Palladium(II) co-ordination by linear *N*-methylated polyamines: a solution and solid-state study

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Palladium(II) co-ordination by the tertiary polyamines 2,5,8-trimethyl-2,5,8-triazanonane, 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane, 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane, 2,6,9,13-tetramethyl-2,6,9,13-tetra-azatetradecane, 2,5,8,11,14-pentamethyl-2,5,8,11,14-pentaazapentadecane, 2,5,8,11,14,17-hexamethyl-2,5,8,11,14,17-hexaazaoctadecane and by the new compound 2,5,8,11,14,17,20,23-octamethyl-2,5,8,11,14,17,20,23-octaazatetracosane has been investigated by means of potentiometric (0.1 M NMe$_4$Cl aqueous solution, 298.1 K) and spectrophotometric measurements. The species present in solution and their stability constants have been determined. The first five amines form only mononuclear complexes, while the last two can give both mono- and bi-nuclear complexes in aqueous solution. The thermodynamic data show that the complexes with *N*-methylated polyamines are tremendously less stable than their non-methylated counterparts. The UV/VIS spectra of the complexes exhibit a marked red shift of the L→M charge-transfer bands with respect to the complexes of the non-methylated ligands. As a consequence of the reduced thermodynamic stability, both mono- and bi-nuclear complexes show a particular acid–base behavior with respect to those of the non-methylated amines. Such complexes can easily bind a proton or a hydroxide anion in aqueous solution, with consequent detachment of a co-ordinated nitrogen. The crystal structures of two binuclear complexes were determined. In both the metals show distorted square-planar arrangements of the donors.
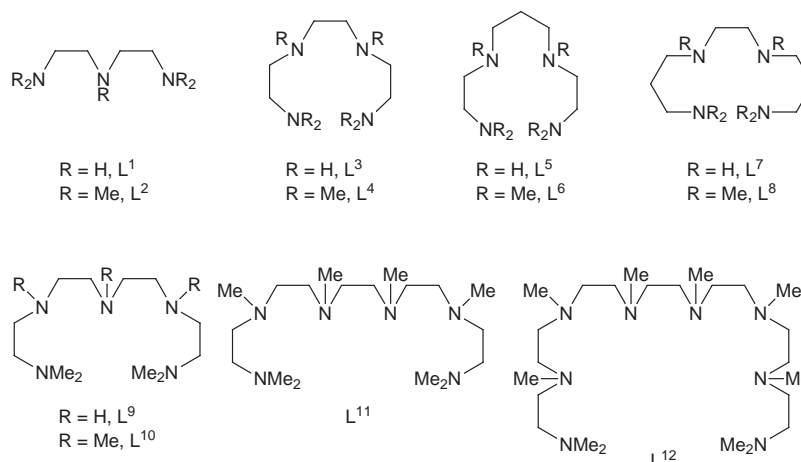
There is a current interest in the chemistry of cyclic and acyclic polyamines because of their special ligational properties which give rise to both anion and cation complexation.[1] The presence in such molecules of large numbers of amine groups allows the modulation of their co-ordinative characteristics through nitrogen functionalization.[2–5]

Recently, it has been shown that nitrogen methylation produces significant changes in the cation binding features of both open-chain and macrocyclic polyamine ligands.[6–9] In particular, we analysed copper(II) complexation with linear polyamines L^2, L^4, L^6, L^8, L^{10} and L^{11}.[8] All these form 1:1 complexes. In the case of the tetraamines L^4, L^6 and L^8 the metal is four-co-ordinated by the tertiary nitrogens, while L^{10} and L^{11} are pentadentate in their complexes.

It was found that the copper(II) complexes with *N*-methylated ligands are considerably less stable than the corresponding complexes with the non-methylated ones. This was mainly attributed to the poorer solvation of the *N*-methylated complexes. The effect of *N*-methylation on the solvation of the complexes is due to two factors. (1) The absence of Cu−N−H · · · O hydrogen bonds to the solvent for the *N*-methylated complexes decreases the σ-donating ability of the nitrogen donors, as the hydrogen bonds increase the electron density on the nitrogen atoms, thus making them better σ donors. Moreover, the absence of the hydrogen bonds reduces the charge transfer from the metal ion to the solvent, destabilizing the copper(II) complexes. (2) The *N*-methylation considerably increases the radii of the complexes, thus decreasing their solvation energy. Furthermore, the stability of the copper(II) complexes is also affected by the strain due to *N*-methylation on the ligand backbone when all the nitrogens are bound to the central copper.

The aim of the present paper is to shed further light on how these factors may affect the co-ordination ability of *N*-methyl-

R$_2$N, N(R), NR$_2$
R = H, L^1
R = Me, L^2

R = H, L^3
R = Me, L^4

R = H, L^5
R = Me, L^6

R = H, L^7
R = Me, L^8

R = H, L^9
R = Me, L^{10}

L^{11}

L^{12}

Table 1 Stability constants of palladium(II) complexes with polymethylated polyamines, determined by potentiometric measurements (0.1 M NMe$_4$Cl, 298.1 K)^a

Reaction^c	log K with ligand^b							
	L^1	L^2	L^3	L^4	L^5	L^6	L^8	L^{10}
Pd + L ⇌ PdL			40.1^{d,e}	23.38(6)^f	46.3^d	28.3(1)	22.95(2)	21.41
PdL + Cl + H ⇌ PdCl(HL)				6.85(7)		3.6(1)	9.30(2)	
PdCl(HL) + H + Cl ⇌ PdCl$_2$(H$_2$L)							4.52(1)	
PdL + H ⇌ Pd(HL)								8.68(7)
Pd(HL) + H + Cl ⇌ PdCl(H$_2$L)								5.76(6)
Pd + L + Cl ⇌ PdClL	35.2^g	24.9(1)						
Pd + L + H$_2$O ⇌ PdL(OH) + H		14.1(1)		13.9(1)		16.9(1)	13.96(2)	10.95(7)
PdL + OH ⇌ PdL(OH)				4.3(1)		2.4(1)	4.84(2)	3.4(1)

