Conversion of Acetonitrile into Acetamide in the Co-ordination Spheres of *cis*- and *trans*-$M^{II}(amine)_2$ (M = Pt or Pd). Solution and Crystal Structural Studies†

Andrea Erxleben,[a] Ilpo Mutikainen[b] and Bernhard Lippert*[,a]

[a] *Fachbereich Chemie, Universität Dortmund, 44221 Dortmund, Germany*

[b] *Department of Chemistry, University of Helsinki, 00100 Helsinki, Finland*

The preparation and solution behaviour of mono- and bis-acetonitrile complexes of *cis*-$[Pt(NH_3)_2Cl_2]$, $[Pt(en)Cl_2]$ (en = ethane-1,2-diamine) and *trans*-$[Pt(NH_3)_2Cl_2]$ has been investigated. The nitrile complexes are hydrolysed to acetamidate, acetamidate-bridged and mixed acetamidate–acetonitrile species. It is shown that an essential feature of monomeric acetamidate complexes with *cis* configuration is their tendency to dimerize to dinuclear platinum compounds having bridging amidate ligands. The resulting dimers undergo a facile head-to-tail to head-to-head rearrangement without any detectable intermediate. Solution studies of the mononitrile complex *trans*-$[Pt(NH_3)_2(MeCN)(OH)]^+$ at around neutral pH reveal the formation of *trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]^+$, suggesting a preceding ligand exchange. The reactions of platinum with MeCN are compared with those of the kinetically labile palladium. The nitrile complex *cis*-$[Pt(NH_3)_2(MeCN)Cl]ClO_4$ and the mixed-ligand complex *trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]ClO_4$ were characterized by X-ray crystallography: *cis*-$[Pt(NH_3)_2(MeCN)Cl]ClO_4$, monoclinic, space group $P2_1/c$, a = 10.618(10), b = 10.625(8), c = 9.176(7) Å, β = 111.20(6)°, Z = 4; *trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]ClO_4$, monoclinic, space group $P2_1/c$, a = 8.601(6), b = 19.508(19), c = 7.625(4) Å, β = 115.29(5)°, Z = 4.

The susceptibility of platinum-bound nitriles to nucleophilic attack by water, amines, alcohols, thiols[1,2] and aprotic nucleophiles like alkoxides[3] yielding amidates, amides, amidines, iminoethers, iminothioethers and cyclic imidoesters is extensively documented in the literature.

In particular the facile hydrolysis of acetonitrile in the co-ordination sphere of platinum has been known for a long time: in 1908 Hoffmann and Bugge[4] prepared the first 'platinum blue', when they treated $[Pt(MeCN)_2Cl_2]$ with silver salts. They obtained a deep blue reaction product, which they called 'Platinblau'. Although the exact structure remained unknown, the platinum blue was postulated to contain deprotonated acetamide, derived from hydrolysis of MeCN. Since then various platinum blues have been prepared by reaction of linear and cyclic amides with platinum complexes, including the antitumour drug *cis*-$[Pt(NH_3)_2Cl_2]$ (cisplatin). Especially the 'platinum pyrimidine blues' of cisplatin, obtained by reaction with pyrimidine nucleobases and related cyclic amide ligands, have attracted much interest as second generation antitumour drugs.[5] Several platinum blues were studied by X-ray crystallography[6] and shown to consist of tetra- or octa-nuclear amidate-bridged cations with platinum in the formal oxidation states of 2.25 and 2.5.

More recently Rochon *et al.*[7] prepared a platinum blue analogue, the acetamidate-bridged diplatinum(II) complex $[(dmso)ClPt(\mu\text{-}C_2H_4NO)_2PtCl(dmso)]$ by reaction of $K[Pt(dmso)Cl_3]$ (dmso = dimethyl sulfoxide) with MeCN. To our knowledge this is the only structurally characterized dimeric platinum(II) complex with bridging acetamidate. In contrast, several structures of platinum compounds with terminal amides have been described.[8]

Here we report on the formation, structure and hydrolysis of acetonitrile complexes of *cis*-$[Pt(NH_3)_2Cl_2]$ and the related compounds *cis*-$[Pt(NH_2Me)_2Cl_2]$ and $[Pt(en)Cl_2]$[9] (en = ethane-1,2-diamine) as well as of the corresponding *trans* isomer *trans*-$[Pt(NH_3)_2Cl_2]$. The hydrolysis reactions lead to amidate, dimeric amidate-bridged and mixed nitrile–amidate species. Solution studies of the nitrile compounds and the hydrolysis products were performed in order to get information about the ligand properties of platinum-bound nitriles and linear amidates. An essential feature is the tendency of monomeric acetamidate species to dimerize to dinuclear platinum complexes with bridging amidate ligands. The resulting dimers were shown to undergo a facile head-to-tail to head-to-head rearrangement.

Several studies have demonstrated the ability of palladium to catalyse the hydration of nitriles to the corresponding amides.[9] The formulated reaction mechanisms include the formation of amide complexes and so we were also interested in the isolation and characterization of palladium amide compounds.

Experimental

Starting Materials.—The complexes *cis*-$[Pt(NH_3)_2Cl_2]$,[10] *cis*-$[Pt(NH_2Me)_2Cl_2]$,[10] $[Pt(en)Cl_2]$,[11] *trans*-$[Pt(NH_3)_2Cl_2]$[12] and $[Pd(en)Cl_2]$[13] were prepared from $K_2[PtCl_4]$ and $K_2[PdCl_4]$ (Degussa) by literature methods. 1-Methylcytosine (mcyt) was prepared from cytosine (Fluka) according to ref. 14. Acetonitrile and CD_3CN were obtained from Merck.

Preparations.—*cis*-$[Pt(NH_3)_2(MeCN)Cl]X$ (X = ClO_4 **1a** *or* NO_3 **1b**). The complex *cis*-$[Pt(NH_3)_2Cl_2]$ (600 mg, 2.00 mmol) was stirred in water (120 cm^3) with acetonitrile (6 cm^3) at 60 °C for 1.5 h (pH 4). After addition of NaX (2.00 mmol) the colourless solution was concentrated to 2 cm^3 and kept at 4 °C. After a few days colourless, cubic crystals of complexes **1a** (407 mg, 50%) and **1b** (395 mg, 54%) were obtained (Found: C, 5.8; H, 2.3; N, 10.4. Calc. for $C_2H_9Cl_2N_3O_4Pt$ **1a**: C, 5.9; H, 2.2; N, 10.4. Found: C, 6.4; H, 2.5; N, 15.0. Calc. for $C_2H_9ClN_4O_3Pt$ **1b**: C, 6.5; H, 2.5; N, 15.2%).

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

[Pt(en)(MeCN)Cl]ClO_4 **1c**. Compound **1c** was prepared as described for **1a** starting from $[Pt(en)Cl_2]$ (100 mg, 0.31 mmol) and MeCN (1 cm^3). The product (73 mg) was obtained as thin needles in 55% yield (Found: C, 11.0; H, 2.6; N, 9.7. Calc. for $C_4H_{11}Cl_2N_3O_4Pt$: C, 11.1; H, 2.6; N, 9.8%).

cis-$[Pt(NH_3)_2(MeCN)_2][ClO_4]_2 \cdot 0.5NaClO_4$ **2a**. The complex *cis*-$[Pt(NH_3)_2Cl_2]$ (150 mg, 0.50 mmol) and $AgNO_3$ (171 mg, 1.01 mmol) were stirred in water (20 cm^3) overnight. After filtration of AgCl, MeCN (3 cm^3) was added and the reaction mixture was stirred at room temperature for 1 d. Addition of $NaClO_4 \cdot H_2O$ (1 g, 7.12 mmol) and concentrating the solution to 1 cm^3 yielded a white precipitate (149 mg, 52%) (Found: C, 8.3; H, 2.1; N, 9.9. Calc. for $C_4H_{12}Cl_{2.5}N_4Na_{0.5}O_{10}Pt$: C, 8.4; H, 2.1; N, 9.8%).

$[Pt(en)(MeCN)_2][ClO_4]_2$ **2b**. Complex **2b** was obtained like **2a**, starting from $[Pt(en)Cl_2]$ (149 mg, 0.46 mmol), $AgNO_3$ (153 mg, 0.90 mmol), MeCN (3 cm^3) and $NaClO_4 \cdot H_2O$ (260 mg, 1.85 mmol), as a white powder in 20% yield (50 mg) (Found: C, 13.2; H, 2.5; N, 10.5. Calc. for $C_6H_{14}Cl_2N_4O_8Pt$: C, 13.4; H, 2.6; N, 10.5%).

cis-$[Pt(NH_3)_2(NHCOMe)Cl]$ **3a**. Compound **1b** (204 mg, 0.56 mmol) was dissolved in water (8 cm^3) and cooled in an ice-bath. Potassium hydroxide (37 mg, 0.66 mmol) was added and the solution was stirred at 0 °C for 75 min. After reducing the volume to 0.5 cm^3, the pale yellow reaction product (105 mg) was isolated in 59% yield (Found: C, 7.4; H, 3.1; N, 12.8. Calc. for $C_2H_{10}ClN_3OPt$: C, 7.5; H, 3.1; N, 13.0%).

