DALTON

First examples of polymeric mixed-metal (Pt–Ag) complexes containing single acetamidate bridges: *cis*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}4H_2O$ and *trans*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}1.5H_2O$

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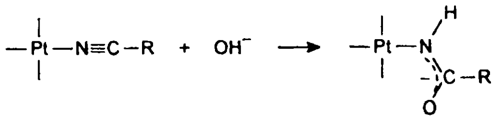
The reaction of $AgNO_3$ with *trans*- and *cis*-$[Pt(NH_3)_2(NHCOMe\text{-}N)_2]$ **1** and **2** yielded the heteronuclear polymeric complexes *cis*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}4H_2O$ **3** and *trans*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}1.5H_2O$ **4**. Complexes **3** and **4** have been studied in solution and characterised by X-ray analysis: **3**, tetragonal, space group $I4_1/a$, $a = b = 15.874(2)$, $c = 22.918(5)$ Å, $Z = 16$; **4**, triclinic, space group $P\bar{1}$, $a = 7.143(3)$, $b = 8.416(5)$, $c = 11.544(6)$ Å, $\alpha = 78.61(4)$, $\beta = 89.67(4)$, $\gamma = 83.79(4)°$, $Z = 2$. The Pt • • • Ag distances are 2.897(1) and 2.903(1) (**3**) and 2.925(2) and 2.919(2) Å (**4**). Possible metal–metal bonding interactions are discussed.

The co-ordination chemistry of acetamide and related molecules toward Pt^{II}, and in particular the aspect of multinuclear complex formation, has been studied since the days of Hoffmann and Bugge.[1] In a number of cases, formation of acetamidate complexes originated from hydrolysis of a co-ordinated acetonitrile ligand (Scheme 1).[2] Outstanding features of platinum(II) amidate complexes, especially when derived from *cis*-$Pt^{II}(NH_3)_2$, are (*i*) the pronounced tendency to form dinuclear complexes with the two amidate ligands arranged head-to-head,[1k] (*ii*) the stacking of these dinuclear entities and (*iii*) easy oxidation to either mixed-valence[3] and/or diplatinum(III) species.[4] A point of interest relates also to the antitumour activity of some of these compounds.[5]

Here we report on two heteronuclear complexes derived from *cis*- and *trans*-$[Pt(NH_3)_2(NHCOMe\text{-}N)_2]$ and $AgNO_3$ which appear to be the first examples of polymeric acetamidate compounds containing single acetamidate bridges rather than consisting of discrete di- or tri-nuclear complexes of types $PtML_2$ or Pt_2ML_4 (L = acetamidate) or oligo- or poly-meric species built up of the latter.



Scheme 1

Experimental

Preparations

The complexes *cis*-$[Pt(NH_3)_2(MeCN)(NHCOMe\text{-}N)]ClO_4$ and *trans*-$[Pt(NH_3)_2(NHCOMe\text{-}N)_2]$ **1** were prepared as previously described.[2j]

***cis*-$[Pt(NH_3)_2(NHCOMe\text{-}N)_2]{\cdot}H_2O$ 2.** The complex *cis*-$[Pt(NH_3)_2(MeCN)(NHCOMe\text{-}N)]ClO_4$ (1.05 mmol in 25 cm^3 water) was treated with 1.2 equivalents of NaOH at 0 °C. After 1 h the solvent was completely evaporated, whereby a dark oil was obtained. Stirring with acetone (40 cm^3) yielded **2** as a slightly yellow precipitate (73%) (Found: C, 13.1; H, 3.9; N, 15.5. Calc. for $C_4H_{16}N_4O_3Pt$: C, 13.2; H, 4.4; N, 15.4%).

***cis*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}4H_2O$ 3.** Complex **2** (0.17 mmol in 3 cm^3 water) was treated with $AgNO_3$ (0.44 mmol) in the dark. The product crystallised at 4 °C as colourless needles (yield 16%) (Found: C, 8.5; H, 3.0; N, 12.6. Calc. for $C_4H_{22}AgN_5O_9Pt$: C, 8.2; H, 3.8; N, 11.9%).

