DALTON COMMUNICATION

Ready formation of water-stable Pt^{II}-(μ-NH_2)-Pd^{II} species through combination of *trans*-[$(NH_3)_2Pt^{II}L_2$] (L = N,N′-heterocycle) and [$enPd(H_2O)_2$]$^{2+}$

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Received 17th January 2000, Accepted 7th February 2000
Published on the Web 24th February 2000

Mixed-metal (Pt^{II}, Pd^{II}) μ-NH_2-complexes are readily formed upon reaction of *trans*-[$(NH_3)_2PtL_2$] (L = 2-aminopyridine-N^1 or pyrazolate-N^1; charges omitted) with [$enPd(H_2O)_2$]$^{2+}$.

Amide (NH_2, NHR, NRR′) complexes of the late transition metals are, unlike those of the early transition elements and the alkali metal ions, relativly rare.[1] Although occasionally suspected intermediates in various catalytic processes such as the Pd catalysed amination of aryl bromides,[2] their formation in general requires harsh conditions[3] and the absence of water, especially in the case of NH_2 compounds. There are very few crystal structures on NH_2 complexes of Pt available,[4] and there appears to be none for Pd. With alkyl- and aryl-amides the situation is different. Others[5] and ourselves[6–8] have described a series of complexes containing transition metal ions (Pt^{II}, Pt^{IV}, Hg^{II}) bound to deprotonated exocyclic amino groups of nucleobases. Here we report on mixed-metal (Pt^{II}, Pd^{II}) NH_2 complexes which are formed under mild reaction conditions (room temperature, pH 8–9) in water from *trans*-[$(NH_3)_2PtL_2$] (L = pyrazolate, pz, or 2-aminopyridine, Hampy, charges omitted) and [$enPd(H_2O)_2$]$(NO_3)_2$. The role of Pt^{II} is to orient the NH_3 ligands and to acidify the protons, while the N-bonded heterocyclic ligand L provides an additional anchoring group N′ for the $enPd^{II}$ entity. The OH ligand of Pd^{II} (average pK_a of [$enPd(H_2O)_2$]$^{2+}$ *ca.* 7.8)[9] functions as a base to deprotonate the NH_3 ligand. As we show, the anchoring group N′ may be an endocyclic (N^2 in pyrazolate) or an exocyclic N-atom (NH_2 in 2-aminopyridine).

Starting from *trans*-[$(NH_2)_2Pt$(pz-N^1)$_2$] **1** † reaction with [$enPd(H_2O)_2$]$^{2+}$ and crystallizaton in the presence of Br^- yields the trinuclear complex *trans*-[Pt(μ-NH_2)$_2$(μ-pz-N^1,N^2)$_2${enPd}$_2$]-Br_2·$2H_2O$ **2a**.‡ In a similar fashion [$enPd(H_2O)_2$]$^{2+}$ reacts with *trans*-[$Pt(NH_3)_2$(Hampy-N^1)$_2$]$(NO_3)_2$ **3**† at the exocylic amino group of the heterocyclic ligand and the NH_3 ligands of Pt^{II} to give *trans*-[Pt(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2${enPd}$_2$Pd(H_2O)]-$(NO_3)_4$·$2H_2O$ **4a**.§ We assume that initially the exocyclic amino group of the Hampy ligand is not deprotonated but rather that its deprotonation is the consequence of insertion of an additional *trans*-square planar Pd^{II} entity between the amino groups of the two aminopyridine ligands, which leads to the tetranuclear $PtPd_3$ species **4**. Formation of the Pd^{II} ion apparently has occurred through loss of the en ligand of $enPd^{II}$. Compound **4** has been isolated in three different forms (**4a**–**4c**), depending on the anions present in solution (Scheme 1).

