Preparation and Interconversion of Dimeric Di-μ-hydroxo and Tri-μ-hydroxo Complexes of Platinum(II) and Palladium(II) with 2,2′-Bipyridine and 1,10-Phenanthroline

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Treatment of $[Pt(L)I_2]$ [L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] with $AgNO_3$ in acetone gives the nitrato complexes $[PtL(ONO_2)_2]$. The palladium analogues were prepared from $[Pd(L)Cl_2]$ in dilute nitric acid. Dissolution of $[ML(ONO_2)_2]$ (M = Pd or Pt) in water results in the formation of the hydroxo-bridged dimers $[LM(\mu\text{-}OH)_2ML][NO_3]_2$ plus nitric acid. Reaction of $[M(L)Cl_2]$ with $AgNO_3$ in water gives $[LM(\mu\text{-}OH)_2ML][NO_3]_2$ directly as the sole product. The dimers are resistant to substitution, although prolonged heating in aqueous nitric acid reforms $[ML(ONO_2)_2]$. The dimers add 1 mol of OH^- to form the very stable trihydroxo-bridged compounds $[LM(\mu\text{-}OH)_3ML]^+$ (M = Pt, deep red; M = Pd, deep yellow) where each metal is five-co-ordinate. These complexes are slowly cleaved by hydroxide to give $[ML(OH)_2]$, which was also prepared either by base hydrolysis or by reaction of $[M(L)Cl_2]$ with Ag_2O. Addition of HX (X = NO_3 or ClO_4) to $[PtL(OH)_2]$ affords $[LPt(\mu\text{-}OH)_3PtL]^+$, $[LPt(\mu\text{-}OH)_2PtL]^{2+}$ or $[PtL(ONO_2)_2]$ at pH 8, 4, and 1 respectively. The complexes have been characterised by i.r., u.v., and n.m.r. (^{195}Pt, ^{13}C, and ^1H) spectroscopy.

Although aqua complexes of Pt^{II} and Pd^{II} can be prepared in solution,[1,2] crystalline compounds containing a co-ordinated water molecule have rarely been isolated.[3] Water molecules co-ordinated to a metal ion are more acidic than the solvent water molecules. The resulting aquahydroxo complexes usually react further[4] to give hydroxo-bridged oligomers of the type $[\{ML_2(\mu\text{-}OH)\}_n]^{n+}$ (L = N-, P-, or S-donor ligand; n = 2 or 3). This is exemplified by $[Pt(PR_3)_2Cl_2]$ (R = Et or Ph) where removal of the chloride ions using silver nitrate leads to the formation of $[\{Pt(PR_3)_2(\mu\text{-}OH)\}_2]^{2+}$ rather than the expected diaqua complexes.[5]

The hydroxo-bridged oligomers $[\{Pt(NH_3)_2(\mu\text{-}OH)\}_n]X_n$ (n = 2 or 3) have been characterised crystallographically[6,7] for X = NO_3,[†] $\frac{1}{2}CO_3$, or $\frac{1}{2}SO_4$. These complexes do not have any antitumour activity and their toxicity is higher than that of the parent compound *cis*-$[Pt(NH_3)_2Cl_2]$ (cisplatin). However, these oligomers may be formed during aquation of cisplatin at physiological pH values at low chloride concentrations.

The aqueous chemistry of the complexes $[ML_2Cl_2]$ (M = Pt^{II} or Pd^{II}, L = N-donor ligand) is rather limited due to their lack of solubility. However, the reactions with nucleophiles have been studied for the soluble tetrasubstituted complexes $[ML_2L'_2]^{2+}$ (L = $\frac{1}{2}$ bipy, $\frac{1}{2}$ phen, or py; L'_2 = L_2 or en[‡]).[9–11] These form initially a five-co-ordinate species with the subsequent substitution of one of the ligands L.

Recently, alkalimetric titrations were reported for $[PdL(ONO_2)_2]$ (L = bipy or phen) in water.[12] This was based on the assumption that $[PdL(ONO_2)_2]$ dissociates in water to give $[PdL(OH_2)_2]^{2+}$, but the pH of the solution before the addition of any base was found to be concentration dependent. This implies that the species formed in water has already undergone substantial hydrolysis.

As part of a study to synthesise water-soluble complexes of Pt^{II} and Pd^{II} for pharmacological studies, we have examined the halide replacement in bipy and phen complexes with aqua ligands using silver(I) salts. This system was, however, more complex than envisaged.

Results and Discussion

Nitrato Complexes.—Reaction of $[Pt(L)I_2]$ (L = bipy or phen) with 2 mol of $AgNO_3$ in acetone gives the dinitrato complex $[PtL(ONO_2)_2]$ as pale yellow needles. The corresponding dinitrato complexes of Pd^{II} were prepared from the reaction of $[Pd(L)Cl_2]$ with $AgNO_3$ in dilute nitric acid. Anderegg and Wanner[12] prepared the palladium(II) nitrato complexes by the reaction of bipy or phen with $Pd(NO_3)_2$ in concentrated nitric acid.

The i.r. spectra of the compounds show characteristic bands for co-ordinated nitrate (see Table 1) which compare favourably with those reported by Gillard and co-workers[13] for $[Pt(bipy)(ONO_2)_2]$ and by Gatehouse *et al.*[14] for $[Pd(bipy)(ONO_2)_2]$. Co-ordinated nitrate has six i.r. active bands.[14–16] The absorption due to ν_3 (*ca.* 750 cm^{-1}) could not be assigned with any certainty due to the ligand C–H out-of-plane deformation bands in this region. There is considerable splitting of the bands ν_4, ν_1, and ν_2 for these complexes. Gatehouse *et al.* also comment on this fact for $[Pd(bipy)(ONO_2)_2]$ and ascribed it to the lower symmetry of the compound owing to the *cis* disposition of the nitrato ligands. A similar splitting occurs in the spectra of *cis*-$[Pt(NH_3)_2(ONO_2)_2]$[17] and *cis*-$[Pt(NH_3)_2(ONO_2)_4]$.[14]

[†] This dimer was first isolated and studied by King[8] who identified it as *cis*-$[Pt(NH_3)_2(OH)(NO_3)]$. Examination of his conductance values clearly demonstrates that the compound in solution behaves as a 2:1 electrolyte.

[‡] Abbreviations used in this paper: bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; py = pyridine; dppm = bis(diphenylphosphino)methane; en = 1,2-diaminoethane; dach = 1,2-diaminocyclohexane; dmso = dimethyl sulphoxide; tmso = tetramethylene sulphoxide; dpso = di-n-propyl sulphoxide. Unless otherwise stated, L means bipy and phen collectively.

Table 1. Infrared bands (cm^{-1})[a] of co-ordinated nitrate

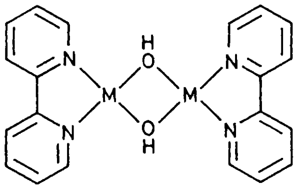
Complex	Δ[b]	ν_4	ν_1	ν_2	ν_6	ν_5	ν(M–O)
$[Pt(bipy)(ONO_2)_2]$	245	1 552	1 284	961	795m	719w	350m
		1 521	1 265	950		705w	340m
$[Pd(bipy)(ONO_2)_2]$[c]	225	1 505	1 289	991	802w	706w	360m
		1 491	1 271	981			350 (sh)
$[Pt(phen)(ONO_2)_2]$	240	1 522	1 282	975	795wm	704w	353m
		1 512	1 272	963			340 (sh)
$[Pd(phen)(ONO_2)_2]$	225	1 501	1 284	988 (sh)	802m	708w	363m
		1 490	1 265	984			355 (sh)

[a] Nujol mull; m = medium, w = weak, sh = shoulder, and sp = sharp. All other bands are strong (s). [b] $\Delta = \nu_4 - \nu_1$; the mean position of each band was used to calculate the difference. [c] $0.5H_2O$ of crystallisation; ν(OH) 3 590, 3 520ms, sp, δ(OH) 1 625 cm^{-1}.