^{a} Stability constants of the chloride complexes with Pd^{II}: Pd + Cl ⇌ PdCl, log K = 3.48; Pd + 2Cl ⇌ PdCl$_2$, log K = 6.27; Pd + 3Cl ⇌ PdCl$_3$, log K = 8.62; Pd + 4Cl ⇌ PdCl$_4$, log K = 9.72 (from ref. 15). ^{b} Protonation constants of methylated ligands are from refs. 8(a) and 8(b). Protonation constants of L^{12}: log K_1 = 9.86(1), log K_2 = 8.78(1), log K_3 = 8.24(1), log K_4 = 7.58(1), log K_5 = 5.91(2), log K_6 = 3.37(2), log K_7 = 2.05(2). K_x = [H$_x$L^{x+}]/[H$_{x-1}$L$^{(x-1)+}$] [H$^+$]. ^{c} Charges omitted for clarity. ^{d} From ref. 13(b) (1 M NaClO$_4$). ^{e} L^3 can also form a protonated [Pd(HL)X] species (X = Br$^-$ or SCN$^-$) in 1 M KBr or 0.1 M NaSCN aqueous solution. log K = 40.1, K = [PdX(HL)]/[Pd][X][H][L] (X = SCN$^-$ or Br$^-$) (from ref. 3). ^{f} Values in parentheses are standard deviations on the last significant figure. ^{g} From ref. 13(a) (1 M NaClO$_4$).

ated ligands toward metal ions with different stereochemical requirements than those of Cu^{II}. In particular, we have chosen Pd^{II} because this metal usually imposes its own stereochemical requirements on ligands.[10–14] A further interest in palladium(II) complexes is the ability of this metal to form polynuclear complexes with ligands containing six or more nitrogen donors.[11,12] For example, the macrocyclic octaamine 1,4,7,10,13,16,19,22-octaazacyclotetracosane, [24]aneN$_8$, can form a binuclear palladium(II) complex.[11c] In order to investigate the formation and the structural characteristic of polynuclear palladium(II) complexes with ligands with tertiary amine groups we have also synthesized the ligand L^{12}, which contains eight tertiary nitrogens.

Results and Discussion

Solution studies

Palladium(II) complex stability. As encountered in other investigations of palladium(II) complexes,[11] it is difficult to determine the stability of the complexes of this metal with polyamines because the aqua-ion undergoes hydrolysis even at pH 1, and its complexes are too stable to be investigated using the customary pH method. As a consequence, thermodynamic data for the binding of Pd^{II} in aqueous solution by amine ligands are rare.[11,13,14] Fortunately, in 0.1 M NMe$_4$Cl solution at acidic pH values, PdCl$_4$$^{2-}$ is in equilibrium with the palladium(II) complexes with polyamines.[15] Using Cl$^-$ as competing ligand, exchange equilibria can be followed both by spectrophotometry and by alkalimetric titrations. The speciation of the complexes was determined in 0.1 M NMe$_4$Cl aqueous solution by computer analysis of the pH-metric data using the HYPERQUAD[16] program. The calculated equilibrium constants are listed in Tables 1 and 2. Table 1 also reports the stability constants for the complexes with the non-methylated ligands L^1, L^3 and L^5, which have been determined by Anderegg.[13] Ligands containing up to five nitrogen donors form only mononuclear complexes in aqueous solution (Table 1), while L^{11} and L^{12}, containing six and eight nitrogens respectively, can form both mono- and bi-nuclear complexes (Table 2). Considering the mononuclear complexes, all the N-methylated ligands show similar binding features toward Pd^{II} giving [PdL]$^{2+}$ species in aqueous solution. Only L^{11} does not give such a complex, due to the formation of stable mono- and di-protonated species, [Pd(HL)]$^{3+}$ and [Pd(H$_2$L)]$^{4+}$, at neutral pH.

The results in Table 1 clearly show that N-methylation of the ligands induces a tremendous destabilization of the palladium(II) complexes. The complexes of L^2, L^4 and L^6 are many orders of magnitude less stable than the corresponding complexes with the unmethylated L^1, L^3 and L^5 ligands. In

Table 2 Stability constants of palladium(II) complexes with polymethylated polyamines L^{11} and L^{12}, determined by potentiometric measurements 0.1 M (NMe$_4$Cl, 298.1 K)

| Reaction^a	log K	
	L^{11}	L^{12}
Pd + L ⇌ PdL		22.85(8)^b
Pd + L + H ⇌ Pd(HL)	30.83(6)	
Pd(HL) + H ⇌ Pd(H$_2$L)	7.16(5)	
Pd + L + H$_2$O ⇌ PdL(OH) + H	10.75(8)	
PdL + 3H ⇌ Pd(H$_3$L)		22.68(8)
2Pd + L + 2Cl ⇌ Pd$_2$Cl$_2$L	44.0(1)	
Pd$_2$LCl$_2$ + H + Cl ⇌ Pd$_2$Cl$_3$(HL)	5.8(1)	
2Pd + L + Cl + H$_2$O ⇌ Pd$_2$ClL(OH) + H	33.9(1)	
2Pd + L ⇌ Pd$_2$L		44.7(1)
Pd$_2$L + H + Cl ⇌ Pd$_2$Cl(HL)		6.5(1)
Pd$_2$(HL)Cl + H + Cl ⇌ Pd$_2$Cl(H$_2$L)		5.8(1)
Pd$_2$L + 2OH ⇌ Pd$_2$L(OH)$_2$		8.8(1)

^{a} Charges omitted for clarity. ^{b} Values in parentheses are standard deviations on the last significant figure.

order to obtain further insight into the source of the effect of N-methylation the UV spectra were recorded. The spectral features of the [PdL]$^{2+}$ complexes are summarized in Table 3, together with those of the binuclear complex of L^{12}. The percentage of the [PdL^6]$^{2+}$ complex is too low at any pH value (less than 50%) to determine confidently its spectral characteristics, while L^2 and L^{11} do not form [PdL]$^{2+}$ species in aqueous solution. The UV spectra of the [PdL]$^{2+}$ complexes are pH dependent, due to their protonation or hydroxide binding. As an example, Fig. 1 shows the spectra recorded in 0.1 M NMe$_4$Cl solutions containing L^4 and Pd^{II} in equimolar ratio at different pH values, together with the spectrum of the [PdL^3]$^{2+}$ complex. As shown by the distribution diagram in Fig. 2, the spectrum recorded at pH 7.8 can be attributed to the [PdL^4]$^{2+}$ complex, which is the only species present in solution at this pH. Comparing the [PdL^4]$^{2+}$ spectrum with that of its non-methylated counterpart, [PdL^3]$^{2+}$, there is a remarkable red shift of the band attributed to a charge-transfer transition from 295 nm for [PdL^3]$^{2+}$ to 320 nm for [PdL^4]$^{2+}$. As summarized in Table 3, a similar behavior is found for the other complexes with polyamine ligands of this series, indicating that N-methylation of ligands induces a marked red shift of the L→M charge-transfer bands. This red shift stems probably from an anodic shift of the redox potentials of the corresponding palladium-(II) and -(I) complexes[8] which cannot be observed experimentally in aqueous solution.