***trans*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}1.5H_2O$ 4.** Complex **4** was prepared in the same way as **3** with a $AgNO_3$: **1** ratio of 3 : 1. Colourless needles were isolated in 36% yield (Found: C, 8.9; H, 2.8; N, 13.3. Calc. for $C_4H_{17}AgN_5O_{6.5}Pt$: C, 8.9; H, 3.2; N, 12.9%).

Instrumentation

The NMR spectra were recorded on a Bruker AC200 spectrometer: ^1H using D_2O or $(CD_3)_2SO$ solutions and 3-trimethylsilylpropane-1-sulfonate as internal reference; ^{195}Pt with $K_2[PtCl_6]$ as external reference. Infrared spectra (KBr pellets) were recorded on Perkin-Elmer 580 B and Bruker IFS 113v spectrometers, Raman spectra on a T64000 Instruments SA spectrometer with argon-laser excitation (514.5 nm).

X-Ray crystallography

Crystal data for compounds **3** and **4** were taken at room temperature on a Nicolet R3m/V single-crystal diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit-cell parameters were obtained by least-squares fit of the 2θ values of 49 (**3**) and 25 (**4**) randomly selected reflections ($15 \leqslant 2\theta \leqslant 30°$). Intensity data were collected at variable scan speeds in the ranges $3 \leqslant 2\theta \leqslant 48$ (**3**) and $2 \leqslant 2\theta \leqslant 55°$ (**4**) using an ω–2θ scan technique. Six standard reflections measured at regular intervals showed no systematic variation in intensity. For both compounds an empirical absorption correction *via* ψ scans was applied. No correction was made for extinction.

The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least squares on F^2 to $R = 0.077$ (**3**) and on F to 0.065 (**4**) using the SHELXTL PLUS and SHELXL93 programs.[6] The nitrate oxygens of complex **3** are disordered. The Fourier-difference syntheses revealed six oxygens to which occupancy factors of 0.7 [O(10), O(11) and O(12)] and 0.3 [O(20), O(21) and O(22)] were assigned. In both structures water molecules of crystallisation were found. On the basis of the peak height in the Fourier map a site occupancy factor of 0.5 was assigned to O(2w) in **4**.

Crystallographic data and details of refinement are reported in Table 1.

Table 1 Crystallographic data and experimental details of the X-ray studies

	3	**4**
Formula	$C_4H_{22}AgN_5O_9Pt$	$C_4H_{17}AgN_5O_{6.5}Pt$
M	587.23	542.161
Crystal dimensions/mm	0.576 × 0.16 × 0.16	0.74 × 0.26 × 0.16
Crystal system	Tetragonal	Triclinic
Space group	$I4_1/a$	$P\bar{1}$
a/Å	15.874(2)	7.143(3)
b/Å	15.874(2)	8.416(5)
c/Å	22.918(5)	11.544(6)
α/°		78.61(4)
β/°		89.67(4)
γ/°		83.79(4)
U/Å^3	5775(2)	676.23(61)
D_c/g cm^{-3}	2.702	2.663
Z	16	2
μ(Mo-Kα)/mm^{-1}	11.17	11.91
F(000)	4448	514.0
$2\theta_{max}$/°	48.1	55.0
No. reflections	2474	3275
No. independent reflections	1268	2425
$[F > 4\sigma(F)]$	173	166
No. variables	$R1 = 0.0765^a$	$R1 = 0.065^a$
Final R indices	$wR2 = 0.1847^a$	$wR1 = 0.083^b$

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w^{-1} = \sigma^2(F_o^2) + (0.1172P)^2$, $P = (F_o^2 + 2F_c^2)/3$. ^{b} $wR1 = \Sigma w(F_o - F_c)/\Sigma w(F_o)$, $w^{-1} = \sigma^2(F) + (0.005\,09F^2)$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/14.

