Di- and Tripalladium(II) and -platinum(II) Complexes Containing 7-Amino-1,8-naphthyridin-2-one as a Bridging Ligand − Oxidation of a $[Pt_3]^{6+}$ Core to $[Pt_3]^{8+}$

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All three dinuclear complexes $[Pd_2(donp)_2(bpy)_2]$ (**1**) (H_2donp = 1,8-naphthyridin-2,7-dione), $[Pd_2(H_2nonp)_2(bpy)_2](ClO_4)_2$ (**2**), and $[Pt_2(H_2nonp)_2(bpy)_2](PF_6)_2$ (**3**) (H_3nonp = 7-amino-1,8-naphthyridin-2-one) exhibit the μ-1κN^1:2κN^8 bridging mode for their *head/tail* orientated naphthyridine ligands. Whereas **1** and **3** may be prepared by direct reaction of the dinucleating ligand with $[MCl_2(bpy)]$, formation of competing tripalladium(II) complexes must be avoided for **2** by employment of the precursor H_2acnonp (7-acetamido-1,8-naphthyridin-2-one), which affords $[H_2nonp]^-$ on cleavage of its original acetyl group. A mixture of the *head/tail* (**4a**) and *head/head* (**4b**) isomers of $[Pd_3(Hnonp)_2(bpy)_3](ClO_4)_2$ is obtained when H_3nonp is treated with $[PdCl_2(bpy)]$ and LiOH at room temperature for 2 d, followed by precipitation with $LiClO_4$. Contrastingly exclusive formation of **4a** is observed upon refluxing this reaction mixture for 3 d in aqueous solution. The $[Hnonp]^{2-}$ ligands exhibit a $μ_3$-1κN^1:2κN^8:3κN^7 bridging mode that leads to short Pd···Pd interactions of 2.781(2) and 2.775(2) Å. Similar metal–metal distances of 2.771(3) and 2.816(3) Å are observed in *head/head*-$[Pt_3(acnonp)(Hnonp)(bpy)_3]Cl_2$ (**5**). An in situ $2e^-$-oxidation (Ag^+/Ag) of the $[Pt_3]^{6+}$ core in triplatinum(II) species such as **5** formed by the reaction of $[PtCl_2(bpy)]$ with H_2acnonp allows the isolation of diamagnetic dark-brown *head/head*-$[Pt_3(Hnonp)_2(NO_3)(bpy)_3](ClO_4)_2(NO_3)$ (**6**) with an average oxidation state of Pt (2.67+). The Pt–Pt distances of 2.723(2) and 2.670(2) Å are markedly shorter than in **5**.

Although the oligomeric class of molecules known as the platinum blues all formally contain Pt^{III}, the average oxidation state of their Group 10 metal atoms is usually much lower than +3.0.[1] Following the first report of the prototype platinum-acetamide blues in 1908,[2] some 70 years were to pass before Lippard et al.[3] were finally successful in structurally characterising *cis*-$[\{Pt_2(μ\text{-}C_5H_4NO)_2(NH_3)_4\}_2](NO_3)_5$ (C_5H_4NO = α-pyridonate) as an adequate model analog. This paramagnetic tetranuclear complex ($S = 1/2$), with its average oxidation state of +2.25, exhibits a Pt−Pt distance of 2.775(1) Å in its outer α-pyridonate bridged dimeric sub-units, that are linked through an inner Pt−Pt interaction of length 2.877(1) Å. Similar alternating short supported [2.880(2), 2.778(1) Å] and longer unsupported [2.900(1), 2.934(1) Å] Pt−Pt bonds were subsequently established for the diamagnetic centrosymmetric octanuclear platinum−acetamide complex $[\{Pt_2(NHCOCH_3)_2(NH_3)_4\}_4](NO_3)_{10} \cdot 4\,H_2O$, in which the average oxidation state is once again +2.25.[4] Significantly shorter metal-metal distances of 2.702(6), 2.710(5), and 2.706(6) Å in the linear Pt_4 chain of $[\{Pt_2(C_4H_3NO)_2(NH_3)_4\}_2](NO_3)_6 \cdot 2\,H_2O$[5] ($C_4H_3NO$ = α-pyrrolidonate) are consistent with this so-called "α-pyrrolidone tan" being in the higher average oxidation state of Pt (2.5+). The spectroscopic, redox, and chemical properties of μ-*N,O*-pyrimidinate bridged (1-MeU = 1-methyluracilate, 1-MeT = 1-methylthyminate) blue and green oligomeric platinum complexes closely mirror those of the α-pyridone blues and an average oxidation state of Pt (2.75+) has been established for $[\{Pt_2Cl_2(1\text{-MeT})_2(NH_3)_2\}_2Cl]PtCl_6 \cdot 6\,H_2O$.[6] However, this complex contains two individual diplatinum units [Pt−Pt distance, 2.699(1) Å], that are connected by a single chloride bridge, and is not, therefore, strictly comparable with the typical Pt_4 linear clusters discussed above.

Mixed intensely golden-tan trinuclear Pt_2Pd complexes of the type *cis*-$[L_2'Pt(μ\text{-}L)_2Pd(μ\text{-}L)_2PtL_2']X_2$ (L′ = en/2, NH_3; L = 1-MeU, 1-MeT; X = NO_3^-, ClO_4^-) have been characterised by Lippert and co-workers[7][8] and can be oxidised by conc. HNO_3 to deep purple-blue trications with an average oxidation state M (2.33+) and Pt−Pd distances in the range 2.634(1)−2.646(1) Å. This posed the question as to whether similar linear homonuclear Pt_3 complexes can also be prepared in the presence of suitable di- or trinucleating ligands and led to our recent characterisation[9] of the 1,8-naphthyridin-2,7-dionato (H_2donp, Scheme 1) compounds *cis*-$[M_3(donp)_2(bpy)_3]^{2+}$ (M = Pd, Pt), which exhibit relatively short supported $\mathbf{M}^{II}\cdots M^{II}$ distances in the range 2.801−2.807 Å. The blue-green triplatinum(II) complex displays one-electron transfer waves at $E_{1/2}$ = 0.65 V to blue-violet *cis*-$[Pt_3(donp)_2(bpy)_3]^{3+}$ and $E_{1/2}$ = 1.30 V (in CH_3CN, vs. Ag/AgCl) to violet *cis*-$[Pt_3(donp)_2(bpy)_3]^{4+}$. As we were unsuccessful in isolating either the Pt (2.33+) or the Pt (2.67+) complex, we have now extended our studies to 7-amino-1,8-naphthyridin-2-one (H_3nonp) and 7-acetamido-1,8-naphthyridin-2-one (H_2acnonp, Scheme 1), in the expectation that the change in the sites of protonation from

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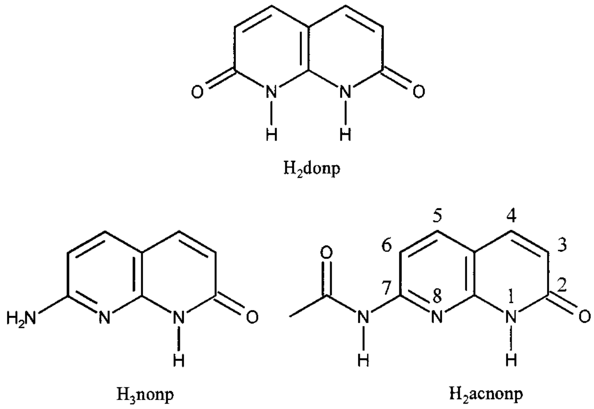
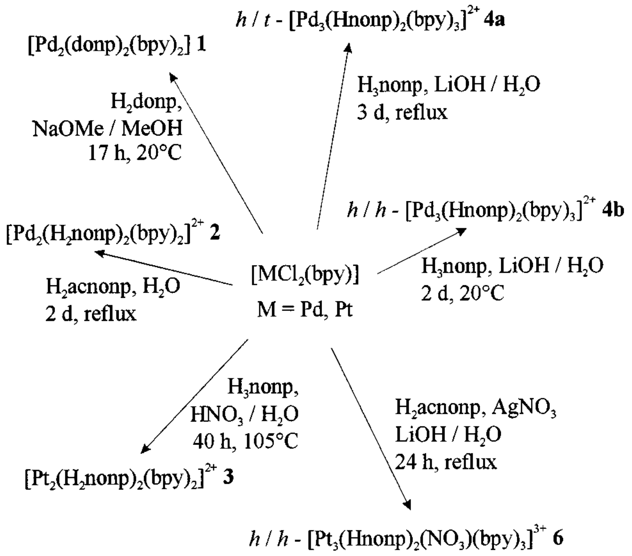
N^1/N^8 in H_2donp to N^1/N^7 in these ligands might help to stabilise a triplatinum(III, II, III) species.