Similar thermodynamic and spectroscopic considerations can be also made for methylated ligands containing more than

Table 3 The UV/VIS data of the palladium(II) complexes

	$[PdL^3]^{2+}$	$[PdL^4]^{2+}$	$[PdL^5]^{2+}$	$[PdL^6]^{2+}$	$[PdL^9]^{2+}$	$[PdL^{10}]^{2+}$	$[Pd_2L^{12}]^{4+}$
λ/nm	295	320	284	316	298	324	320
$\varepsilon/M^{-1}\,cm^{-1}$	800	1800	410	830	720	1280	3830
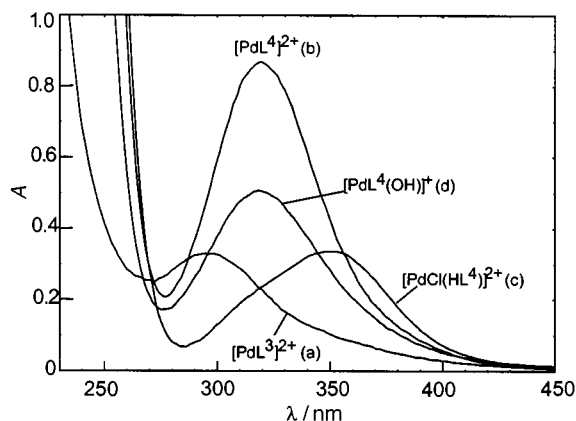
Fig. 1 Charge-transfer absorption bands of the palladium(II) complexes with L^3 and L^4 in 0.1 M NMe$_4$Cl aqueous solution: (a) $[PdL^3]^{2+}$: $[Pd^{2+}] = [L^3] = 4.3 \times 10^{-4}$, (b) $[PdL^4]^{2+}$: $[Pd^{2+}] = [L^4] = 4.3 \times 10^{-4}$, pH 7.8; (c) $[PdCl(HL^4)]^{2+}$: $[Pd^{2+}] = [L^4] = 4.3 \times 10^{-4}$, pH 2.9; (d) $[PdL^4-(OH)]^{+}$: $[Pd^{2+}] = [L^4] = 4.3 \times 10^{-4}$ M, pH 11.5
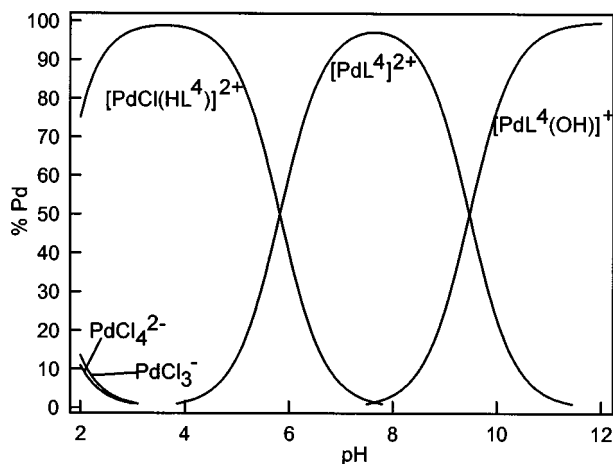
Fig. 2 Distribution diagram of the species for the system L^4–Pd^{II} (0.1 M NMe$_4$Cl, 298.1 K, $[L^4] = 1 \times 10^{-3}$, $[Pd^{2+}] = 1 \times 10^{-3}$ M)

four nitrogen donors. Actually both the mononuclear $[PdL^{10}]^{2+}$ and $[PdL^{12}]^{2+}$ complexes show thermodynamic stability and spectral features similar to those found for the L^4 and L^6 complexes (Tables 1 and 3), indicating that in both complexes the palladium(II) ion is four-co-ordinated by a N$_4$ moiety.

The reduced thermodynamic stability of the palladium(II) complexes and the red energy shift of their charge-transfer bands can be ascribed to decreased solvation of the complexes with tertiary amine ligands and to the poorer σ-donating ability of these ligands in comparison with secondary and primary amine ligands.[8] The effect of *N*-methylation on the σ-donating properties of the non-bonding electron pairs of the nitrogens can be attributed to two main factors: the effect of the M–N–H···O hydrogen bonds to the solvent on the σ-donating properties of primary and secondary amines (absence of this effect in tertiary nitrogens ligands make them weaker σ donors); steric hindrance due to the insertion of methyl groups within the ligand framework which can cause elongation of the M–N bond as well as distortions of the co-ordination sphere of Pd^{II} in its complexes and thus reduces their stabilities.

As noted above, *N*-methylation also leads to a decrease of

the stability of the copper(II) complexes with linear amines. However, it should be noted that this decrease in the thermodynamic stability constants is more pronounced for the palladium(II) complexes. For instance, *N*-methylation of L^3 reduces the stability constant of its copper(II) complex by *ca.* 7 log units (log $K = 20.1$ for $[CuL^3]^{2+}$, 12.6 for $[CuL^4]^{2+}$),[8] while the palladium(II) complex of L^4 is almost eighteen orders of magnitude less stable than the L^3 complex (Table 1). Such a different behavior for the complexes of Cu^{II} and Pd^{II} may be ascribed to the higher tendency of Pd^{II} to impose its own geometry on the ligands. Indeed, *N*-methylation leads to a molecular crowding and stiffening of polyamines. Such an increased rigidity reduces the ability of ligands to adapt to the stereochemical requirements of Pd^{II}, which are much stricter than those of Cu^{II}. Therefore, *N*-methylation produces a larger decrease in thermodynamic stability in palladium(II) than in copper(II) complexes.

