Heteronuclear Pt–Pd, Pt$_2$Cu and Pt$_2$Ni complexes with bridging acetamidate crystal structures and spectroscopic studies

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The reaction of *trans-* and *cis*-[Pt(NH$_3$)$_2$(NHCOMe-N)$_2$] 1 and 2 with heterometals [(en)Pd^{II} (en = ethane-1,2-diamine), Cu^{2+} or Ni^{2+}] has been investigated. Dinuclear compounds of stoichiometry PtML$_2$ and trinuclear Pt$_2$ML$_4$ complexes with the heterometals co-ordinating through the amide oxygens have been characterised and studied in solution. The crystal structures of *cis*-[(NH$_3$)$_2$Pt(NHCOMe)$_2$Pd(en)][ClO$_4$]$_{1.5}$[NO$_3$]$_{0.5}$ 3, *cis*-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$Cu][ClO$_4$]$_2$ 4 and *cis*-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$Ni][ClO$_4$]$_2$ 5 have been determined.

In a previous paper we reported on the formation and solution behaviour of acetamidate complexes of *cis-* and *trans*-Pt^{II}(am)$_2$ (am = amine ligand).[1] The spontaneous dimerisation of the monoacetamidate complex *cis*-[Pt(NH$_3$)$_2$(NHCOMe-N)Cl] to the dinuclear, amidate-bridged complex *cis*-[Pt(NH$_3$)$_2$(μ-NHCOMe)]$_2$Cl$_2$ reflected the tendency of N-co-ordinated acetamidate to bind additional metal ions *via* the amide oxygen which can be attributed to the increased basicity of the latter due to co-ordination of platinum to the deprotonated amide nitrogen.

The excellent ligating properties of acetamidate and its derivatives are well established and reflected by the isolation and characterisation of mixed-valent platinum acetamidate 'blues': in the octanuclear platinum blue compounds [(NH$_3$)$_2$Pt(μ-NHCOMe)$_2$Pt(NH$_3$)$_2$]$_4$[NO$_3$]$_{10}$·4H$_2$O and [(NH$_3$)$_2$Pt(μ-NHCOCH$_2$F)$_2$Pt(NH$_3$)$_2$]$_4$[NO$_3$]$_{8.66}$·H$_2$O, which consist of four pairs of dinuclear species stacked on top of each other, pairs of metal centres are bridged by two acetamidate and fluoroacetamidate ligands, respectively.[2] Besides these mixed-valent compounds, dinuclear platinum-(II) and -(III) complexes of the type [{Pt(Me$_2$SO)Cl(μ-NHCOR)}$_2$],[3] [Pt$_2$(μ-NHCOMe)$_4$X$_2$][4] and [Pt$_2$(μ-NHCOMe)$_2$(NHCOMe)$_2$(en)$_2$]I$_2$ (en = ethane-1,2-diamine),[5] as well as several dirhodium(II),[6] dicobalt(III)[7] and dichromium(III)[8] complexes were shown to contain bridging acetamidate. All these acetamidate-bridged compounds are homonuclear. In contrast, a large number of heteronuclear complexes consisting of the *cis*-Pt^{II}(am)$_2$ entity and cyclic amidate or amide ligands like 1-methylthymine,[9] 1-methyluracil[10] [uracil = (1H,3H)-pyrimidine-2,4-dione] and 1-methylcytosine (Hmcyt)[11] has been described. Depending on the heterometal, the counter anions and the concentration conditions, complexes with different stoichiometries (*e.g.* PtML$_2$, Pt$_2$ML$_4$, Pt$_2$M$_2$L$_2$; L = cyclic amidate) and different metal geometries (*e.g.* square planar with Pd^{II}, Mn^{II} and Cu^{II}, distorted tetrahedral with Ag^{I} and square pyramidal with Zn^{II} are observed. Polynuclear amidate-bridged complexes with *trans* geometry for the metals are rare due to steric hindrance and only a few examples are described in the literature.[12]

Frequently, rather short distances between the metal centres bridged by the amidate ligands are found and in the related complexes of the type *trans*-[(am)$_2$Pt(mcyt-N^3,N^4)$_2$PdY]$^{n+}$ and *trans*-[(am)$_2$Pt(mcyt-N^3,N^4)$_2$Hg]$^{2+}$ [mcyt = 1-methylcytosine deprotonated at N^4, Y = variable ligand] metal–metal bonds are formed.[13]

In continuation of our work on platinum acetamidate complexes we have studied the reaction of *cis-* and *trans*-[Pt(NH$_3$)$_2$(NHCOMe-N)$_2$] with various metal ions [Cu^{2+},

Ni^{2+}, Ag$^+$, (en)Pd^{II} and (am)$_2$Pt^{II}]. In particular, we were interested in the co-ordination pattern formed and the electronic interactions between the metal centres. Whereas Ag$^+$ yielded the first examples of polymeric compounds,[14] di- and tri-nuclear complexes were obtained with (en)Pd^{II}, Cu^{2+} and Ni^{2+}. Two complexes of the stoichiometry Pt$_2$ML$_4$, *cis*-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$M][ClO$_4$]$_2$ (M = Cu or Ni), as well as the dimeric complex *cis*-[(NH$_3$)$_2$Pt(NHCOMe)$_2$Pd-(en)][ClO$_4$]$_{1.5}$[NO$_3$]$_{0.5}$ were characterised by X-ray analysis. To our knowledge no di- or tri-meric heteronuclear complexes with metal centres bridged by linear amidates have yet been described.