Scheme 1. The ligands H_2donp, H_3nonp and H_2acnonp with the numbering scheme



Scheme 2. Synthesis of complexes **1−6**

Results

The reaction of H_2donp with $[MCl_2(bpy)]$ (M = Pd, Pt) and LiOH at 1:1:2 molar ratio in refluxing aqueous solution generates the trinuclear complexes *cis*-$[M_3(donp)_2(bpy)_3]^{2+}$ rather than the stoichiometrically expected μ-N^1,N^8-bridged dimers *cis*-$[M_2(donp)_2(bpy)_2]$.[9] Lowering the reaction temperature to 20 °C does, indeed, lead to precipitation of a sparingly soluble dinuclear Pd neutral complex, albeit in low yield. We could now show that *cis*-$[Pd_2(donp)_2(bpy)_2]$ (**1**) can, in fact, be isolated as an orange precipitate in satisfactory yield (63%) by changing the solvent/base combination to CH_3OH/CH_3ONa and performing the reaction at room temperature. The formation of tripalladium(II) complexes of the type $[Pd_3(Hnonp)_2(bpy)_3]^{2+}$ (**4a**, **4b**) can likewise be avoided by treating $[PdCl_2(bpy)]$ with H_2acnonp at an equimolar ratio in refluxing water in the absence of base. Addition of $LiClO_4$ leads to precipitation of *cis*-$[Pd_2(H_2nonp)_2(bpy)_2](ClO_4)_2$ (**2**), in which the naphthyridine monoanions H_2nonp^-, formed by cleavage of the acetyl group in the original ligand, adopt the bridging μ-N^1,N^8 coordination mode. The analogous diplatinum(II) complex *cis*-$[Pt_2(H_2nonp)_2(bpy)_2](PF_6)_2$ (**3**) can be isolated by adding an excess of NH_4PF_6 to an aqueous reaction solution of $[PtCl_2(bpy)]$ and H_3nonp kept at pH 2 to suppress the metalation of the 7-amino function, which leads to formation of the preferred trinuclear dications.

Figures 1 and 2 depict the structures of the neutral dipalladium(II) complex **1** and the dication of the $Pt^{(II,II)}$ complex **3**. All three dinuclear species **1−3** display the μ-$1\kappa N^1$:$2\kappa N^8$ coordination mode with *head*/*tail* positioning of their bridging naphthyridine ligands. This binding pattern was also established for $[Ru_2(monp)_4]$[10] (Hmonp = 7-methyl-1,8-naphthyridin-2-one) and $[Ru_2(mphonp)_4(H_2O)]$[11] (Hmphonp = 5-methyl-7-phenyl-1,8-naphthyridin-2-one) and should be electronically favourable for $[M_2]^{4+}$ cores with occupied antibonding orbitals (e.g. $[Ru_2]^{4+}$, $[Rh_2]^{4+}$, $[Pd_2]^{4+}$), as it will enhance the interaction between the δ* orbitals of the dimetal unit and the π* molecular orbitals of the bridging aromatic anions[11]. In contrast, the dinucleating $monp^-$ ligands in $[Mo_2(monp)_4]$ exhibit the alternative μ_2-$1\kappa N^1$:$2\kappa O^2$ coordination mode[10].

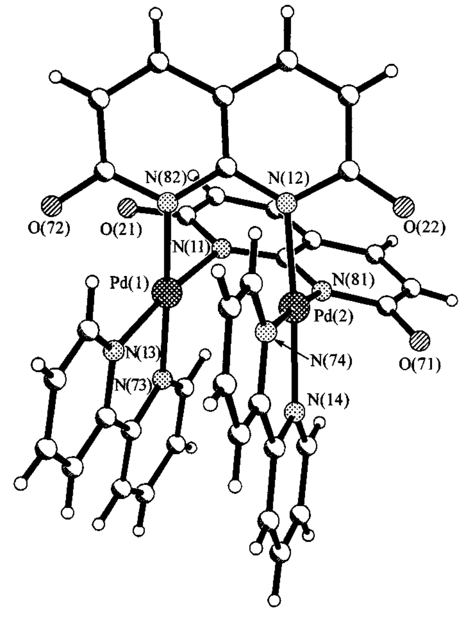


Figure 1. Molecular structure of $[Pd_2(donp)_2(bpy)_2]$ (**1**)

The M···M distances of respectively 2.779(1) (M = Pd) and 2.789(1) Å (M = Pt) in the H_2nonp^- complexes **2** and **3** are marginally shorter than that of 2.797(1) Å in the $Pd^{(II,II)}$ compound **1** (Table 1). This latter value lies in the range 2.794−2.804 Å established[9] for the analogous dinuclear complexes $[M_2(onp)_2(bpy)_2]^{2+}$ (Honp = 1,8-naphthyridin-2-one) and $[M_2(monp)_2(bpy)_2]^{2+}$ (M = Pd, Pt), which themselves are markedly shorter than the metal−metal distances of 2.841−2.974 Å previously reported for similar 1-methylthyminato- and 1-methyluracilato-bridged complexes.[12−17] The Pt···Pt separation of 2.899(2) Å in the di-

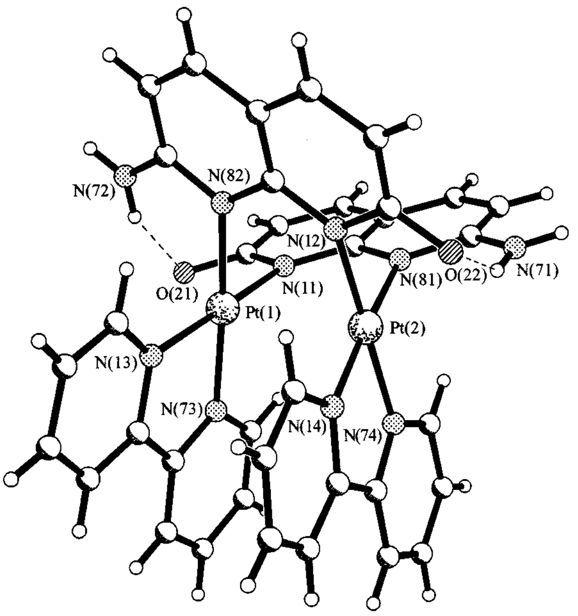


Figure 2. Structure of dication $[Pt_2(H_2nonp)_2(bpy)_2]^{2+}$ of **3**

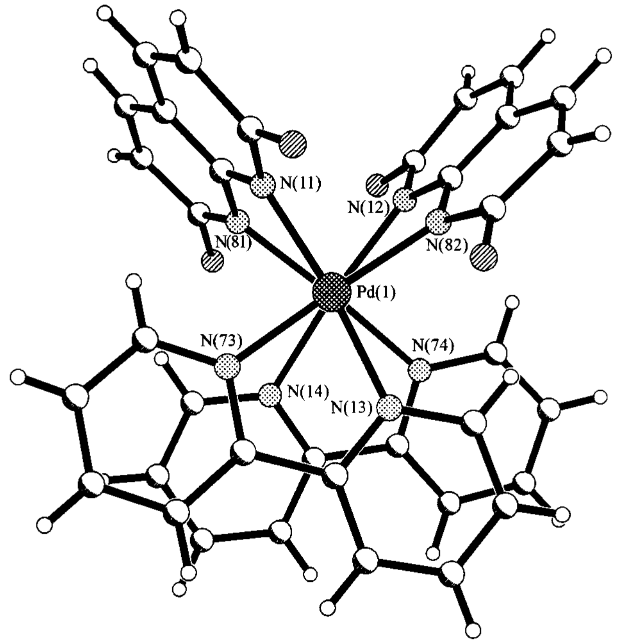


Figure 3. Projection of the structure of (**1**) along the Pd(1)···Pd(2) axis to demonstrate the pronounced relative twisting of the $donp^{2-}$ and bpy ligands

