

Ready formation of water-stable $\text{Pt}^{\text{II}}-(\mu\text{-NH}_2)\text{-Pd}^{\text{II}}$ species through combination of $\text{trans}[(\text{NH}_3)_2\text{Pt}^{\text{II}}\text{L}_2]$ ($\text{L} = \text{N}, \text{N}'\text{-heterocycle}$) and $[\text{enPd}(\text{H}_2\text{O})_2]^{2+}$

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Mixed-metal (Pt^{II} , Pd^{II}) $\mu\text{-NH}_2$ -complexes are readily formed upon reaction of $\text{trans}[(\text{NH}_3)_2\text{PtL}_2]$ ($\text{L} = 2\text{-aminopyridine-}N^1$ or pyrazolate- N^1 ; charges omitted) with $[\text{enPd}(\text{H}_2\text{O})_2]^{2+}$.

Amide (NH_2 , NHR , NRR') complexes of the late transition metals are, unlike those of the early transition elements and the alkali metal ions, relatively 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 conditions³ 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. Others⁵ 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 $\text{trans}[(\text{NH}_3)_2\text{PtL}_2]$ ($\text{L} = \text{pyrazolate}$, pz , or 2-aminopyridine , Hampy , charges omitted) and $[\text{enPd}(\text{H}_2\text{O})_2](\text{NO}_3)_2$. 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 (average pK_a of $[\text{enPd}(\text{H}_2\text{O})_2]^{2+}$ 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 $\text{trans}[(\text{NH}_3)_2\text{Pt}(\text{pz-}N^1)_2] \mathbf{1}^+$ reaction with $[\text{enPd}(\text{H}_2\text{O})_2]^{2+}$ and crystallization in the presence of Br^- yields the trinuclear complex $\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2(\mu\text{-pz-}N^1, N^2)_2\{\text{enPd}\}_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ **2a**.[†] In a similar fashion $[\text{enPd}(\text{H}_2\text{O})_2]^{2+}$ reacts with $\text{trans}[\text{Pt}(\text{NH}_3)_2(\text{Hampy-}N^1)_2](\text{NO}_3)_2$ **3**[†] at the exocyclic amino group of the heterocyclic ligand and the NH_3 ligands of Pt^{II} to give $\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2(\text{ampy-}N^1, N^2, N^2)_2\{\text{enPd}\}_2\text{Pd}(\text{H}_2\text{O})](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ **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; $\text{Pd}(1)\text{--N}(21)$ is significantly (6σ) longer than $\text{Pd}(1)\text{--N}(22)$. The cations in **2a** are stacked, in such a way as to form $\text{Pd} \cdots \text{Pt} \cdots \text{Pd}$ of ca. 3.5 \AA contacts. Br^- ions and water molecules are arrayed in a honeycomb pattern.

The structure of the cation of $\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2(\text{ampy-}N^1, N^2, N^2)_2\{\text{enPd}\}_2\text{Pd}(\text{H}_2\text{O})](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ **4a**|| (Fig. 2) consists of the four heavy metal ions, two $\mu\text{-NH}_2$ groups and two bridging $\mu\text{-aminopyridine}$ ligands, as well as an aqua and two en ligands. In addition, there is a weak contact between $\text{Pt}(1)$ 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 $\text{Pt}(1)\text{--Pd}(1)$ representing a metal–metal bond. The torsion between the two ampy ligands makes the cation chiral. The cations of $\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2(\text{ampy-}N^1, N^2, N^2)_2\{\text{enPd}\}_2\text{PdCl}](\text{NO}_3)_3 \cdot 1.3\text{H}_2\text{O}$ **4b**|| and of $\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2\text{--}$