Acid–base behavior of the complexes. The reduced thermodynamic stability of the palladium(II) complexes and the weakening of the Pd–N bonds in tertiary polyamines remarkably affect their acid–base behavior. The ability of these complexes to bind protons or hydroxides has been analysed by means of both potentiometric and spectrophotometric measurements. All the complexes with tertiary amines show a marked tendency to form protonated species, as shown in Tables 1 and 2. In the case of the tetraamines L^4, L^6 and L^8 the formation of a mono-protonated $[PdCl(HL)]^{2+}$ species is observed in aqueous solution and L^8 can also form a diprotonated $[PdCl_2(H_2L)]^{2+}$ species at strong acidic pH. Table 1 also reveals that the metal complexes with the methylated ligands display a higher tendency to protonation than do the corresponding unmethylated ones. Among the complexes with the unmethylated ligands L^1, L^3 and L^5, only $[PdL^3]^{2+}$ can bind a proton, only at strong acidic pH,[13b] while the analogous complexes with the corresponding methylated ligands protonate at neutral or slight acidic pH values. The distribution diagram for the system Pd^{II}/L^4 (Fig. 2) shows that protonation of the complex takes place at neutral pH.

Since in the $[PdL]^{2+}$ species the metal is co-ordinated by four amine groups, in the case of the L^4, L^6 and L^8 complexes protonation of the $[PdL]^{2+}$ complex implies detachment of a nitrogen donor and co-ordination of one chloride ion in NMe$_4$Cl aqueous solutions to give a $[PdCl(HL)]^{2+}$ species. As shown in Fig. 1, the spectrum recorded at pH 3.0, {at which $[PdCl-(HL^4)]^{2+}$ species is largely prevalent in solution, see Fig. 2} exhibits a marked red shift of the charge-transfer band ($\lambda_{max} = 355$ nm) with respect to the $[PdL^4]^{2+}$ spectrum ($\lambda_{max} = 320$ nm), as expected for the replacement of a tertiary nitrogen donor with a chloride anion, which is a better electron donor. Similar spectral features are also observed for the $[PdCl(HL)]^{2+}$ complexes formed by the ligands L^6 and L^8 {$\lambda_{max} = 353$ and 360 nm for $[PdCl(HL^6)]^{2+}$ and $[PdCl(HL^8)]^{2+}$, respectively}. The spectral features of the latter complexes are similar to those found for the palladium(II) complex of L^2 ($\lambda_{max} = 350$ nm), which forms only a $[PdClL^2]^{+}$ species at neutral as well as at acidic pH. In this complex the metal is bound by the triamine ligand and one chloride anion. As a consequence a similar co-ordination environment can be proposed for the protonated $[PdCl(HL)]^{2+}$ complexes (L = L^4, L^6 or L^8). In other words, protonation of the ligand is accomplished with the opening of the terminal chelate ring and chloride co-ordination to form the $[PdCl(HL)]^{2+}$ complex, as in Scheme 1.

The mononuclear complexes with ligands L^{10}, L^{11} and L^{12},
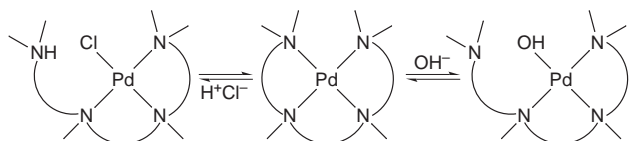
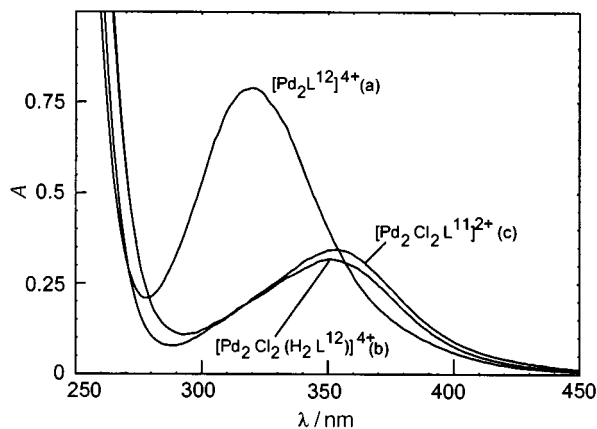**Scheme 1** Proposed mechanism for proton and hydroxide binding by palladium(II) complexes with methylated tetraamines
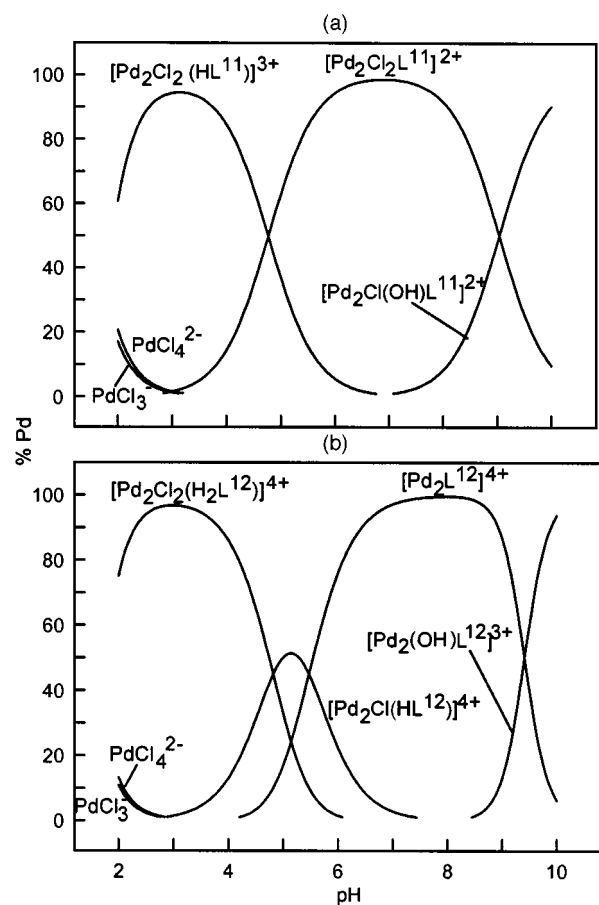
Fig. 3 Distribution diagrams of the species for the systems (a) L^{11}–Pd^{II} and (b) L^{12}–Pd^{II} (0.1 M NMe$_4$Cl, 298.1 K, [L] = 1 × 10^{-3}, [Pd^{2+}] = 2 × 10^{-3} M) as a function of pH

Fig. 4 Charge-transfer absorption bands of the binuclear palladium(II) complexes in 0.1 M NMe$_4$Cl aqueous solution: (a) [Pd$_2$L^{12}]$^{4+}$: [Pd^{2+}] = 4.1 × 10^{-4}, [L^{12}] = 2.05 × 10^{-4}, pH 6.9; (b) [Pd$_2$Cl$_2$(H$_2$L^{12})]$^{4+}$: [Pd^{2+}] = 4.1 × 10^{-4}, [L^{12}] = 2.05 × 10^{-4}, pH 2.7; (c) [Pd$_2$Cl$_2$L^{11}]$^{2+}$: [Pd^{2+}] = [L^{11}] = 2.4 × 10^{-4} M, pH 7.3

which contain more than four nitrogens show a somewhat different behavior. In their [PdL]$^{2+}$ complexes one (L^{10}) or more amine groups (L^{11} and L^{12}) are not bound to the metal and facile protonation occurs on nitrogens not involved in co-ordination, giving [Pd(H$_x$L)]$^{(2+x)+}$ species.