Experimental

Starting materials

The complexes *trans*-[Pt(NH$_3$)$_2$(NHCOMe)$_2$] 1 and *cis*-[Pt(NH$_3$)$_2$(NHCOMe)$_2$] 2 were prepared as previously described;[1,14] [Pd(en)Cl$_2$] was obtained from K$_2$[PdCl$_4$] (Degussa) according to ref. 15.

Preparations

cis-[(NH$_3$)$_2$Pt(NHCOMe)$_2$Pd(en)][ClO$_4$]$_{1.5}$[NO$_3$]$_{0.5}$ 3. The complex [Pd(en)Cl$_2$] (59 mg, 0.25 mmol) was stirred with AgNO$_3$ (84 mg, 0.50 mmol) in water (6 cm^3) overnight. After filtration of AgCl, compound 2 (86 mg, 0.24 mmol) was added, and the pale yellow solution (pH 6.6) changed to deep yellow. After addition of NaClO$_4$·H$_2$O (7 mg, 0.50 mmol) the reaction mixture was stirred for 30 min at room temperature, slow evaporation of the solvent at room temperature yielded orange-yellow cubes of 3 (63 mg, 36%) (Found: C, 10.2; H, 3.0; N, 13.2. Calc. for C$_6$H$_{22}$Cl$_{1.5}$N$_{6.5}$O$_{9.5}$PdPt: C, 10.4; H, 3.2; N, 13.2%).

cis-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$Cu][ClO$_4$]$_2$ 4. Compounds 2 (60 mg, 0.17 mmol) and Cu(NO$_3$)$_2$·3H$_2$O (42 mg, 0.17 mmol) were dissolved in water (3 cm^3), giving a green solution immediately. After filtration of a small amount of Cu(OH)$_2$, NaClO$_4$·H$_2$O (42 mg, 0.30 mmol) was added. The solution (pH 5.7) was kept at room temperature in an open beaker. After 10 d, green, cubic crystals of 4 (14 mg, 19%) were obtained (Found: C, 10.1; H, 3.0; N, 11.8. Calc. for C$_8$H$_{28}$Cl$_2$CuN$_8$O$_{12}$Pt$_2$: C, 10.1; H, 3.0; N, 11.8%).

cis-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$Ni][ClO$_4$]$_2$ 5. Compound 2 (60 mg, 0.17 mmol) and Ni(ClO$_4$)$_2$·6H$_2$O (45 mg, 0.12 mmol) were dissolved in water (2.5 cm^3). A small amount of Ni(OH)$_2$ was

filtered off. After addition of NaClO$_4$·H$_2$O (49 mg, 0.35 mmol), the yellow solution (pH 5.6) was kept at room temperature in an open beaker. After 1 d, greenish yellow cubes of **5** crystallised (10 mg, 14%) (Found: C, 10.1; H, 2.9; N, 11.7. Calc. for C$_8$H$_{28}$Cl$_2$N$_8$NiO$_{12}$Pt$_2$: C, 10.1; H, 3.0; N, 11.8%).

***trans*-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$Cu][ClO$_4$]$_2$ 6.** The salt Cu(NO$_3$)$_2$·3H$_2$O (35 mg, 0.15 mmol) was added to a solution of compound **1** (50 mg, 0.15 mmol) in water (4 cm^3). The pH was adjusted to 5.7, a small amount of Cu(OH)$_2$ was filtered off and NaClO$_4$·H$_2$O (41 mg, 0.29 mmol) was added. After 2 weeks, reddish brown crystals of **6** were isolated (20 mg, 29%) (Found: C, 10.2; H, 3.0; N, 11.9. Calc. for C$_8$H$_{28}$Cl$_2$CuN$_8$O$_{12}$Pt$_2$: C, 10.1; H, 3.0; N, 11.8%).

***trans*-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$Ni][ClO$_4$]$_2$ 7.** Greenish yellow crystals of complex **7** were obtained as described for **6** in 41% yield starting from **1** (51 mg, 0.15 mmol) and Ni(ClO$_4$)$_2$·6H$_2$O (54 mg, 0.15 mmol) (Found: C, 10.0; H, 2.9; N, 11.9. Calc. for C$_8$H$_{28}$Cl$_2$N$_8$NiO$_{12}$Pt$_2$: C, 10.1; H, 3.0; N, 11.8%).

Instrumentation

The NMR spectra were recorded on a Bruker AC 200 spectrometer, ^{1}H for D$_2$O or (CD$_3$)$_2$SO solutions using sodium 3-trimethylsilylpropane-1-sulfonate as internal reference, and for ^{195}Pt with K$_2$[PtCl$_6$] as external reference. Infrared spectra of KBr pellets were recorded on Perkin-Elmer 580B and Bruker IFS 113v FT spectrometers, EPR spectra (X-band) on a Varian spectrometer, and electronic spectra on a Perkin-Elmer (Lambda 15) spectrometer.