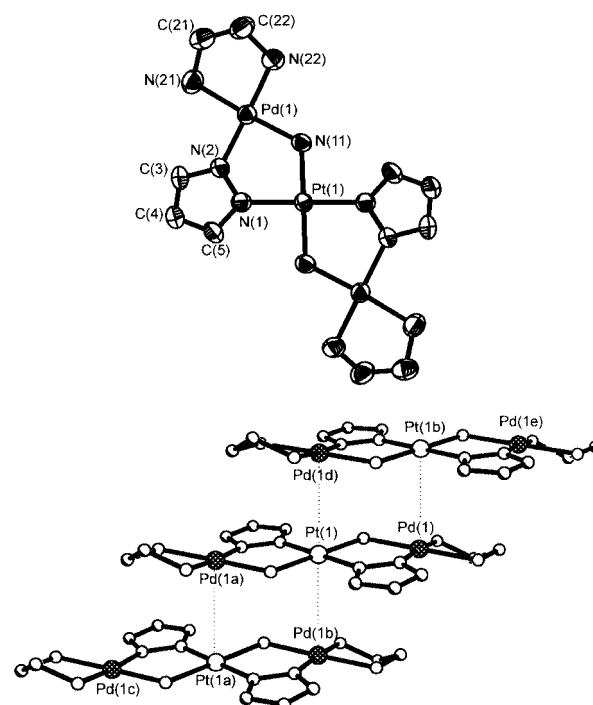
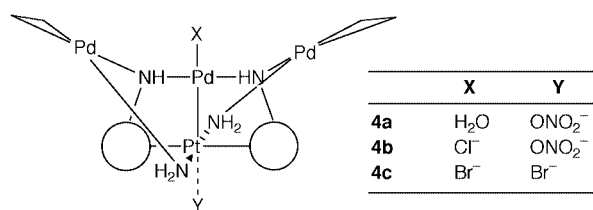


Fig. 1 View of the cation of **2a** with atom numbering scheme and section of the crystal packing. Bond lengths (\AA): $\text{Pd}(1)\text{--N}(2)$ 2.001(5), $\text{Pd}(1)\text{--N}(11)$ 2.011(5), $\text{Pt}(1)\text{--N}(11)$ 2.044(5), $\text{Pt}(1)\text{--N}(1)$ 2.010(5), $\text{Pt}(1)\text{--Pd}(1)$ 3.486(1), $\text{Pt}(1)\text{--Pd}(1d)$ 3.516(2). Bond angles ($^\circ$): $\text{N}(2)\text{--Pd}(1)\text{--N}(11)$ 88.4(2), $\text{Pd}(1)\text{--N}(11)\text{--Pt}(1)$ 118.5(2), $\text{N}(11)\text{--Pt}(1)\text{--N}(1)$ 92.0(0).



Scheme 1

$\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2\{\text{enPd}\}_2\text{Pd}(\text{H}_2\text{O})](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ **4a**|| (Fig. 2) consists of the four heavy metal ions, two $\mu\text{-NH}_2$ groups and two bridging $\mu\text{-aminopyridine}$ ligands, as well as an aqua and two en ligands. In addition, there is a weak contact between $\text{Pt}(1)$ 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 $\text{Pt}(1)\text{--Pd}(1)$ representing a metal–metal bond. The torsion between the two ampy ligands makes the cation chiral. The cations of $\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2(\text{ampy-}N^1, N^2, N^2)_2\{\text{enPd}\}_2\text{PdCl}](\text{NO}_3)_3 \cdot 1.3\text{H}_2\text{O}$ **4b**|| and of $\text{trans}[\text{Pt}(\mu\text{-NH}_2)_2\text{--}$

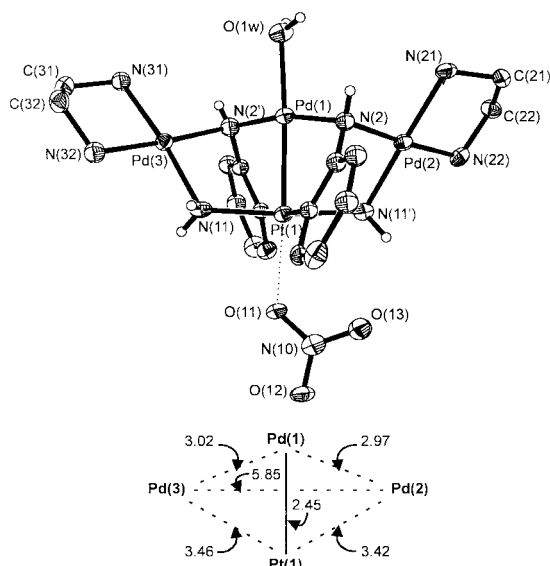


Fig. 2 View of the cation of **4a** and schematic disposition of the heavy metals. Bond lengths (Å): Pt(1)–N(1) 2.026(5), Pt(1)–N(1') 2.016(5), Pt(1)–N(11) 2.038(6), Pt(1)–N(11') 2.041(6), Pd(2)–N(11') 2.039(6). Bond angles (°): N(1')–Pt(1)–N(1) 175(2), N(2')–Pd(1)–N(2) 168.0(2).