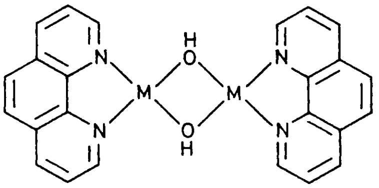
Table 2. Characteristic i.r. absorptions (cm^{-1}) for $[\{ML(\mu\text{-}OH)\}_2]X_2$[a]

M	L	X	OH stretch	OH bend	MO stretch	Other bands
Pt	bipy	NO_3[b]	3 440m, br	1 032s	576s	520wm, 302w[c]
Pt	bipy	ClO_4	3 380m, br	*d*	560m	520w, 306w
Pt	bipy	BF_4	3 620, 3 410m, br	*d*	573m	*d*, 304wm
Pd	bipy	NO_3	3 400m, br	1 025s	560s	520w, 300w
Pd	bipy	ClO_4	3 440 (sh), 3 400s, br	*d*	550 (sh), 545s	520ms, 302w
Pt	phen	NO_3	3 410s, br	1 036m	582m	536w
Pt	phen	ClO_4	3 200m, br	1 018s	575s	309vw
Pd	phen	NO_3	3 400s, br	1 033s	564s, 557s	526m, 313w
Pd	phen	ClO_4	3 600, 3 300m, br	1 019 (sh)	553s, 550 (sh)	312w

[a] Nujol mull; br = broad, v = very. [b] 0.5 H_2O of crystallisation. [c] Tentatively ν(Pt–N). [d] Masked by the anion absorption.



(**1**; M = Pt)
(**3**; M = Pd)



(**2**; M = Pt)
(**4**; M = Pd)

The separation between ν_1 and ν_4 ($\Delta = \nu_4 - \nu_1$) (Table 1) may be taken as a measure of the covalent character of the M–O bond.[18] The value for a covalently bound nitrate such as CH_3ONO_2 is 385 cm^{-1} while that for an ionic nitrate is zero. The frequency of the N–O stretching mode also depends on the degree of covalent character of the M–O bond, with the value for the ν_2 band varying from 1 050 (ionic nitrate) to 854 cm^{-1} for CH_3ONO_2.

The medium-intensity bands in the region 360—320 cm^{-1} are identified as the Pt–O stretching modes based on the assignments of Nuttal and Taylor[19] and Frank and Rogers.[20] Lippert *et al.*[17] reported a broad absorption suggestive of two overlapping vibrations at 330 cm^{-1} for *cis*-$[Pt(NH_3)_2(ONO_2)_2]$. The ν(Pt–N) for $[Pt(bipy)Cl_2]$ has been assigned[21] to the medium-intensity band at 295 cm^{-1}. The spectra of the bipy nitrato complexes have a weak band near 280 cm^{-1}.

Hydroxo-bridged Dimers.—When water is used as the solvent for the reaction of $[M(L)Cl_2]$ with $AgNO_3$ [equation (1)] the

$$[M(L)Cl_2] + 2AgNO_3 \longrightarrow 0.5[LM(\mu\text{-}OH)_2ML]^{2+} + H^+ + 2NO_3^- + 2AgCl \quad (1)$$
$$+ H_2O$$

corresponding hydroxo-bridged dimers $[\{ML(\mu\text{-}OH)\}_2][NO_3]_2$ (**1**)—(**4**) are obtained after heating for 30 min for Pt^{II} and 10 min for Pd^{II}. It is necessary to remove the silver chloride from the hot solution at the end of the reaction, since the products crystallise on cooling. The pH of the resulting solution is *ca.* 1.5. The reaction of $AgNO_3$ with $[Pt(bipy)Cl_2]$ was described by Morgan and Burstall[22] who identified the product as $[Pt(bipy)(ONO_2)_2]$. However, their elemental analyses (Pt, N) are not very convincing. Further, this product is unlikely, since for the palladium system two different products are obtained on treating $[Pd(L)Cl_2]$ with silver nitrate depending on the conditions, *viz.* in water or in dilute nitric acid. Similarly, for the platinum system a concentrated solution of nitric acid is required to give the dinitrato complex (see below).

The hydroxo-bridged dimers (**1**)—(**4**) were also isolated as the perchlorate and tetrafluoroborate salts by metathesis in hot water. All these complexes crystallise as fine hairy needles. The platinum(II) dimers (**1**) and (**2**) are deep yellow-orange and the palladium(II) complexes (**3**) and (**4**) are fawn-yellow.

The i.r. spectra (Table 2) of $[\{ML(\mu\text{-}OH)\}_2][NO_3]_2$ show a strong band at 1 370 and a weak band at 830 cm^{-1} which are characteristic of ionic nitrate.[14–16,18] The presence of a co-ordinated hydroxide group is confirmed[15a,23,24] by the OH stretching absorption at *ca.* 3 400 cm^{-1} (Table 2), whereas there is no OH bending band at 1 630 cm^{-1}. Therefore, the formulation $[ML(OH_2)(OH)]^+$ can be eliminated. Further, there are strong bands at *ca.* 1 030 and at *ca.* 575 cm^{-1} (Table 2) which are not present in the spectra of the dinitrato

Table 3. Absorption spectra for the hydroxo-bridged dimers [$\lambda_{max.}$ nm (ε/dm^3 mol^{-1} cm^{-1})]

Complex					
(**1**) [{Pt(bipy)(μ-OH)}$_2$][NO$_3$]$_2$		358 (2 410)[a] (2 410)[b]	318 (7 470)[a] (10 700)[b]	307 (8 020)[a] (9 450)[b]	250 (16 000)[a] (17 800)[b]
(**3**) [{Pd(bipy)(μ-OH)}$_2$][NO$_3$]$_2$				307 (10 700)	244 (16 600)
(**2**) [{Pt(phen)(μ-OH)}$_2$][NO$_3$]$_2$	372 (2 250)	352 (2 250)			270 (15 300)
(**4**) [{Pd(phen)(μ-OH)}$_2$][NO$_3$]$_2$		355 (1 360)	337 (1 560)		272 (13 000)

[a] 1.995 × 10^{-3} mol dm^{-3}. [b] 1.995 × 10^{-4} mol dm^{-3}.

complexes. The former band is assigned as the OH bending mode and the latter as the MO stretching vibration for a bridging hydroxide group.[25] For the salts [{ML(μ-OH)}$_2$]X$_2$ (X = ClO$_4$ or BF$_4$) the δ(OH) mode is obscured by the intense anion absorption. The ν(M–O) frequency depends on the nature of the anion, as was observed for [{Pt(NH$_3$)$_2$(μ-OH)}$_2$]X$_2$ (X = NO$_3$, $\frac{1}{2}$SO$_4$, or $\frac{1}{2}$CO$_3$).[7] In addition there is an unidentified weak band at 520 cm^{-1}. There are no bands in the region 400—310 cm^{-1}, while the weak absorption at 300 cm^{-1} may be the ν(Pt–N) mode.