$[Pt(en)(NHCOMe)Cl] \cdot 1.5H_2O$ **3b**. Compound **3b** was obtained as pale yellow precipitate by stirring **1c** (203 mg, 0.47 mmol) with NaOH (23 mg, 0.58 mmol) in water (10 cm^3) for 1 h at 0 °C. The yield was 42% (73 mg) (Found: C, 12.8; H, 3.8; N, 11.1. Calc. for $C_4H_{15}ClN_3O_{2.5}Pt$: C, 12.8; H, 4.0; N, 11.2%).

cis-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2][ClO_4]_2$ **4a**. Complex **1a** (300 mg, 0.74 mmol) was treated at room temperature with an aqueous solution of $AgClO_4$ (0.74 mmol) in water (30 cm^3). After 24 h the AgCl was filtered off and the solution was brought to pH 8.5 by adding NaOH. After stirring at 60 °C for 2.5 h most of the solvent was evaporated under reduced pressure, whereby a deep green solution was obtained. By keeping the sample at 4 °C small green cubes were obtained (23 mg). Further concentration of the solution gave 76 mg of compound **4a** as a dark reddish brown powder [Found (crystals): C, 6.1; H, 2.8; N, 11.0. Found (powder): C, 6.0; H, 2.6; N, 10.7. Calc. for $C_4H_{20}Cl_2N_6O_{10}Pt_2$: C, 6.2; H, 2.6; N, 10.9%].

cis-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2][NO_3]_2 \cdot 2H_2O$ **4b**. Complex **4b** was prepared in the same way as **4a** by reaction of **1b** (300 mg, 0.82 mmol) with $AgNO_3$ (138 mg, 0.81 mmol). The product was obtained in low yield as a brownish green powder (37 mg, 12%) (Found: C, 6.5; H, 3.0; N, 15.3. Calc. for $C_4H_{24}N_8O_{10}Pt_2$: C, 6.5; H, 3.3; N, 15.3%).

Compound **4b** was also formed by adding MeCN (1 cm^3) to an aqueous solution of *cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$, which was prepared from *cis*-$[Pt(NH_3)_2Cl_2]$ (250 mg, 0.83 mmol) and $AgNO_3$ (277 mg, 1.63 mmol). The reaction mixture was brought to pH 6.0 and stirred at room temperature for 1 d. Keeping the red solution at 4 °C for 1 week yielded 65 mg of a dark red powder, which was identified as a mixture of compound **4b** and a platinum(III) dimer (see text).

$[\{Pt(en)(\mu\text{-}C_2H_4NO)\}_2][ClO_4]_2$ **4c**. Compound **4c** was prepared like **4a**, starting from **1c** (100 mg, 0.23 mmol), as a dark powder in low yield (31 mg, 8%) (Found: C, 11.5; H, 2.8; N, 10.0. Calc. for $C_8H_{24}Cl_2N_6O_{10}Pt_2$: C, 11.6; H, 2.9; N, 10.2%)

cis-$[\{Pt(NH_2Me)_2(\mu\text{-}C_2H_4NO)\}_2][ClO_4]_2$ **4d**. The complex *cis*-$[Pt(NH_2Me)_2Cl_2]$ (164 mg, 0.50 mmol) was dissolved in water (10 cm^3). An aqueous solution of $AgClO_4$ (1.0 mmol) was added and the reaction mixture stirred overnight at room temperature. After filtration of AgCl, MeCN (1.5 cm^3) was added and the solution heated at 60 °C for 2 h. The solvent was completely evaporated and the product obtained as dark red-brown oil.

cis-$[Pt(NH_3)_2(MeCN)(NHCOMe)]ClO_4$ **5**. Complex **2a** (100 mg, 0.175 mmol) was dissolved in water (6 cm^3) and cooled at 0 °C. After adding 0.1 mol dm^{-3} NaOH (2.35 cm^3) the reaction mixture was stirred at 0 °C for 70 min. The solution was then concentrated to 0.5 cm^3. After 3 d a colourless microcrystalline precipitate of **5** (36 mg, 43%) was obtained (Found: C, 11.0; H, 2.9; N, 13.1. Calc. for $C_4H_{13}ClN_4O_5Pt$: C, 11.2; H, 3.1; N, 13.1%).

$[\{Pd(en)(\mu\text{-}C_2H_4NO)\}_2][ClO_4]_2$ **7**. The complex $[Pd(en)Cl_2]$ (95 mg, 0.40 mmol) and $AgNO_3$ (136 mg, 0.80 mmol) were stirred in water (10 cm^3) at room temperature for 3.5 h. Then AgCl was filtered off and the pH was adjusted to 6.5. After heating with MeCN (2 cm^3) at 60 °C for 2.5 h, $NaClO_4$ (98 mg, 0.80 mmol) was added. The yellow solution was concentrated to 3 cm^3 and kept at 4 °C. After 3 d yellow cubes were separated (35 mg, 27%) (Found: C, 15.1; H, 3.9; N, 13.2. Calc. for $C_8H_{24}Cl_2N_6O_{10}Pd_2$: C, 14.8; H, 3.7; N, 13.0%).

trans-$[Pt(NH_3)_2(MeCN)Cl]ClO_4$ **8**. Compound **8** was obtained by reaction of *trans*-$[Pt(NH_3)_2Cl_2]$ (399 mg, 1.33 mmol) and MeCN (4 cm^3) in water (60 cm^3) at acidic pH. After stirring at 60 °C for 2.5 h and adding $NaClO_4 \cdot H_2O$ (414 mg, 2.95 mmol), unreacted *trans*-$[Pt(NH_3)_2Cl_2]$ was filtered off. The colourless solution was concentrated to 10 cm^3 and left at 4 °C. After a few days colourless cubes were isolated (441 mg, 82%) (Found: C, 5.6; H, 2.2; N, 10.6. Calc. for $C_2H_9Cl_2N_3O_4Pt$: C, 5.9; H, 2.2; N, 10.4%).

trans-$[Pt(NH_3)_2(MeCN)_2][ClO_4]_2$ **9**. Compound **9** was prepared in the same way as **2a** starting from *trans*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ (0.51 mmol). The yield was 63% (165 mg, 0.32 mmol) (Found: C, 9.5; H, 2.4; N, 11.2. Calc. for $C_4H_{12}Cl_2N_4O_8Pt$: C, 9.4; H, 2.4; N, 11.0%).

trans-$[Pt(NH_3)_2(NHCOMe)Cl]$ **10**. Compound **8** (100 mg, 0.25 mmol) was dissolved in water (10 cm^3), the solution was brought to pH 11.4 and then stirred at room temperature for 75 min. After reducing the volume to 1 cm^3 the product (20 mg, 25%) was precipitated by adding acetone (Found: C, 8.0; H, 3.2; N, 13.0. Calc. for $C_2H_{10}ClN_3OPt$: C, 7.5; H, 3.1; N, 13.0%).

trans-$[Pt(NH_3)_2(MeCN)(NHCOMe)]ClO_4$ **11**. The complex *trans*-$[Pt(NH_3)_2Cl_2]$ (200 mg, 0.67 mmol) was treated in water (10 cm^3) with an aqueous solution of $AgClO_4$ (1.3 mmol) at room temperature. After 19 h, AgCl was filtered off. The pH of the solution was adjusted to 8.4 and MeCN (2 cm^3) was added. The sample was stirred for 1.5 h at 60 °C, then concentrated to 2.5 cm^3. The solution was kept at 4 °C. After 9 d colourless crystals were isolated (53 mg, 19%) (Found: C, 11.1; H, 3.2; N, 13.0. Calc. for $C_4H_{13}ClN_4O_5Pt$: C, 11.2; H, 3.1; N, 13.1%).

trans-$[Pt(NH_3)_2(NHCOMe)_2]$ **12**. Compound **9** (250 mg, 0.49 mmol) was dissolved in water (8 cm^3). By addition of $NaHCO_3$ (108 mg, 1.29 mmol) the pH was raised to 7.1. The solution was stirred at 40 °C for 2 d, then concentrated to 1 cm^3, whereby a white precipitate formed. The product (52 mg, 31%) was filtered off and dried with acetone (Found: C, 13.7; H, 3.8; N, 16.2. Calc. for $C_4H_{14}N_4O_2Pt$: C, 13.9; H, 4.1; N, 16.2%).

trans-$[Pt(NH_3)_2(MeCN)(mcyt\text{-}N^3)][ClO_4]_2 \cdot 0.5H_2O$ **13**. Silver nitrate (140 mg, 0.82 mmol) was added to an aqueous solution (25 cm^3) of complex **8** (335 mg, 0.83 mmol). After 22 h the AgCl was removed and 1-methylcytosine (105 mg, 0.84 mmol) and $NaClO_4 \cdot H_2O$ (240 mg, 1.71 mmol) were added. The reaction mixture was stirred for 2 d at room temperature. By concentrating the sample to 6 cm^3 and keeping it at 4 °C a colourless, microcrystalline product was formed (216 mg, 43%) (Found: C, 13.9; H, 2.9; N, 13.9. Calc. for $C_7H_{17}Cl_2N_6O_9Pt$: C, 13.9; H, 2.8; N, 13.9%).

trans-$[Pt(NH_3)_2(NHCOMe)(mcyt\text{-}N^3)]ClO_4$ **14**. Complex **14** was prepared by reaction of **13** (200 mg, 0.33 mmol) with NaOH (16 mg, 0.40 mmol) in water (25 cm^3) at 0 °C. After stirring for 45 min the solvent was evaporated under reduced pressure until a white precipitate formed. The product (122 mg, 71%) was filtered off and washed with acetone (Found: C, 16.1;

H, 3.6; N, 16.1. Calc. for $C_7H_{17}ClN_6O_6Pt$: C, 16.1; H, 3.5; N, 16.1%).