The X-ray structure determination of **2a**¶ proves that the cation is trinuclear and centrosymmetric (Fig. 1). Except for the en ligands, the cation is planar. The geometry of the pz ligands is normal.[10] Comparison of the M–N bond lengths reveals the *trans* influence of the amide group; Pd(1)–N(21) is significantly (6σ) longer than Pd(1)–N(22). The cations in **2a** are stacked, in such a way as to form Pd · · · Pt · · · Pd of *ca.* 3.5 Å contacts. Br^- ions and water molecules are arrayed in a honeycomb pattern.

The structure of the cation of *trans*-[Pt(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2${enPd}$_2$Pd(H_2O)]$(NO_3)_4$·$2H_2O$ **4a**‖ (Fig. 2) consists of the four heavy metal ions, two μ-NH_2 groups and two bridging μ-amidopyridine ligands, as well as an aqua and two en ligands. In addition, there is a weak contact between Pt(1) and one of the nitrate anions which effectively leads to a (5 + 1) co-ordination at the Pt atom. The four heavy metals form a slightly irregular but planar diamond (Fig. 2) with only the short diagonal Pt(1)–Pd(1) representing a metal–metal bond. The torsion between the two ampy ligands makes the cation chiral. The cations of *trans*-[Pt(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2$-{enPd}$_2$PdCl]$(NO_3)_3$·$1.3H_2O$ **4b**‖ and of *trans*-[Pt(μ-NH_2)$_2$-

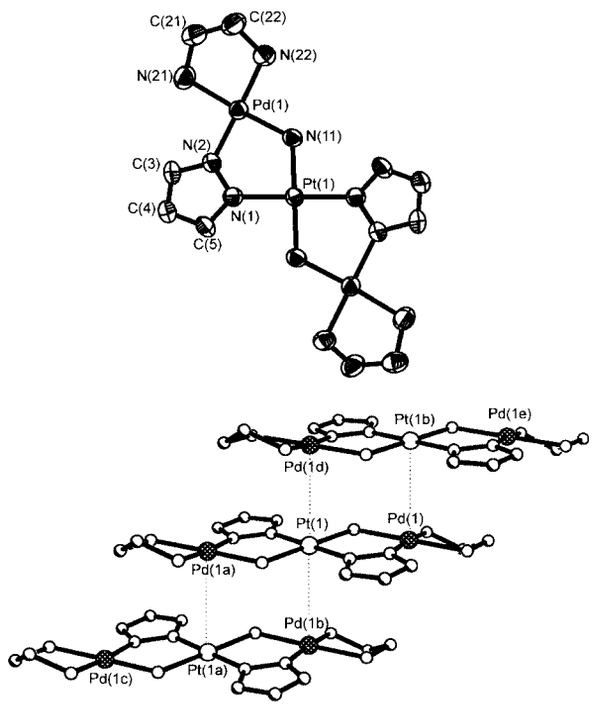
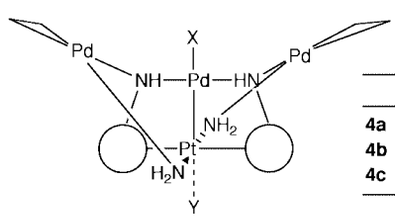


Fig. 1 View of the cation of **2a** with atom numbering scheme and section of the crystal packing. Bond lengths (Å): Pd(1)–N(2) 2.001(5), Pd(1)–N(11) 2.011(5), Pt(1)–N(11) 2.044(5), Pt(1)–N(1) 2.010(5), Pt(1)–Pd(1) 3.486(1), Pt(1)–Pd(1d) 3.516(2). Bond angles (°): N(2)–Pd(1)–N(11) 88.4(2), Pd(1)–N(11)–Pt(1) 118.5(2), N(11)–Pt(1)–N(1) 92.0(0).