Results and Discussion

Crystal structures

A section of the polymeric cation *cis*-$[\{(NH_3)_2Pt(NHCOMe)_2Ag\}_n]^+$ **3** is depicted in Fig. 1 and selected bond lengths, angles and short contacts are presented in Table 2. The cation is built up of infinite chains of alternating Pt and Ag atoms bridged by the amidate ligands. The metal–metal distances in the chain are 2.897(1) (Pt···Ag) and 2.903(1) Å [Pt···Ag(a), symmetry operation $y + \frac{3}{4}, -x + \frac{3}{4}, z - \frac{1}{4}$]. The angles Ag–Pt–Ag(a) and Pt–Ag–Pt(a) are 176.1(3) and 165.7(1)°. The acetamidate is assumed to co-ordinate to Ag through the amide oxygen and to Pt through the deprotonated amide nitrogen. The assignment of the donor atoms is not straightforward on crystallographic arguments, but is reasonable on the basis of the method of preparation and substantiated by the solution studies (^{195}Pt NMR spectroscopy) described below. The mean planes through the ligands are nearly perpendicular to each other [84.9(2)°]. The co-ordination geometry of Pt is square planar, and the valence angles around Pt range from 88.1(2) to 93.6(2)°. The Pt–N (amide) and Pt–N (amine) bond lengths are in the normal range. Disregarding metal–metal interactions, Ag is approximately linearly co-ordinated by the amide oxygens [O(1)–Ag–O(2) 172.5(2)°]. The Ag–O bond lengths compare well with those observed in related complexes.[7,8] Contacts to the nearest-neighbour nitrate oxygen or water of crystallisation [Ag···O(4w) 3.079(9), Ag···O(20) 2.815(6), Ag···O(11) 3.376(5) Å] are too long for any significant bonding interactions. As can be seen from Fig. 1, the platinum co-ordination plane and the plane defined by O(1a), O(2) and Ag are substantially tilted toward each other [21.61(8)°]. The amidate ligands are planar [maximum deviation from the best weighted plane 0.008(4) Å for C(3)], and angles between the acetamidate and the platinum co-ordination planes are 80.4(2) and 83.5(2)°.

Table 2 Selected bond lengths (Å) and angles (°), possible hydrogen-bonding interactions and short contacts in complex **3**

Pt···Ag	2.897(1)	Pt···Ag^a	2.903(1)
Pt–N(1)	2.020(4)	Pt–N(2)	1.980(4)
Pt–N(3)	2.118(4)	Pt–N(4)	2.062(5)
Ag–O(1)	2.222(4)	Ag–O(2)^b	2.236(4)
N(1)–C(1)	1.324(7)	N(2)–C(3)	1.257(7)
O(1)–C(1)	1.257(7)	C(3)–O(2)	1.268(7)
N(1)–Pt–N(2)	93.6(2)	N(1)–Pt–N(3)	88.5(2)
N(1)–Pt–N(4)	177.9(2)	N(2)–Pt–N(3)	177.8(2)
N(2)–Pt–N(4)	88.1(2)	N(3)–Pt–N(4)	89.9(2)
N(1)–Pt–Ag	83.04(12)	N(2)–Pt–Ag	88.72(13)
N(3)–Pt–Ag	90.63(13)	N(4)–Pt–Ag	98.23(13)
O(1)–Ag–O(2)^b	172.5(2)	C(1)–N(1)–Pt	128.7(4)
C(3)–N(2)–Pt	129.7(4)	C(1)–O(1)–Ag	125.2(4)
O(1)–C(1)–N(1)	122.1(5)	O(1)–C(1)–C(2)	118.2(6)
N(2)–C(3)–O(2)	123.4(6)		
O(1w)···O(21)^c	3.15(1)	O(1w)···O(2)^d	2.78(1)
O(2w)···O(4w)^e	2.90(1)	O(4w)···O(2w)^c	2.90(1)
O(1)···O(1w)^f	2.85(1)	N(1)···O(21)^g	3.15(1)
N(3)···O(4w)^h	3.08(1)	N(4)···O(1w)^e	2.94(1)
N(2)···O(20)^f	2.74(1)	N(4)···O(3w)^e	3.02(1)
N(4)···O(4w)^e	3.03(1)		
Ag···O(4w)^h	3.079(9)	Ag···O(20)^g	2.815(6)
Ag···O(11)^f	3.376(5)		
O(1)–Ag–O(4w)^h	91.0(1)	O(2)–Ag–O(4w)^h	82.1(1)
O(1)–Ag–O(20)^f	91.8(1)	O(2)–Ag–O(20)^f	95.4(1)
O(1)–Ag–O(11)^f	68.7(1)	O(2)–Ag–O(11)^f	117.8(1)