Crystallography

Crystal data were measured at room temperature on an Enraf-Nonius CAD4 diffractometer for complexes **3** and **4** and on a Nicolet R3m/V diffractometer for **5** using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit-cell dimensions were obtained by least-squares fit of the 2θ values of 25 high-order reflections for **3** and **4** and of 47 randomly selected reflections (15.8 ⩽ 2θ ⩽ 29.7°) for **5**. Data were measured with variable scan speed to ensure constant statistical precision for the collected intensities. Three standard reflections were used to check the stability of the crystals and of the experimental conditions and measured every hour. Data were corrected for Lorentz-polarisation factors and for decay (**3**) using the data-reduction programs of the MOLEN package (**3** and **4**).[16a] The data reduction for **5** was carried out using the appropriate routine of the SHELXTL PLUS program.[16b] Empirical absorption corrections were applied using azimuthal (ψ) scans of three (**3** and **4**) and six (**5**) 'high-χ' angle reflections. Selected crystallographic and other relevant data are listed in Table 1.

The structures were solved by a combination of Patterson and Fourier methods and refined on F by full-matrix least squares (the function minimised being $\Sigma\{w[F_o - (1/k)F_c]^2\}$); no extinction correction was found to be necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from ref. 17. The contributions of the hydrogen atoms, in idealised positions [C–H 0.95 (Å), B(H) = 1.3B(C$_{bonded}$) Å^2], were taken into account, but not refined. The anions in complex **3** were found to be disordered, as judged from the high value of some of the displacement parameters, in particular the ClO$_4$$^-$ and the NO$_3$$^-$ groups lying on the symmetry elements. Even though it proved impossible to refine a meaningful model for the disorder, three types of refinement were attempted: (1) with all atoms treated isotropically, (2) all atoms anisotropic and (3) only one ClO$_4$$^-$ anisotropic with the remaining groups refined isotropically. The latter model was significantly[18] better than the other two and this type of refinement was retained.

Atom 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 186/15.

Results and Discussion

Heteronuclear complexes of *cis*-[Pt(NH$_3$)$_2$(NHCOMe-*N*)$_2$] with the stoichiometry PtML$_2$

The acetamidate-bridged complex *cis*-[{Pt(NH$_3$)$_2$(μ-NH-COMe)}$_2$][NO$_3$]$_2$ is formed by reaction of **2** with *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$][NO$_3$]$_2$. In solution two isomers of the dimer exist corresponding to a head-to-head (hh) and head-to-tail (ht) orientation of the ligands. The facile head-to-head to head-to-tail rearrangement of the dinuclear complex as well as of the analogous [{Pd(en)(μ-NHCOMe)}$_2$][ClO$_4$]$_2$ has been described elsewhere.[1] Reaction of **2** with [Pd(en)(H$_2$O)$_2$]$^{2+}$ leads to the mixed Pt–Pd complex hh-[(NH$_3$)$_2$Pt(μ-NH-COMe)$_2$Pd(en)][ClO$_4$]$_{1.5}$[NO$_3$]$_{0.5}$ **3** which was characterised by X-ray crystallography.

Crystal structure and spectroscopic characterisation of complex 3. The cation of complex **3** is depicted in Fig. 1, and selected bond lengths, angles and possible hydrogen interactions are presented in Table 2. The (en)Pd^{II} entity is bound to the amide oxygens of *cis*-[Pt(NH$_3$)$_2$(NHCOMe)$_2$] so that acet-amidate acts as a bridging, bidentate ligand. As evident from solution studies (see below) there is no ambiguity with respect to the mutual interchange of amide oxygen and nitrogen. The intermetallic distance is 3.038(1) Å, thus pointing against a strong bonding interaction. The Pt–N, Pd–N and Pd–O bond lengths are in the normal range. The co-ordination geometries of Pt and Pd are square planar with the valence angles around Pd deviating slightly from the ideal geometry [O(1)–Pd–N(10) 171.2(5) and O(2)–Pd–N(11) 172.9(4)°]. Palladium lies slightly out of the co-ordination plane formed by N(10), N(11), O(1) and O(2), pointing away from Pt. The dihedral angles between the ligands and the co-ordination planes of the metals are 97.3(3) and 103.8(4)° (Pd) and 65.7(4) and 78.9(4)° (Pt). The amidate ligands form an angle of 85.9(5)° with each other. The metal co-ordination planes are significantly tilted. The dihedral angle of 39.1(4)° lies in the upper range of the values reported for dinuclear complexes of cyclic amidates, *e.g.* 35.8° in hh-[{Pt(NH$_3$)$_2$(mura)}$_2$]$^{2+}$ (mura = 1-methyluracil anion),[19] 25.8° in *cis*-[(NH$_3$)$_2$Pt(mura)$_2$Cu(H$_2$O)$_2$]SO$_4$·4.5H$_2$O,[20] 34.2° in *cis*-[(NH$_3$)$_2$Pt(mura)$_2$Pd(en)]NO$_3$·6H$_2$O,[21] 36.1° in ht-[{Pt-(NH$_3$)$_2$(mthy)}$_2$][NO$_3$]$_2$·6H$_2$O (mthy = 1-methylthymine anion)[22] and 29.5° in hh-[{Pt(NH$_3$)$_2$(mthy)}$_2$][NO$_3$]$_2$,[23] and parallels the relatively long Pt•••Pd distance. In related
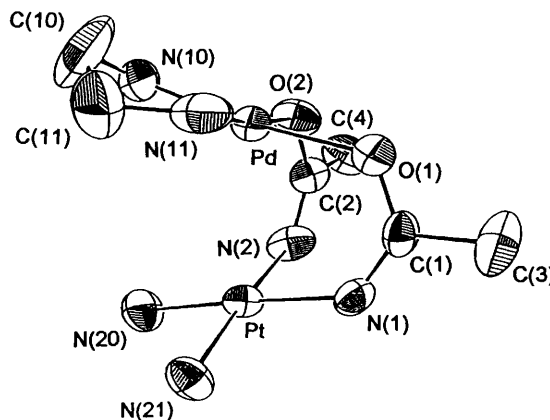