Instrumentation.—The NMR spectra were recorded on a Bruker AC 200 spectrometer. Proton NMR spectra were run in D_2O or $(CD_3)_2SO$ solutions using sodium 3-trimethylsilylpropanesulfonate as internal reference. For the ^{195}Pt chemical shift data, $K_2[PtCl_6]$ was used as external reference. The pD values of D_2O solutions were obtained by use of a glass electrode and addition of 0.4 to the pH meter reading. Infrared spectra of KBr pellets were taken on Perkin-Elmer 580B and Bruker IFS 113v FT spectrometers.

Crystal Structure Analysis.—Crystal data for compounds **1a** and **11** 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 from least-squares fits to 17 randomly selected reflections in the range $5.70 \leqslant 2\theta \leqslant 24.44°$ (**1a**) and to 15 reflections in the range $16.36 \leqslant 2\theta \leqslant 29.82°$ (**11**). Intensity data were collected at variable scan speeds in the range $4.1 \leqslant 20 \leqslant 50.0$ (**1a**) and $4.2 \leqslant 2\theta \leqslant 50.1°$ (**11**) using an ω–2θ scan technique. An empirical absorption correction *via* ψ scans was applied for both compounds. No correction was made for extinction. Crystal data and experimental details are listed in Table 3.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares using the SHELXTL PLUS and SHELX 93 programs.[15] All non-hydrogen atoms of compound **11** were refined anisotropically; in the case of compound **1a** only the platinum, chlorine and the perchlorate oxygens were refined anisotropically. Idealized hydrogen positions were calculated geometrically with fixed X–H bond distances and fixed isotropic U values. The scattering factors are taken from ref. 16. Final non-hydrogen positional parameters are listed in Tables 4 and 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Table 1 Infrared data (cm^{-1}) for the acetonitrile complexes

Compound		ν(C≡N)
1a	*cis*-$[Pt(NH_3)_2(MeCN)Cl]ClO_4$	2334
1b	*cis*-$[Pt(NH_3)_2(MeCN)Cl]NO_3$	2334
1c	$[Pt(en)(MeCN)Cl]ClO_4$	2334
2a	*cis*-$[Pt(NH_3)_2(MeCN)_2][ClO_4]_2$	2330
2b	$[Pt(en)(MeCN)_2][ClO_4]_2$	2329
5	*cis*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]ClO_4$	2320
8	*trans*-$[Pt(NH_3)_2(MeCN)Cl]ClO_4$	2355
9	*trans*-$[Pt(NH_3)_2(MeCN)_2][ClO_4]_2$	2330
11	*trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]ClO_4$	2336
13	*trans*-$[Pt(NH_3)_2(MeCN)(mcyt\text{-}N^3)][ClO_4]_2$	2340

Results and Discussion

Acetonitrile Complexes with cis-$Pt^{II}(amine)_2$.—Reaction of *cis*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(en)Cl_2]$ with MeCN leads to the nitrile complexes **1a–1c**, while reaction of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ and $[Pt(en)(H_2O)_2]^{2+}$ in acidic solution gives the bis(acetonitrile) complexes **2a** and **2b**.

Infrared and ^1H NMR data are reported in Tables 1 and 2. The ν(C≡N) stretching vibrations are near 2330 cm^{-1} as expected for end-on bound nitriles.[1,17] Some of the nitrile complexes give two bands in this region, one resulting from ν(C≡N), the other assignable to a combination band of $\delta_{sym}(CH_3)$ and ν(C–C) vibrations of the nitrile ligand. The correct assignment of the ν(C≡N) band was verified by comparison with the IR spectrum of the deuteriated complex *cis*-$[Pt(NH_3)_2(CD_3CN)Cl]ClO_4$, which only shows the ν(C≡N) band. Co-ordination of MeCN to platinum results in a shift of the NMR resonance of the methyl group to lower field by about 0.5 ppm; $^4J(^{195}Pt–^1H)$ coupling constants typically are between 10 and 14 Hz. For compound **1a** crystals suitable for X-ray diffraction analysis were obtained and the crystal structure of the complex was determined.

Crystal structure of complex **1a**. Fig. 1 shows the cation, and bond lengths and angles are presented in Table 5. The co-ordination geometry of the Pt atom is slightly distorted square planar with deviations (Å) from the best weighted plane as follows: Pt 0.001(2), Cl(2) 0.003(6), N(1) −0.076(21), N(2)

Table 2 Proton NMR data for compounds **1–12**

Complex	δ(CH_3) (nitrile)	$^4J(^{195}Pt–^1H)$/ Hz	δ(CH_3) (amide)	δ(NH) (amide)	δ($NH_{2/3}$)[a]	δ($CH_{2/3}$) (en, NH_2Me)
1a, **1b**[b]	2.53	12.7	—	—	—	—
1c[b]	2.52	12.4	—	—	—	2.57–2.71 (m)
2a[b]	2.59	10.6	—	—	—	—
2b[b]	2.58	—	—	—	—	2.70
3a[b]	—	—	1.95	—	—	—
3c[b]	—	—	1.95	—	—	2.62
4a, **4b**[c]	—	—	1.90	6.22 6.27	4.02 4.10 4.26 4.33	—
4c[c]	—	—	1.92	6.31 6.36	5.03–6.18 (m)	1.85
4d[c]	—	—	1.92	6.50 6.54	4.76–5.08	2.17–2.40
5[b]	2.46	11.0	1.96	—	—	—
6[b]	—	—	1.95	—	—	—
7[c]	—	—	1.83	5.64 5.78	4.39–5.64 (m)	*d*
8[b]	2.54	—	—	—	—	—
9[b]	2.67	14.4	—	—	—	—
10[b]	—	—	1.95	—	—	—
11[b]	2.49	10.7	1.96	—	—	—
11[c]	2.56	—	1.75	5.44	4.65	—
12[b]	—	—	1.95	—	—	—

[a] NH_3, NH_2 of NH_2Me or NH_2 of en. [b] Spectra recorded in D_2O. [c] Spectra recorded in $(CD_3)_2SO$. [d] Signal probably obscured by the Me_2SO resonance.

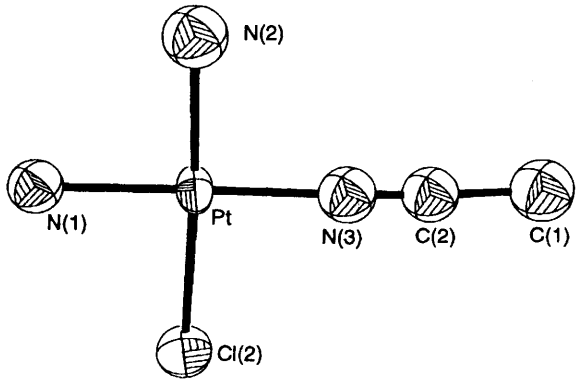


Fig. 1 View of the cation of complex **1a** with the atom numbering scheme

Table 3 Crystallographic data and experimental details of the X-ray studies*

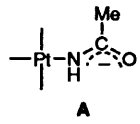
Complex	**1a**	**11**
Formula	$C_2H_9Cl_2N_3O_4Pt$	$C_4H_{13}ClN_4O_5Pt$
M	405.11	427.72
a/Å	10.618(10)	8.601(6)
b/Å	10.625(8)	19.508(19)
c/Å	9.176(7)	7.625(4)
β/°	111.20(6)	115.29(5)
U/Å^3	965.1(14)	1156.8(15)
D_c/g cm^{-3}	2.788	2.456
Crystal dimensions/mm	0.64 × 0.54 × 0.48	0.45 × 0.18 × 0.26
μ(Mo-Kα)/mm^{-1}	15.08	12.37
F(000)	744	800
No. measured reflections	1517	1812
No. independent reflections	761	898
No. observed reflections [$F > 4\sigma(F)$]	657	735
No. parameters	84	116
R_1	0.0492	0.0355
wR_2	0.1214	0.0912

* Details in common: monoclinic, space group $P2_1/c$; $Z = 4$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2$; $P = (F_o^2 + 2F_c^2)/3$; $a = 0.0715$ for complex **1a** and 0.0554 for **11**.