nuclear (bpy)Pt^{II} cation of $[Pt_2(C_4H_6NO)_2(bpy)_2](ClO_4)_2$ (C_4H_6NO = α-pyrrolidonate) also lies within this typical longer range.[18] μ-1κN^1:2κN^8 metal coordination in **1−3** leads to a significant widening of the N^1···N^8 bite distance (respectively 2.34, 2.35, 2.40 Å) in comparison to the separation of these donor atoms in free naphthyridine ligands [e.g. 2.293(6) Å in Hmonp[19]]. Interestingly, the $N^1-M^1\cdots M^2$ angles in the H_2nonp^- complexes **2** [81.6(2)°] and **3** [81.5(4), 82.3(4)°] are considerably narrower than those observed for $N^8-M^2\cdots M^1$ [85.8(2)° in **2**, 85.8(4) and 86.3(5)° in **3**]. The analogous angles for the symmetrically 2,7-disubstituted $donp^{2-}$ ligands of **1** all lie within the range 81.3(2)−83.0(2) and are, therefore, similar to those for $N^1-M^1\cdots M^2$ in **2** and **3**. As the Pd^{II} and Pt^{II} atoms in **1−3** are not significantly displaced from the least-squares planes of their respective coordination spheres, the narrow $N^1\cdots N^8$ separations of the bridging naphthyridine ligands cause the square-planar MN_4 units to tilt away from one another at dihedral angles of 19.4(3) (**1**), 17.9(2) (**2**), and 18.0(4)° (**3**). Close intramolecular contacts between adjacent O^2 and O^7 atoms of the *cis*-positioned $donp^{2-}$ ligands in **1** lead to pronounced rotation of the naphthyridine (npy) and 2,2′-bipyridyl moieties relative to one another about the Pd(1)···Pd(2) axis. This state of affairs is illustrated in Figure 3 and manifests itself in the large average N(npy)−Pd(1)−Pd(2)−N(npy)′ and N(bpy)−Pd(1)−Pd(2)−N(bpy)′ torsion angles of 19.4(3) and 22.6(3)° in this compound. In contrast to **1**, the *head/tail* arrangement of the bridging H_2nonp^- ligands in **2** and **3** is stabilised by the formation of intramolecular $O2\cdots H-N^7$ hydrogen bonds (Figure 2), with the consequence that the degree of twisting for the naphthyridine and 2,2′-bipyridyl ligands is significantly less pronounced in these complexes (Table 1).

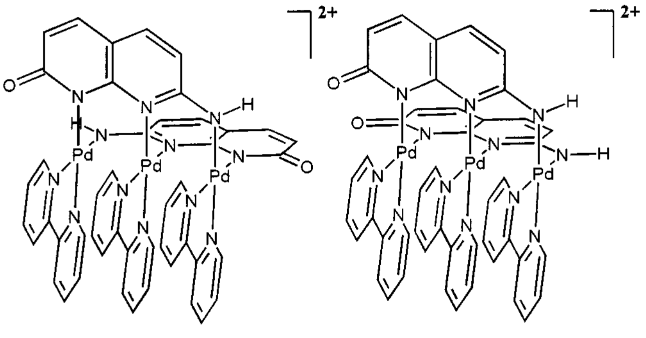
Trinuclear Pd^{II} and Pt^{II} Complexes

Treatment of H_2donp[9] and H_3nonp with $[MCl_2(bpy)]$ (M = Pd, Pt) in aqueous solution in the presence of base leads to preferred formation of trinuclear complexes even at an equimolar ratio of the starting materials. A *head/head* positioning of the μ_3-1κN^1:2κN^8:3κO^7 coordinated $donp^{2-}$ ligands in $[M_3(donp)_2(bpy)_3]^{2+}$ (M = Pd, Pt) would afford the less favourable polar complexes, with formal charge balance at M^1 and M^2. Such isomers would also exhibit unfavourable short intramolecular contacts between adjacent O^2 atoms. As a result of these electronic and steric factors, favoured formation of the charge balanced *head/tail* isomers is observed upon refluxing aqueous solutions of this naphthyridine derivative with $[MCl_2(bpy)]$ and LiOH for 1−3 d at a 2:3:4 molar ratio.[9] In contrast to H_2donp with its protonated aromatic nitrogen atoms N^1 and N^8, the likewise dibasic H_3nonp is protonated at N^1 and the endocyclic amino nitrogen N^7, with the consequence that for a μ_3-1κN^1:2κN^8:3κN^7 bridging mode both the *head/head* and *head/tail* isomers of $[M_3(Hnonp)_2(bpy)_3]^{2+}$ will exhibit formal charge balance at M^1 and M^3 of a linear $[M_3]^{6+}$ core. Inspection of the structures of these isomers (Scheme 3) indicates, however, that, whereas the *head/tail* isomers could be stabilised by intramolecular $N^7-H\cdots O^2$ bonding between adjacent substituents, close contacts between neighbouring O^2 atoms of the *cis* sited $Hnonp^{2-}$ ligands in the *head/head* isomer would lead to pronounced relative twisting of the naphthyridine and 2,2′-bipyridyl ligands about the M···M axes, as in $[Pd_2(donp)_2(bpy)_2]$ **1**.

The reaction of H_3nonp with $[PdCl_2(bpy)]$ and LiOH in refluxing water does, indeed, lead to exclusive formation of the preferred isomers, *head/tail* $[Pd_3(Hnonp)_2(bpy)_3]^{2+}$ after 3 d. This dication, whose X-ray structure is depicted in Fig-

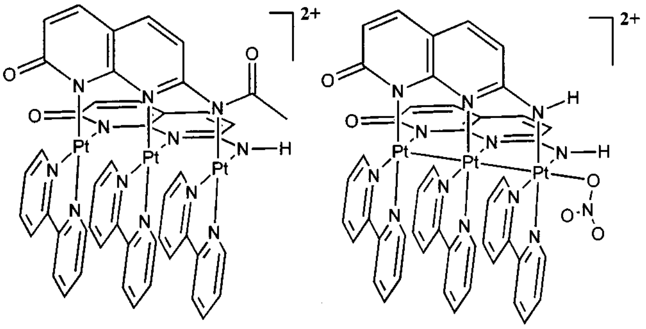
Table 1. M−M distances [Å] and average N−M−M′−N′ torsion angles in di- and trinuclear naphthyridine-bridged complexes

Complex	Coordination mode	*d*(M−M′)	N(npy)−M−M′−N(npy)′	N(bpy)−M−M′−N(bpy)′
1, *cis*-$[Pd_2(donp)_2(bpy)_2]$	μ-1κ*N*^{1}:2κ*N*^{8}	2.797(1)	19.4(3)	22.6(3)
2, *cis*-$[Pd_2(H_2nonp)_2(bpy)_2]^{2+}$	μ-1κ*N*^{1}:2κ*N*^{8}	2.779(1)	9.9(2)	13.7(2)
3, *cis*-$[Pt_2(H_2nonp)_2(bpy)_2]^{2+}$	μ-1κ*N*^{1}:2κ*N*^{8}	2.789(1)	12.2(1)	14.2(5)
4a, *h*/*t*-$[Pd_3(Hnonp)_2(bpy)_3]^{2+}$	μ$_3$-1κ*N*^{1}:2κ*N*^{8}:3κ*N*^{7}	2.781(1), 2.775(2)	14(1), 19.3(5)	17(1)
5, *h*/*h*-$[Pt_3(acnonp)(Hnonp)(bpy)_3]^{2+}$	μ$_3$-1κ*N*^{1}:2κ*N*^{8}:3κ*N*^{7}	2.771(3), 2.816(3)	20(2), 21(1)	23(3)
6, *h*/*h*-$[Pt_3(Hnonp)_2(NO_3)(bpy)_3]^{3+}$	μ$_3$-1κ*N*^{1}:2κ*N*^{8}:3κ*N*^{7}	2.723(2), 2.670(2)	2(1), 3(1)	2(1)



4a (h / t) **4b (h / h)**

Scheme 3. *head*/*tail* and *head*/*head* isomers (**4a**, **4b**) of [Pd$_3$(Hnonp-μ$_3$-1κ*N*^{1}:2κ*N*^{8}:3κ*N*^{7})$_2$(bpy)$_3$](ClO$_4$)$_2$