Bands associated with the OH bending vibration occur in the region 900—1 100 cm^{-1} for inorganic compounds.[7,23,26,27] Further, di-μ-hydroxo complexes give strong bands in the region 600—400 cm^{-1} due to the M–O stretching mode,[5a,25,28] *e.g.* [{Pt(NH$_3$)$_2$(μ-OH)}$_2$][NO$_3$]$_2$ (495 cm^{-1}).[27,29]

The other potential structure for the product of reaction (1) is the monomer [ML(OH)(ONO$_2$)]. This can, however, be rapidly rejected since (*a*) the i.r. spectrum of the reaction product shows that the nitrate is ionic and (*b*) the perchlorate and tetrafluoroborate salts can be prepared by metathesis with no significant changes in the spectrum. The formation in solution of a complex such as [ML(OH)(ONO$_2$)] would present a number of problems since nitrato complexes are completely hydrolysed in aqueous solution to the corresponding aqua complex, as shown by solution Raman spectroscopy,[17,30] conductance,[8] and pH titration.[31] The addition[32] of a large excess of nitrate to a solution of *cis*-[Pt(NH$_3$)$_2$(OH$_2$)$_2$]$^{2+}$ results in the formation of only a small amount of *cis*-[Pt(NH$_3$)$_2$(OH$_2$)(ONO$_2$)]$^+$ with an equilibrium constant of 0.17. Diaqua complexes are very soluble and can be isolated only by evaporation to dryness,[33] whereupon, if nitrate is present, [Pt(NH$_3$)$_2$(ONO$_2$)$_2$] is reformed,[8,17,32] as is [Pt(dien)(ONO$_2$)]NO$_3$ from [Pt(dien)(OH$_2$)][NO$_3$]$_2$.[30] In the present study the complexes (**1**)—(**4**) crystallise from solution indicating the formation of a salt.

The nitrato compounds [PtL(ONO$_2$)$_2$] dissolve in water on warming (50 °C) to give a yellow solution which becomes deep orange over a period of several minutes. On cooling to room temperature, orange needles of the corresponding hydroxo-bridged dimers (**1**) or (**2**) separate. The palladium dinitrato complexes dissolve in water at 30 °C and on cooling to 25 °C the dimers (**3**) or (**4**) separate as fine needles.* The other product of the reaction is nitric acid. All attempts to grow crystals suitable for a crystallographic study were unsuccessful.

The platinum(II) dimers (**1**) and (**2**) are resistant to substitution. Thus, there is no reaction with an excess of LiCl at 100 °C, and the dimer crystallises on cooling as the chloride salt. Furthermore, the dimers can be recrystallised from hot dilute nitric acid. A similar lack of reactivity for [{Pt(PEt$_3$)$_2$(μ-OH)}$_2$][BF$_4$]$_2$ has been observed by Bushnell *et al.*[5a] The stability of such a dimer is further exemplified by the oxidation of [{Pt(NH$_3$)$_2$(μ-OH)}$_2$]$^{2+}$ with hydrogen peroxide without cleavage of the bridge.[36] Attempts to oxidise [{PtL(μ-OH)}$_2$]$^{2+}$ (L = bipy or phen) with hydrogen peroxide gave yellow solids of variable composition (L = bipy) or a green-yellow uncharacterised precipitate (L = phen).

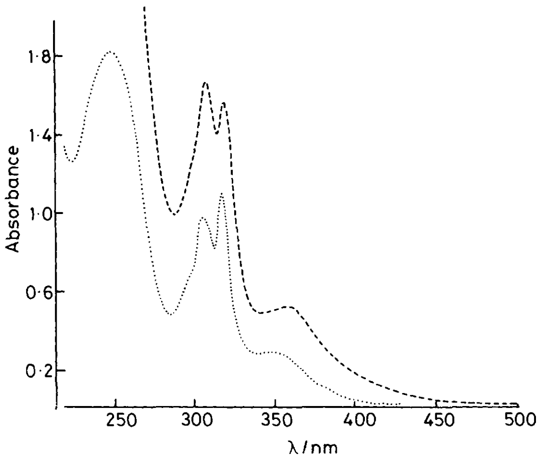


Figure 1. Electronic spectra of [{Pt(bipy)(μ-OH)}$_2$][NO$_3$]$_2$ in water at concentrations of 1.99 × 10^{-3} (– – – –, 1-mm cell) and 1.99 × 10^{-4} mol dm^{-3} (· · · ·, 5-mm cell)

Boiling in dilute nitric acid for 30 min (the solution changes from deep orange to lemon-yellow) is required to cleave the dimers (**1**) and (**2**). Yellow [PtL(ONO$_2$)$_2$] was isolated by removal of the solvent. The dinitrato complex did not crystallise from the reaction mixture. The palladium dimers (**3**) and (**4**) are more reactive than the platinum analogues, thus only slight heating in dilute nitric acid is required to form the dinitrato complex [PdL(ONO$_2$)$_2$]. These complexes separate from the reaction mixture as yellow crystals.

The electronic spectra of the hydroxo-bridged dimers in water are given in Table 3. The compounds obey the Beer–Lambert law in the concentration range 10^{-3}—10^{-4} mol dm^{-3} except for (**1**) (see Figure 1), for which the plot of absorption *versus* concentration for all the peaks is linear with an intercept at the origin, except for the peak at 318 nm which exhibits a linear plot with a positive *y* intercept.

Reactions with Base.—When aqueous sodium hydroxide is added to an aqueous solution of complex (**1**) and (**2**) until the pH is 8, a deep red solution is rapidly formed from which a red precipitate slowly separates. A conductimetric titration at 25 °C (Figure 2) shows that the conductance remains

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* Although the existence of palladium(II) hydroxo-bridged dimers has been demonstrated in solution,[34] such a complex has been isolated only for *S*-propylenediamine.[35]

Table 4. Absorption spectra[a] of $[ML(OH)_2]\cdot 2H_2O$ [$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})]

Complex						
$[Pt(bipy)(OH)_2]$[b]	375 (3 110)	321 (7 910)	308 (6 780)	270 (21 200)	248 (14 400)	
$[Pd(bipy)(OH)_2]$			309 (12 900)	300 (12 000)	250 (14 400)	
$[Pt(phen)(OH)_2]$	385 (2 160)	330 (3 020)		275 (13 800)	252 (19 100)	222 (18 800)
$[Pd(phen)(OH)_2]$	356 (1 170)	338 (1 530)	296 (sh) (8 040)	273 (23 700)		222 (25 900)

[a] Solvent = water. Except for $[Pt(bipy)(OH)_2]$, the spectra did not alter on addition of base. [b] pH 10 (NaOH).

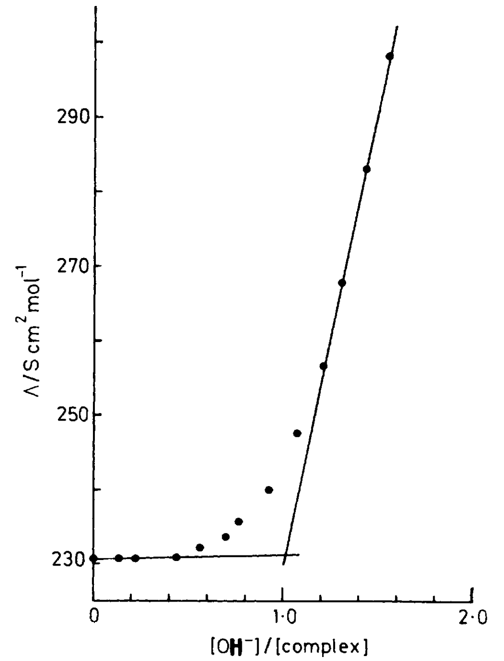

Figure 2. Conductimetric titration of $[\{Pt(bipy)(\mu\text{-}OH)\}_2][NO_3]_2$ (15 cm^3, 1.04×10^{-3} mol dm^{-3}) in water at 25 °C with aqueous NaOH (0.04 mol dm^{-3})

relatively constant up to 1 mol of OH^- added, whereupon it increases rapidly as the concentration of free OH^- increases, suggesting that 1 mol of hydroxide adds to the complex. A similar spectrophotometric titration with NaOH also shows that the dimers react with 1 mol of OH^- (Figure 3, example given for the bipy system).