As shown in Table 1, all *N*-methylated ligands give hydroxylated [PdL(OH)]$^+$ species at alkaline pH. On the contrary, the non-methylated tetraamines L^3 and L^5 do not form such a species in aqueous solution. The higher tendency to bind OH$^-$, exhibited by *N*-methylated ligands, can again be ascribed to weakening of the Pd^{II}–N bonds, since binding of OH$^-$ likely involves detachment of one terminal nitrogen donor, as depicted in Scheme 1. The formation of [PdL(OH)]$^+$ leads to changes in the electronic spectra, with a marked reduction of molar absorbance, and a slight blue shift with respect to the [PdL]$^{2+}$ spectrum, as shown in Fig. 1 for the L^4 complex.

The formation of binuclear complexes. As shown in Table 2, the L^{11} and L^{12} ligands can give binuclear metal complexes in aqueous solutions. In both cases, these complexes are prevalent in aqueous solutions containing ligand and Pd^{II} in 1 : 2 molar ratio as shown by the distribution diagrams in Fig. 3. On the other hand these two ligands show different binding features due to the different number of nitrogens available for co-ordination. Ligand L^{11} does not contain enough nitrogen
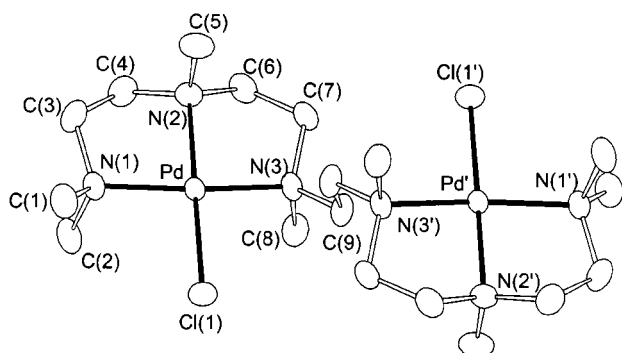
donors to fulfil the co-ordination sphere of two palladium(II) ions. As a consequence it gives a binuclear [Pd$_2$Cl$_2$L^{11}]$^{2+}$ complex in NMe$_4$Cl aqueous solutions. This species is prevalent in aqueous solutions in a wide pH range [4–9, Fig. 3(a)]. Its electronic spectrum displays a maximum at 350 nm (Fig. 4), as does the mononuclear [PdClL^2]$^+$ complex, and a ε value which is about twice that found for the latter {820 M^{-1} cm^{-1} for [PdClL^2]$^+$, *vs.* 1480 M^{-1} cm^{-1} for [Pd$_2$Cl$_2$L^{11}]$^{2+}$}. Since in [PdClL^2]$^+$ the metal ion is co-ordinated by the triamine ligand and one chloride anion, it can be assumed that in the binuclear [Pd$_2$Cl$_2$L^{11}]$^{2+}$ complex L^{11} behaves as two tridentate ligands. Each metal is co-ordinated by a triamine unit and a chloride anion, as confirmed by the crystal structure of the [Pd$_2$Cl$_2$L^{11}]-[ClO$_4$]$_2$ complex (see below).

A similar palladium(II) complex is formed by the macrocyclic hexamine ligand [18]aneN$_6$, which contains six secondary nitrogens.[11a,c] In [Pd$_2$Cl$_2$([18]aneN$_6$)]$^{2+}$ each metal has a N$_3$Cl co-ordination environment. Although in this complex the two palladium(II) ions are kept in close proximity by the macrocyclic framework, it shows a remarkably higher stability than [Pd$_2$Cl$_2$L^{11}]$^{2+}$ {log K = 51.8 for [Pd$_2$Cl$_2$([18]aneN$_6$)]$^{2+}$ *vs.* log K = 44.0 for [Pd$_2$Cl$_2$L^{11}]$^{2+}$}.[11c] Such a decrease in thermodynamic stability can be reasonably ascribed to the tertiary nature of the nitrogen donors in L^{11}, thus indicating that *N*-methylation strongly affects the binding features of polyamine ligands also in their binuclear complexes. As far as L^{12} is concerned, it is of interest that the formation constant of the binuclear [Pd$_2$L^{12}]$^{4+}$ complex is about twice that of the mononuclear [PdL^4]$^{2+}$ complex (log K = 44.7 for the equilibrium 2Pd^{2+} + L^{12} $\rightleftharpoons$ [Pd$_2$L^{12}]$^{4+}$ *vs.* log K = 23.38 for the equilibrium Pd^{2+} + L^4 $\rightleftharpoons$ [PdL^4]$^{2+}$). Moreover, the electronic spectrum of [Pd$_2$L^{12}]$^{4+}$ shows a maximum at 320 nm (ε = 3830 M cm^{-1}), similar to that found for the mononuclear palladium(II) complexes with tetraamine ligands L^4, L^6 and L^8. These observations indicate that the binuclear palladium(II) complex of L^{12} behaves simply as two PdN$_4$ subunits linked by an ethylenic chain, without any interaction between the two metal centers. This conclusion is strongly confirmed by the crystal structure of the [Pd$_2$L^{12}]$^{4+}$ cation (see below), in which each metal is loaded in a tetraamine subunit, far apart from each other [Pd$\cdots$Pd 7.396(3) Å]. It also shows a rather distorted square-planar co-ordination environment for the metal ions, with two elongated Pd–N bonds in each tetraamine unit. These structural data confirm that *N*-methylation causes distortion of the inner co-ordination sphere and weakening of the Pd–N bonds, as proposed above for the mononuclear palladium(II) complexes on the basis of the thermodynamic results. It is to be noted that the [Pd$_2$L^{12}]$^{4+}$ species can easily add protons to give