5 (h / h) **6 (h / h)**

Scheme 4. *head*/*head*-$[Pt_3(acnonp)(Hnonp)(bpy)_3]^{2+}$ (**5**) and *head*/*head*-[Pt$_3$(Hnonp-μ$_3$-1κ*N*^{1}:2κ*N*^{8}:3κ*N*^{7})$_2$(NO$_3$)(bpy)$_3$](ClO$_4$)$_2$(NO$_3$) (**6**)

ure 4, can be precipitated as its dark-orange perchlorate (**4a**) by addition of LiClO$_4$ to the reaction solution. The closely similar Pd(1)···Pd(2) and Pd(2)···Pd(3) distances of 2.781(2) and 2.775(2) Å in **4a**, which are associated with a Pd(1)···Pd(2)···Pd(3) angle of 170.9(1)° are significantly shorter than those in the analogous donp^{2-} complex [Pd$_3$(donp)$_2$(bpy)$_3$](PF$_6$)$_2$ (2.801(1), 2.804(1) Å). As observed in the dinuclear complexes **1−3**, tilting of the metal coordination planes dihedral angles Pd(1)N$_4$−Pd(2)N$_4$ 19.2(5)°, Pd(2)N$_4$−Pd(3)N$_4$ 19.6(4)°] is accompanied by marked twisting of the Hnonp^{2-} and bpy ligand positions relative to the Pd(1)···Pd(2) and Pd(2)···Pd(3) vectors in **4a** (Table 1). Due to the fact that the Pd···Pd separations are markedly longer than the bridging N1···N8 and N8···N7 bite distances, wide C^9−N^1−Pd [128.0(7), 128.3(7)°) and C^7−N^7−Pd (129.3(8), 128.9(8)°] angles are required in this trinuclear complex.

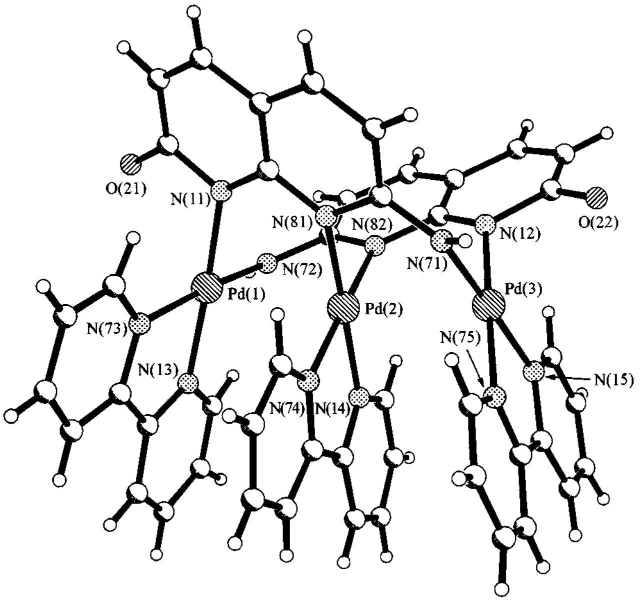


Figure 4. X-ray structure of the dication of *head*/*tail*-[Pd$_3$(Hnonp)$_2$(bpy)$_3$](ClO$_4$)$_2$ (**4a**)

A mixture of the *head*/*head* and *head*/*tail* isomers of $[Pd_3(Hnonp)_2(bpy)_3]^{2+}$ is obtained when H$_3$nonp is treated with [PdCl$_2$(bpy)] and LiOH at room temperature for 2 d. The major product of this reaction **4b** (*head*/*head*) can be isolated in 32% yield by extracting the more soluble *head*/*tail* isomer **4a** with pyridine. **4b** was characterised by elemental analysis, mass spectrometry, and ^{1}H NMR spectroscopy. As both the *C*$_2$ symmetric *head*/*tail* and *C*$_s$ symmetric *head*/*head* isomers exhibit 5 naphthyridine and 12 2,2′-bipyridyl magnetically inequivalent protons, it is not possible to distinguish **4a** and **4b** on the basis of their ^{1}H-NMR patterns. However, characteristic differences are apparent in Figure 5 for the bpy chemical shifts and the Hnonp^{2-} amino H^7 resonance, which moves upfield from δ = 6.49 in **4a** to 6.28 in **4b**.

In contrast to the tripalladium(II) complex, an aqueous reaction solution of Hnonp^{2-} and [PtCl$_2$(bpy)] still contains a mixture of the *head*/*head* and *head*/*tail* isomers of $[Pt_3(Hnonp)_2(bpy)_3]^{2+}$, even after refluxing for periods longer than 3 d. It proved impossible to separate these products by solvent extraction or liquid chromatography, even though ^{1}H-NMR spectra indicated a predominance

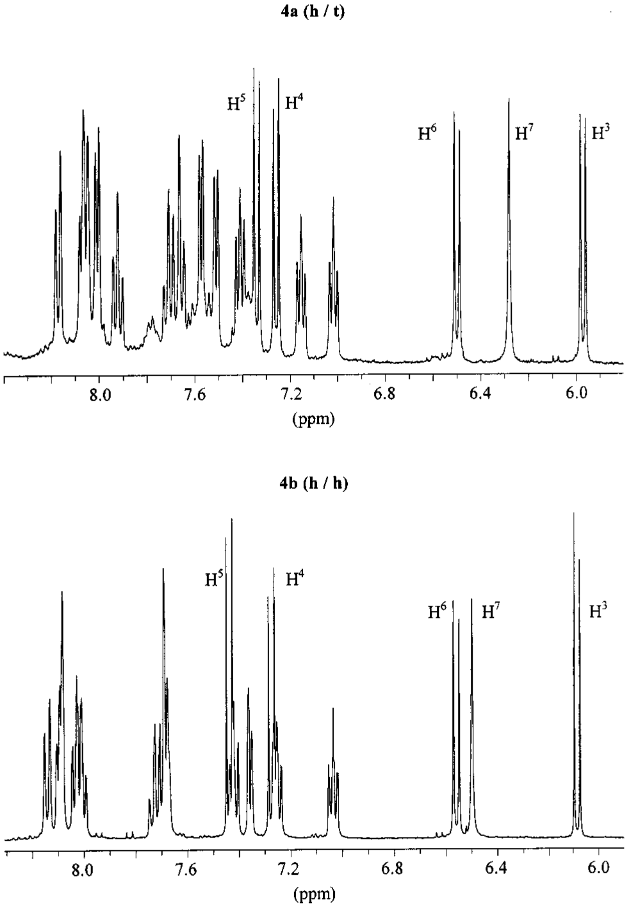


Figure 5. Proton NMR spectra ([D$_6$]DMSO) of the *head/tail* and *head/head* isomers (**4a**, **4b**) of [Pd$_3$(Hnonp)$_2$(bpy)$_3$](ClO$_4$)$_2$

(ca. 4:1) of the energetically more favourable *head/tail* isomer. The formation of trimers was confirmed by the presence of molecular ions [M − PF$_6$]$^+$ (*m/z* 1517) and [M − 2 PF$_6$]$^+$ (*m/z* 1371) in the FAB mass spectrum of the product mixture. This lack of success in separating the isomers of [Pt$_3$(Hnonp)$_2$(bpy)$_3$]$^{2+}$ prompted us to study the reaction of H$_2$acnonp with [PtCl$_2$(bpy)] in alkaline solution. As discussed previously, the facile cleavage of the 7-acetyl function of this naphthyridine derivative (presumably after initial coordination) enables the preparation of [Pd$_2$(H$_2$nonp)$_2$(bpy)$_2$](ClO$_4$)$_2$ **2**. After refluxing an aqueous 2:3:4 molar mixture of H$_2$acnonp, [PtCl$_2$(bpy)] and LiOH for 1 d, addition of excess NH$_4$PF$_6$ leads to precipition of a dark-green solid, whose FAB mass spectrum contains (among others) the following molecular ions (*m/z*, %): 1559 (23) [Pt$_3$(acnonp)(Hnonp)(bpy)$_3$(PF$_6$)]$^+$, 1518 (4) [Pt$_3$(Hnonp)$_2$(bpy)$_3$(PF$_6$)]$^+$, 1414 (14) [Pt$_3$(acnonp)(Hnonp)(bpy)$_3$]$^+$, 1375 (5) [Pt$_3$(Hnonp)$_2$(bpy)$_3$]$^+$. Although satisfactory separation of the products contained in this mixture could not be achieved, a few green-blue crystals of *head/head*-[Pt$_3$(Hacnonp)(Hnonp)(bpy)$_3$]Cl$_2$ · *x* H$_2$O (**5**) could, on one occasion, be isolated by slow evaporation of a reaction solution. The X-ray structure of this triplatinum(II) complex, which exhibits Pt(1)···Pt(2) and Pt(2)···Pt(3) separations of 2.771(3) and 2.816(3) Å, is depicted in Figure 6. Tilt angles of 19.3(8) and 22.0(9)° are observed for the terminal PtN$_4$ coordination planes relative to the central PtN$_4$ unit and are associated with a Pt(1)···Pt(2)···Pt(3) angle of 168.0(1)°.