Treatment of the dimers with pyridine, 4-methylpyridine, or KCN also gives red complexes, but the solids isolated do not contain any of these ligands and were identical with the solids obtained with NaOH. However, with a less basic pyridine such as 4-cyanopyridine ($pK_a = 1.86$[37]) there is no reaction. Therefore, these reactions with pyridine and cyanide are essentially a reaction with the OH^- produced by these bases in solution. The red complexes were isolated as the NO_3^- and ClO_4^- salts which analyse as $[Pt_2L_2(OH)_3]X\cdot nH_2O$ [L = bipy (**5**) or phen (**6**); X = NO_3 or ClO_4; n = 2, 4, or 5]. They react with acid to reform the hydroxo-bridged dimers. A dilute solution (10^{-3} mol dm^{-3}) of the red complex reacts slowly (12 h, 25 °C) with base (pH 10) to form the dihydroxo complex $[PtL(OH)_2]$, but a concentrated solution can be boiled in 2 mol dm^{-3} sodium hydroxide solution for 1 h without change.

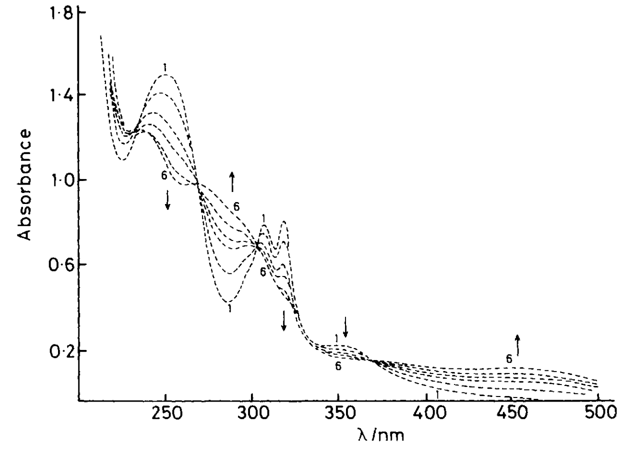

Figure 3. Electronic spectra of $[\{Pt(bipy)(\mu\text{-}OH)\}_2][NO_3]_2$ (2.13×10^{-4} mol dm^{-3}, 2-mm cells) in water with added hydroxide ion. Mole ratios of OH^- :complex are 0:1 (1), 0.327:1 (2), 0.535:1 (3), 0.732:1 (4), 0.901:1 (5), and 1.08:1 (6). The addition of more hydroxide gives spectra identical to curvc 6

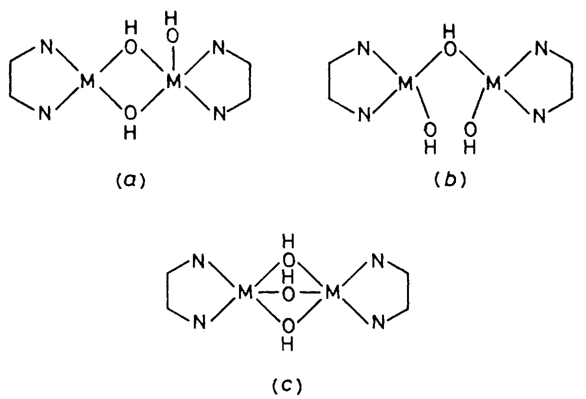

Figure 4. Possible structures for $[M_2L_2(OH)_3]^+$ [M = Pt, (**5**) or (**6**), or Pd; L = bipy or phen (N–N)]

For the formula $[Pt_2L_2(OH)_3]^+$ three possible structures are shown in Figure 4; *viz*. (*a*) an asymmetric dimer, (*b*) a monohydroxo-bridged dimer, and (*c*) a trihydroxo-bridged dimer. This formula is also consistent with a 1:1 mixture of the dimer (**1**) or (**2**) and $[PtL(OH)_2]$. However, this is at variance with the deep red colour of the solution, the spectrophotometric titration, and the lack of reactivity of (**5**) and (**6**).

The ^{195}Pt n.m.r. chemical shifts of $[Pt(bipy)(OH)_2]$, (**1**), and

Table 5. Proton, ^{13}C, and ^{195}Pt n.m.r. parameters

		$\delta(^1H)^b$				J/Hz				
Complex	$\delta(^{195}Pt)^a$	H^6	H^4	H^3	H^5	$H^{3,4}$	$H^{3,5}$	$H^{4,5}$	$H^{4,6}$	$H^{5,6}$
$[Pt(bipy)(OH)_2]^c$	−1 776	8.45	7.98	7.79	7.41	6		8		5
(1) $[\{Pt(bipy)(\mu\text{-}OH)\}_2]^{2+,d}$	−1 340	8.30	7.98	7.68	7.39	8.1		7.6		5.6
(5) $[Pt_2(bipy)_2(\mu\text{-}OH)_3]^{+,e}$	−1 318	8.34	7.78	7.40	7.16	8.1		7.6		5.4
(3) $[\{Pd(bipy)(\mu\text{-}OH)\}_2]^{2+}$		8.16	8.08	7.89	7.50	8.1	1.3	7.7	1.4	5.6

[a] Shifts relative to H_2PtCl_6 (0.1 mol dm^{-3}) in D_2O, spectra recorded at 323 K. [b] Spectra recorded at 303 and 323 K, except for (5) (pH *ca.* 8) at 323 K only. [c] Proton spectrum from ref. 13. [d] ^{13}C (D_2O, 323 K): 126.6 (C^3), 130.7 (C^5), 144.5 (C^4), 151.2 (C^6), and 158.3 (C^2) p.p.m. [e] ^{13}C (D_2O, 323 K): 126.0 (C^3), 130.3 (C^5), 143.5 (C^4), 151.0 (C^6), and 157.5 (C^2) p.p.m.

(**5**) are shown in Table 5.* The red complex is a single distinct species and the presence of only one resonance suggests that the molecule is symmetric and thus structure (*a*) is unlikely. The ^{195}Pt chemical shift for complexes of the type $[Pt(N)_2(O)_2]$, where N and O are N- and O-donor ligands respectively, fall within a rather narrow range of values.[38,39] Nevertheless, the chemical shift is sensitive to the O–Pt–O angle, such that the difference in chemical shift between *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ and *cis*-$[Pt(NH_3)_2(OH)_2]$ is only 12 p.p.m.,[31] whereas $[\{Pt(NH_3)_2(\mu\text{-}OH)\}_2]^{2+}$ is displaced to lower field by 430 p.p.m.[29] For the same reason, the signal for $[\{Pt(bipy)(\mu\text{-}OH)\}_2]^{2+}$ (**1**) is 436 p.p.m. downfield from $[Pt(bipy)(OH)_2]$. The proximity of the resonances for (**1**) and (**5**) implies a common skeleton.

Appleton *et al.*[32] observed a ^{195}Pt n.m.r. signal (pH 2) at −1 549 p.p.m. which they attributed to $[(H_3N)_2(H_2O)Pt(\mu\text{-}OH)Pt(OH_2)(NH_3)_2]^{3+}$ shifting to −1 516 p.p.m. at pH 12.5 due to $[(H_3N)_2(OH)Pt(\mu\text{-}OH)Pt(OH)(NH_3)_2]^+$ {*cf. cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$, −1 584 p.p.m.}. On this basis the mono-hydroxo-bridged complex [Figure 4(*b*)] can be eliminated. Moreover, the rapid formation of (**5**) from (**1**) and its slow reaction with hydroxide argues against a single hydroxo bridge.