Fig. 1 View of the cation of complex **3** with the atom numbering scheme

Table 1 Experimental data for the X-ray diffraction study of compounds 3-5

	3	4	5
Formula	$C_6H_{22}Cl_{1.5}N_{6.5}O_{9.5}PdPt$	$C_8H_{28}Cl_2CuN_8O_{12}Pt_2$	$C_8H_{28}Cl_2N_8NiO_{12}Pt_2$
M	691.95	952.98	948.12
Crystal dimensions/nm	0.20 × 0.30 × 0.35	0.20 × 0.20 × 0.15	0.30 × 0.50 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
$a/Å$	9.096(2)	9.924(1)	9.963(3)
$b/Å$	21.409(1)	7.364(1)	7.356(2)
$c/Å$	20.360(2)	16.589(2)	16.445(3)
$\beta/°$	92.23(1)	91.08(1)	90.91(2)
$U/Å^3$	3962(1)	1212(1)	1205(2)
$D_c/g\ cm^{-3}$	2.320	2.611	2.437
Z	8	2	2
$\mu(Mo\text{-}K\alpha)/mm^{-1}$	8.28	12.796	12.75
θ Range/°	$2.5 < \theta < 25.0$	$2.5 < \theta < 28.0$	$2.5 < \theta < 25.0$
No. data collected (independent)	3467	2484	1268
No. observed reflections $[\lvert F_o \rvert > 3.0\sigma(\lvert F \rvert)]$	2813 $[\lvert F_o \rvert > 3.1\sigma(\lvert F \rvert)]$	2040	912
No. variables	208	193	151
Final R, R'	0.052, 0.065	0.026, 0.035	0.037, 0.046

* $R = \Sigma(\lvert F_o \rvert - (1/k)F_c\rvert)/\Sigma\lvert F_o\rvert$, $R' = [\Sigma w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)]^2/\Sigma w(\lvert F_o\rvert^2)]^{\frac{1}{2}}$, $w = [\sigma^2(F_o)]^{-1}$, $\sigma(F_o) = [\sigma^2(F_o^2) + f^4(F_o^2)]^{\frac{1}{2}}/2F_o$.

Table 2 Selected bond distances (Å), angles (°) and possible hydrogen-bonding interactions with estimated standard deviations (e.s.d.s) for complex 3

Pt · · · Pd	3.038(1)	Pt–N(2)	2.01(1)
Pt–N(1)	2.01(1)	Pt–N(20)	2.05(1)
Pt–N(21)	2.05(1)	Pd–O(1)	2.022(9)
Pd–O(2)	2.030(9)	Pd–N(10)	2.01(1)
Pd–N(11)	2.00(1)	O(1)–C(1)	1.31(1)
O(2)–C(2)	1.28(2)	N(1)–C(1)	1.29(2)
N(2)–C(2)	1.31(2)	N(10)–C(10)	1.53(3)
N(11)–C(11)	1.48(3)	C(1)–C(3)	1.51(2)
C(2)–C(4)	1.50(2)	C(10)–C(11)	1.50(3)
N(1)–Pt–N(2)	92.3(4)	N(1)–Pt–N(20)	177.5(5)
N(1)–Pt–N(21)	86.9(4)	N(2)–Pt–N(20)	89.0(5)
N(2)–Pt–N(21)	174.8(4)	N(20)–Pt–N(21)	91.6(4)
O(1)–Pd–O(2)	90.2(4)	O(1)–Pd–N(10)	171.2(5)
O(1)–Pd–N(11)	90.3(5)	O(2)–Pd–N(10)	94.1(4)
O(2)–Pd–N(11)	172.9(4)	Pd–O(1)–C(1)	124.8(8)
Pd–O(2)–C(2)	124.3(7)	Pt–N(1)–C(1)	131.9(8)
Pt–N(2)–C(2)	131.2(9)	Pd–N(10)–C(10)	108(1)
Pd–N(11)–C(11)	113(1)	O(1)–C(1)–N(1)	123(1)
O(1)–C(1)–C(3)	113(1)	N(1)–C(1)–C(3)	123(1)
O(2)–C(2)–N(2)	124(1)	O(2)–C(2)–C(4)	115(1)
N(2)–C(2)–C(4)	121(1)		
O(1) · · · N(10)[a]	2.93(2)	N(20) · · · O(6)[a]	3.04(3)
O(2) · · · N(11)[a]	2.91(2)	N(20) · · · O(9)[b]	2.98(3)
N(1) · · · O(9)	2.94(3)	N(21) · · · O(8)	3.09(2)
N(11) · · · O(8)	3.06(2)		

Symmetry operations: [a] $-x, -y, -z + 1$; [b] $-x, y, -z + \frac{3}{2}$.