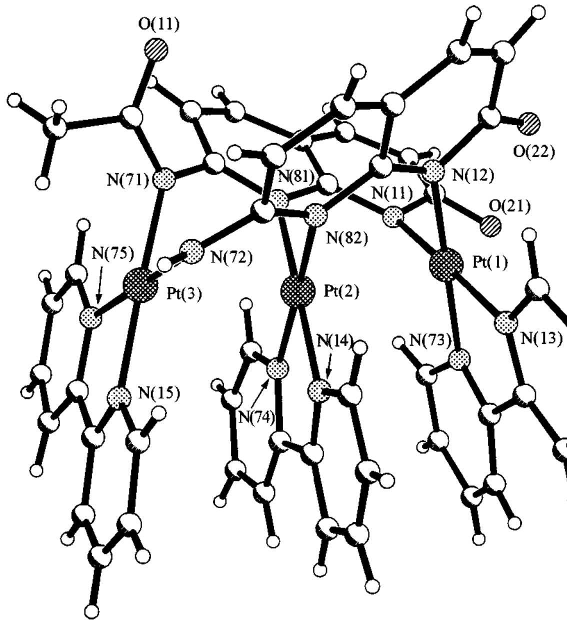


Figure 6. X-ray structure of the dication of *head/head*-[Pt$_3$(acnonp)(Hnonp)(bpy)$_3$]Cl$_2$ · *x* H$_2$O (**5**)

A Linear [Pt$_3$]$^{8+}$ Core

We have previously reported the CV characterisation of reversible one-electron oxidation steps for the [Pt$_3$]$^{6+}$ core in [Pt$_3$(donp)$_2$(bpy)$_3$]$^{2+}$ to [Pt$_3$]$^{7+}$ and [Pt$_3$]$^{8+}$, at respectively $E_{1/2}$ 0.65 and 1.30 V (vs. Ag/AgCl). Oxidation is accompanied by a shift in the main absorption maximum in the visible range to lower wavelengths and the appearance of a second maximum for the tri- and tetracations: [Pt$_3$]$^{6+}$ blue-green, λ_{max} = 710 nm, 555 nm, [Pt$_3$]$^{8+}$ violet, λ_{max} = 695 nm, 540 nm. Attempts to prepare [Pt$_3$]$^{7+}$ or [Pt$_3$]$^{8+}$ species were carried out with oxidants such as HNO$_3$ (conc.), Na$_2$S$_2$O$_8$, and NOBF$_4$. The first member of this list, HNO$_3$, was, for instance, used by Matsumoto to prepare violet [{Pt$_2$(GI)$_2$(bpy)$_2$}$_2$](NO$_3$)$_5$ · 2 H$_2$O (GI = glutarimidate)[20]. However, only the addition of NOBF$_4$ to an acetonitrile solution of [Pt$_3$(donp)$_2$(bpy)$_3$]$^{2+}$ did, in fact, lead to a characteristic colour change from blue-green to violet, but did not allow the isolation of a solid oxidation product. As we had previously been unsuccessful in separating the *head/head* and *head/tail* isomers of [Pt$_3$(Hnonp)$_2$(bpy)$_3$]$^{2+}$, oxidation experiments were carried out directly on the aqueous reaction solutions obtained by treatment of Hnonp^{2-} or acnonp^{2-} with [PtCl$_2$(bpy)]. [Pt$_3$]$^{7+}$, or [Pt$_3$]$^{8+}$ species could, once again, not be isolated with the above oxidants.

The Ag$^+$/Ag couple has also occasionally been employed for the oxidation of platinum(II) complexes. For instance, both Kuyper[21] and Cotton[22] have demonstrated that Ag^I

can extract two electrons from dinuclear Pt^{II} complexes to afford Pt$^{(III,\ III)}$ species with a Pt−Pt single bond. Although the mechanism of this redox process has not been fully elucidated, Lippert et al.[23][24] have isolated heteronuclear Pt_4Ag and Pt_2Ag complexes, which can be regarded as precursors. This approach finally led to the isolation of dark-brown *head*/*head*-[$Pt_3(Hnonp)_2(NO_3)(bpy)_3](ClO_4)_2(NO_3)$ (**6**) in low (23%) but reproducible yields by refluxing 2:3:4 aquous solutions of $H_2acnonp$, [$PtCl_2(bpy)$], and LiOH for 24 h in the presence of an excess of $AgNO_3$. After filtration of a black precipitate and addition of $LiClO_4$, crystals of **6** · 2 H_2O can be grown by gas diffusion of acetone into a nitromethane solution of the resulting dark-brown solid. The δ values of the aromatic protons of **6** (Figure 7) are shifted on average by 0.3 ppm to lower field (^1H NMR spectrum, [D_6]DMSO) in comparision to those recorded for the mixture of *head*/*head* and *head*/*tail* isomers of the triplatinum(II) complex [$Pt_3(Hnonp)_2(bpy)_3]^{2+}$. Cleavage of the original acetyl functions of the bridging naphthyridine ligands is confirmed by the absence of $CH_3C(O)$ methyl resonances in this spectrum and by the X-ray structure presented in Figure 8, which also establishes the presence of the novel $[Pt_3]^{8+}$ core with its average oxidation state of Pt (2.67+). The diamagnetic trinuclear cation exhibits Pt(1)−Pt(2) and Pt(2)−Pt(3) distances of 2.723(2) and 2.670(2) Å, that are similar to those of 2.702(6)−2.710(5) in the respectively tetranuclear Pt (2.5+) and Pt (2.75+) complexes $[\{Pt_2(C_4H_3NO)_2(NH_3)_4\}_2](NO_3)_6 \cdot 3\,H_2O$ and $[\{Pt_2Cl_2(1\text{-}MeT)_2(NH_3)_2\}_2Cl]PtCl_6 \cdot 6\,H_2O$.[6] One of the nitrate counterions in **6** is axially coordinated to Pt(3) at a distance of 2.42(3) Å, that is longer than that of the analogous interaction in the dinuclear complex $[Pt_2(\mu\text{-}C_5H_4NO)_2(NO_3)\,(H_2O)(NH_3)_4](NO_3)_3$ [2.193(7) Å].[25] This axial ligand is disordered in **6** at two different sites with site occupation factors of 0.52 and 0.48. In contrast to **4a** and **5**, the terminal metal atoms in **6**, Pt(1) and Pt(3), are displaced by respectively 0.064(8) and 0.071(8) Å towards the central atom Pt(2) and the chelating 2,2′-bipyridyl ligands adopt an effectively eclipsed orientation (Figure 9). The metrical data for **6** and the fact that the trinuclear cation is diamagnetic are in accordance with the presence of a $[Pt_3]^{8+}$ core, for which the Pt(1) and Pt(3) atoms can be assigned a formal oxidation state of 3+, with the central metal atom Pt(2) remaining at 2+. Interestingly the trimetal core retains the 48E electron count of tripalladium(II) or triplatinum(II) complexes such as **4a** or **5**, by means of its additional axial coordination of an NO_3^- anion.