The ^1H and ^{13}C n.m.r. spectra (for L = bipy) are summarised in Table 5. Platinum coupling was not observed. The ^1H spectra were recorded at both ambient temperature and at 323 K (to augment the solubility), however the spectra are identical. When the spectrum of (**5**) was run at 343 K (pH 8) an additional set of weak resonances was present at 8.76 (d), 8.09 (t), and 7.57 (d), due to further reaction of (**5**). The most likely product, based on the spectrophotometric titration, is $[Pt(bipy)(OH)_2]$. The agreement with the previously reported[13] spectrum of $[Pt(bipy)(OH)_2]$ is only fair. The formation of (**5**) from (**1**) results in an upfield shift of the proton resonances and only a slight modification in the chemical shifts of the carbon atoms. In contrast, the bipy protons for $[Pt(bipy)(OH)_2]$[13] are considerably deshielded. The ^{13}C spectra of (**1**) and (**5**) are similar to that of $[Pt(bipy)_2][NO_3]_2$.[10b]

The complexes $[PtL_2]^{2+}$ (L = bipy or phen) react rapidly[10,11a] in aqueous solution with nucleophiles (X = OH^- or CN^-) to form the five-co-ordinated complexes $[Pt(L)_2X]^+$ which have been characterised by crystal structure determinations. Livingstone and Wheelahan[40] showed that $[Pt(bipy)_2]^{2+}$ adds 1 mol of halide in nitromethane to give $[Pt(L)_2X]^+$. Similarly, $[Pt(dppm)_2]X_2$ (X = Cl, Br, or I) exists as a five-co-ordinate species in organic solvents.[41]

The electronic spectra of five-co-ordinate complexes of platinum(II) and palladium(II) generally have an intense band(s) in the visible or near-visible region arising from a *d–d* transition. The non-centrosymmetric structure accounts for the high intensity due to the lack of an inversion centre and the square planar or trigonal bipyramidal field results in a bathochromic shift of the transition relative to a square planar complex.[42]

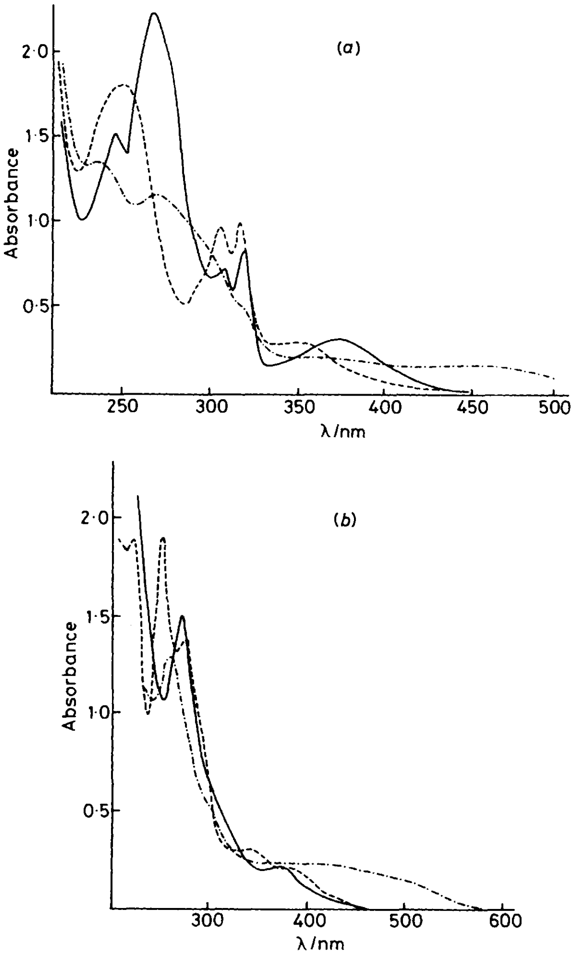

Figure 5. Electronic spectra (*a*) of $[\{Pt(bipy)(\mu\text{-}OH)\}_2][NO_3]_2$ (– – – –), $[Pt_2(bipy)_2(\mu\text{-}OH)_3]NO_3$ (— · — · —) in water, and $[Pt(bipy)(OH)_2]$ (——) in aqueous NaOH (pH 10), (*b*) of $[\{Pt(phen)(\mu\text{-}OH)\}_2][NO_3]_2$ (– – – –), $[Pt_2(phen)_2(\mu\text{-}OH)_3]NO_3$ (— · — · —), and $[Pt(phen)(OH)_2]$ (——) in water

The electronic spectra of $[Pt(L)_2X]^+$ (L = bipy or phen; X = CN or OH) show an intense absorption above 400 nm consistent with their five-co-ordinate structure. In addition,

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* The Pt–phen system was not studied by n.m.r. spectroscopy because of lack of solubility.

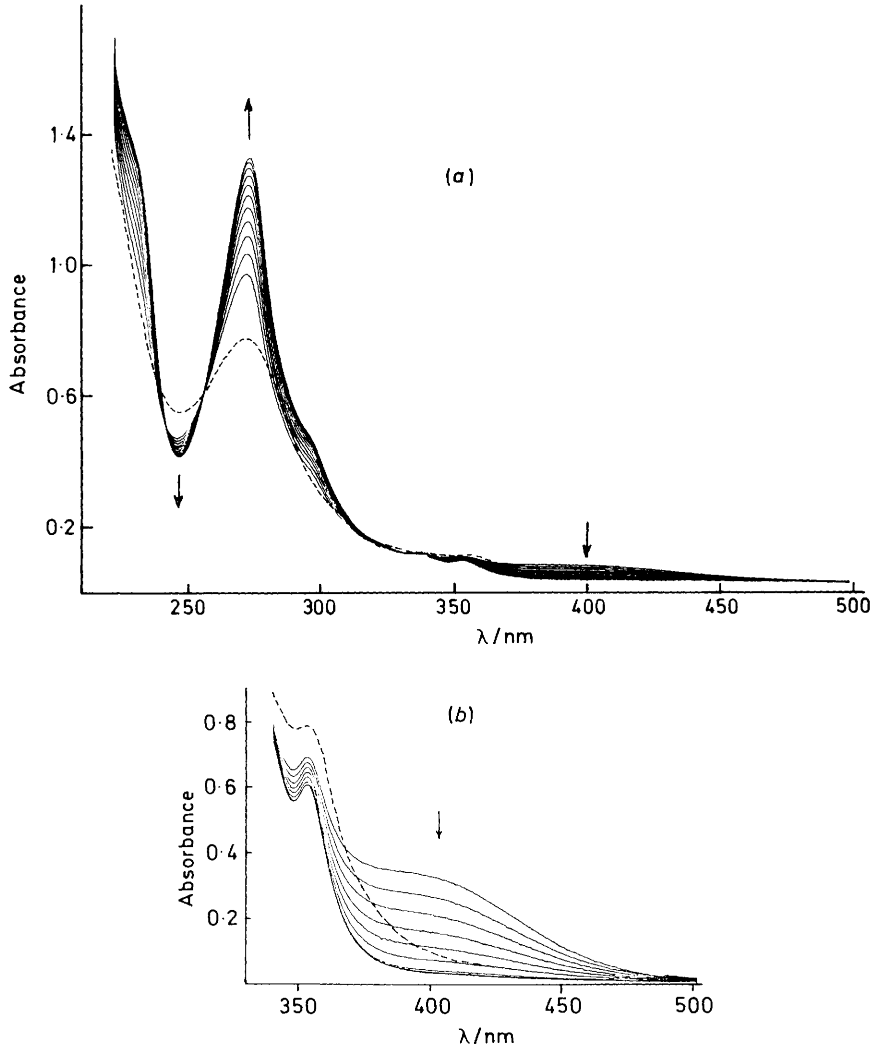

Figure 6. Electronic spectra of $[\{Pd(phen)(\mu\text{-}OH)\}_2][NO_3]_2$ (5.52×10^{-4} mol dm^{-3}) in water ( ) and a repetitive scan study (25 °C, 1.5-min cycles) of the complex (5.52×10^{-4} mol dm^{-3}) in 2 mol dm^{-3} NaOH (——): (*a*) 1-mm cells; (*b*) 10-mm cells. Isosbestic points at 243, 257, and 333 nm

there is a reduction in the intensity of the bands between 350 and 400 nm, which results in a rather featureless spectrum in this region. It would seem that these latter bands are characteristic of square-planar co-ordination for bipy and phen complexes of Pt^{II}; they are also present in the spectra of $[Pt(bipy)Cl_2]$.[43]

Complexes (**5**) and (**6**) each have a broad absorption in the electronic spectrum at 400—550 nm (Figures 3 and 5), suggesting that these complexes are five-co-ordinate. Moreover, there is a reduction in the intensity of the bands between 300 and 380 nm, as observed for the $[PtL_2]^{2+}$ systems.

