissolved, both forms eventually reach an identical equilibrium. The rate of head-to-head ⟶ head-to-tail isomer interconversion has been determined in this case ($k = 1 \times 10^{-4}\ s^{-1}$ at 295 K). For the dmcyt analogue, this rate should be very similar, as judged from the ^1H NMR spectroscopic changes.

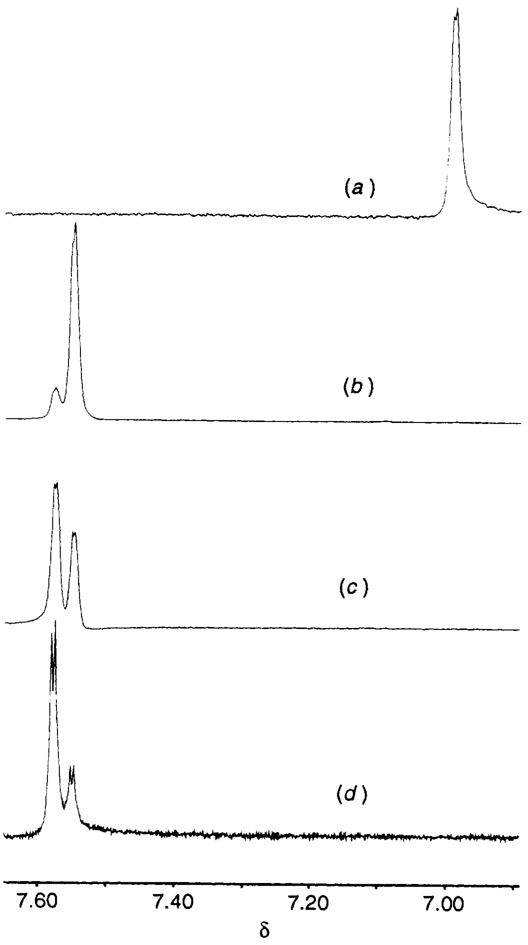
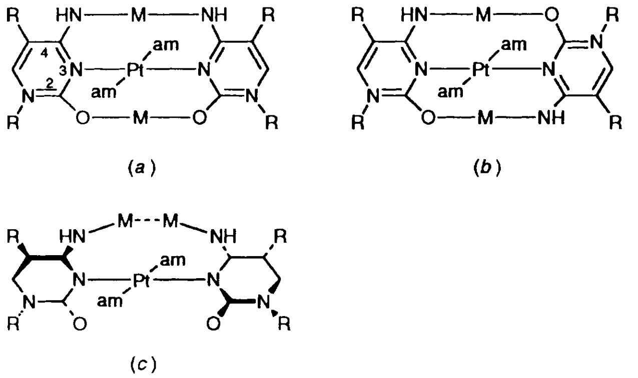


Fig. 4 Section of the ^1H NMR spectra [H(6) protons only] of (*a*) *trans*-$[(NH_2Me)_2Pt(dmcyt)_2Ag_2]^{2+}$ (D_2O, pD 9.8), (*b*) 20 min after addition of DCl and formation of *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2]^{2+}$ and AgCl (D_2O, pD 2.8), (*c*) 210 min after addition of DCl, and (*d*) 24 h after addition of DCl. Resonances at δ 7.55 and 7.57 are assigned to the head-to-head and the head-to-tail rotamers of *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2]^{2+}$, respectively

Conclusion

The head-to-head arrangement of the $dmcyt^-$ nucleobases in compound **1**, as evident both from the solid-state structure and its solution behaviour with HCl, is consistent with the view that binding of Ag^+ to *trans*-$[Pt(NH_2Me)_2(Hdmcyt)_2]^{2+}$ takes place sequentially, that is first at the two N(4) sites (with deprotonation) and then at the two O(2) sites. Most likely this reflects the large differences in basicity of the deprotonated N(4) atoms as compared to the O(2) sites. This situation contrasts with the situation in two mura complexes of PtM_2 stoichiometry, *trans*-$[(NH_3)_2Pt(mura)_2Ag_2]^{2+}$[7] and *trans*-$K_2[PtI_2(mura)_2]$,[29] both of which adopt a head-to-tail orientation of the bases and consequently display mixed O(4), O(2) co-ordination of the heterometal. Similarly, in polymeric



Scheme 1 Representations of PtM_2 complexes with (*a*) head-to-head arrangement of nucleobases as seen in compound **1**, and alternative possibilities with (*b*) head-to-head arrangement and (*c*) M $\cdots$ M interaction in a head-to-head situation. am = Amine

Ag_2L_2 compounds (L = mura[8a] or mthy[8b]), mixed O(4), O(2) co-ordination is observed. We assume that the differences in donor properties of O(4) and O(2) in mura and mthy are less pronounced and therefore favour a head-to-tail arrangement. For a related *cis*-$[(en)Pd(mthy)_2Na_2]^{2+}$ complex (en = ethane-1,2-diamine) this question was not unambiguously solved due to problems in differentiating the two exocyclic oxygens.[30] Another alternative, binding of *two* Ag atoms to the two N(4) sites, which would lead to a triangular arrangement of the three metal ions rather than the observed linear one, is likewise not realized (Scheme 1). This binding pattern would require a substantial propeller-twist of the two nucleobases in order to increase the intramolecular N(4) $\cdots$ N(4) separation. We have evidence[31] that such a possibility exists in principle for heterometals that are capable of interacting with each other, hence forming (weak) M $\cdots$ M interactions.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (Rome), and the HCM programme. We thank Dr. S. Menzer, I. Rombeck and A. Danzmann for recording NMR spectra.