Symmetry operatons: ^{a} $y + \frac{3}{4}, -x + \frac{3}{4}, z - \frac{1}{4}$; ^{b} $-y + \frac{3}{4}, x - \frac{3}{4}, z + \frac{1}{4}$; ^{c} x, y, y; ^{d} $y + \frac{1}{4}, -x + \frac{1}{4} + 1, z + \frac{1}{4}$; ^{e} $-x + 1, -y + \frac{1}{2}, z$; ^{f} $-x + \frac{1}{2} + 1, -y + \frac{1}{2}, -z + \frac{1}{2}$; ^{g} $-y + \frac{1}{4} + 1, x - \frac{3}{4}, -z + \frac{1}{4}$; ^{h} $y + \frac{1}{4}, -x + \frac{1}{4}, z + \frac{1}{4}$.

The crystal lattice is built up of parallel chains along the crystallographic z axis. The polymeric cations are connected *via* extensive hydrogen bonding involving the nitrate oxygens and water of crystallisation (Table 2). The unit cell contains four sets of water molecules which form hydrogen bonds among each other, to the disordered nitrate oxygens, to the ammine ligands as well as to the amide oxygens.

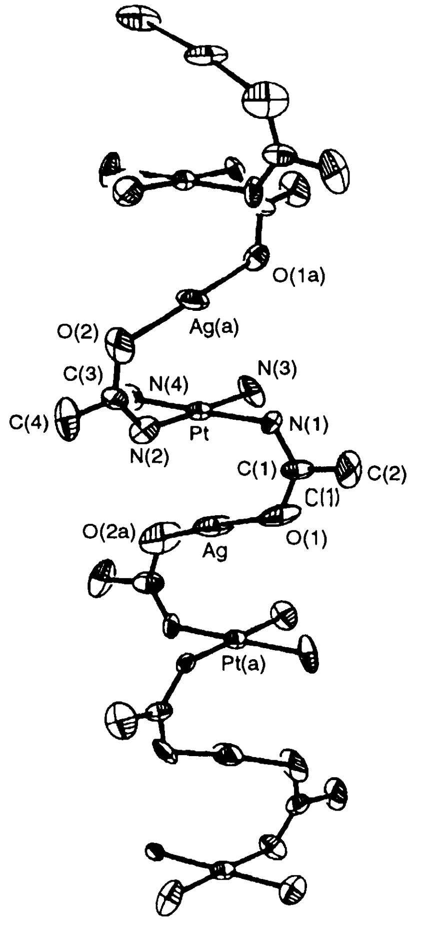


Fig. 1 Section of the polymeric cation of *cis*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}4H_2O$ **3** projected along the *z*-axis