On the other hand, the formation of a mono-μ-hydroxo complex [Figure 4(*b*)] should not drastically perturb the electronic spectrum, but in contrast should give a spectrum similar to that of $[PtL(OH)_2]$ [see Table 4, Figure 5(*a*) and (*b*)] which is typical of a square planar complex. Thus, the electronic spectra provide further support for a tri-μ-hydroxo structure.

The i.r. spectra of (**5**) and (**6**) are similar to those of (**1**) and (**2**) apart from the bands due to the water of crystallisation. The ν(Pt–O) absorption is somewhat broader and there is a broad band at 600—500 cm^{-1} due to the lattice water.

The triply bridged structure [Figure 4(*c*)] is consistent with both the ^{195}Pt n.m.r.† and the electronic spectrum. The facile transformation between (**5**), (**6**), and (**1**), (**2**) respectively on adjusting the pH compared with the forcing conditions required to cleave (**5**) or (**6**) to form $[PtL(OH)_2]$ suggests that the red complexes have a common skeleton with the hydroxo-bridged dimers. A possible mechanism for the reaction is attack on one platinum atom to form structure (*a*) (Figure 4) followed by formation of the third hydroxo bridge. All attempts to grow crystals suitable for an *X*-ray structure determination gave only fine needles.

Addition of NaOH to the palladium complexes (**3**) and (**4**) results in the formation of a deep yellow species, the stability of which depends on the concentration of both the complex and hydroxide. If concentrated solutions are used the yellow complex can be isolated as the nitrate or perchlorate salt, which we believe to have the formulation $[Pd_2L_2(OH)_3]X$ ($X = NO_3$ or ClO_4). Due to the reactivity of these complexes, they could not be isolated in a completely pure state and appeared to contain some of the corresponding dimer.

Dissolution of these complexes in water at the concentration required to measure the electronic spectrum (*ca.* 2×10^{-3} mol

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† T. G. Appleton, personal communication.

dm^{-3}) results in rapid decoloration of the solution so that the spectrum now corresponds to that of the dimer, $[\{PdL(\mu\text{-}OH)\}_2]^{2+}$. A spectroscopic titration of the compounds (**3**) and (**4**) was performed. At a concentration of 2 × 10^{-3} mol dm^{-3}, there is an initial formation of the deep yellow complex which persists for several seconds before decolourising rapidly to form $[PdL(OH)_2]$, so that the spectrum is a composite of two or three species. However, when an excess of hydroxide is used the rate of disappearance of the intermediate yellow compound is reduced. The complex with phenanthroline as ligand is transformed during approximately 20 min at room temperature to $[Pd(phen)(OH)_2]$ (see Figure 6) with isosbestic points at 243, 257, and 333 nm. The most interesting feature of the spectrum is the intense broad band at 400 nm which disappears on cleavage of the dimer. For the bipy complex the rapidity of the reaction does not allow a repetitive scan study at 25 °C but a broad band at *ca.* 400 nm is observed if the spectrum is taken directly after mixing.

These electronic spectra are again indicative of five-co-ordination, and we suggest that these deep yellow palladium complexes are analogous to the deep red platinum(II) complexes [structure (*c*)], but are more reactive.

The complex $[\{Pd(bipy)(\mu\text{-}OH)\}_2][NO_3]_2$ gives a better resolved ^1H n.m.r. spectrum (Table 5) than that of the platinum analogue. The spectra after the addition of hydroxide show that a mixture of species is formed, but they were not interpreted further.

Addition of Acid to $[PtL(OH)_2]$.—Gillard and co-workers[13] were the first to isolate and characterise a monomeric platinum(II) dihydroxo compound, which they prepared by base hydrolysis of $[Pt(bipy)Cl_2]$. We find that the base hydrolysis of $[Pt(bipy)Cl_2]$ is rapid whereas that of $[Pt(phen)Cl_2]$ requires prolonged heating under reflux. The same reaction with the palladium analogues is rapid. These complexes are soluble except for $[Pd(phen)(OH)_2]$ which crystallises from the reaction mixture as pale yellow needles. The complex $[Pd(bipy)Cl_2]$ reacts with base to give a yellow solid which on drying changes to orange; satisfactory analyses could not be obtained. We find that the reactions of $[M(L)Cl_2]$ with Ag_2O are more convenient for the preparation of the dihydroxo complexes, which crystallise with 2 molecules of water of crystallisation. The electronic spectra are summarised in Table 4.

The nature of the species obtained when acid is added to $[PtL(OH)_2]$ is strongly dependent on the final pH. Addition of HX (X = NO_3 or ClO_4) to the deep orange solution of $[PtL(OH)_2]$ to give a pH of 8 does not result in an immediate colour change. However, when this solution is heated (60 °C, 1 h) or allowed to stand at room temperature for 12 h a fine red precipitate of (**5**) and (**6**) respectively separates. The slow formation of the red complex from the dihydroxo species again suggests that the structure of the former is very different to that of the monomer $[PtL(OH)_2]$.

Gillard and co-workers[13] formulated the complexes obtained on acidification of $[Pt(bipy)(OH)_2]$ to pH 4 with HX (X = NO_3, ClO_4, or BF_4) as $[Pt(bipy)(OH)(ONO_2)]$ and $[Pt(bipy)(OH)(H_2O)]X$ (X = ClO_4 or BF_4) respectively. When these preparations were repeated the i.r. spectrum of the complex obtained with nitric acid showed no bands due to co-ordinated nitrate. The spectra of the complexes using $HClO_4$ or HBF_4 show an absorption at 3 450 cm^{-1} but no absorption at 1 630 cm^{-1}, which indicates the presence of only a hydroxo group. The i.r. and electronic spectra of these complexes are identical to those of hydroxo-bridged dimers obtained by the reaction of $[Pt(bipy)Cl_2]$ with AgX (X = NO_3, ClO_4, or BF_4) in water.

The reaction of the dihydroxo compound with acid was repeated for all compounds studied (M = Pt or Pd; L = bipy or phen), and the complex isolated at pH 4 was always $[\{ML(\mu\text{-}OH)\}_2]^{2+}$.

Table 6. Acid dissociation constants of the complexes $[Pt(amine)_2(OH_2)_2]^{2+}$

		Complex		
Amine	pK_a [a]	pK_1	pK_2	Ref.
NH_3	9.25	5.6	7.3	30
en	9.91	5.8	7.6	34
dach [b]	9.77	6.1	7.6	45

[a] 25 °C; J. J. Christensen, R. M. Izatt, D. P. Wrathall, and I. D. Hansen, *J. Chem. Soc. A*, 1969, 1212. [b] *trans* Isomer.

When a solution of $[PtL(OH)_2]$ is lowered very quickly to pH 1 using HNO_3 a bright yellow solution is obtained from which the dinitrato complex can be obtained on evaporation of the solvent. It was purified by extraction into hot acetone in which it is soluble and found to be the only species produced in this reaction. Gillard and co-workers[13] also isolated $[Pt(bipy)(ONO_2)_2]$ on addition of HNO_3 to $[PtL(OH)_2]$. Addition of HNO_3 over a period of 10 min to pH 1 and evaporation of the solvent gives a mixture of the dinitrato complex and the hydroxo-bridged complex (the two compounds can easily be separated by extraction with hot acetone in which the dimer is insoluble).