Table 4 Selected bond lengths (Å) and angles (°) for [Pd$_2$Cl$_2$L^{11}][ClO$_4$]$_2$

Pd–N(2)	2.049(7)	Pd–N(3)	2.074(6)
Pd–N(1)	2.063(6)	Pd–Cl(1)	2.306(3)
N(2)–Pd–N(1)	86.0(3)	N(2)–Pd–Cl(1)	177.4(2)
N(2)–Pd–N(3)	86.6(3)	N(1)–Pd–Cl(1)	94.4(2)
N(1)–Pd–N(3)	165.6(3)	N(3)–Pd–Cl(1)	93.5(2)

Table 5 Selected bond lengths (Å) and angles (°) for [Pd$_2$L^{12}][ClO$_4$]$_4$·2H$_2$O

Pd–N(2)	2.04(2)	Pd–N(4)	2.12(1)
Pd–N(3)	2.05(2)	Pd–N(1)	2.14(2)
N(2)–Pd–N(3)	84.0(6)	N(2)–Pd–N(1)	85.3(6)
N(2)–Pd–N(4)	168.4(6)	N(3)–Pd–N(1)	167.9(6)
N(3)–Pd–N(4)	85.2(6)	N(4)–Pd–N(1)	105.0(6)

Fig. 5 An ORTEP drawing of the [Pd$_2$Cl$_2$L^{11}]$^{2+}$ cation

Fig. 6 An ORTEP drawing of the [Pd$_2$L^{12}]$^{4+}$ cation

the mono- and di-protonated species [Pd$_2$Cl(HL^{12})]$^{4+}$ and [Pd$_2$Cl$_2$(H$_2$L^{12})]$^{4+}$ even at slightly acidic pH. Most likely, protonation of the ligand takes place *via* terminal Pd–N bond cleavage followed by co-ordination of chloride anions. In the [Pd$_2$Cl$_2$(H$_2$L^{12})]$^{4+}$ cation each metal is likely co-ordinated by a triamine chain and a chloride anion, as found in the binuclear L^{11} complex [Pd$_2$Cl$_2$(H$_2$L^{11})]$^{4+}$. The electronic spectrum of [Pd$_2$Cl$_2$(H$_2$L^{12})]$^{4+}$ (Fig. 4) confirms this hypothesis, showing a band with λ$_{max}$ = 351 nm (ε = 1540 M^{-1} cm^{-1}). These spectral features are almost the same as those found for [Pd$_2$Cl$_2$(H$_2$L^{11})]$^{4+}$, and can be attributed, as discussed above, to the presence of N$_3$PdCl chromophores.
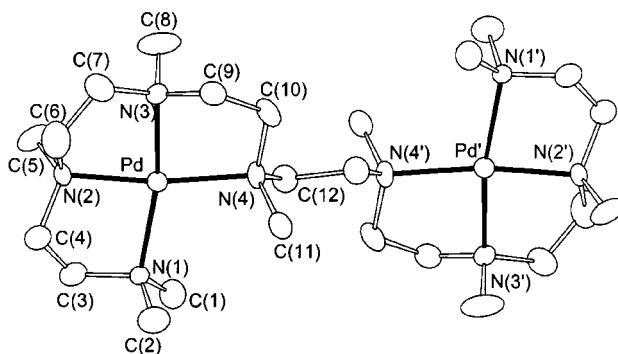
Structural studies

Crystal structure of [Pd$_2$Cl$_2$L^{11}][ClO$_4$]$_2$. The molecular structure consists of binuclear complexes [Pd$_2$Cl$_2$L^{11}]$^{2+}$ and perchlorate anions. An ORTEP[17] drawing of the cation is shown in Fig. 5 and selected bond angles and distances are reported in Table 4. Each cation lies around a crystallographic inversion center. The palladium is co-ordinated by three nitrogen atoms [N(1), N(2) and N(3)] and by the Cl(1) anion in a distorted square-planar environment; the deviations from the mean plane, defined by N(1), N(2) and N(3) and Cl(1), range from 0.018(3) Å for Cl(1) to 0.199(7) Å for N(2). The palladium atom is located 0.0639(6) Å from this plane. The overall conformation of the acyclic ligand is approximately Z-shaped, with the metal ions lying at each extremity, 6.160(3) Å from each other. Owing to the presence of the crystallographic inversion centre the chloride ions are in *trans* conformation with respect to the intermetallic axis and the two co-ordination planes are parallel and form an angle of 117.(1)° with the internuclear axis.

A similar co-ordination environment for Pd^{II} has been found in the binuclear complex with the macrocyclic ligand [18]aneN$_6$, which contains six secondary nitrogen donors connected by ethylenic chains.[11a,c] In [Pd$_2$Cl$_2$([18]aneN$_6$)]$^{2+}$ each metal is co-ordinated in a square-planar manner by three nitrogens and one Cl$^-$ anion and the two complexed moieties are staggered. The cyclic nature of the ligand results in a shorter Pd···Pd distance (3.04 Å) and a higher displacement of the metal from the co-ordination plane (0.14 Å) in comparison with the present [Pd$_2$Cl$_2$L^{11}]$^{2+}$ cation. On the other hand in [Pd$_2$Cl$_2$([18]aneN$_6$)]$^{2+}$ the Pd–N distances range from 1.99 to 2.05 Å, while in [Pd$_2$Cl$_2$L^{11}]$^{2+}$ they are somewhat longer (see Table 4). In [Pd$_2$Cl$_2$([18]aneN$_6$)]$^{2+}$ the distortions from the ideal square-

planar geometry can reasonably be attributed to the lodging of two metals within the cyclic framework of the ligand; in [Pd$_2$Cl$_2$L^{11}]$^{2+}$ the rather distorted co-ordination geometry as well as the elongation of Pd–N bond distances can be ascribed to *N*-methylation, which leads to an increased rigidity of the backbone and weakening of the Pd–N bonds.

Crystal structure of [Pd$_2$L^{12}][ClO$_4$]$_4$·2H$_2$O. The molecular structure consists of [Pd$_2$L^{12}]$^{4+}$ complex cations, perchlorate anions and water solvent molecules. An ORTEP[17] drawing of the cation is shown in Fig. 6 and selected bond angles and distances are reported in Table 5.