Table 4 Atomic positional parameters with estimated standard deviations (e.s.d.s) for complex **1a**

Atom	x	y	z
Pt	0.1140(1)	0.0781(5)	0.1542(1)
Cl(1)	0.3462(9)	−0.0576(5)	0.6823(10)
Cl(2)	−0.0245(6)	0.2485(4)	0.0670(7)
C(1)	0.4126(30)	0.2325(26)	−0.0664(36)
C(2)	0.3038(29)	0.1770(23)	−0.0045(31)
N(1)	0.0020(23)	0.0355(17)	0.2856(25)
N(2)	0.2269(27)	−0.0776(15)	0.2340(30)
N(3)	0.2274(25)	0.1323(20)	0.0399(25)
O(1)	0.4778(23)	−0.0071(22)	0.7449(31)
O(2)	0.3526(46)	−0.1686(24)	0.5915(45)
O(3)	0.3030(43)	−0.0894(28)	0.8071(48)
O(4)	0.2574(23)	0.0247(21)	0.5814(28)

0.047(24) and N(3) −0.088(22) Å. The acetonitrile ligand is linear [N(3)–C(2)–C(1) 177.3(27)°] and is bound to platinum through the electron lone pair on the nitrogen atom forming a Pt–N(3)–C(2) angle of 168.0(20)°. Deviations from linearity of the M–N–C moiety are also observed in other metal nitrile complexes and attributed to partial sp^2 character of the donor nitrogen atom.[17] The Pt–N(1), Pt–N(2) and Pt–Cl(2) bond distances are normal, the Pt–N(3) bond length is in good



A

agreement with values found in other platinum acetonitrile complexes.[1,17]

The packing of the molecules in the crystal is depicted in Fig. 2. The cations form layers parallel to the *ac* plane with a Pt ··· Pt distance of 3.42(1) Å (symmetry operation: $-x$, $-y$, $-z$).

Hydrolysis of complexes **1a**–**1c**. The nitrile complexes **1a**–**1c** are converted into the corresponding amidate species *cis*-$[Pt(NH_3)_2(NHCOMe)Cl]$ **3a** and [Pt(en)(NHCOMe)Cl] **3b** by reaction with base at low temperature. The products were characterized by IR and ^1H NMR spectroscopy (Table 2).

Co-ordination *via* the deprotonated amide nitrogen is assumed for the following reasons. In principle, acetamide can bind through oxygen and nitrogen of both the keto and enol forms, but co-ordination through nitrogen is preferred.[18] The analytical results are consistent with acetamide functioning as an anionic ligand. The IR data support binding through the deprotonated amide nitrogen: the vibrations of the amide group at 1550 and 1593 (**3a**) and 1565 and 1589 cm^{-1} (**3b**) coincide with an amidate anion co-ordinating through nitrogen.[19] Furthermore the IR spectrum exhibits a strong band at 1478 (**3a**) and 1487 cm^{-1} (**3b**), which can be assigned to skeleton vibrations and which is characteristic for the proposed co-ordination mode.[19] Finally, the reaction scheme suggests N-co-ordination of the amide ligand: **3a** and **3b** are formed by hydrolysis of (N-)co-ordinated acetonitrile and a subsequent isomerization seems unlikely due to the preference of Pt for nitrogen. For this reason we postulate the binding mode **A**. Unfortunately this cannot be unambiguously proven by means of a ^1H–^{195}Pt HMQC (heteronuclear multiple-quantum coherence) spectrum, since the compound is decomposed in aprotic solvents like Me_2SO or dimethylformamide (dmf).

Dimerization of complex **3a**. When an aqueous solution of complex **3a** is kept at room temperature for several days (pH 6.7) the dimeric complex *cis*-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2]Cl_2$ **4** is formed. The dimerization reaction was monitored by ^1H NMR spectroscopy (Fig. 3). During the reaction, the CH_3 resonance of **3a** at δ 1.95 decreases while two new singlets at δ 2.01 and 2.00 appear assigned to complex **4**. The appearance of two singlets is due to the occurrence of two isomers [head-to-head (hh) and head-to-tail (ht), Scheme 1] as discussed below. After 13 d the reaction was nearly complete. Addition of $AgNO_3$ accelerates the dimerization. No intermediate is detectable in the NMR spectra, neither during the reaction of the chloro species nor during the reaction in the presence of Ag^+. Integration of the NMR signals showed roughly a 1:1 ratio of the hh and ht isomers. During the reaction time no significant changes in the ratio of the two species were found. No resonances due to the hydroxo species *cis*-$[Pt(NH_3)_2(NHCOMe)(OH)]$, which is expected as an intermediate during the reaction with $AgNO_3$, were observed.

The dimer was also obtained by heating *cis*-$[Pt(NH_3)_2(MeCN)(OH)]^+$ or by reaction of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with MeCN in basic or slightly acidic solution. In this way compounds **4a** and **4b** were prepared on a preparative scale and characterized by IR, ^1H and ^{195}Pt NMR spectroscopy. In contrast to compounds **3a** and **3b**, the IR spectra show only one amide band at 1606 (**4a**) and 1596 cm^{-1} (**4b**), respectively. In the region around 340 cm^{-1} no ν(Pt–Cl) vibrations are detected.

The proton NMR spectrum in $(CD_3)_2SO$ immediately after dissolving (Fig. 4) reveals two inequivalent amide protons (δ 6.22 and 6.27) and four inequivalent amine protons (δ 4.02, 4.10, 4.26 and 4.33). One CH_3 resonance appears at δ 1.90.

In the ^{195}Pt NMR spectrum (Fig. 5) three resonances at δ −1415, −1898 and −2354 are observed. According to estab-

Table 5 Bond distances (Å) and angles (°) with e.s.d.s for complex **1a**

Pt–N(1)	2.03(3)	Pt–N(2)	2.02(2)
Pt–N(3)	1.95(4)	Pt–Cl(2)	2.286(5)
Cl(1)–O(1)	1.41(2)	Cl(1)–O(2)	1.46(3)
Cl(1)–O(3)	1.42(6)	Cl(1)–O(4)	1.37(2)
C(2)–N(3)	1.14(4)	C(2)–C(1)	1.57(5)
N(1)–Pt–N(2)	90.0(13)	N(1)–Pt–Cl(2)	86.8(6)
N(3)–Pt–N(1)	174.8(7)	N(2)–Pt–Cl(2)	176.5(10)
N(3)–Pt–N(2)	92.0(13)	N(3)–Pt–Cl(2)	91.3(6)
O(1)–Cl(1)–O(2)	107.2(22)	O(1)–Cl(1)–O(3)	108.9(18)
O(3)–Cl(1)–O(2)	111.3(26)	O(4)–Cl(1)–O(1)	111.8(16)
O(4)–Cl(1)–O(2)	107.0(20)	O(4)–Cl(1)–O(3)	110.7(23)
C(2)–N(3)–Pt	168.0(20)	N(3)–C(2)–C(1)	177.3(27)

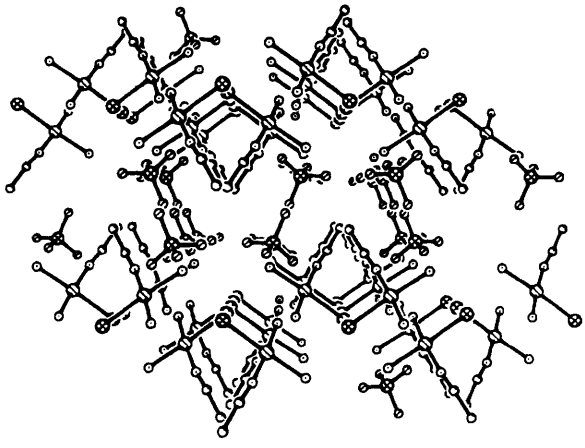
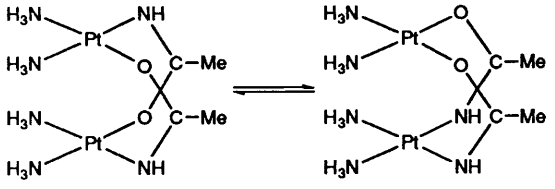


Fig. 2 Crystal packing of complex **1a** along the *y* axis



Scheme 1 Head-to-tail ⟶ head-to-head isomerization equilibrium of *cis*-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2]^{2+}$

lished ^{195}Pt chemical shift trends the downfield resonance has to be assigned to a N_2O_2 environment whereas the upfield resonance corresponds to a N_4 co-ordination sphere.[20] The third signal occurs midway between the N_2O_2 and N_4 resonances and therefore suggests a N_3O environment. The ^1H and ^{195}Pt NMR spectra are consistent with the hh and ht isomers of the dimer existing in nearly equal concentrations in solution. The ratio of the two isomers is independent of the method of preparation and, as mentioned above, independent of the reaction time. Concerning the reaction of **3a**, the combination of two monomeric amidate complexes should lead exclusively to the head-to-tail isomer. A rearrangement of the monomeric complex seems unlikely since N-co-ordination is thermodynamically favoured.[18] Therefore a rapid isomerization of the ht to the hh dimer without any detectable intermediate has to be postulated. The ht ⇌ hh equilibrium is reached rapidly after the formation of the dimer, since the ratio of the two species is constant with time. A fast hh ⇌ ht isomerization was also observed for the amidate-bridged platinum dimers hh-$[\{Pt_2(NH_3)_4(C_4H_6NO)_2\}_2][PF_6]_3[NO_3]\cdot H_2O$ and hh-$[Pt_2(en)_2(C_5H_4NO)_2][NO_3]_2$. The isomerization equilibrium of the former is established rapidly after dissolution whereas the hh ⇌ ht equilibrium of the latter is reached within several hours.[21,22] No intermediates were detected and a reversible, intramolecular, dissociatively activated rearrangement was proposed for hh-$[Pt_2(en)_2(C_5H_4NO)_2][NO_3]_2$. A similar mechanism for the facile isomerization of *cis*-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2]^{2+}$ seems reasonable.