PtPd[21] and PtPdPt[24] compounds containing bridging mura ligands (all metal ions in +II oxidation state) the intermetallic distances are significantly shorter, 2.927(1) and 2.837(1)–2.839(1) Å, respectively. Upon partial oxidation to $Pt^{II}Pd^{III}Pt^{II}$ these distances shrink by ca. 0.2 Å. The co-ordination of Pt and Pd has no marked influence on the geometry of the acetamidate. The O–C–N bond angle does not differ significantly from that found in free acetamide [122.6(5)° in acetamide,[25] 123(1) and 124(1)° in 3]. The C–O and C–N bond lengths are equal within experimental error which indicates extensive electron delocalisation within the ligand. The acetamidate ligands are planar, with Pd being slightly out of the mean planes through the ligands [0.368(1) and −0.254(1) Å].

In the crystal lattice rather short Pd · · · Pd' contacts between adjacent dimers are found [3.159(2) Å] which are almost comparable to the Pt · · · Pd distance within the cations [3.038(1) Å]. Two neighbouring cations are centrosymmetrically

related through an inversion centre at the midpoint of the Pd · · · Pd' vector. The resulting 'dimer-of-dimer' structure is stabilised by four hydrogen bonds formed between the amine nitrogens and the amide oxygens of the two hh dimers (Table 2). The 'dimer-of-dimer' entities are connected to zigzag chains parallel to the yz plane with Pt · · · Pt' contacts of 4.22 Å. The Pt · · · Pt' distances are considerably longer than the Pd · · · Pd' distances, as no hydrogen bonds are possible between amine ligands of neighbouring cations. Cations of parallel strands stack along the x axis. Weak hydrogen interactions between the perchlorate oxygens and the amide nitrogens stabilise the structure. The same packing pattern with infinite strands of hh dimers in a sequence (Pt–Pd)·(Pd–Pt)·(Pt–Pd) has been reported for cis-$[(NH_3)_2Pt(mura)_2Pd(en)][NO_3]_2$·$6H_2O$.[21] It represents a combination observed in both type I^{10d} and type II diplatinum(II) complexes. As to the 'dimer-of-dimer' structure, 3 may be compared with platinum α-pyridone blue which is built up of tetranuclear cations containing two dimeric cis-$[\{Pt(NH_3)_2(C_5H_4NO)\}_2]^{n+}$ entities or with the corresponding diplatinum(II) precursor.[26]

Solution behaviour of complex 3. In the ^{195}Pt NMR spectrum (D_2O) of complex 3 one resonance at δ −2466 is observed. According to established ^{195}Pt chemical shift trends[27] the signal is assigned to a N_4 co-ordination sphere; N_3O or N_2O_2 spheres should lead to shifts of around δ −2000 and −1500, respectively.[28] The ^{195}Pt NMR spectrum therefore is consistent with a head-to-head orientation with the (en)Pd^{II} entity binding through the amide oxygens. No evidence for a stereochemical rearrangement, as observed for the homonuclear Pt_2 and Pd_2 dimers, was obtained. The small chemical shift difference in the ^{195}Pt NMR spectra of 2 (δ −2514) and 3 excludes strong metal–metal interactions.

The proton NMR spectra of complexes 2 and 3 in $(CD_3)_2SO$ are shown in Fig. 2. Binding of the (en)Pd^{II} entity leads to a downfield shift of the amide protons of nearly 1 ppm [$\delta(NH)$ 5.33 for 2 and 6.28 for 3]. The broad singlet of the ammine protons occurs at δ 4.45 for 2 (with ^{195}Pt coupling of 49.6 Hz) and at 4.09 for 3, and the CH_3 signal is shifted to lower field due to the palladium co-ordination [$\delta(CH_3)$ 1.71 for 2 and 1.82 for 3]. The CH_2 resonances of the en ligand are obscured by the solvent signal. The spectrum of 3 reveals two inequivalent NH_2 (en) protons (δ 5.19 and 4.83). In D_2O two singlets are observed for the methyl (δ 1.94) and methylene protons (δ 2.71).

A mixture of complexes 2 and 3 gives two distinct sets of resonances due to the two components. Thus, the Pt–Pd dimer is non-labile on the NMR time-scale. Equilibrium (1) clearly
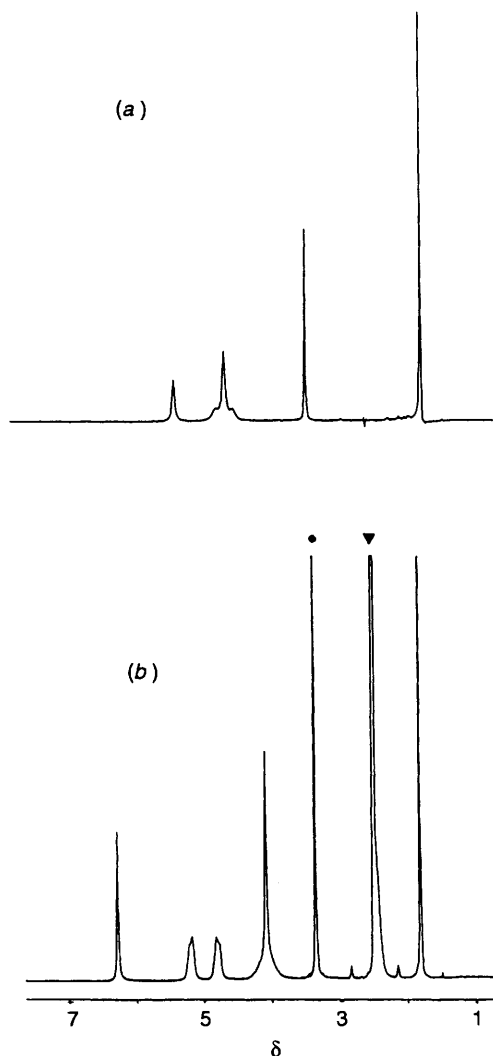
(a)