	X	Y
4a	H_2O	ONO_2^-
4b	Cl^-	ONO_2^-
4c	Br^-	Br^-

Scheme 1

DOI: 10.1039/b000456l

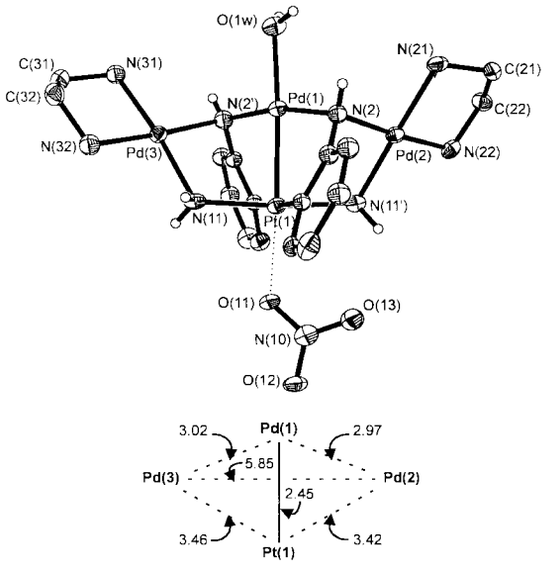


Fig. 2 View of the cation of **4a** and schematic disposition of the heavy metals. Bond lengths (Å): Pt(1)–N(1) 2.026(5), Pt(1)–N(1′) 2.016(5), Pt(1)–N(11) 2.038(6), Pt(1)–N(11′) 2.041(6), Pd(2)–N(11′) 2.039(6). Bond angles (°): N(1′)–Pt(1)–N(1) 175(2), N(2′)–Pd(1)–N(2) 168.0(2).

(ampy-N^1,N^2,$N^{2'}$)$_2${enPd}$_2$PdBr]Br$(NO_3)_2$·4.6H_2O **4c**‖ are very similar to that of **4a**. As expected,[11] distances between Pd(1) and X as well as between Pd(1) and Pt(1) effect each other mutually. There are no unusual bond distances between the metal ions and their N ligands.

Both **2** and **4** display NH_2 resonances at around δ 1–2 (D_2O, pD 7.8). The isotopic exchange of ^{1}H by ^{2}D of these groups is surprisingly slow (3 d). $^2J(^{195}Pt–^1H)$ coupling of *ca*. 45 Hz is observed, as confirmed by an HMQC experiment.

Our findings suggest that it might be possible to develop a similar chemistry with Pt–diam(m)ine compounds of *cis* geometry and of species with other bridging groups such as hydroxo, methoxo, thiolato or phosphido ligands. The latter are generally obtained *via* substitution of μ-Cl groups by ligands.[12]

Notes and references

† **1** was synthesised in a way analogous to **3**[13] from its protonated form followed by treatment with aqueous NH_3 to give poorly soluble **1**.

‡ To a suspension of **1** (0.2 mmol in 10 mL of H_2O) [enPd$(H_2O)_2$]$(NO_3)_2$ (0.4 mmol in 5 mL H_2O) is added. The pH of the mixture is adjusted with 1 M NaOH to 8–9. After 24 h stirring at room temperature slightly green needles of [Pt(μ-NH_2)$_2$(μ-pz-N^1,N^2)$_2$-{enPd}$_2$]$(NO_3)_2$·3H_2O **2** are formed, 73 mg, (42%). Anal. Calc. for $C_{10}H_{32}N_{12}O_9Pd_2Pt$: C, 13.8; N, 19.3; H, 3.7. Found: C, 13.8; N, 19.3; H, 3.4%. Crystals suitable for X-ray crystallography of the Br salt **2a** were obtained by following recrystallization of **2** from an aqueous solution containing trimethylammonium bromide.

§ A solution of *trans*-[Pt$(NH_3)_2$(Hampy)$_2$]$(NO_3)_2$ **3** (0.2 mmol in 10 mL of H_2O) is combined with [enPd$(H_2O)_2$]$(NO_3)_2$ (0.8 mmol in 10 mL H_2O) and the pH is adjusted with 1 M NaOH to 8–9. The mixture is stirred for 2 d at room temperature. Upon slow reduction of the volume in a stream of nitrogen dark brown crystals of trans-[Pt(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2${enPd}$_2$Pd(H_2O)][$(NO_3)_4$·2H_2O **4a** are formed which are suitable for X-ray analysis, 65 mg (29%). Anal. Calc. for $C_{14}H_{36}N_{14}O_{15}Pd_3Pt$: C, 14.6; N, 17.0; H, 3.1. Found: C, 14.4; N, 17.1; H, 3.3%. **4b** and **4c** are obtained from solutions of **4a** in water in the presence of 1 equiv of NaCl and 2 equiv of KBr, respectively.