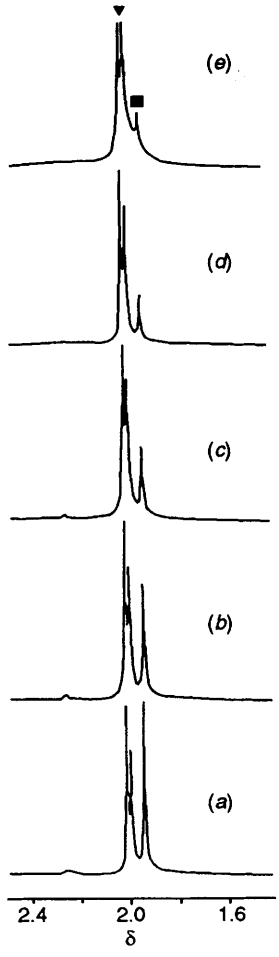


Fig. 3 Dimerization of complex **2a**. Proton NMR spectra were taken after (*a*) 1, (*b*) 2, (*c*) 3, (*d*) 6 and (*e*) 13 d at room temperature. Resonances are assigned as follows: (■) *cis*-$[Pt(NH_3)_2(NHCOMe)Cl]$ and (▼) hh,ht-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2]^{2+}$

As expected the same behaviour in aqueous solution was found for compound **3b**: At room temperature, it is slowly converted into the dimeric complex **4c**, existing as hh and ht isomers as observed for **4a** and **4b**. The complex [Pt(en)(MeCN)(OH)]ClO_4 in basic solution at 60 °C gives **4c** on a preparative scale. Proton NMR data are presented in Table 2.

Although attempts to isolate a nitrile complex of *cis*-$[Pt(NH_2Me)_2Cl_2]$ failed, the dimeric acetamidate complex **4d** could be obtained as an oily product from the reaction of *cis*-$[Pt(NH_2Me)_2(H_2O)_2]^{2+}$ with MeCN. Proton NMR data are reported in Table 2. The same hh ⇌ ht equilibrium was observed as for **4a**–**4c**.

Oxidation of complex **4b**. When compound **4b** was prepared by reaction of *cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$ with MeCN at pH 6 a mixture of **4b** and a by-product, probably resulting from air oxidation of the platinum(II) dimer, was isolated. The ^{195}Pt NMR spectrum shows, besides the signals of the hh and ht isomers of **4b**, an additional resonance at δ −552. From the chemical shift it can be concluded that it is due to a platinum(III) compound.[20] The diamagnetism requires a dimeric structure with a Pt–Pt bond. The reaction mixture is ESR silent. No hints for mixed-valence intermediates could be obtained. Unfortunately all attempts to isolate the oxidation product were unsuccessful, so a full characterization has not been possible.

Hydrolysis of complex **2**. Keeping complex **2a** in slightly basic solution (pD ≈ 8) at 40 °C for some hours yields free acetamide and hh,ht-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2]^{2+}$. When the pD is kept

constant by use of a buffer the ^{1}H NMR spectrum recorded after 1 d reveals a mixture consisting of free MeCN, hh,ht-$[\{Pt(NH_3)_2(\mu\text{-}C_2H_4NO)\}_2]^{2+}$ as well as the mixed-ligand complex *cis*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]^+$ **5** and the bis(acetamidate) complex *cis*-$[Pt(NH_3)_2(NHCOMe)_2]$ **6**. Complexes **5** and **6** cannot be observed in unbuffered solution, as the pD decreases significantly during the reaction (down to 4–5), so that the amidate ligand becomes protonated and the Pt–N (amide) bond is cleaved. The dimeric complex is more stable against acid (up to pD ≈ 3). The complex *cis*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]ClO_4$ is formed as the only product (besides a by-product in low concentration giving an NMR resonance at δ 2.24, which may be attributed to an O-coordinated amide species), when **2a** is treated with 1.2 equivalents of base at 0 °C. The IR spectrum shows a ν(C≡N) stretching vibration at 2320 cm^{-1} and amide bands at 1605 and 1550 cm^{-1}; ^{1}H NMR data are given in Table 2.

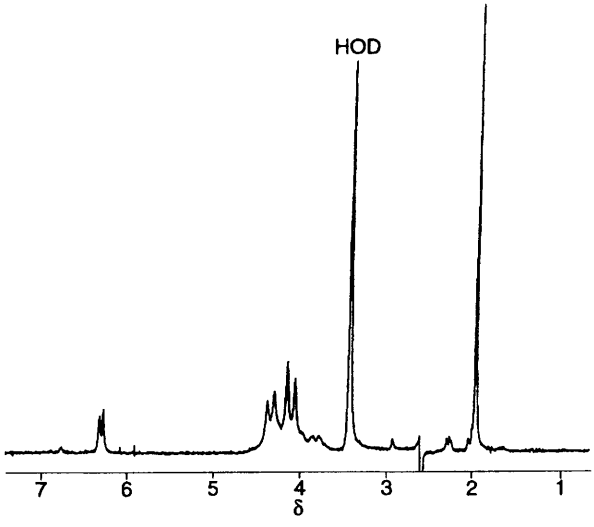


Fig. 4 Proton NMR spectrum in $(CD_3)_2SO$ of complexes **4a**/**4b** recorded immediately after dissolution

Complex **5** is completely converted into the bis(acetamidate) **6** by reaction with base at low temperature within 1 h. The hydrolysis of the acetonitrile ligand, which was followed by ^{1}H NMR spectroscopy, is confirmed by loss of the acetonitrile resonance. After 1 h the spectrum shows only one singlet at δ 1.95, which is assigned to compound **6**. Attempts to isolate **6** yielded oils, which could not be characterized by IR spectroscopy or elemental analysis.

Reaction of $Pd^{II}(en)$ *with acetonitrile*. The ability of palladium to catalyse the hydration of nitriles yielding the corresponding amides is well established.[9] We were able to prepare a dinuclear acetamidate complex of $Pd^{II}(en)$ by reaction of $[Pd(en)(H_2O)_2]^{2+}$ with MeCN. Proton NMR data (Table 2) clearly reveal a structure analogous to that of compound **4c**. A ht ⇌ hh isomerization equilibrium immediately established after dissolution was likewise observed. In contrast to the reactions carried out with platinum, an acetonitrile complex could not be detected when the hydrolysis was followed by ^{1}H NMR spectroscopy. The fact that no intermediate could be

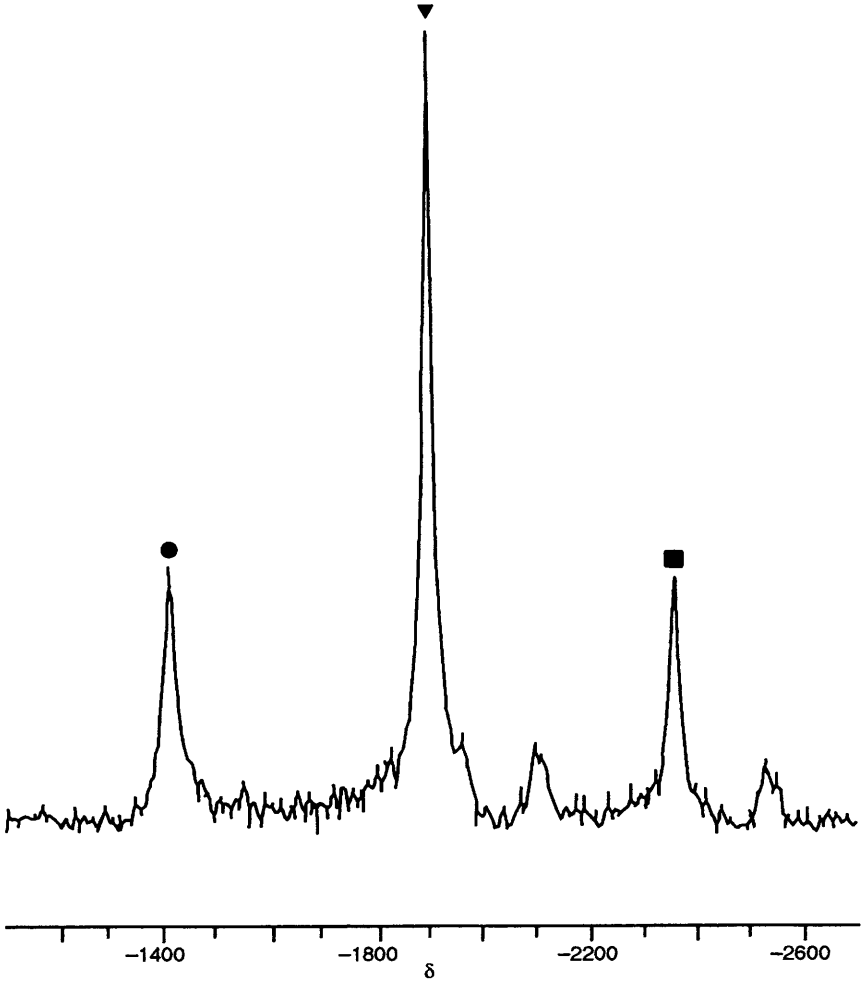
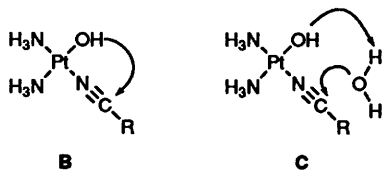