The conformation of the ligand is similar to that of L^{11} in the [Pd$_2$Cl$_2$L^{11}]$^{2+}$ complex; the ligand is Z-shaped and lies around a crystallographic inversion centre. The octaamine molecule behaves as two tetradentate ligands; each palladium atom is surrounded by four nitrogen atoms [N(1), N(2), N(3), N(4)] in a distorted square-planar co-ordination geometry. The deviations from the mean plane defined by the donors are lower than 0.016 Å and the metal atom lies 0.098(2) Å above this plane. The two metals are far apart from each other [7.396(3) Å], with an angle of 108.6(2)° between the Pd···Pd axis and the co-ordination planes.

A crystal structure of a binuclear palladium(II) complex with an octaamine ligand has been previously reported. In fact, the macrocycle [24]aneN$_8$ can bind two palladium ions giving the [Pd$_2$([24]aneN$_8$)][ClO$_4$]$_4$ complex which was structurally characterized.[11b] In the [Pd$_2$([24]aneN$_8$)]$^{4+}$ each metal is co-ordinated by four secondary amine groups with a rather distorted square-planar goemetry. Since the two metals are lodged inside the macrocyclic cavity the Pd···Pd distance is remarkably shorter than that found in [Pd$_2$L^{12}]$^{4+}$ (5.447 *vs.* 7.396 Å). In [Pd$_2$([24]aneN$_8$)]$^{4+}$ the Pd–N distances are in the range 1.98–2.10 Å, somewhat shorter than those found in [Pd$_2$L^{12}]$^{4+}$, which range from 2.04 to 2.14 Å (see Table 5). In particular, in [Pd$_2$L^{12}]$^{4+}$ N(1) and N(4) show longer bond distances in comparison with N(2) and N(3), and a broadened N(1)–Pd–N(4) angle. Distortion of the palladium(II) co-ordination sphere from the ideal square-planar geometry and elongation of the Pd–N distances may be ascribed to *N*-methylation of amine groups, which leads to some strain on the ligand backbone when all nitrogens are bound to the central palladium and weakening of the Pd–N bonds.

Conclusion

N-Methylation of linear polyamines causes a dramatic decrease in stability of their palladium(II) complexes, together with a marked red shift of the L→M charge-transfer band. Such effects are observed in both mono- and bi-nuclear palladium(II) complexes mainly due to the following reasons: decreased outer-sphere solvation of the complexes due to their increased radii; weaker σ-donating properties due to the exclusion of hydrogen bonds of the type Pd−N−H · · · O; distortion of the inner co-ordination sphere and/or Pd−N bond elongation. These conclusions are supported by the crystal structures of the [Pd₂Cl₂L¹¹]²⁺ and [Pd₂L¹²]⁴⁺ binuclear complexes, which show the metal ions in distorted square-planar co-ordination environments. The distortion from the ideal square-planar geometry can be attributed to molecular crowding and stiffening of ligands, due to *N*-methylation.

The increased molecular rigidity, due to *N*-methylation, leads to a reduced ability of the ligands to adapt to steric requirements of metals. Palladium(II) has a marked tendency to impose its own geometry on ligands. Therefore, as a consequence of the increased molecular rigidity, the decrease in the stability constants of the palladium(II) complexes is considerably larger than that observed for the copper(II) complexes. *N*-Methylation also changes the solution behaviour of the mono- and bi-nuclear palladium(II) complexes. The [PdL]²⁺ complexes with tetraamines L⁴, L⁶ and L⁸ show a considerably larger tendency to bind a proton than the corresponding unmethylated counterparts L³, L⁵ and L⁷. This process is favoured by the weakening of the Pd−N bonds, since it requires detachment of a nitrogen donor. The subsequent binding of a chloride anion from the medium gives [PdCl(HL)]²⁺ species. The observation that *N*-methylation weakens the M−N bonds is also confirmed by the formation at alkaline pH of hydroxylated species. This process occurs *via* dissociation of a Pd−N bond and OH⁻ binding, and, similarly to proton binding, is thermodynamically favoured for *N*-methylated polyamines relative to their unmethylated counterparts.

Experimental

General

2,5,8-Trimethyl-2,5,8-triazanonane (L²), 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane (L⁴), 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane (L⁶), 2,6,9,13-tetramethyl-2,6,9,13-tetraaza-tetradecane (L⁸), 2,5,8,11,14-pentamethyl-2,5,8,11,14-pentaaza-pentadecane (L¹⁰), 2,5,8,11,14,17-hexamethyl-2,5,8,11,14,17-hexaazaoctadecane (L¹¹) were synthesized as previously described.[8a,b] All compounds had satisfactory elemental analyses and ¹H and ¹³C NMR spectra. Compounds L¹, L³, L⁵, L⁷ and L⁹ were from Aldrich Chemical Co. The 50.32 MHz ¹³C NMR spectra in D₂O solution were recorded at 298 K on a Bruker AC-200 spectrometer with 1,4-dioxane as reference standard. The UV/VIS spectra at different pH values were recorded on a Shimadzu UV-2101PC spectrophotometer.

Synthesis

2,5,8,11,14,17,20,23-Octamethyl-2,5,8,11,14,17,20,23-octa-azatetracosane octahydrochloride (L¹²·8HCl·2H₂O). To a solution of 2,23-dimethyl-2,5,8,11,14,17,20,23-octaazatetracosane[2a] (0.5 g, 0.0014 mol) in refluxing formic acid (15 cm³) was added paraformaldehyde (0.6 g, 0.019 mol) in small portions over a period of 3 h. The resulting suspension was refluxed for 24 h then cooled at 0 °C and water (10 cm³) added. The solution was made strongly alkaline by addition of 5 M NaOH, extracted with chloroform (6 × 15 cm³), and the combined extracts were dried over sodium sulfate. The solvent was removed under reduced pressure to give a colorless oil. The octahydrochloride salt L¹²·8HCl·2H₂O was obtained by the addition of an excess

of HCl to an ethanolic solution containing the free amine. Yield: 0.7 g (64%). ¹³C NMR (D₂O): δ 41.2 (2C), 44.3 (1C), 44.5 (1C), 44.7 (1C), 52.1 (1C), 52.7 (1C), 52.9 (1C), 53.1 (1C), 53.4 (1C), 53.5 (1C) and 53.6 (1C) (Found: C, 36.7; H, 8.8; N, 14.2. Calc. for C₁₂H₃₅Cl₄N₄O: C, 36.65; H, 8.97; N, 14.25%).