Conclusions

In general nitrato groups are reactive[44] and in aqueous solution the nitrate ligand is completely displaced by a water molecule.[17] The aqua complexes thus formed behave as weak acids.[31,45,46] For a diaqua complex $[ML_2(OH_2)_2]^{2+}$ (L = any ligand) the equilibria (2) and (3) exist in solution. The aquahydroxo species

$$[ML_2(OH_2)_2]^{2+} \rightleftharpoons [ML_2(OH)(OH_2)]^{+} + H^{+} \quad (2)$$

$$[ML_2(OH)(OH_2)]^{+} \rightleftharpoons [ML_2(OH)_2] + H^{+} \quad (3)$$

formed during the first acid dissociation contains both a good ligand and a good leaving group. Thus, an alternative reaction for this species is dimerisation (or trimerisation).* The rate of dimerisation of platinum(II) complexes depends on the pH, concentration,[29,45,48,49] and probably the nature of the ligand L. For N-donor (NH_3[7] or dach[45]) and S-donor ligands (dmso, tmso, or dpso[50]) the preparation of oligomeric complexes is essentially similar, *viz.* neutralisation of the diaqua complexes to pH 6—6.5 and often storage of the solution near 0 °C for several days for complete crystallisation. The ratio of dimer/trimer depends on the temperature, concentration, pH, and the nature of the counter ion.[7,29] The pH dependence follows from the fact that the reactive species for oligomerisation is the aquahydroxo complex.

In comparison, for the hypothetical complexes $[PtL(OH_2)_2]^{2+}$ (L = bipy or phen) the rate of dimer formation is considerably faster than for amine analogues, and there is no indication of the existence of a trimer. The increased reactivities of $[Pt(bipy)Cl_2]$ and $[Pt(phen)Cl_2]$ with respect to $[Pt(en)Cl_2)]$ has been observed by Conrad and Rund[51] and Haake and Cronin[52] and was rationalised on the basis that bond making dominates the transition state. The pK_a values for some $[Pt(amine)_2(OH_2)_2]^{2+}$ complexes are summarised in Table 6. In acidic media these aqua complexes are fully

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* Rochon *et al.*[47] reported the isolation of a tetramer for the Pt(en) system.

Table 7. Elemental analyses

		Analysis*/%			
Complex	Colour	C	H	N	O
$[Pt(bipy)I_2]$	Bright yellow	19.6	1.3	4.5	
		(19.8)	(1.3)	(4.6)	
$[Pt(phen)I_2]\cdot H_2O$	Bright yellow	21.6	1.1	4.3	
		(22.3)	(1.2)	(4.3)	
$[Pt(bipy)(ONO_2)_2]$	Yellow	25.1	1.7	11.5	
		(25.3)	(1.7)	(11.7)	
$[Pt(phen)(ONO_2)_2]$	Yellow	28.4	1.6	10.9	
		(28.8)	(1.6)	(11.2)	
$[Pd(bipy)(ONO_2)_2]\cdot 0.5H_2O$	Orange	30.4	2.2	14.2	
		(30.3)	(2.3)	(14.2)	
$[Pd(phen)(ONO_2)_2]$	Orange	35.1	1.9	13.4	23.3
		(35.1)	(1.9)	(13.6)	(23.4)
$[\{Pt(bipy)(\mu\text{-}OH)\}_2][NO_3]_2\cdot 0.5H_2O$	Bright orange	27.2	2.1	9.5	
		(27.3)	(2.3)	(9.5)	
$[\{Pt(bipy)(\mu\text{-}OH)\}_2][ClO_4]_2$	Bright orange	25.5	2.1	6.1	
		(25.7)	(1.9)	(6.0)	
$[\{Pt(bipy)(\mu\text{-}OH)\}_2][BF_4]_2$	Bright orange	26.0	2.0	6.6	
		(26.4)	(2.0)	(6.2)	
$[\{Pt(phen)(\mu\text{-}OH)\}_2][NO_3]_2$	Bright yellow	31.4	1.9	9.1	
		(31.7)	(2.0)	(9.2)	
$[\{Pt(phen)(\mu\text{-}OH)\}_2][ClO_4]_2$	Orange	29.5	1.8	5.9	
		(29.3)	(1.8)	(5.7)	
$[\{Pd(bipy)(\mu\text{-}OH)\}_2][NO_3]_2$	Pale yellow	34.5	2.7	11.6	
		(35.0)	(2.6)	(11.6)	
$[\{Pd(bipy)(\mu\text{-}OH)\}_2][ClO_4]_2$	Pale yellow	31.5	2.3	7.4	
		(31.6)	(2.4)	(7.3)	
$[\{Pd(phen)(\mu\text{-}OH)\}_2][NO_3]_2$	Pale yellow	39.0	2.3	11.3	17.8
		(39.4)	(2.5)	(11.5)	(17.6)
$[\{Pd(phen)(\mu\text{-}OH)\}_2][ClO_4]_2$	Pale yellow	35.6	2.2	6.9	
		(35.8)	(2.3)	(7.0)	
$[Pt(bipy)(OH)_2]\cdot 2.5H_2O$	Orange	27.5	2.9	6.0	17.2
		(27.9)	(3.5)	(6.5)	(16.8)
$[Pd(bipy)(OH)_2]\cdot 2H_2O$	Yellow	35.5	3.6	8.3	21.6
		(36)	(4.2)	(8.4)	(21.1)
$[Pd(phen)(OH)_2]\cdot 2H_2O$	Yellow	40.5	3.9	7.8	
		(40.4)	(3.9)	(7.8)	
$[Pt_2(bipy)_2(\mu\text{-}OH)_3]NO_3\cdot 2H_2O$	Red	28.9	2.70	8.2	15.8
		(28.3)	(2.75)	(8.2)	(15.0)
$[Pt_2(bipy)_2(\mu\text{-}OH)_3]ClO_4\cdot 4H_2O$	Red	26.4	2.0	6.2	15.9
		(26.5)	(2.7)	(6.2)	(17.6)
$[Pt_2(phen)_2(\mu\text{-}OH)_3]ClO_4\cdot 5H_2O$	Red	29.0	2.1	5.7	
		(29.1)	(2.9)	(5.7)	

* Theoretical values in parentheses.

protonated and stable. Oligomer formation is not observed[4,45,48] until pH > 3 as the ionisation of the first aqua ligand begins to change the distribution of the species in solution. The bipy and phen complexes are completely dimerised at *ca.* pH 2 {the natural pH of a solution of $[ML(ONO_2)_2]$ in water}, indicating that the first ionisation is already complete and that the complexes $[ML(OH_2)_2]^{2+}$ are considerably more acidic than the analogues with amine ligands. Perhaps the diaqua complexes can be stabilised in concentrated acidic media but we have not yet demonstrated this possibility.

There have been several reports on the isolation and reactions of '$[ML(OH_2)_2]^{2+}$' (M = Pd or Pt; L = bipy or phen).[4,12,53,54] Examination of the various experimental methods and spectroscopic properties invariably indicates that the dimer $[LM(\mu\text{-}OH)_2ML]^{2+}$ was actually studied.

Experimental

Infrared spectra were recorded (4 000—200 cm^{-1}) on a Perkin-Elmer 983 spectrophotometer using both Nujol mulls (CsI plates) and alkali halide discs. Electronic spectra were recorded on a Varian Cary 2300 spectrophotometer at room temperature. Conductance measurements in water were made at 25 °C with a Beckman conductivity bridge. The C, H, N, and O analyses were carried out by the Interuniversity Microanalytical Services, Ecole Nationale Supérieure de Chimie de Toulouse. Proton-decoupled ^{195}Pt n.m.r. spectra were recorded at 53.65 MHz in D_2O on a WH-250 Bruker Fourier-transform spectrometer at 323 K, pulse width 20 μs, using H_2PtCl_6 in D_2O as external reference at 53 770 768 MHz. Data were collected on freshly prepared samples. The ^1H (250.13 MHz) and ^{13}C (62.89 MHz) (323 K) n.m.r. spectra in D_2O were run on a WH-250 Bruker Fourier spectrometer.