Fig. 5 The ^{195}Pt NMR spectrum in $(CD_3)_2SO$ of complexes **4a**/**4b** recorded immediately after dissolution. Resonances are assigned as follows: (■) $Pt(N_2N'_2)$, (●) $Pt(N_2, O_2)$ and (▼) $Pt(N_2, N', O)$



B C

observed demonstrates the strong ability of palladium to promote the hydration of nitriles.

All attempts to isolate a palladium acetonitrile complex analogous to **1c** were unsuccessful. No nitrile complex could be obtained from acidic solution starting with $[Pd(en)Cl_2]$, but in basic solution reactions of $[Pd(en)Cl_2]$ with MeCN yielded free acetamide.

Acetonitrile Complexes with trans-$Pt^{II}(amine)_2$.—Reaction of *trans*-$[Pt(NH_3)_2Cl_2]$ with MeCN gives the nitrile complex **8**. When MeCN is added to an acidic aqueous solution of *trans*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ the bis(acetonitrile) complex **9** is formed. The IR and ^1H NMR data of both compounds are given in Tables 1 and 2.

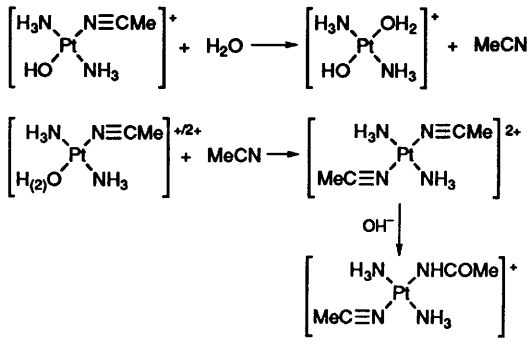
Hydrolysis of complexes **8** *and* **9**. Treating complex **8** with base at room temperature gives the acetamidate **10**, which was characterized by IR and ^1H NMR spectroscopy. The IR spectrum shows amide bands at 1590 and 1555 cm^{-1}, which compare well with the values found for the *cis* isomer. The ν(Pt–Cl) stretching vibration occurs at 325 cm^{-1}. Proton NMR data are listed in Table 2.

The bis(acetonitrile) complex **9** is converted into the mixed-ligand complex *trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]^+$ **11** when kept in nearly neutral solution at 40 °C. Proton NMR spectra showed that hydrolysis of one of the nitrile ligands was complete within 24 h. The bis(acetamide) complex **12** is obtained when the solution is buffered with $NaHCO_3$. Its IR spectrum reveals an amide band at 1595 cm^{-1}; ^1H NMR data are presented in Table 2.

The reactions of the described nitrile complexes demonstrate that hydrolysis of platinum-bound acetonitrile is possible under mild conditions. In the case of the bis(nitrile) complexes and the mononitrile complexes with *trans* configuration, conversion of acetonitrile into acetamidate should take place *via* external attack of hydroxide, the hydrolysis being facilitated by Lewis-acid activation of the metal. For the hydroxo species of mononitrile complexes with *cis* configuration a combined Lewis-acid and metal hydroxide activation is possible, whereby the hydroxide can act as a nucleophile (**B**) or as a base (**C**).

The mechanism of hydration of acetonitrile catalysed by the cobalt complex $[Co(cyclen)(H_2O)_2]^{3+}$ (cyclen = 1,4,7,10-tetraazacyclododecane) was investigated by Chin and co-workers.[23] They showed that the hydrolysis takes place by intramolecular nucleophilic attack of the hydroxo group in *cis* position to the co-ordinated nitrile.

Reaction of complex **8** *with* Ag^+. When complex **8** is treated with $AgNO_3$ and the resulting hydroxo species *trans*-$[Pt(NH_3)_2(MeCN)(OH)]^+$ is kept in nearly neutral solution (pD 6.6) over several days, signals of the mixed-ligand complex *trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]^+$ **11** and free acetamide are observed in the ^1H NMR spectrum. At the beginning of the reaction small amounts of the bis(acetonitrile) complex *trans*-$[Pt(NH_3)_2(MeCN)_2]^{2+}$ are detected. The reaction of the hydroxo species to give **11** is depicted in Scheme 2. First the nitrile ligand of the hydroxonitrile complex is exchanged by water. Free acetonitrile, which is observed in the ^1H NMR spectra in low concentrations, attacks a mononitrile species forming the bis(acetonitrile) complex, which is hydrolysed to *trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]^+$. Another feasible mechanism is hydrolysis of *trans*-$[Pt(NH_3)_2(MeCN)(OH)]^+$ to *trans*-$[Pt(NH_3)_2(NHCOMe)(OH)]$ and attack of free acetonitrile on it, but this seems unlikely as there is no evidence for an amidatehydroxo species. No ligand exchange is observed



Scheme 2 Formation of *trans*-$[Pt(NH_3)_2(MeCN)(NHCOMe)]^+$ from *trans*-$[Pt(NH_3)_2(MeCN)(OH)]^+$

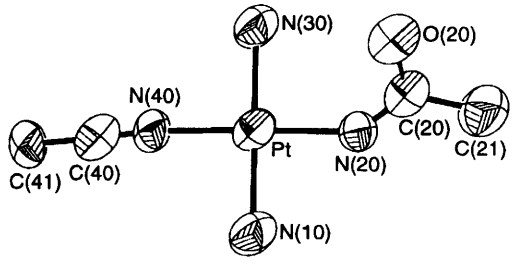


Fig. 6 View of the cation of complex **11** with the atom numbering scheme

Table 6 Atomic positional parameters with estimated standard deviations (e.s.d.s) for complex **11**

Atom	*x*	*y*	*z*
Pt	0.1469(1)	0.1507(1)	0.2432(1)
Cl	−0.7546(5)	−0.4028(2)	−0.0287(6)
N(10)	0.2529(21)	0.0919(6)	0.4929(21)
N(20)	0.3527(17)	0.2125(5)	0.3528(22)
N(30)	0.0394(19)	0.2109(5)	−0.0019(21)
N(40)	−0.0511(17)	0.0843(6)	0.1347(22)
C(20)	0.3677(21)	0.2776(8)	0.3554(24)
C(21)	0.5371(5)	0.3113(2)	0.4645(6)
C(40)	−0.1489(21)	0.0431(7)	0.0851(26)
C(41)	−0.2761(22)	−0.0089(9)	0.0195(32)
O(20)	0.2391(14)	0.3172(5)	0.2755(16)
O(1)	−0.6309(5)	−0.4313(2)	0.1348(6)
O(2)	−0.7979(5)	−0.3380(2)	0.0149(6)
O(3)	−0.9002(5)	−0.4433(2)	−0.1033(6)
O(4)	−0.6919(5)	−0.3873(2)	−0.1611(6)

in acidic media. Therefore the cleavage of the nitrile–platinum bond may be attributed to the higher *trans* effect of OH^- as compared to H_2O. The presence of free acetamide can be explained by slow decomposition of **11** upon long reaction times, or alternatively by rapid cleavage of *trans*-$[Pt(NH_3)_2(NHCOMe)(OH)]$ as a consequence of the *trans* effect of OH^-. Since the free amidate will immediately be protonated at around neutral pH and as free acetamide does not react with *trans*-platinum compounds to give amidate complexes under these conditions, the cleavage is irreversible. Although there is no spectroscopic evidence for *trans*-$[Pt(NH_3)_2(NHCOMe)(OH)]$, its formation as a short-lived intermediate by hydrolysis of *trans*-$[Pt(NH_3)_2(MeCN)(OH)]^+$ cannot be excluded.