(b)

7   5   3   1

δ

Fig. 2 Proton NMR spectra of complexes **2** (a) and **3** (b) in $(CD_3)_2SO$. ● HOD, ▼ solvent. In spectrum (a) the solvent signal was suppressed
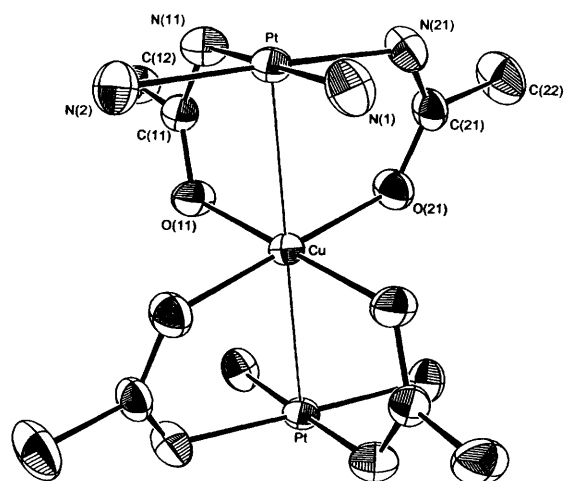

Fig. 3 View of the cation of complex **4** with the atom numbering scheme

Fig. 4 View of the cation of complex **5** with the atom numbering scheme

lies to the left-hand side, as no monomeric species are detected in D_2O or $(CD_3)_2SO$ solutions of **3**.

$$cis\text{-}[(NH_3)_2PtL_2Pd(en)]^{2+} \rightleftharpoons$$
$$cis\text{-}[Pt(NH_3)_2L_2] + [Pd(en)(solv)_2]^{2+} \quad (1)$$
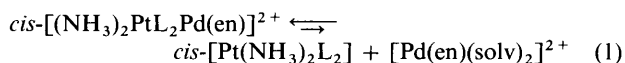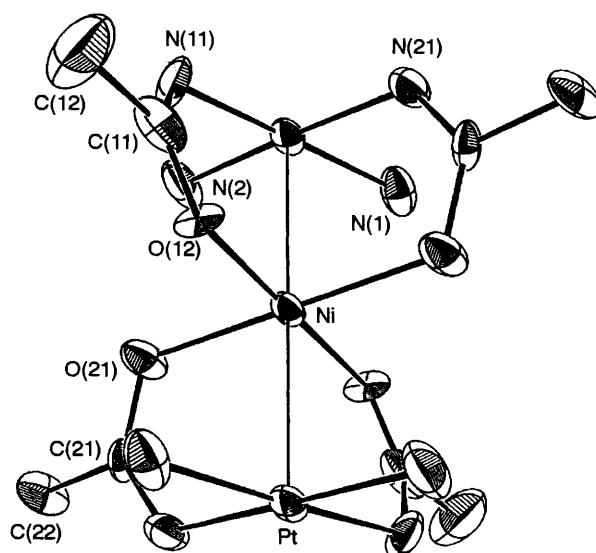
Heteronuclear complexes of cis-[Pt(NH₃)₂(NHCOMe-N)₂] with the stoichiometry Pt₂ML₄

Reaction of complexes **1** and **2** with Cu^{2+} and Ni^{2+} leads to trinuclear complexes of composition $cis\text{-}[\{Pt(NH_3)_2(NH\text{-}COMe)_2\}_2Cu][ClO_4]_2$ **4**, $cis\text{-}[\{Pt(NH_3)_2(NHCOMe)_2\}_2Ni]\text{-}[ClO_4]_2$ **5**, $trans\text{-}[\{Pt(NH_3)_2(NHCOMe)_2\}_2Cu][ClO_4]_2$ **6** and $trans\text{-}[\{Pt(NH_3)_2(NHCOMe)_2\}_2Ni][ClO_4]_2$ **7**. Visible spectra of solutions with different molar ratios of the platinum complexes and Cu or Ni gave no hint of Pt–M complexes with a stoichiometry other than Pt_2ML_4. For **4** and **5** crystals suitable for X-ray analysis were obtained, and the crystal structures of the trimers were determined.

Crystal structure and spectroscopic characterisation of complexes 4 and 5. The cations of complexes **4** and **5**, which are isostructural, are shown in Figs. 3 and 4, and selected bond lengths and angles are presented in Tables 3 and 4.