6 represents, to our knowledge, the first example of a homonuclear triplatinum complex with an average oxidation state above 2+. Its isolation confirms the suitability of 2(7)-substituted naphthyridines as trinucleating ligands capable of supporting two metal−metal bonds. Previous examples are limited to the 46E $[Ru_3]^{2+}$ complex $[Ru_3(\mu\text{-}mponp)_2(CO)_6]$ (hpmonp = 5-methyl-7-phenyl-1,8-naphthyridin-2-one)[26] with its Ru−Ru distances of 2.701(2) and 2.702(3) Å and the paramagnetic 47E complexes $[Rh_xIr_y(\mu\text{-}dmonp)_2(CO)_2\,(cod)_2]^{2+}$ ($x = 0, 2$; $y = 3 - x$; Hdmonp = 5,7-dimethyl-1,8-naphthyridin-2-one), for which the Rh_2Ir cluster could be characterised by X-ray anaysis (Rh−Ir bond lengths, 2.768(2), 2.773(2) Å].[27]

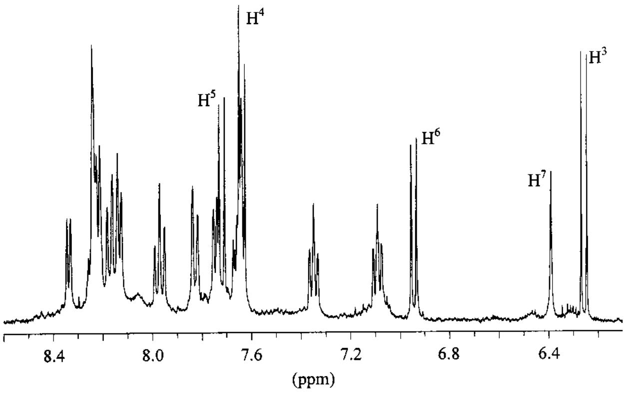


Figure 7. ^1H NMR spectrum of *head*/*head*-$[Pt_3(Hnonp)_2(NO_3)(bpy)_3]^{3+}$ (**6**) in [D_6]DMSO solution

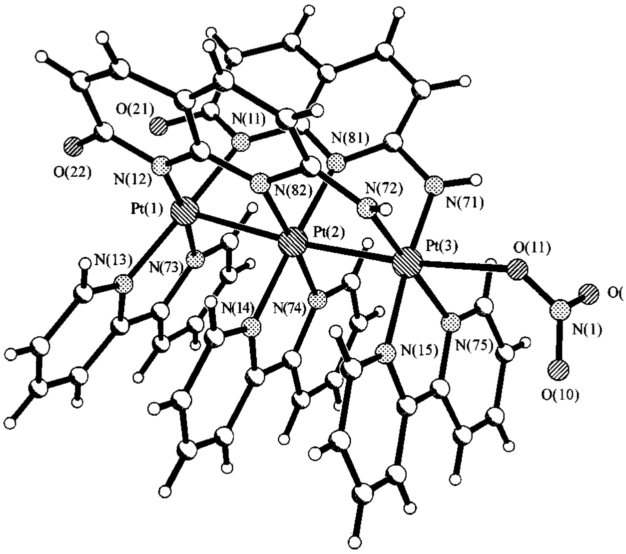


Figure 8. X-ray structure of the trication of *head*/*head*-$[Pt_3(Hnonp)_2(NO_3)(bpy)_3](ClO_4)_2(NO_3)$ (**6**)

Experimental Section

FAB MS: Fisons VG Autospec with 3-nitrobenzyl alcohol as matrix. − ^1H NMR: Bruker DRX 400; chemical shifts are reported as δ values relative to the signal of the deuterated solvent. − ^{195}Pt NMR: Bruker DRX 400, using a saturated K_2PtCl_4 solution as external standard with δ = −1628. − UV/Vis: Perkin−Elmer Lambda 15, λ_{max} is in nm, ε $dm^3 \cdot mol^{-1} \cdot cm^{-1}$. − Elementary analyses: Beller, Mikroanalytisches Labor, Göttingen. The naphthyridine derivatives H_3nonp[28] and $H_2acnonp$[29] were synthesized according to literature procedures; the starting compounds [$MCl_2(bpy)$] (M = Pd, Pt) were prepared[30] from K_2MCl_4.

[$Pd_2(donp)_2(bpy)_2$] (1): H_2donp (16.2 mg, 0.1 mmol) were stirred with 0.2 mL of 1 M NaOMe in 15 mL of MeOH for 30 min. [$PdCl_2(bpy)$] (33.2 mg, 0.1 mmol) was added to the yellow solution and the suspension stirred for 17 h at room temperature. The resulting light orange precipitate was filtered off, washed with MeOH, and dried in vacuo to afford **1**. Yield 28.9 mg (63%). − $C_{36}H_{24}N_8O_4Pd_2 \cdot 4\,H_2O$ (917.5): calcd. C 47.1, H 3.5, N 12.2;

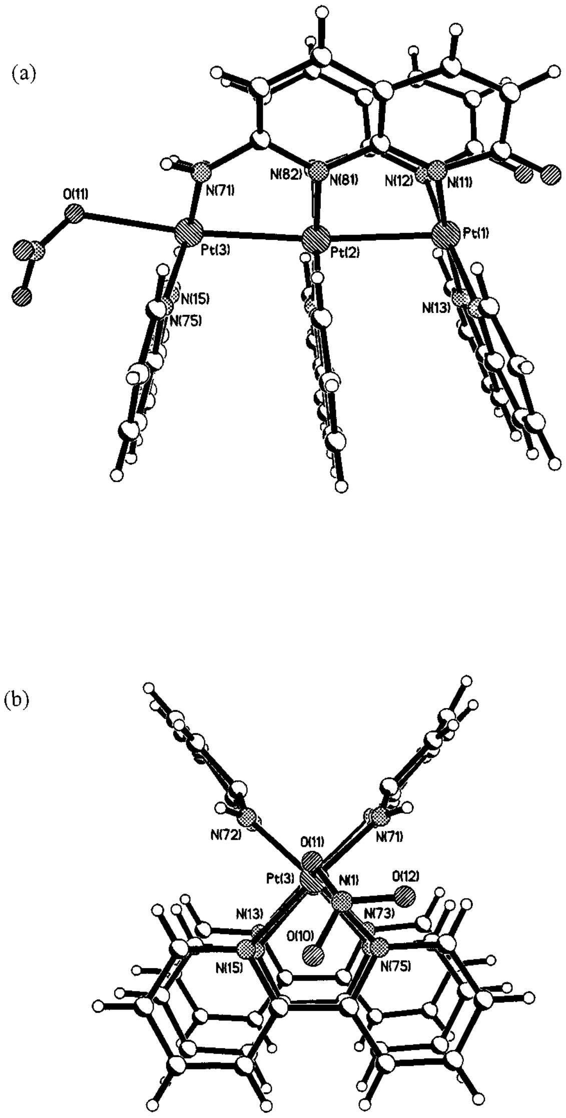


Figure 9. Projections of the trication of *head/head*-$[Pt_3(Hnonp)_2(NO_3)(bpy)_3](ClO_4)_2(NO_3)$ **6**: (a) parallel to the plane of the central 2,2′-bipyridyl plane and (b) along the Pt_3 axis

found C 47.7, H 3.7, N 12.2. − FAB MS; *m*/*z* (%): 845 (36) $[M]^+$, 685 (12) $[M - donp]^+$, 534 (29) $[M - 2\,bpy]^+$, 422 (100) $[M - donp - bpy - Pd]^+$. − UV/Vis (DMSO): λ_{max} (ε): 258 (2642), 308 (2637), 330 (2567), 344 (2561), 360 sh (1480), 440 sh (133). Crystals of **1** · 3.5 $C_7H_7NO_3$ for X-ray analysis were obtained by gas diffusion of acetone into a 3-nitrobenzyl alcohol solution of **1**.

$[Pd_2(H_2nonp)_2(bpy)_2](ClO_4)_2$ (2): $[PdCl_2(bpy)]$ (33.2 mg, 0.1 mmol) and H_2acnonp (20.3 mg, 0.1 mmol) were stirred in 20 mL of refluxing water for 2 d. After cooling, an excess of $LiClO_4$ was added to the solution and following centrifugation the resulting yellow precipitate dried in vacuo to afford **2**. Yield 45.4 mg (87%). − $C_{36}H_{28}Cl_2N_{10}O_{10}Pd_2 \cdot 2\,H_2O$ (1080.5): calcd. C 40.0, H 3.0, N 13.0; found C 40.0, H 3.0, N 13.1. − FAB MS; *m*/*z* (%): 945(31) $[M - ClO_4]^+$, 846 (27) $[M - 2\,ClO_4]^+$, 688 (19) $[M - 2\,ClO_4 - bpy]^+$, 534 (38) $[M - 2\,ClO_4 - 2\,bpy]^+$, 422 (100) $[M - 2\,ClO_4]^{2+}$, 260 (52) $[Pd(bpy)]^+$. − ^1H NMR ($[D_6]$DMSO): δ = 6.50 (d, 2 H, 3-H), 6.62 (d, 2 H, 6-H), 7.08 (m, 4 H, bpy), 7.53 (dd, 2 H, bpy), 7.61 (d, 2 H, bpy), 7.81 (d, 2 H, 4-H), 7.93 (d, 2 H, 5-H), 8.07 (dd, 2 H, bpy), 8.16 (dd, 2 H, bpy), 8.21 (d, 2 H, bpy), 8.26 (d, 2 H, bpy), 8.94 (s, 4 H, NH_2). − UV/Vis (DMSO): λ_{max} (ε): 262 (3501), 308 (5006), 325 sh (5000), 343 (7156), 368 sh (3012), 420 sh (216).