Spectroscopic characterisation and crystal structure of complex **11**. Compound **11** was obtained on a preparative scale by reaction of *trans*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with MeCN in basic solution at 60 °C. Proton NMR resonances are listed in Table 2. In the IR spectrum the ν(C≡N) vibration is observed at 2336 cm^{-1} and a strong amide band appears at 1602 cm^{-1}.

The cation of compound **11** is depicted in Fig. 6 and

interatomic distances and angles are given in Table 7. The co-ordination geometry of the platinum atom is square planar [maximum deviation from the best weighted plane: 0.053(17) Å for N(20)]. The Pt–N bond distances are in the range 2.00(1)–2.07(1) Å as expected for platinum(II) complexes. The linear acetonitrile ligand [N(40)–C(40)–C(41) 179.1(14)°] co-ordinates through the lone pair of electrons on the nitrogen. The Pt–N(40)–C(40) angle [173.3(10)°] deviates slightly from linearity as already discussed for compound **1a**. The N(40)–C(40) bond length [1.11(2) Å] corresponds well with the values found in **1a** and other platinum nitrile complexes.[17] The acetamide ligand is assumed to co-ordinate through the deprotonated amide nitrogen. The Pt–N(20)–C(20) angle is 132.1(12)°. Although the nitrogen and oxygen of the amide group are crystallographically not distinguishable, this co-ordination pattern seems reasonable on the basis of ^{195}Pt NMR data (δ −2667). The position of the signal clearly rules out co-ordination of acetamide through oxygen.[20] The N(20)–C(20) and O(20)–C(20) bond distances are equal within experimental error. This suggests extensive electron delocalization within the amide group. The best weighted plane through the acetamide forms an angle of 40.8(7)° with the platinum co-ordination plane. An intramolecular hydrogen bond [2.94(2) Å] is formed between O(20) and N(30) with the O(20)–N(30)–Pt and N(30)–O(20)–C(20) angles being 81.4(9) and 92.1(10)°.

The packing of the molecules in the crystal is shown in Fig. 7. The cations are connected *via* hydrogen bonds between amide oxygen and the amine ligands (Table 7).

Reaction of complex **11** *with chloride*. In order to get information about the ligand properties of acetonitrile and acetamidate we investigated the reaction of complex **11** with chloride. With 1 equivalent of NaCl at room temperature in neutral solution [where cleavage of the Pt–N (amidate) bond due to protonation of the ligand can be excluded] small amounts of free acetamide, free acetonitrile and *trans*-[Pt(NH$_3$)$_2$(MeCN)Cl]$^+$ are seen in the ^{1}H NMR spectrum within 1 d, with acetamide and consequently *trans*-[Pt(NH$_3$)$_2$(MeCN)Cl]$^+$ existing in slightly higher concentration than that of acetonitrile. With longer reaction times the formation of free acetamide and acetonitrile increases, while the concentration of *trans*-[Pt(NH$_3$)$_2$(MeCN)Cl]$^+$ decreases. After 8 d the signal of *trans*-[Pt(NH$_3$)$_2$(MeCN)Cl]$^+$ disappeared and yellow *trans*-[Pt(NH$_3$)$_2$Cl$_2$] precipitated. During the reaction no signal assignable to *trans*-[Pt(NH$_3$)$_2$(NHCOMe)Cl] is observed, indicating that cleavage of the Pt–N (amidate) bond is the preferred reaction of **11** with chloride and that the free acetonitrile results exclusively from reaction of *trans*-[Pt(NH$_3$)$_2$(MeCN)Cl]$^+$ with chloride (Scheme 3). This behaviour was unexpected in view of the stability of platinum complexes with N-bound cyclic amidates to chloride. The *trans* effect of nitriles is not well studied, but it is expected to be high due to the multiple bond of the C≡N group. The fact that **11** reacts with 1 equivalent of NaCl not completely to *trans*-[Pt(NH$_3$)$_2$(MeCN)Cl]$^+$, but that rather a mixture of **11** and *trans*-[Pt(NH$_3$)$_2$Cl$_2$] results, needs an explanation: the Pt–N(nitrile) bond of **11** is not cleaved, so that normally the nitrile complex should be stable against chloride. The cleavage of the Pt–N bond of *trans*-[Pt(NH$_3$)$_2$(MeCN)Cl]$^+$ can be explained with a higher *trans* effect of chloride as compared to that of the amidate ligand and/or with the low solubility of *trans*-[Pt(NH$_3$)$_2$Cl$_2$].

Mixed nitrile– and amidate–pyrimidine complexes. The aqua species obtained by treating complex **8** with AgNO$_3$ reacts with 1-methylcytosine to give the mixed nitrile–pyrimidine complex **13**, with 1-methylcytosine co-ordinating through N^3 as expected for platinum complexes. The IR spectrum shows the ν(C≡N) stretching vibration at 2340 cm^{-1}. A strong, broad band at 1645 cm^{-1} with shoulders at 1610 and 1670 cm^{-1} is observed for the ν(C=O) and ν(C=C) stretching modes of mcyt. The following IR bands are typical for N^3-co-ordinated 1-methylcytosine: 1540 and 1520 (ring stretching modes) and 775 and 648 cm^{-1} (ring breathing modes).[24] Proton NMR resonances of **13** in D$_2$O are observed at δ 7.63 (d, ^3J = 7.4, H^6), 6.02 (d, ^3J = 7.4 Hz, H^5), 3.42 (CH$_3$, mcyt) and 2.64 (MeCN).

The nitrile ligand in complex **13** is hydrolysed to the corresponding amidate by reaction with base at 0 °C (Scheme 4). The mixed amidate–pyrimidine complex **14** was character-

Table 7 Bond distances (Å), angles (°) and possible hydrogen-bonding interactions with e.s.d.s for complex **11**

Pt–N(10)	2.071(13)	Pt–N(20)	2.004(11)
Pt–N(30)	2.062(12)	Pt–N(40)	2.016(12)
Cl–O(1)	1.365(13)	Cl–O(2)	1.40(2)
Cl–O(3)	1.38(2)	Cl–O(4)	1.37(7)
N(20)–C(20)	1.28(2)	N(40)–C(40)	1.11(2)
C(40)–C(41)	1.42(2)	C(20)–O(20)	1.27(2)
C(20–C(21)	1.49(2)		
N(20)–Pt–N(10)	89.2(6)	N(20)–Pt–N(30)	90.6(5)
N(20)–Pt–N(40)	176.8(6)	N(40)–Pt–N(10)	89.1(6)
N(30)–Pt–N(10)	178.6(8)	N(40)–Pt–N(30)	91.2(5)
O(1)–Cl–O(2)	109.5(10)	O(1)–Cl–O(3)	111.0(10)
O(1)–Cl–O(4)	111.4(17)	O(3)–Cl–O(2)	109.2(13)
O(4)–Cl–O(2)	101.9(14)	O(4)–Cl–O(3)	113.4(14)
C(20)–N(20)–Pt	132.1(12)	C(40)–N(40)–Pt	173.3(10)
N(40)–C(40)–C(41)	179.1(14)	O(20)–C(20)–C(21)	116.4(14)
N(20)–C(20)–C(21)	121.1(19)		
N(10)···O(20^{I})	2.83(3)	N(30)···O(20^{II})	2.94(3)
N(30)···O(20^{III})	2.94(2)		
O(20)–N(10)–Pt^{I}	102.0(10)	N(10)–O(20)–C(20^{I})	115.4(10)
O(20)–N(30)–Pt^{II}	105.7(10)	N(30)–O(20)–C(20^{II})	102.7(10)
O(20)–N(30)–Pt^{III}	81.4(9)	N(30)–O(20)–C(20^{III})	92.1(10)

Symmetry operations: I $x, -y + \frac{1}{2}, z + \frac{1}{2}$; II $x, -y + \frac{1}{2}, z - \frac{1}{2}$; III x, y, z.