The basic structure of the two compounds is very similar. The trinuclear, centrosymmetric cations of **4** and **5** are built up of two $cis\text{-}Pt(NH_3)_2(NHCOMe\text{-}N)_2$ entities and one Cu^{II} or Ni^{II} bound to the four amide oxygens. The Pt–Cu distance of 2.705(2) Å in **4** is close to the values found in Pt_2M complexes

derived from cyclic amidates, e.g. 2.681(1) Å for $cis\text{-}[\{Pt(NH_3)_2(mura)(Hmcyt)\}_2Cu]^{4+}$ (Hmcyt = 1-methylcytosine),[11] 2.684(1) Å for $cis\text{-}[\{Pt(NH_3)_2(mura)_2\}_2Cu]^{2+29}$ and 2.704(1) Å for $cis\text{-}[\{Pt(NH_3)_2(mthy)_2\}_2Mn]Cl_2\cdot10H_2O$.[30] The intermetallic distance in **5** is considerably shorter [2.611(1) Å]. The rather short metal–metal distances within the complex cations do not necessarily imply strong interactions, but may be mainly a consequence of the bite distance of N and O in the ligand [2.253(6)/2.277(6) in **4** and 2.27(1)/2.31(1) Å in **5**] or of the number of d electrons (d^9 vs. d^8) and of the square-planar co-ordination geometries of the metals. In both structures the heterometal lies on a crystallographic inversion centre so that it and the amide oxygens are rigorously coplanar. The valence angles around Pt, Ni and Cu are close to 90°, and the Ni–O and Cu–O bond lengths are in good agreement with values found in related Pt_2Cu compounds. The Pt–N distances of **5** are in the normal range, with the Pt–N (amide) bonds [1.99(1) and 2.01(2) Å] being slightly shorter than the Pt–N (amine) bonds [2.08(2) and 2.09(2) Å]. This finding also holds for **4** [Pt–N (amine) 2.051(5)/2.049(4) and Pt–N (amide) 2.011(5)/1.995(4) Å]. The C–N and C–O bond lengths do not differ significantly from those observed in free acetamide.[25]

In both structures the amidate ligands are planar within the standard deviations. They form angles of 94.4 (**4**) and 107.1° (**5**) with each other, so they are tilted away from the perpendicular

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s for complex **4**

Pt–Cu	2.705(2)	Pt–N(1)	2.051(5)
Pt–N(2)	2.049(4)	Pt–N(11)	1.995(4)
Pt–N(21)	2.011(5)	Cu–O(11)	1.999(4)
Cu–O(21)	1.949(3)	C(11)–O(11)	1.265(6)
C(11)–C(12)	1.512(8)	C(21)–N(21)	1.304(6)
C(21)–O(21)	1.251(7)	C(21)–C(22)	1.507(8)
N(2)–Pt–N(11)	89.4(2)	N(2)–Pt–N(21)	176.0(2)
N(2)–Pt–N(1)	89.3(2)	N(21)–Pt–N(11)	87.7(2)
N(21)–Pt–N(1)	93.6(2)	N(11)–Pt–N(1)	178.7(2)
O(11)–Cu–O(21)	90.1(2)	Cu–O(11)–C(11)	120.0(3)
Cu–O(21)–C(21)	123.6(3)	Pt–N(21)–C(21)	123.8(4)
O(21)–C(21)–N(21)	123.7(5)	O(21)–C(21)–C(22)	116.4(4)
N(21)–C(21)–C(22)	119.9(5)	O(11)–C(11)–C(12)	117.9(4)

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s for complex **5**

Pt–Ni	2.611(1)	Pt–N(1)	2.09(2)
Pt–N(2)	2.08(2)	Pt–N(11)	2.01(2)
Pt–N(21)	1.99(1)	Ni–O(12)	2.01(2)
Ni–O(21)	2.05(1)	C(11)–N(11)	1.35(3)
C(11)–O(12)	1.22(3)	C(11)–C(12)	1.49(5)
C(21)–O(21)	1.30(2)	C(21)–C(22)	1.48(2)
N(1)–Pt–N(11)	176.7(6)	N(1)–Pt–N(21)	88.0(7)
N(2)–Pt–N(11)	93.8(8)	N(2)–Pt–N(21)	176.3(7)
N(11)–Pt–N(21)	89.8(8)	O(12)–Ni–O(21)	89.8(6)
Ni–O(12)–C(11)	120(1)	Ni–O(21)–C(21)	118(1)
Pt–N(11)–C(11)	121(1)	O(12)–C(11)–N(11)	125(2)
O(12)–C(11)–C(12)	118(2)	N(11)–C(11)–C(12)	117(2)
O(21)–C(21)–C(22)	118(1)		

position relative to each other as required by the square-planar co-ordination spheres of the three metals. The dihedral angles of the ligand planes with the platinum co-ordination plane are 71.6 and 96.6° for **5** and 90.9 and 73.3° for **4**. The copper co-ordination plane forms angles of 104.9 and 84.2° with the ligands; in **5** the angles between the nickel co-ordination plane and the ligand are 98.3 and 75.8°. As observed in Pt_2M compounds with cyclic amidates, the heavy metals are arranged in a face-face-orientation, although the metal co-ordination planes are not exactly parallel to each other but are slightly tilted as observed in related Pt_2M complexes of 1-methyl-uracil or -thymine.

The crystal lattices of complexes **4** and **5** are built up of layers of the dimeric cations with metal–metal distances of 7.364 (**4**) and 7.356 Å (**5**). The perchlorate oxygen atoms are involved in weak hydrogen-bonding interactions with the ammine and/or amide nitrogen [**4**: N(11)···O(1) 3.14(1); **5**: O(3)···N(2) 3.11(4), $-x + 1, -y + 1, -z + 2$; O(4)···N(1) 3.18(3) Å, x, $y + 1, z$]. In **5** intermolecular hydrogen bonding also occurs between the amide oxygen and the ammine nitrogen [N(2)···O(21) 3.12(2) Å, $x, y + 1, z$].