References

1 B. Lippert, *Handbook of Nucleobase Complexes*, ed. J. R. Lusty, CRC Press, Boca Raton, 1990, vol. 1, pp. 9–46.
2 M. Krumm, B. Lippert, L. Randaccio and E. Zangrando, *J. Am. Chem. Soc.*, 1991, **113**, 5129; M. Krumm, E. Zangrando, L. Randaccio, S. Menzer and B. Lippert, *Inorg. Chem.*, 1993, **32**, 700.
3 M. Krumm, E. Zangrando, L. Randaccio, S. Menzer, A. Danzmann, D. Holthenrich and B. Lippert, *Inorg. Chem.*, 1993, **32**, 2183.
4 G. Fusch, E. C. Fusch and B. Lippert, unpublished work.
5 C. Mealli, F. Pichierri, L. Randaccio, E. Zangrando, M. Krumm, D. Holthenrich and B. Lippert, *Inorg. Chem.*, 1995, **34**, 3418.
6 (*a*) B. Lippert and D. Neugebauer, *Inorg. Chem.*, 1982, **21**, 451; (*b*) U. Thewalt, D. Neugebauer and B. Lippert, *Inorg. Chem.*, 1984, **23**, 1713; (*c*) B. Lippert, H. Schöllhorn and U. Thewalt, *Inorg. Chem.*, 1987, **26**, 1736.
7 H. Schöllhorn, U. Thewalt and B. Lippert, *J. Chem. Soc., Chem. Commun.*, 1984, 769; I. Dieter, B. Lippert, H. Schöllhorn and U. Thewalt, *Z. Naturforsch., Teil B*, 1990, **45**, 731.
8 (*a*) F. Guay and A. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 6260; (*b*) K. Aoki and W. Saenger, *Acta Crystallogr., Sect. C*, 1984, **40**, 775.
9 J. Arpalahti, B. Lippert, H. Schöllhorn and U. Thewalt, *Inorg. Chim. Acta*, 1988, **153**, 45.
10 R. Lumry, E. L. Smith and R. R. Glantz, *J. Am. Chem. Soc.*, 1951, **73**, 4335.
11 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
12 MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, 1990.
13 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
14 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187; CSD Version 5.08, October 1994.
15 H. H. Murray, D. A. Briggs, G. Garzon, R. G. Raptis, L. C. Porter and J. P. Fackler, jun., *Organometallics*, 1987, **6**, 1992.
16 T. F. Carlson, J. P. Fackler, jun., R. J. Staples and R. E. P. Winpenny, *Inorg. Chem.*, 1995, **34**, 426.
17 H. Schmidbaur, C. Hartmann, G. Reber and G. Muller, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1146.
18 A. L. Balch, E. Y. Fung and M. M. Olmstead, *Inorg. Chem.*, 1990, **29**, 3203.
19 A. L. Balch, V. J. Catalano and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 2010.
20 A. L. Balch, V. J. Catalano, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 7558.
21 H. Schöllhorn, U. Thewalt and B. Lippert, *Inorg. Chim. Acta*, 1987, **135**, 155.
22 F. A. Cotton, L. R. Falvello, R. Uson, J. Fornies, M. Tomas, J. M. Casas and I. Ara, *Inorg. Chem.*, 1987, **26**, 1366.
23 R. Uson, J. Fornies, M. Tomas, I. Ara, J. M. Casas and A. Martin, *J. Chem. Soc., Dalton Trans.*, 1991, 2253.
24 A. F. M. J. van der Ploeg, G. van Koten and C. Brevard, *Inorg. Chem.*, 1982, **21**, 2878.
25 M. Ebihara, K. Tokoro, K. Imaeda, K. Sakurai, H. Masuda and T. Kawamura, *J. Chem. Soc., Chem. Commun.*, 1992, 1591.
26 P. S. Pregosin, in *Annu. Rep. N. M. R. Spectrosc.*, 1986, 285.
27 G. J. Arsenault, C. M. Anderson and R. J. Puddephatt, *Organometallics*, 1988, **7**, 2094.
28 D. Holthenrich, I. Sóvágó, G. Fusch, A. Erxleben, E. C. Fusch, I. Rombeck and B. Lippert, *Z. Naturforsch., Teil B*, in the press.
29 O. Renn, I. Mutikainen and B. Lippert, *Inorg. Chim. Acta*, 1994, **218**, 117.
30 W. Micklitz, B. Lippert, F. Lianza and A. Albinati, *Inorg. Chim. Acta*, 1994, **227**, 5.
31 G. Fusch, E. Zangrando, L. Randaccio and B. Lippert, unpublished work.

Received 18*th April* 1995; *Paper* 5/02465J