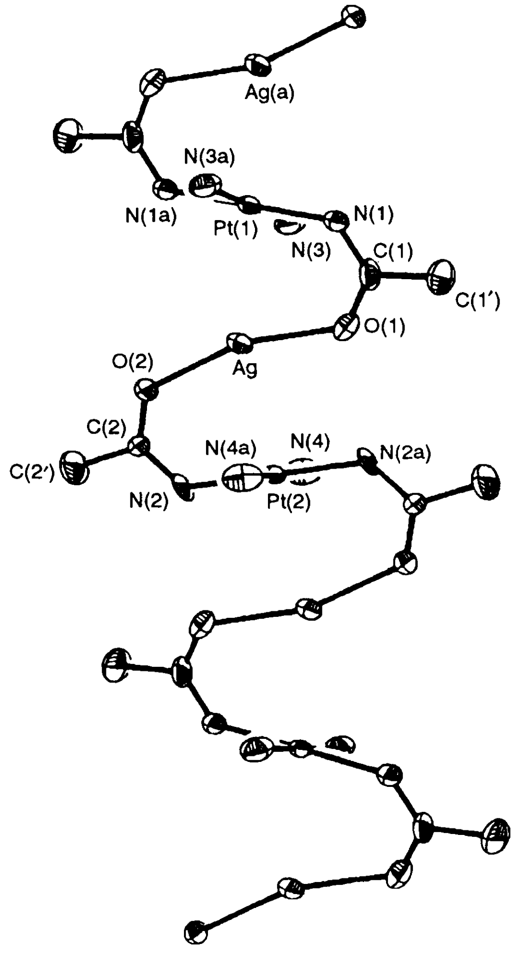


Fig. 2 Section of the polymeric cation of *trans*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}1.5H_2O$ **4** projected along the *z* axis

Fig. 2 gives a view of *trans*-$[\{(NH_3)_2Pt(NHCOMe)_2Ag\}_n]^+$ **4**. Selected bond lengths, angles and short contacts are listed in Table 3. The polymeric cations are built up of two crystallographically independent Pt atoms sitting on inversion centres ($\frac{1}{2}$, 0, 0 and $\frac{1}{2}$, 0, $\frac{1}{2}$), separated from Ag by 2.925(2) and 2.919(2) Å. The Pt–Ag–Pt unit is significantly bent [Pt(1)–Ag–Pt(2) 162.0(1)°, torsion angle Pt(1)–Ag–Pt(2)–Ag(a) −78.6°]. The valence angles around Pt are close to 90°, and the Pt–N and Ag–O bond lengths are normal. The shortest contact of Ag to an adjacent nitrate oxygen is 2.95(1) Å. The O–Ag–O entity deviates severely from linearity [O(1)–Ag–O(2) 161.9(4)°] and Ag lies significantly out of the ligand planes [−0.407(3) and 0.813(3) Å]. The dihedral angle between the amidate planes is 13.7(6)°. The C–N and C–O bond lengths are equal within the standard deviations. The C–N bond distances are slightly shorter, the C–O bond distances slightly longer than the bond lengths found in free acetamide [C–O 1.258(6) Å, C–N 1.338(7) Å],[9] thus indicating extensive electron delocalisation.

In the crystal packing of complex **4** (Fig. 3) parallel chains of the cations in the crystallographic *z* direction are held together by hydrogen bonds. Short contacts occur between the nitrate oxygens, the ammine and amide nitrogens, amide oxygens and water molecules.

Infrared and Raman spectra

Although the co-ordination of silver to the amide oxygen has been established by the X-ray analyses, the IR spectra of complexes **3** and **4** are very similar to those of the parent compounds except for nitrate bands. The same feature has been reported for Pt–Ag compounds derived from cyclic amidates like 1-methyluracil [uracil = (1*H*,3*H*)-pyrimidine-2,4-dione] and 1-methylthymine.[10] The amide I bands at 1595 (**1**) and 1570 cm^{-1} (**2**) which are in the typical range of amidate anions co-ordinating *via* the deprotonated amide nitrogen[11] are only moderately shifted due to the binding of the heterometal (**3**, 1560; **4**, 1600 cm^{-1}). The amide vibrations of free acetamide as well as of complexes with neutral acetamide occur in the range 1650–1750 cm^{-1}.[12] The shift of the amide I band to lower wavenumbers in the spectra of **1**–**4** is consistent with an extensive electron delocalisation within the amide group.[13] The skeletal vibrations at 1498 (**1**) and 1470 cm^{-1} (**2**) and δ(NCO) bands at 608 (**1**) and 605 cm^{-1} (**2**) are not drastically affected by silver co-ordination (**3**, 1465 and 605; **4**, 1495 and 608 cm^{-1}). The rocking vibrations of the amidate NH groups which occur in the spectra of free acetamide and complexes of neutral acetamide at around 1120–1150 cm^{-1} (ref. 12) are observed at 1253 (**1**), 1248 (**2**), 1245 (**3**) and 1255 cm^{-1} (**4**), the out-of-plane vibration of the NH groups at 728 (**1**), 785 (**2**), 772 (**3**) and 728 cm^{-1} (**4**).