Preparation of Complexes.—$[Pd(L)Cl_2]$.[55] 2,2′-Bipyridine (0.48 g, 3.09 mmol) or 1,10-phenanthroline (0.56 g, 3.31 mmol) dissolved in acetonitrile was added to a hot filtered solution of $PdCl_2$ (0.55 g, 3.0 mmol) in acetonitrile. The orange needles of $[Pd(L)Cl_2]$, which separated on cooling, were filtered off, washed with acetonitrile, acetone, and dried *in vacuo*. The yield was almost quantitative. This method is preferred to that using

$K_2[PdCl_4]$ in water[56] as the formation of the double salt $[PdL_2][PdCl_4]$ is avoided.

$[Pt(L)Cl_2]$. This complex was prepared by heating $K_2[PtCl_4]$ with L in dilute hydrochloric acid.[22,51]

$[Pt(bipy)I_2]$. Morgan and Burstall[22] described a preparation of $[Pt(bipy)I_2]$. This involves the preparation of $[Pt(bipy)_2]I_2$ which dissociates on heating to give $[Pt(bipy)I_2]$ and bipy. However, using this method we found that the separation of $[Pt(bipy)I_2]$ from bipy was not obvious and several extractions with hot diethyl ether were necessary to remove the bipy. The complex $[Pt(bipy)I_2]$ can easily be prepared in good yield *via* the base hydrolysis of $[Pt(bipy)Cl_2]$.

The complex $[Pt(bipy)Cl_2]$ (0.63 g, 1.5 mmol) was heated in sodium hydroxide solution (0.2 g in 50 cm^3) to form a golden yellow solution. Silver nitrate was added to the cooled solution to precipitate the chloride as AgCl until the solid turned black due to the onset of the formation of the more soluble Ag_2O. The solids were removed, an excess of KI was added, and the resulting mixture adjusted to pH 3 using nitric acid whereupon a green-yellow complex separated. The solid was collected and then heated in ethanol (96%) until it gradually became yellow, and the supernatant orange. The di-iodo complex was isolated, washed liberally with water and ethanol, and dried *in vacuo*. The yield was almost quantitative.

The complex $[Pt(phen)I_2]$ was prepared in similar manner. The base hydrolysis of $[Pt(phen)Cl_2]$ was slower and heating under reflux for 3 h was necessary for complete reaction. The product separated as a bright yellow solid and no impurities such as are found in the preparation of $[Pt(bipy)I_2]$ were observed.

$[PtL(ONO_2)_2]$ (L = bipy *or* phen). Finely ground $AgNO_3$ (340 mg, 2.05 mmol) was added to a suspension of $[Pt(L)I_2]$ (1.0 mmol) in acetone (65 cm^3) and the mixture stirred vigorously for 30 min. The volume was then increased to 170 cm^3 with acetone and the precipitate of AgI was removed by filtration of the hot solution through cellulose. The product was obtained as yellow microcrystals (75%) by concentrating the solution. It can be recrystallised from hot acetone.

$[PdL(ONO_2)_2]$ (L = bipy *or* phen). Silver nitrate (340 mg, 2.0 mmol) in the minimum amount of water was added to a warm suspension of $[Pd(L)Cl_2]$ (1.0 mmol) in dilute nitric acid (pH 1, 90 cm^3). The precipitation of AgCl commenced immediately. The mixture was stirred for 20 min, and the AgCl removed by centrifugation of the hot solution. The pale yellow solution was evaporated to dryness. The complex was recrystallised from hot nitric acid (pH 1).

$[\{PtL(\mu\text{-}OH)\}_2][NO_3]_2$ (L = bipy *or* phen). A mixture of $[Pt(L)Cl_2]$ (1.0 mmol) and $AgNO_3$ (340 mg, 2.0 mmol) in water (65 cm^3) was heated (60 °C) with stirring for 30 min. The precipitate of AgCl was removed from the hot solution by centrifugation and the resulting orange solution concentrated to 40 cm^3. The product (75—80%) crystallised as fine needles which were separated, washed with cold water, and dried *in vacuo*.

$[\{PdL(\mu\text{-}OH)\}_2][NO_3]_2$ (L = bipy *or* phen). These complexes were prepared in a similar manner as for $[PdL(ONO_2)_2]$, except that the reaction was carried out in water. The precipitate of silver chloride was removed from the hot solution, from which the dimer separated on cooling as a fawn-yellow fibrous precipitate. The product (80%) was collected, washed with cold water, and dried *in vacuo*.

When the dinitrato complex $[ML(ONO_2)_2]$ was dissolved in a minimum amount of hot water and the solution cooled to room temperature, the hydroxo-bridged dimer separated in quantitative yield.

$[\{ML(\mu\text{-}OH)\}_2]X_2$ (M = Pd *or* Pt; L = bipy *or* phen; X = ClO_4 *or* BF_4). An aqueous solution of NaX (X = ClO_4 or BF_4) was added to a hot aqueous solution of $[\{ML(\mu\text{-}OH)\}_2][NO_3]_2$. After cooling to room temperature, the solid was collected, washed with cold water, and dried *in vacuo*.

$[Pt(phen)(OH)_2]\cdot 2H_2O$. A suspension of $[Pt(phen)Cl_2]$ (115 mg, 0.26 mmol) in hot water (30 cm^3) was treated with Ag_2O (59 mg, 0.26 mmol) and the mixture heated with stirring for 1 h. The precipitate of AgCl was removed, the orange solution concentrated to 1 cm^3, and acetone was added to precipitate the product. The complex (60%) was collected, washed with acetone and ether, and dried *in vacuo*.

The complex $[Pt(bipy)(OH)_2]\cdot 2.5H_2O$ was prepared by the same method except that the reaction was carried out under slightly basic conditions to prevent formation of the red complex. Yield: 60%. The complex $[Pd(bipy)(OH)_2]\cdot 2H_2O$ was prepared in a similar manner but the mixture of Ag_2O and $[Pd(bipy)Cl_2]$ was stirred for 15 min. Yield: 80%.

$[Pd(phen)(OH)_2]\cdot 2H_2O$. To a hot suspension of $[Pd(phen)Cl_2]$ (145 mg, 0.40 mol) in water (30 cm^3) was added a solution of sodium hydroxide (75 mg, 1.8 mmol). The original suspension gradually dissolved to form a light yellow solution. Silver nitrate (147 mg, 0.87 mmol) dissolved in the minimum amount of water was added, the precipitate of AgCl removed, and the solution concentrated to 5 cm^3. The yellow needles (80%) that separated were collected, washed with cold water, and dried *in vacuo*.

$[Pt_2L_2(\mu\text{-}OH)_3]ClO_4$. The method of synthesis for L = bipy or phen is similar and is described for the phen complex.

(*a*) The complex $[Pt(phen)Cl_2]$ (130 mg, 0.28 mmol) was heated in a solution of sodium hydroxide (pH 13.5) until the initial suspension dissolved to give an orange solution (3 h). A concentrated solution of $AgClO_4$ (128 mg, 0.567 mmol) was added and the precipitate of AgCl removed. The resulting solution was adjusted to pH 8 with perchloric acid. The orange-red solution obtained was allowed to stand at room temperature for 48 h and the red precipitate was collected, washed with water, and dried *in vacuo*. The complex as the nitrate salt was prepared by the same method, except that $AgNO_3$ was used to remove the chloride ions and the pH of the solution was adjusted with HNO_3.

(*b*) Treatment of a solution of $[\{Pt(phen)(\mu\text{-}OH)\}_2][NO_3]_2$ (0.3 mmol) in water (20 cm^3) with base to pH 7.5—9 gave a deep red solution from which the red complex precipitated after 10 min. The solid was isolated, washed with water, and dried *in vacuo*. The perchlorate salt was prepared by redissolving the nitrate complex in the mother-liquor by warming and adding a concentrated solution of $NaClO_4$ whereupon $[Pt_2(bipy)_2(\mu\text{-}OH)_3]ClO_4$ precipitated.

Method (*a*) for preparing the red complexes as the perchlorate salts is preferred as the product obtained from method (*b*) was often contaminated with the nitrate salt.

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