[Pd₂Cl₂L¹¹][ClO₄]₂. A solution of Na₂PdCl₄·2H₂O (11 mg, 0.032 mmol) in water (5 cm³) was slowly added to an aqueous solution (20 cm³) containing L¹¹·6HCl (28 mg, 0.016 mmol) and NaCl (20 mg). The pH was adjusted to 7 with 0.1 M NaOH. After heating at 50 °C for 1 h, NaClO₄ (100 mg) was added. Yellow crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature. Yield: 10 mg (75%) (Found: C, 26.1; H, 5.3; N, 10.2. Calc. for C₉H₂₂Cl₂N₃O₄Pd: C, 26.14; H, 5.36; N, 10.16%).

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive; these compounds must be handled with great care.

[Pd₂L¹²][ClO₄]₄·2H₂O. A solution of Na₂PdCl₄·2H₂O (10 mg, 0.03 mmol) in water (5 cm³) was slowly added to an aqueous solution (20 cm³) containing L¹²·8HCl·2H₂O (12 mg, 0.015 mmol) and NaCl (20 mg). The pH was adjusted to 7 with 0.1 M NaOH. After heating at 50 °C for 2 h, NaClO₄ (100 mg) was added. Yellow crystals of the complex suitable for X-ray analysis were obtained by slow evaporation at room temperature. Yield: 15 mg (91%) (Found: C, 26.1; H, 5.3; N, 10.3. Calc. for C₁₂H₃₁Cl₂N₄O₉Pd: C, 26.07; H, 5.65; N, 10.14%).

Potentiometric measurements

Equilibrium constants for complexation reactions of Pdᴵᴵ with ligands were determined by pH-metric measurements (pH = −log [H⁺]) in 0.1 M NMe₄Cl at 298.1 ± 0.1 K, by using potentiometric equipment that has been described.[18] The combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO₂-free NaOH solutions and determining the equivalence point by Gran's method[19] which allows one to determine the standard potential E°, and the ionic product of water [pK_w = 13.83(1) at 298.1 K in 0.1 M NMe₄Cl]. Concentrations 1 × 10⁻³–2 × 10⁻³ M of amines and metal ions, were employed in the potentiometric measurements, three titration experiments (about 100 data points each) being performed in the pH range 2–11. Owing to some slowness encountered in the complexation reactions with Pdᴵᴵ, titrations were performed with waiting times of at least 10 min between successive titrant additions to ensure the attainment of equilibrium. In the case of L⁶ the stability constant of the complex is too high to be determined by a simple alkalimetric titration. For this reason complexation of Pdᴵᴵ was studied by performing a competitive titration using L⁴ as competing ligand. The computer program HYPERQUAD[16] was used to calculate equilibrium constants from electromotive force data. All titrations were treated either as single sets or as separate entities, for each system, without significant variation in the values of the determined constants.

Crystallography

Crystal data and data collection parameters. [Pd₂Cl₂L¹¹]-[ClO₄]₂, C₁₈H₄₄Cl₄N₆O₈Pd₂, M = 827.2, monoclinic, space group P2₁/n, a = 7.70(1), b = 12.298(2), c = 16.41(1) Å, β = 97.3(1)°, U = 1541(2) Å³ (by least-squares refinement on diffractometer angles from 25 centred reflections, 14.6 < 2θ < 24°), T = 298 K, graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å, Z = 2, D_c = 1.782 Mg m⁻³, F(000) = 836, yellow prism with approximate dimensions 0.035 × 0.04 × 0.15 mm (the rather high cell dimension errors are probably related to the small crystal size), μ = 1.563 mm⁻¹, Enraf–Nonius CAD4 X-ray diffractometer, θ–2θ scans, data collection range 5 < 2θ < 50°, h, k, ± l, two standard reflections showed no loss of intensity;

2909 reflections collected, 2112 unique observed reflections with $I > 2\sigma(I)$. Absorption correction performed by means of the DIFABS [20] program once the structure had been solved (correction in φ and μ, maximum = 1.27, minimum = 0.79; correction in θ, maximum = 1.08, minimum = 0.75).

$[Pd_2L^{12}][ClO_4]_4\cdot2H_2O$, $C_{24}H_{62}Cl_4N_8O_{18}Pd_2$, $M = 1101.38$, monoclinic, space group $P2_1/c$, $a = 7.986(8)$, $b = 29.98(1)$, $c = 9.040(2)$ Å, $\beta = 95.24(4)°$, $U = 2155(2)$ Å³ (by least-squares refinement on diffractometer angles from 25 centred reflections, $12 < 2\theta < 20°$), $Z = 2$, $D_c = 1.697$ Mg m^{-3}, $F(000) = 1124$, yellow prism with approximate dimensions $0.02 \times 0.05 \times 0.1$ mm, $\mu = 1.159$ mm^{-1}, data collection range $5 < 2\theta < 44°$, $\pm h, k, l$, two standard reflections showed no loss of intensity; 2388 reflections collected, 1244 unique observed with $I > 2\sigma(I)$. Absorption correction in φ and μ: maximum = 1.15, minimum = 0.89; correction in θ, maximum = 1.05, minimum = 0.97. Other details as above.

Structure solution and refinement. The structure of $[Pd_2\text{-}Cl_2L^{11}][ClO_4]_2$ was solved by using the Patterson method and subsequent Fourier maps. Anisotropic displacement parameters were used for all the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions, with overall refined isotropic thermal parameters. Final agreement factors for 177 refined parameters $R1 = 0.056$ $[I > 2\sigma(I)]$ and $wR2 = 0.1822$ (all data) (maximum shift/e.s.d. -0.05).

The structure of $[Pd_2L^{12}][ClO_4]_4\cdot2H_2O$ was solved similarly. The hydrogen atoms of the water molecule were located in the ΔF map. Five peaks were introduced as oxygen atoms (each with population parameter 0.8) for one perchlorate ion [Cl(1)] due to rotational disorder. The SIMU restraint of the SHELXL 93 program, [21b] with the relative default options, was applied to these oxygen atoms. Final agreement factors for 269 refined parameters $R1 = 0.072$ $[I > 2\sigma(I)]$ and $wR2 = 0.2340$ (all data) (maximum shift/e.s.d. -0.02).

Refinements were performed by full-matrix least squares minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2 F_c^2)/3$. Calculations, carried out on a DEX 486-DX computer, were performed with the SHELXL 93 [21b] program, which uses the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref. 22.

CCDC reference number 186/934.

See http://www.rsc.org/suppdata/dt/1998/1625/ for crystallographic files in .cif format.

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