The Raman spectra reveal ν(Pt–N) vibrations at 532 and 550 (**1**), 502 and 558 (**2**), 511 and 521 (**3**) as well as at 536 cm^{-1} (**4**). The δ(N–Pt–N) bands are observed at 308 and 240 (**1**) and at 314 and 257 cm^{-1} (**4**). The band at 330 cm^{-1} in the spectrum of **3** is tentatively assigned to a ν(Ag–O) vibration. No ν(Ag–O) band could be detected for **4**, but the δ(N–Pt–N) band at 314 cm^{-1} increases in intensity which may be due to a superimposition of the two vibrations. Silver co-ordination to **1** leads to a decrease in intensity of the ρ(N–H) band at 1557 cm^{-1} and of the δ(N–C–O) band at 607 cm^{-1}. The skeleton vibration is slightly shifted to lower wavenumbers (1498 for **1** and 1489 cm^{-1} for **4**) and its intensity is diminished. The sharp amide I band at 1550 cm^{-1} is significantly broadened, whereas the out-

Table 3 Selected bond lengths (Å) and angles (°), possible hydrogen-bonding interactions and short contacts in complex **4**

Ag···Pt(1)	2.925(2)	Ag···Pt(2)	2.919(2)
Ag–O(1)	2.23(1)	Ag–O(2)	2.20(1)
Pt(1)–N(1)	2.03(1)	Pt(2)–N(2)	2.01(1)
Pt(1)–N(3)	2.05(1)	Pt(2)–N(4)	2.02(1)
C(1)–N(1)	1.30(2)	C(1)–O(1)	1.30(2)
C(2)–O(2)	1.26(2)	C(2)–N(2)	1.30(2)
O(1)–Ag–O(2)	161.9(4)	Pt(1)–Ag–O(1)	77.8(3)
Pt(1)–Ag–O(2)	119.8(3)	Pt(2)–Ag–O(1)	84.4(3)
Pt(2)–Ag–O(2)	78.1(3)	Pt(1)–Ag–Pt(2)	162.0(1)
Ag–Pt(1)–N(1)	81.0(3)	Ag–Pt(1)–N(3)	85.8(3)
N(3)–Pt(1)–N(1)	90.1(5)	Ag–Pt(2)–N(4)	89.0(4)
Ag–Pt(2)–N(2)	83.4(4)	N(2)–Pt(2)–N(4)	91.2(5)
Ag–O(1)–C(1)	119.2(9)	Ag–O(2)–C(2)	125.2(9)
Pt(1)–N(1)–C(1)	127.2(10)	Pt(2)–N(2)–C(2)	127.6(10)
O(1)–C(1)–N(1)	123.0(14)	N(2)–C(2)–O(2)	123.7(13)
O(1w)···N(3)[a]	2.96(2)	O(1w)···O(2w)[b]	2.91(4)
O(1)···N(2)[c]	2.98(2)	O(2)···O(1w)[d]	2.72(2)
O(10)···N(4)[e]	2.90(2)	O(12)···O(2w)[d]	2.84(3)
N(2)···N(4)[c]	2.82(2)	N(3)···N(1)[f]	2.88(2)
N(3)···O(11)[e]	2.95(2)	N(3)···O(1w)[g]	2.96(2)
N(4)···O(10)[e]	2.90(2)	N(4)···O(12)[h]	3.10(2)
Ag–O(12)[i]	2.95(1)	Ag–O(11)[j]	3.14(2)
Ag–O(10)[j]	3.50(2)		
O(1)–Ag–O(12)[i]	55.7(2)	O(2)–Ag–O(12)[i]	141.5(2)
O(1)–Ag–O(11)[j]	59.3(2)	O(2)–Ag–O(11)[j]	136.3(3)
O(1)–Ag–O(11)[j]	57.0(3)	O(2)–Ag–O(10)[j]	138.1(3)

Symmetry operations: [a] $x, y-1, z$; [b] $x, y, z+1$; [c] $-x+1, -y, -z-1$; [d] x, y, z; [e] $-x, -y-1, -z-1$; [f] $-x+1, -y, -z$; [g] $x, y+1, z$; [h] $x, y+1, z$; [i] $-x+1, -y+1, -z+1$; [j] $-x, -y+1, -z+1$.