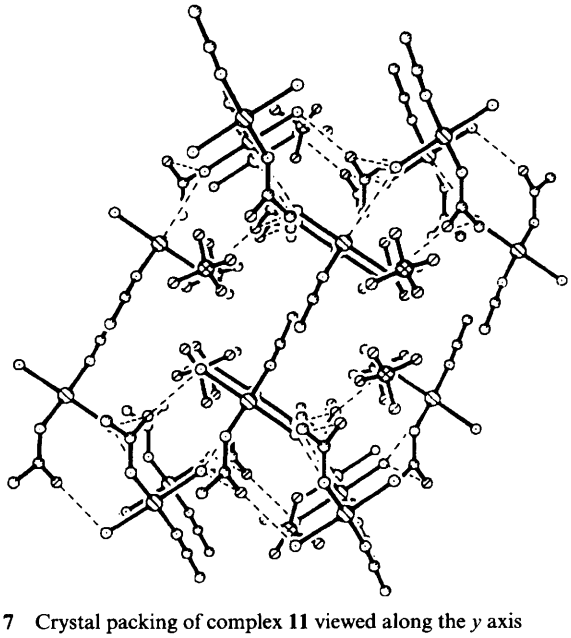
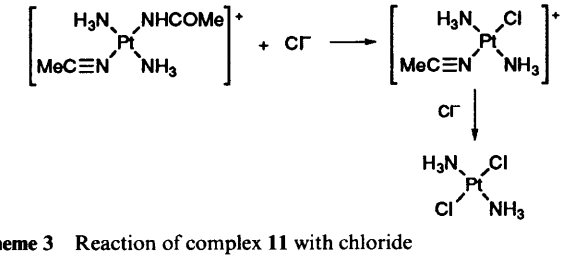
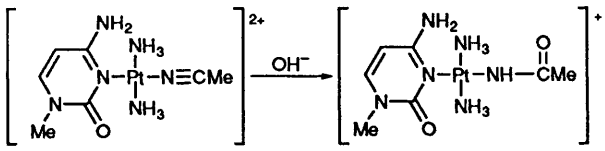


Fig. 7 Crystal packing of complex **11** viewed along the *y* axis



Scheme 3 Reaction of complex **11** with chloride



Scheme 4 Hydrolysis of *trans*-$[Pt(NH_3)_2(MeCN)(mcyt)][ClO_4]_2$

ized by IR and ^1H NMR spectroscopy: Although no amide band can be identified in the IR spectrum, as it is probably buried under the strong, broad ν(C=O) and ν(C=C) stretching bands around 1660 cm^{-1}, hydrolysis of the nitrile ligand is confirmed by loss of the ν(C≡N) vibration. Characteristic 1-methylcytosine bands occur at 1535 (ring stretching mode) and 772 and 650 cm^{-1} (ring breathing mode). Proton NMR resonances of **14** in $(CD_3)_2SO$ occur at δ 8.51 and 7.92 (NH_2, mcyt), 7.75 (d, ^3J = 7.3, H^6), 5.85 (d, ^3J = 7.3 Hz, H^5), 5.45 (NH, acetamidate), 4.31 (NH_3), 3.34 (CH_3, mcyt) and 1.79 (CH_3, acetamidate). When the NMR spectrum is recorded in D_2O the H^5 and H^6 doublets are split (H^6, δ 7.61/7.59; H^5, δ 6.04/6.02 at pD 9.3) indicating the presence of two species with a nearly 1:1 abundance ratio due to hindered rotation about the Pt–mcyt bond.

Conclusion

This work described the synthesis and hydrolysis of acetonitrile complexes of *cis*- and *trans*-$Pt^{II}(amine)_2$. The hydrolysis of platinum-bound nitriles proceeds fairly easily compared to unco-ordinated nitriles due to Lewis-acid activation of the metal. Depending on the reaction conditions, free acetamide, mono- and bis-acetamidate, acetamidate-bridged as well as acetamidateacetonitrile complexes are formed. In contrast, reactions of the kinetically labile palladium with acetonitrile yield in general free acetamide, the only palladium complex isolated being the dinuclear $[\{Pd(en)(\mu\text{-}C_2H_4NO)\}_2][ClO_4]_2$.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, DFG, and the Fonds der Chemischen Industrie. We thank Degussa for a loan of $K_2[PtCl_4]$ and the University of Dortmund for a fellowship (for A. E.). We also thank Mr. G. Fusch and Mrs. A. Danzmann for recording NMR spectra.

References

1 B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, 1977, **23**, 1 and refs. therein.
2 L. Maresca, G. Natile, F. P. Intini, F. Gasparini, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Am. Chem. Soc.*, 1986, **108**, 1180; F. P. Fanizzi, F. P. Intini and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1989, 947.
3 R. A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo and R. J. Angelici, *Organometallics*, 1991, **10**, 1751; *J. Chem. Soc., Dalton Trans.*, 1993, 959.
4 K. A. Hoffmann and G. Bugge, *Ber. Dtsch. Chem. Ges.*, 1908, **41**, 312.
5 J. P. Davidson, P. J. Faber, R. G. Fischer, S. Mansy, H. J. Peresie, B. Rosenberg and L. VanCamp, *Cancer Chemother. Rep.*, 1975, **59**, 287; B. Rosenberg, *Cancer Chemother. Rep.*, 1975, **59**, 589; B. Lippert, *J. Clin. Hematol. Oncol.*, 1977, **7**, 26.
6 J. K. Barton, H. N. Rabinowitz, D. J. Szalda and S. J. Lippard, *J. Am. Chem. Soc.*, 1977, **99**, 2827; J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszczak and S. J. Lippard, *J. Am. Chem. Soc.*, 1979, **101**, 1434; S. J. Lippard, *Science*, 1982, **218**, 1075; T. V. O'Halloran, P. K. Mascharak, I. D. Williams, M. M. Roberts and S. J. Lippard, *Inorg. Chem.*, 1987, **26**, 1261; K. Matsumoto and K. Fuwa, *J. Am. Chem. Soc.*, 1982, **104**, 897; K. Matsumoto, H. Takahashi and K. Fuwa, *Inorg. Chem.*, 1983, **22**, 4086; K. Sakai and K. Matsumoto, *J. Am. Chem. Soc.*, 1989, **111**, 3074; K. Sakai, K. Matsumoto and K. Nishio, *Chem. Lett.*, 1991, 1081; K. Matsumoto, K. Sakai, K. Nishio, Y. Tokisue, R. Ito, R. Nishide and Y. Shichi, *J. Am. Chem. Soc.*, 1992, **114**, 8110.
7 F. D. Rochon, P. C. Kong and R. Melanson, *Inorg. Chem.*, 1990, **29**, 1352.
8 R. Cini, F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Am. Chem. Soc.*, 1993, **115**, 5123 and refs. therein.
9 G. Villain, P. Kalck and A. Gaset, *Tetrahedron Lett.*, 1980, **21**, 2901; G. Villain, G. Constant, A. Gaset and P. Kalck, *J. Mol. Cat.*, 1980, **7**, 355; M. Louey, C. J. McKenzie and R. Robson, *Inorg. Chim. Acta*, 1986, **111**, 107; C. J. McKenzie and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1988, 112.
10 S. C. Dhara, *Indian J. Chem.*, 1970, **8**, 143; G. Raudaschl, B. Lippert, J. D. Hoeschele, H. E. Howard-Lock, C. J. L. Lock and P. Pilon, *Inorg. Chim. Acta*, 1985, **106**, 141.
11 F. Basolo, J. C. Bailar, jun. and B. R. Tarr, *J. Am. Chem. Soc.*, 1950, **72**, 2433.
12 G. B. Kaufmann and D. O. Cowan, *Inorg. Synth.*, 1963, **7**, 239.
13 J. McCormick, E. N. Jaynes, jun. and R. J. Kaplan, *Inorg. Synth.*, 1972, **13**, 216.
14 T. T. Sakai, A. L. Pogolotti and D. V. Santi, *J. Heterocycl. Chem.*, 1968, **5**, 849.
15 G. M. Sheldrick, (*a*) SHELXTL PLUS (Release 3.4) for Nicolet R3m/V Crystallographic Systems, University of Göttingen, 1987; (*b*) SHELX 93, University of Göttingen, 1993.
16 *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer, Dordrecht, 1992, vol. C, Tables 6.1.1.4 (pp. 500–502) and 4.2.6.8. (pp. 219–222).
17 F. D. Rochon, R. Melanson, H. E. Howard-Lock, C. J. L. Lock and G. Turner, *Can. J. Chem.*, 1984, **62**, 860 and refs. therein; M. M. Muir, G. M. Gomez and J. A. Muir, *Acta Crystallogr., Sect. C*, 1986, **42**, 1699; F. D. Rochon and L. Fleurent, *Inorg. Chim. Acta*, 1988, **143**, 81; V. K. Belsky, V. E. Konovalov, V. Y. Kukushkin and A. I. Moiseev, *Inorg. Chim. Acta*, 1990, **169**, 101.
18 S. J. S. Kerrison and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1981, 61; M. B. Krogh-Jespersen and A. Altonen, *Inorg. Chem.*, 1987, **26**, 2084; T. C. Woon and D. P. Fairlie, *Inorg. Chem.*, 1992, **31**, 4069.
19 D. H. Kerridge, *Chem. Soc. Rev.*, 1988, **17**, 181.
20 P. Pregosin, *Annu. Rep. N.M.R. Spectrosc.*, 1986, **17**, 285.
21 K. Matsumoto, H. Miyamae and H. Moriyama, *Inorg. Chem.*, 1989, **28**, 2964.
22 T. V. O'Halloran and S. J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 3341; *Inorg. Chem.*, 1989, **28**, 1289.
23 J. Chin and J. H. Kim, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 523; J. H. Kim, J. Britten and J. Chin, *J. Am. Chem. Soc.*, 1993, **115**, 3618.
24 R. Faggiani, B. Lippert, C. J. L. Lock and R. Pfab, *Inorg. Chem.*, 1981, **20**, 2381.

Received 4*th July* 1994; *Paper* 4/04023F