$[Pt_2(H_2nonp)_2(bpy)_2](PF_6)_2$ (3): $[PtCl_2(bpy)]$ (42.2 mg, 0.1 mmol) and H_3nonp (16.2 mg, 0.1 mmol) were mixed in 15 mL of water, whose pH was subsequently adjusted to 2 by addition of 0.1 M HNO_3. After heating for 40 h at 105 °C the deep-red solution was filtered and an excess of NH_4PF_6 added to the filtrate. The resulting violet precipitate was filtered off and dried in vacuo to afford **3**. Yield 45.9 mg (70%). − $C_{36}H_{28}F_{12}N_{10}O_2P_2Pt_2$ (1312.8): calcd. C 32.9, H 2.1, N 10.7; found C 32.3, H 1.9, N 10.8. − FAB MS; *m*/*z* (%): 1167 (30) $[M - PF_6]^+$, 1022 (60) $[M - 2\,PF_6]^+$, 861 (6) $[M - 2\,PF_6 - H_2nonp]^+$, 704 (11) $[M - 2\,PF_6 - H_2nonp - bpy]^+$, 511 (100) $[M - 2\,PF_6 - H_2nonp - bpy - Pt]^+$. − ^1H NMR ($[D_6]$DMSO): δ = 6.49 (d, 2 H, 3-H), 6.60 (d, 2 H, 6-H), 7.14 (dd, 2 H, bpy), 7.49 (d, 2 H, bpy), 7.53 (dd, 2 H, bpy), 7.79 (d, 2 H, 4-H), 7.91 (d, 2 H, 5-H), 8.01 (d, 2 H, bpy), 8.12 (dd, 2 H, bpy), 8.22 (d, 4 H, bpy), 8.27 (d, 2 H, bpy), 8.76 (s, 4 H, NH_2). − ^{195}Pt NMR ($[D_6]$DMSO): δ = −2285. − UV/Vis (DMSO): λ_{max} (ε): 259 (3442), 311 (3258), 349 (3960), 370 sh (2262), 460 sh (155), 550 (166). Crystals of **3** · 3 C_3H_7NO for X-ray analysis were grown by gas diffusion of *tert*-butyl methyl ether into a dimethylformamide (dmf) solution.

***head/tail*-$[Pd_3(Hnonp)_2(bpy)_3](ClO_4)_2$ (4a):** A mixture of H_3nonp (32.2 mg, 0.2 mmol), $[PdCl_2(bpy)]$ (100.1 mg, 0.3 mmol) and $LiOH \cdot H_2O$ (16.8 mg, 0.4 mmol) was stirred at reflux in 40 mL of H_2O for 3 d. Following cooling, addition of an excess of $LiClO_4$ led to precipitation of dark-orange **4a**, which was dried in vacuo after centrifugation. Yield 79.6 mg (61%). − $C_{46}H_{34}Cl_2N_{12}O_{10}Pd_3 \cdot 4\,H_2O$ (1377.1): calcd. C 40.1, H 3.1, N 12.2; found C 40.3, H 3.7, N 12.3. − FAB MS; *m*/*z* (%): 1205 (43) $[M - ClO_4]^+$, 1106 (49) $[M - 2\,ClO_4]^+$, 951 (17) $[M - 2\,ClO_4 - bpy]^+$, 792 (31) $[M - 2\,ClO_4 - 2bpy]^+$, 638 (74) $[M - 2\,ClO_4 - 3\,bpy]^+$, 552 (100) $[M - 2\,ClO_4]^{2+}$. − ^1H NMR ($[D_6]$DMSO): δ = 6.08 (d, 2 H, 3-H), 6.49 (s, 2 H, NH), 6.55 (d, 2 H, 6-H), 7.03 (dd, 2 H, bpy), 7.25 (dd, 2 H, bpy), 7.27 (d, 2 H, 4-H), 7.35 (d, 2 H, bpy), 7.41 (dd, 2 H, bpy), 7.43 (d, 2 H, 5-H), 7.72 (m, 6 H, bpy), 8.00 (dd, 2 H, bpy), 8.02 (dd, 2 H, bpy), 8.09 (m, 4 H, bpy), 8.13 (d, 2 H, bpy). − UV/Vis (DMSO): λ_{max} (ε): 263 (7242), 307 (9065), 325 sh (7102), 352 (6250), 440 sh (1208), 530 sh (277). Crystals of **4a** · 7 H_2O for X-ray diffraction were obtained by slowly evaporating an acetone/water solution of the product.

***head/head*-$[Pd_3(Hnonp)_2(bpy)_3](ClO_4)_2$ (4b):** $[PdCl_2(bpy)]$ (100.1 mg, 0.3 mmol) was added to a suspension of H_3nonp (32.2 mg, 0.2 mmol) and $LiOH \cdot H_2O$ (16.8 mg, 0.4 mmol) in 40 mL of H_2O and the reaction mixture then stirred for 2 d at room temperature. After addition of an excess of $LiClO_4$, the resulting orange precipitate was washed with acetone and **4a** extracted with pyridine to leave **4b**, which was dried in vacuo. Yield 41.8 mg (32%). − $C_{46}H_{34}Cl_2N_{12}O_{10}Pd_3$ (1305.0): calcd. C 42.3, H 2.6, N 12.9; found C 42.5, H 2.7, N 12.8. − FAB MS; *m*/*z* (%): 1205 (51) $[M - ClO_4]^+$, 1106 (35) $[M - 2\,ClO_4]^+$, 951 (21) $[M - 2\,ClO_4 - bpy]^+$, 792 (36) $[M - 2\,ClO_4 - 2\,bpy]^+$, 638 (70) $[M - 2\,ClO_4 - 3\,bpy]^+$, 552 (100) $[M - 2\,ClO_4]^{2+}$. − ^1H NMR ($[D_6]$DMSO): δ = 5.97 (d, 2 H, 3-H), 6.28 (s, 2 H, NH), 6.50 (d, 2 H, 6-H), 7.03 (dd, 2 H, bpy), 7.16 (dd, 2 H, bpy), 7.26 (d, 2 H, 4-H), 7.34 (d, 2 H, 5-H), 7.41 (dd, 4 H, bpy), 7.52 (d, 2 H, bpy), 7.57 (d, 2 H, bpy), 7.68 (m, 2 H, bpy), 7.93 (dd, 2 H, bpy), 8.01 (d, 2 H, bpy), 8.07 (m, 4 H, bpy), 8.17 (d, 2 H, bpy). − UV/Vis (DMSO): 263 (5888), 306 (7221), 325 (5211), 353 (5549), 440 sh (1201), 530 sh (331).

***head/head*-$[Pt_3(Hnonp)_2(NO_3)(bpy)_3](ClO_4)_2(NO_3)$ (6):** H_2acnonp (20.3 mg, 0.1 mmol), $LiOH{\cdot}H_2O$ (8.4 mg, 0.2 mmol) and $[PtCl_2(bpy)]$ (63.4 mg, 0.15 mmol) were stirred at reflux in 30 mL of H_2O for 24 h in the presence of $AgNO_3$ (203.8 mg, 1.2 mmol). After filtration of the black precipitate and addition of an excess of $LiClO_4$ to the filtrate, the resulting dark-brown solid was dried in vacuo. Crystals of **5** · 2 H_2O were obtained from a nitromethane solution of the product mixture by gas diffusion of acetone. Yield 19.9 mg (23%). − $C_{46}H_{34}Cl_2N_{14}O_{16}Pt_3 \cdot 2 H_2O$ (1731.0): calcd. C 31.9, H 2.2, N 11.3; found C 31.6, H 2.3, N 11.1. − ^1H NMR ([D$_6$]DMSO): δ = 6.26 (d, 2 H, 3-H), 6.39 (s, 2 H, NH), 6.94 (d, 2 H, 6-H), 7.09 (dd, 2 H, bpy), 7.35 (dd, 2 H, bpy), 7.63 (d, 2 H, 4-H), 7.64 (m, 2 H, bpy), 7.72 (d, 2 H, 5-H), 7.74 (d, 2 H, bpy), 7.83 (d, 2 H, bpy), 7.97 (dd, 2 H, bpy), 8.13 (d, 2 H, bpy), 8.16 (dd, 2 H, bpy), 8.23 (m, 6 H, bpy), 8.34 (d, 2 H, bpy). − UV/Vis (DMSO): 259 (8418), 309 (7288), 327 sh (6242), 388 sh (4749), 437 sh (1734), 478 sh (1274), 539 sh (678), 773 (364).