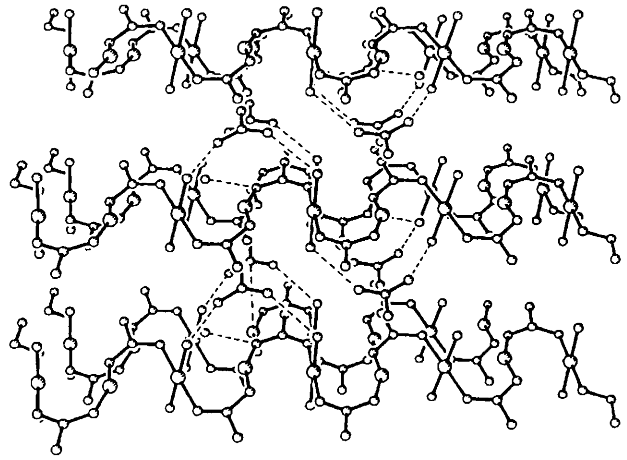


Fig. 3 Crystal packing of complex **4** along the *z* axis, which is perpendicular to the paper plane

of-plane vibration of the NH group remains essentially unchanged. The Raman spectra of **2** and **3** differ mainly in the carbonyl range: for **3** a sharp band at 1536 cm^{-1} is observed, whereas **2** gives a broad band of 150 cm^{-1} halfwidth with a maximum at 1586 cm^{-1}.

Solution studies

The proton NMR resonances of the acetamidate methyl group of complexes **1** and **2** are hardly sensitive to silver co-ordination (Table 4). Compared to the starting compounds, the methyl groups are shifted to lower field by 0.05 (**3**) and 0.06 ppm (**4**). Addition of increasing amounts of $AgNO_3$ has only a small effect on the spectra, *e.g.* addition of 10 equivalents to a solution of **3** resulted in a further 0.03 ppm downfield shift.

The ^{195}Pt NMR spectra of complexes **3** and **4** are consistent with a PtN_4 co-ordination sphere,[14] rather than PtN_3O or PtN_2O_2, for which very different shifts of δ −2000 and −1500 would have been expected.[15] Compared to the spectra of **1** (δ −2521) and **2** (δ −2512), the ^{195}Pt resonances of **3** and **4** are shifted downfield by about 100 ppm each. The influence of silver co-ordination on the ^{195}Pt chemical shift thus is much less pronounced than that of the heterometal in heteronuclear Pt–Pd and Pt–Hg complexes of the type *trans*-$[(am)_2Pt(mcyt\text{-}N^3,N^4)_2PdX]^{n+}$ and *trans*-$[(am)_2Pt(mcyt\text{-}N^3,N^4)_2Hg]^{2+}$ (mcyt = 1-methylcytosinate, am = NH_3 or NH_2Me), where Pt–M donor–acceptor bonds of considerable strength are present (Δδ = 400 ppm),[16] but significantly larger than the downfield shift due to palladium co-ordination observed for the dinuclear acetamidate complex *cis*-$[(NH_3)_2Pt(NHCOMe)_2Pd(en)]^{2+}$ (en = ethane-1,2-diamine) derived from **2** (Δδ = 48 ppm).[17] The ^{195}Pt NMR data therefore suggest weak Pt–Ag interactions only. The ^{195}Pt–^{107,109}Ag coupling cannot be resolved which may be due to the relatively large halfwidth of the ^{195}Pt signals (>250 Hz) as compared to typical coupling constants (160–200 Hz).[14,18] Addition of NaCl to aqueous solutions of **3** and **4** leads to instantaneous precipitation of AgCl. The ^{195}Pt NMR spectra are then identical with those of the starting compounds **1** and **2**, thereby ruling out any linkage isomerisation during reaction of **1** and **2** with $AgNO_3$ and confirming the PtN_4 co-ordination sphere.