¶ Crystal data of **2a**: $C_5H_{15}N_5OBrPdPt_{0.5}$; triclinic, space group $P\bar{1}$; a = 5.0470(10), b = 9.580(2), c = 13.568(3) Å; α = 105.65(3), β = 98.84(3), γ = 98.60(3)°; V = 611.5(2) Å^3; ρ_{calc} = 2.417 g cm^{-3}; $2\theta_{max}$ = 54.2°; μ = 10.452 mm^{-1}; crystal dimensions: 0.56 × 0.13 × 0.04 mm, R_1 = 0.0325, wR_2 = 0.0827. Unique diffractometer data sets were measured at T = 293(2) K (Enraf-Nonius-κCCD-diffractometer) using MoKα radiation λ = 0.71069 Å, N = 2464 independent reflections were obtained N_0 = 2070 ($I > 2\sigma(I)$) being considered 'observed'; integration and Lp-corrections of the frames were performed using the DENZO-package.[14] The structures were solved using SHELXS-86 and developed *via* alternating least squares cycles and Fourier difference syntheses with the aid of the SHELXTL-PLUS programs and SHELXL-93.[14]

‖ Crystal data of **4a**: $C_{14}H_{36}N_{14}O_{15}Pd_3Pt$; monoclinic, space group $P2_1/c$; a = 8.274(2), b = 13.653(3), c = 27.992(6) Å; β = 92.56(3)°; V = 3159.0(12) Å^3; ρ_{calc} = 2.428 g cm^{-3}; $2\theta_{max}$ = 43.4°; μ = 6.182 mm^{-1}; crystal dimensions: 0.38 × 0.13 × 0.06 mm, MoKα (λ = 0.71069 Å); T = 136(2) K; N = 3631, N_0 = 2810 ($I > 2\sigma(I)$); R_1 = 0.0248, wR_2 = 0.0458. Crystal data of **4b**: $C_{14}H_{32.6}N_{13}O_{10.3}ClPd_3Pt$; triclinic, space group $P\bar{1}$; a = 11.046(2), b = 12.056(2), c = 12.971(3) Å; α = 101.93(3), β = 102.74(3), γ = 112.30(3)°; V = 1475.9(5) Å^3; ρ_{calc} = 2.470 g cm^{-3}; $2\theta_{max}$ = 50.0°; μ = 6.685 mm^{-1}; crystal dimensions: 0.88 × 0.19 × 0.13 mm, MoKα (λ = 0.71069 Å); T = 293(2) K; N = 4835, N_0 = 2893 ($I > 2\sigma(I)$); R = 0.0369, R_W = 0.0597. Crystal data of **4c**: $C_{14}H_{39.2}N_{12}O_{10.6}Br_2Pd_3Pt$; triclinic, space group $P\bar{1}$; a = 11.641(2), b = 11.757(2), c = 14.136(3) Å; α = 111.96(3), β = 105.48(3), γ = 100.62(3)°; V = 1639.6(5) Å^3; ρ_{calc} = 2.470 g cm^{-3}; $2\theta_{max}$ = 46.6°, μ = 8.374 mm^{-1}; crystal dimensions: 0.38 × 0.13 × 0.13 mm, MoKα (λ = 0.71069 Å); T = 293(3) K; N = 4217, N_0 = 2844 ($I > 2\sigma(I)$); R_1 = 0.0412, wR_2 = 0.0835. CCDC reference number 186/1844. See http://www.rsc.org/suppdata/dt/b0/b000456l/ for crystallographic files in .cif format.

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Communication b000456l