X-ray Structural Analyses: Siemens P4 diffractometer graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), T = 295 K. Semi-empirical absorption corrections were applied to the intensity data for **1**, **3**, **4a**, and **5** on the basis of ψ scans; DIFABS[31] was employed for the data set of **3**. The structures were solved by Patterson syntheses or direct methods and refined by full-matrix least squares against F^2 using SHELXL-93.[32] Where appropriate, hydrogen atoms were included at calculated positions with isotropic temperature factors.[33]

[Pd$_2$(donp)$_2$(bpy)$_2$]·3.5C$_7$H$_7$NO$_3$ (1): $C_{36}H_{24}N_8O_4Pd_2 \cdot 3.5 C_7H_7NO_3$ $_M$ = 1381.4, monoclinic space group $P2_1/c$ (no. 14), a = 17.193(3), b = 23.616(4), c = 15.747(2) Å, β = 96.60(1)°, V = 6352(2) Å^3, Z = 4, D_{calcd} = 1.445 g·cm^{-3}, μ = 0.64 mm^{-1}. Crystal size: 0.65 × 0.45 × 0.22 mm; ω-scan; scan range 4° ≤ 2θ ≤ 50° (−20 ≤ h ≤ 20, 0 ≤ k ≤ 28, 0 ≤ l ≤ 18), 11169 symmetry independent reflections; max./min. transmission 0.93/0.86; 704 parameters refined; R = 0.082 [$I > 2\sigma(I)$], wR_2 = 0.271 (all data), Δρ max./min 1.39/−0.78 eÅ^{-3}. With one exception, all of the solvent 3-nitrobenzyl alcohol molecules are disordered.

[Pd$_2$(H$_2$nonp)$_2$(bpy)$_2$](ClO$_4$)$_2$ · 2 H$_2$O (2): $C_{36}H_{32}Cl_2N_{10}O_{12}Pd_2$ $_M$ = 1080.4, orthorhombic space group $Pbcm$ (no. 57), a = 12.708(2), b = 14.639(3), c = 23.702(3) Å, V = 4409.1(13) Å^3, Z = 4, D_{calcd} = 1.628 g·cm^{-3}, μ = 1.01 mm^{-1}. Crystal size: 0.68 × 0.22 × 0.20 mm; ω scan; scan range 4° ≤ 2θ ≤ 50° (0 ≤ h ≤ 15, 0 ≤ k ≤ 17, 0 ≤ l ≤ 28), 3978 symmetry-independent reflections; max./min. transmission 0.33/0.31; 305 parameters refined; R = 0.048 [$I > 2\sigma(I)$], wR_2 = 0.198 (all data), Δρ max./min. 0.83/−0.76 eÅ^{-3}. The water oxygens exhibit multiple disorder.

[Pt$_2$(H$_2$nonp)$_2$(bpy)$_2$](PF$_6$)$_2$ · 3 C$_3$H$_7$NO (3): $C_{45}H_{49}F_{12}N_{13}O_5P_2Pt_2$, M = 1532.1, triclinic space group $P\bar{1}$ (no. 2), a = 14.436(2), b = 15.684(2), c = 16.036(3) Å, α = 62.01(1), β = 70.36(1), γ = 68.47(1)°, V = 2922.4(7) Å^3, Z = 2, D_{calcd} = 1.741 g·cm^{-3}, μ = 4.93 mm^{-1}. Crystal size: 0.42 × 0.33 × 0.09 mm; ω scan; scan range 4° ≤ 2θ ≤ 45° (−14 ≤ h ≤ 15, 0 ≤ k ≤ 16, −15 ≤ l ≤ 17), 7553 symmetry-independent reflections; max./min. transmission 0.70/0.26; 707 parameters refined; R = 0.070 [$I \leq 2\sigma(I)$], wR_2 = 0.198 (all data), Δρ max./min. 0.91/−0.99 eÅ^{-3}. The F atoms of the counterions are disordered, as is one of the solvent dmf molecules.

***head/tail*-[Pd$_3$(Hnonp)$_2$(bpy)$_3$](ClO$_4$)$_2$ · 7 H$_2$O (4a):** $C_{46}H_{48}Cl_2N_{12}O_{17}Pd_3$, M = 1431.1, triclinic space group $P\bar{1}$ (no. 2), a = 12.651(3), b = 14.248(3), c = 18.427(3) Å, a = 81.87(2), β = 70.34(1), γ = 79.75(2)°, V = 3066(1) Å^3, Z = 2, D_{calcd} = 1.550 g·cm^{-3}, μ = 1.03 mm^{-1}. Crystal size: 0.72 × 0.30 × 0.12 mm; ω scan; scan range 4° ≤ 2θ ≤ 45° (−14 ≤ h ≤ 15, 0 ≤ k ≤ 16, −21 ≤ l ≤ 21), 10758 symmetry-independent reflections, max./min. transmission 0.88/0.83; 674 parameters refined; R = 0.082 [$I \leq 2\sigma(I)$], wR_2 = 0.294 (all data), Δρ max./min. 0.91/−0.82 eÅ^{-3}. Wheareas the first of the ClO_4^- counterions is disordered with s. o. f. s of 0.8 and 0.2, the second perchlorate could not be satisfactorily located in difference syntheses.

***head/head*-[Pt$_3$(acnonp)(Hnonp)(bpy)$_3$]Cl$_2$ · *x* H$_2$O (5):** $C_{48}H_{58}Cl_2N_{12}O_{14}Pt_3$ (x = 11), M = 1683.2, monoclinic space group $P2_1/c$ (no. 14), a = 12.045(2), b = 22.696(5), c = 22.236(4) Å, β = 92.96(3)°, V = 6071(2) Å^3, Z = 4, $D_{calcd.}$ = 1.842 g·cm^{-3}, μ = 7.05 mm^{-1}. Crystal size: 0.22 × 0.15 × 0.13 mm; ω scan; scan range 4° ≤ 2θ ≤ 47.5° (0 ≤ h ≤12, 0 ≤ k ≤24, −23 ≤ l ≤ 23), 6951 symmetry-independent reflections, max. /min. transmission 0.94/0.45; 415 parameters refined; R = 0.083 [$I \leq 2\sigma(I)$], wR_2 = 0.196 (all data), Δρ max./min. 0.89/−0.70 eÅ^{-3}. The disordered water oxygens were assigned appropriate s. o. f. s for x = 11. One of the chloride counterions is disordered with s. o. f. s 0.4, 0.3 and 0.3.

***head/head*-[Pt$_3$(Hnonp)$_2$(NO$_3$)(bpy)$_3$](ClO$_4$)$_2$(NO$_3$) · 2 H$_2$O (6):** $C_{46}H_{38}Cl_2N_{14}O_{18}Pt_3$, M = 1731.1, monoclinic space group $P2_1/n$ (no. 14), a = 12.233(2), b = 18.126(4), c = 27.234(5) Å, β = 90.01(3)°, V = 6039(2) Å^3, Z = 4, $D_{calcd.}$ = 1.904 g·cm^{-3}, μ = 7.10 mm^{-1}. Crystal size: 0.24 × 0.22 × 0.18 mm; ω scan; scan range 4° ≤ 2θ ≤ 45° (−1 ≤ h ≤ 13, −1 ≤ k ≤ 19, −29 ≤ l ≤ 29), 7723 symmetry-indepent reflections, max./min. transmission 0.045/0.028; 323 parameters refined; R = 0.070 [$I \leq 2\sigma(I)$], wR_2 = 0.182 (all data), Δρ max./min. 0.71/−0.75 eÅ^{-3}. Both NO_3^- counterions are disordered, with that coordinated directly to Pt(3) displaying s. o. f. s of 0.52 and 0.42 and the other s. o. f. s of 0.57, 0.25 and 0.18.

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[33] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data (deposit numbers (CCDC-113920−113925) may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44−1223/ 336-033, E-mail: deposit@ccdc. cam. ac. uk).

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