As expected the IR spectra of complexes **4** and **5** are very similar. Compared to the spectrum of **2**, the amide I band is shifted by 20 cm^{-1} to higher wavenumbers (**2**, 1570; **4** and **5**, 1590 cm^{-1}). Such a shift is unusual as co-ordination of the heterometal should decrease the double-bond character of the carbonyl group and may be attributed to a higher contribution of δ(NH) to the amide I vibration. The value for the amide I band is in the same range as that found for the acetamidate-bridged diplatinum(II) complexes cis-[{Pt(am)$_2$(NHCO-Me)}$_2$]X$_2^1$ [am = NH$_3$, (am)$_2$ = en, 1596–1606 cm^{-1}] and slightly lower than those found in dinuclear platinum(III) complexes, e.g. [{Pt(NHCOMe)$_2$X}$_2$]^{31} (1615–1628 cm^{-1}). The band at 1470 cm^{-1} of **2**, assigned to a skeleton vibration, is shifted to 1493 (**4**) and 1498 cm^{-1} (**5**). The out-of-plane

vibrations of the NH group at 785 cm^{-1} (**2**) occur in the spectra of the trimers at lower wavenumbers [768 (**4**) and 774 cm^{-1} (**5**)]. All other bands of the parent compound remain essentially unchanged.

Characterisation of complexes 6 and 7. Co-ordination of Cu and Ni to complex **1** via the amide oxygens is established by a shift of the amide I band to lower wavenumbers (1600, **1**; 1566, **6**; 1560 cm^{-1}, **7**). All other vibration bands of the ligand compare well with those in the spectra of **4** and **5**. As the crystals obtained for **6** and **7** were not suitable for X-ray analyses, the co-ordination of the heterometals and the trinuclear structure with the Pt having $trans$ configuration has to rely on IR data and the results of the elemental analyses.

EPR and electronic spectra of complex **6**. Complex **4** displays the characteristic greenish colour [absorption maxima in the visible spectrum at 682 (ε = 3.06 × 10^4) and 879 nm (ε = 2.53 × 10^4 cm^2 mol^{-1})] generally observed for heteronuclear Pt_nCu (n = 1 or 2) complexes derived from cis-Pt(am)$_2$L(L′) (L, L′ = cyclic amide or amidate) with square-planar or tetragonally elongated co-ordination geometries for Cu.^{20,32} In contrast, co-ordination of Cu^{II} to **1** gives a reddish brown complex. The visible spectrum of a solution of **6**, recorded in the range from 400 to 900 nm, shows two absorption maxima at 379 (ε = 9.68 × 10^4) and 824 nm (ε = 1.28 × 10^4 cm^2 mol^{-1}). Light orange or orange-red colours have been found for $trans$-[{Pt(NH$_2$Me)$_2$(urd)$_2$}$_2$Cu]$^{2+}$ (urd = uridinate) and $trans$-[{Pt(am)$_2$(C$_5$H$_4$NO)$_2$}$_2$Cu]$^{2+}$ (C$_5$H$_4$NO = 2-pyridonate, am = NH$_3$ or NH$_2$Me)^{12a} and have been attributed to a severe distortion of the copper co-ordination geometry from square planar toward distorted tetrahedral due to steric hindrance.

Complex **6** exhibits an axial EPR symmetry. The X-band spectrum (solid) shows two resonances with $g_\perp$ = 2.082 and $g_{||}$ = 2.191. This $g_\perp$ value compares well with those found for $trans$-[{Pt(am)$_2$(C$_5$H$_4$NO)$_2$}$_2$Cu]$^{2+}$ ($g_\perp$ = 2.083, $g_{||}$ = 2.430) and $trans$-[{Pt(NH$_3$)$_2$(Hmcyt)(mura)}$_2$Cu]$^{2+}$ ($g_\perp$ = 2.070, $g_{||}$ = 2.384), whereas $g_{||}$ is significantly smaller.^{11,12} The fact that the $g_\perp$ band occurs at higher field than the $g_{||}$ absorption indicates a tetragonal elongation of the ligand field of the Cu.

Conclusion

This work describes the preparation and characterisation of heteronuclear Pt–M complexes of type $PtML_2$ and Pt_2ML_4 with L being acetamide. The group (en)Pd^{II} co-ordinates through the amide oxygens of cis-[Pt(NH$_3$)$_2$(NHCOMe)$_2$] forming a dinuclear, mixed Pt–Pd complex. In the crystal lattice neighbouring cations are connected through hydrogen bonds involving the amine (en) nitrogens and the amide oxygens leading to infinite chains of the sequence (Pt–Pd)·(Pd–Pt)·(Pt–Pd)·(Pd–Pt) with surprisingly short intermolecular Pd···Pd′ contacts.

Copper(II) and Ni^{II} react with [Pt(NH$_3$)$_2$(NHCOMe-N)$_2$] to give trinuclear compounds with both cis and $trans$ configuration at the Pt. The co-ordination geometry of Cu and Ni in cis-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$M][ClO$_4$]$_2$ is planar, whereas the reddish brown colour of $trans$-[{Pt(NH$_3$)$_2$(NHCOMe)$_2$}$_2$Cu]-[ClO$_4$]$_2$ indicates a tetrahedral distortion of the copper(II) co-ordination sphere.

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