(ampy- N^1, N^2, N^2')₂{enPd}₂PdBr][Br(NO₃)₂·4.6H₂O **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 NH₂ resonances at around δ 1–2 (D₂O, pD 7.8). The isotopic exchange of ¹H by ²D of these groups is surprisingly slow (3 d). ²J(¹⁹⁵Pt–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 NH₃ to give poorly soluble **1**.

‡ To a suspension of **1** (0.2 mmol in 10 mL of H₂O) [enPd(H₂O)₂](NO₃)₂ (0.4 mmol in 5 mL H₂O) 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-NH₂)₂(μ-pz- N^1, N^2)₂]{enPd₂}(NO₃)₂·3H₂O **2** are formed, 73 mg, (42%). Anal. Calc. for C₁₀H₃₂N₁₂O₉Pd₂Pt: 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(NH₃)₂(Hampy)₂](NO₃)₂ **3** (0.2 mmol in 10 mL of H₂O) is combined with [enPd(H₂O)₂](NO₃)₂ (0.8 mmol in 10 mL H₂O) 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-NH₂)₂(ampy- N^1, N^2, N^2')₂]{enPd₂}(NO₃)₂·2H₂O **4a** are formed which are suitable for X-ray analysis, 65 mg (29%). Anal. Calc. for C₁₄H₃₆N₁₄O₁₅Pd₂Pt: 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**: C₅H₁₅N₅OBrPdPt_{0.5}; triclinic, space group $P\bar{1}$; $a = 5.0470(10)$, $b = 9.580(2)$, $c = 13.568(3)$ Å; $\alpha = 105.65(3)$, $\beta = 98.84(3)$, $\gamma = 98.60(3)^\circ$; $V = 611.5(2)$ Å³; $\rho_{\text{calc}} = 2.417$ g cm⁻³; $2\theta_{\text{max}} = 54.2^\circ$; $\mu = 10.452$ mm⁻¹; crystal dimensions: $0.56 \times 0.13 \times 0.04$ mm, $R_1 = 0.0325$, $wR_2 = 0.0827$. Unique diffractometer data sets were measured at $T = 293(2)$ K (Enraf-Nonius- κ CCD-diffractometer) using MoK α radiation $\lambda = 0.71069$ 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**: C₁₄H₃₆N₁₄O₁₅Pd₂Pt; monoclinic, space group $P2_1$; $a = 8.274(2)$, $b = 13.653(3)$, $c = 27.992(6)$ Å; $\beta = 92.56(3)^\circ$; $V = 3159.0(12)$ Å³; $\rho_{\text{calc}} = 2.428$ g cm⁻³; $2\theta_{\text{max}} = 43.4^\circ$; $\mu = 6.182$ mm⁻¹; crystal dimensions: $0.38 \times 0.13 \times 0.06$ mm, MoK α ($\lambda = 0.71069$ 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**: C₁₄H_{32.6}N₁₃O_{10.3}ClPd₃Pt; triclinic, space group $P\bar{1}$; $a = 11.046(2)$, $b = 12.056(2)$, $c = 12.971(3)$ Å; $\alpha = 101.93(3)$, $\beta = 102.74(3)$, $\gamma = 112.30(3)^\circ$; $V = 1475.9(5)$ Å³; $\rho_{\text{calc}} = 2.470$ g cm⁻³; $2\theta_{\text{max}} = 50.0^\circ$; $\mu = 6.685$ mm⁻¹; crystal dimensions: $0.88 \times 0.19 \times 0.13$ mm, MoK α ($\lambda = 0.71069$ 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**: C₁₄H_{39.2}N₁₂O_{10.6}Br₂Pd₃Pt; triclinic, space group $P\bar{1}$; $a = 11.641(2)$, $b = 11.757(2)$, $c = 14.136(3)$ Å; $\alpha = 111.96(3)$, $\beta = 105.48(3)$, $\gamma = 100.62(3)^\circ$; $V = 1639.6(5)$ Å³; $\rho_{\text{calc}} = 2.470$ g cm⁻³; $2\theta_{\text{max}} = 46.6^\circ$; $\mu = 8.374$ mm⁻¹; crystal dimensions: $0.38 \times 0.13 \times 0.13$ mm, MoK α ($\lambda = 0.71069$ 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/b000456/> for crystallographic files in .cif format.

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