Table 4 Proton and ^{195}Pt NMR data for compounds **1**–**4** (D_2O, pD 5)

Compound	δ(CH_3)	δ(^{195}Pt)
1	1.95	−2521
2	1.92	−2512
3	1.97	−2420
4	2.01	−2433

Possible metal–metal interactions and comparison with other Pt–Ag complexes

To the best of our knowledge the present compounds are the first examples for heteronuclear, polymeric complexes derived from *cis*- and *trans*-$Pt^{II}(NH_3)_2$ containing single amidate bridges. In contrast to the polymeric nature of **3** and **4**, several Pt–Ag complexes of cyclic amidates like 1-methyl-cytosine, -uracil and -thymine, characterised by X-ray analyses were shown to consist of discrete di-, tri-, tetra- or penta-nuclear cations, always containing pairs of bridging amidate ligands.[10,19–21] Polymeric arrangements are likewise feasible in such systems, as proposed for *cis*-$[\{Pt(NH_3)_2(mura)_2Ag\}_\infty]^+$ (mura = 1-methyluracilate),[22] even though only in the case of *trans*-$[\{Pt(NH_3)_2(mura)_2Ag_2\}_\infty]^{2+}$ the polymeric nature has been established by X-ray crystallography.[7]

The Pt···Ag distances in complexes **3** and **4** are close to those found in cyclic amidate complexes and chloro-bridged $(Pt\text{–}Ag)_n$ complexes, *e.g.* 2.853(1) Å in *cis*-$[(NH_3)_2Pt(mura)Ag]_2[NO_3]_4\cdot 2H_2O$,[10c] 2.860(3) Å in *cis*-$[\{Pt(NH_3)_2(mura)\}_2Ag][NO_3]_3\cdot AgNO_3\cdot 0.5H_2O$,[19] 2.906(1) Å in *cis*-$[(NH_3)_2Pt(mura)(Hmcyt)Ag(OH_2)_2][NO_3]_2\cdot AgNO_3\cdot 2.5H_2O$,[20] 2.787(1) Å in $[\{$*cis*-$[Pt(NH_3)_2(mura)\}_4Ag][NO_3]_5\cdot 4H_2O$,[10b] 2.849(1) and 2.884(1) Å in *cis*-$[(NH_3)_2Pt(mthy)_2Ag]NO_3\cdot 5H_2O$ (mthy = 1-methylthyminate),[10a] 3.040(1) and 2.892(1) Å in *trans*-$[(NH_2Me)_2Pt(dmcyt)_2Ag_2][NO_3]_2$ (dmcyt = 1,5-dimethylcytosinate),[21] 2.945(1) Å in $[(Ph_3P)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)]$,[23] 2.855(2) Å in $[\{PtAgCl_2(C_6Cl_5)(PPh_3)\}_n]\cdot 1.5CH_2Cl_2$[24] and 2.796(2) Å in $[NBu_4][PtAgCl_2(C_6F_5)_2(PPh_3)]$,[25] and considerably longer than distances reported for structures without bridging ligands [2.637(1)–2.692(2) Å] and indicating a direct Pt–Ag bond.[26] Platinum to silver donor–acceptor bonds have been reported to give Pt–Ag distances up to 2.95 Å.[23] Although the Pt ··· Ag distances of around 2.9 Å found in **3** and **4** are clearly at the high end of this range, metal–metal interactions may be assumed on the basis of the van der Waals radii.[27] The relatively long distances may be partly attributed to geometric requirements of the ligand and to the fact that every metal atom interacts with two neighbouring metal centres in contrast to unbridged di- or tri-metallic complexes.

Conclusion

N-Bound amidate complexes of *cis*- and *trans*-$Pt^{II}(NH_3)_2$ are capable of binding additional heterometals through the amide oxygen. In the case of the reaction of platinum(II) acetamidate complexes with Ag^+, the flexibility of the ligand favours the formation of polymeric structures with both *cis* and *trans* configurations of the $Pt(NH_3)_2$ entity. For the single acetamidate-bridged Pt–Ag compounds *cis*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}4H_2O$ and *trans*-$[(NH_3)_2Pt(NHCOMe)_2Ag]NO_3{\cdot}1.5H_2O$ weak metal–metal interactions can be assumed on the basis of the Pt ··· Ag bond distances and ^{195}Pt NMR chemical shift data.

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