Aqueous Chemistry of Platinum and Palladium Complexes. Part 2.[1] Synthesis and Crystal Structure of a Palladium Hydroxo Complex $[Pd(terpy)(OH)]ClO_4 \cdot H_2O$ (terpy = 2,2′:6′,2″-terpyridine)‡

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The complex $[Pd(terpy)(ONO_2)]NO_3$ (terpy = 2,2′:6′,2″-terpyridine) can be prepared from the reaction of $Pd(NO_3)_2$ with terpy in dilute nitric acid or from metathesis of [Pd(terpy)Cl]Cl using $AgNO_3$. It dissolves in water with hydrolysis of the co-ordinated nitrato group to form $[Pd(terpy)(OH_2)]^{2+}$. Attempts to isolate this complex were unsuccessful. Addition of sodium perchlorate to a solution of $[Pd(terpy)(ONO_2)]NO_3$ at pH 10.5 afforded orange needles of $[Pd(terpy)(OH)]ClO_4 \cdot H_2O$. The Pd–OH bond distance is 1.966(3) Å, and the hydroxo group forms strong hydrogen bonds with the molecule of water of crystallisation.

The study of the aqueous chemistry of platinum complexes has experienced a revival over the past few years especially due to its relevance to anti-cancer platinum(II) compounds.[2] Terminal aqua groups on Pt^{II} and Pd^{II} are generally assumed to exist in aqueous solution due to the hydrolysis of labile ligands such as chloride.[3] However, the number of aqua compounds of Pt^{II} and Pd^{II} known in the solid state is limited.[4] The acidity of the co-ordinated water molecules results in formation of aquahydroxo compounds[3,5,6] which can polymerise to give hydroxo-bridged oligomers.[7] The ease of formation of these polynuclear species is determined by the acidity of the aqua group[6] which in turn depends on the nature of other ligands present in the complex. Hydroxo-bridged dimeric species can be formed from the partially neutralised aqua[1,7,8a] or hydroxo species.[1,8a]

In order to prevent the formation of hydroxo-bridged dimers which arise from *cis*-diaqua complexes, Lock and co-workers[9] attempted to isolate an aqua complex where three of the co-ordination sites around the metal were occupied by dien.§ Instead, however, they isolated the nitrato complex $[Pt(dien)(ONO_2)]NO_3$.

As a continuation of our studies on the aqueous chemistry of complexes of Pt^{II} and Pd^{II} with bipy, phen[1,8a] and cyclometallated bipy,[8b] we report here the behaviour of palladium(II) complexes of terpy in water. We were unable to isolate $[Pd(terpy)(OH_2)]^{2+}$ but were successful in isolating $[Pd(terpy)(OH)]^+$.

Results and Discussion

The conductance of [Pd(terpy)Cl]Cl in water was studied as a function of concentration. At concentrations around 10^{-2} mol dm^{-3} the complex behaves as a 1:1 electrolyte, but on dilution the molar conductance increases until at concentrations below 5×10^{-4} mol dm^{-3} the complex behaves as a 2:1 electrolyte, suggesting that aquation is complete [equation (1)].

$$[Pd(terpy)Cl]^+ \rightleftharpoons [Pd(terpy)(OH_2)]^{2+} + Cl^- \quad (1)$$

The molar absorbance of [Pd(terpy)Cl]Cl in water follows Beer's law at concentrations 0.8×10^{-4}—4×10^{-4} mol dm^{-3} (Table 1). At higher concentrations, the plot of absorption at 345 nm *vs.* concentration is linear but has a positive *y* intercept. Thus, at low concentrations, only $[Pd(terpy)(OH_2)]^{2+}$ is present in accord with the conductance data while at concentrations above 5×10^{-4} mol dm^{-3} aquation of the chloro ligand is incomplete. The hydrolysis of the halide in $[Pt(dien)X]^+$ (X = halide) is minimal[3] compared to $[PtLX_3]^-$ and $[PtL_2X_2]$ (L = nitrogen-donor ligand). Surprisingly, Lippard and co-workers[10] reported conductance measurements which suggest that $[Pt(terpy)X]^+$ (X = Cl or SCH_2CH_2OH) behaves as a 2:1 electrolyte in water, whereas at still lower concentrations the molar conductivity increases sharply. The aquation of the halides in complexes of Pd^{II} would be relatively faster, and for $[Pd(terpy)Cl]^+$ this is observed at low concentrations.

The acidity of the aqua group in $[M(dien)(OH_2)]^{2+}$ has been reported,[11,12] but no such measurements have been undertaken for the terpy analogue. Before embarking on such a study it is important to know the nature of the species present in solution as a function of pH to avoid misinterpretation of the results[8,13] as almost all aquahydroxo complexes tend to undergo olation. Complexes of the type $[M(terpy)X]^+$ are generally more reactive towards substitution than $[M(dien)X]^+$[14] and an increase in reactivity has been observed for $[Pt(bipy)Cl_2]$ and $[Pt(phen)Cl_2]$ with respect to $[Pt(en)Cl_2]$.[15] Such a trend is also found[1,8a] in the acidity (and subsequent dimer formation) of $[M(bipy)(OH_2)_2]^{2+}$ and $[M(phen)(OH_2)_2]^{2+}$ compared to the en, cyclohexane-1,2-diamine, and NH_3 analogues.

In order to increase the concentration range at which $[Pd(terpy)(OH_2)]^{2+}$ exists in aqueous solution, the chloro ligand was replaced by the nitrato group which is known readily to undergo hydrolysis. The complex $[Pd(terpy)(ONO_2)]NO_3$ (1) was prepared from the reaction of $Pd(NO_3)_2$ and terpy in

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‡ Hydroxo(2,2′:6′,2″-terpyridine)palladium(II) perchlorate hydrate.

§ Abbreviations used in this paper: terpy = 2,2′:6′,2″-terpyridine, en = ethylenediamine, dmp = 2-(dimethylaminomethyl)phenyl, bquin = benzo[*h*]quinoline, dien = diethylenetriamine (1,5-diamino-3-azapentane), bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, mbipy = 1-methyl-2,2′-bipyridin-1-ium-3-yl, mcyt = 1-methylcytosine.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Absorption spectra[a] of the complexes [$\lambda_{max.}$ (nm) (ε/dm^3 mol^{-1} cm^{-1})]

Complex						
$[Pd(terpy)Cl]Cl\cdot2H_2O$	360	345	330		272	240
	(6 910)	(7 290)	(6 670)		(18 100)	(25 600)
$[Pd(terpy)(ONO_2)]NO_3\cdot H_2O$	360	345	325		265	240
	(9 960)	(8 960)	(6 550)		(16 750)	(32 770)
$[Pd(terpy)(OH)]^+$ [b]	360	343	330	300	277	273
	(6 660)	(7 760)	(7 210)	(12 060)	(18 520)	(18 350)

[a] Solvent = water. [b] $[Pd(terpy)(ONO_2)]NO_3$ at pH 10 (NaOH).

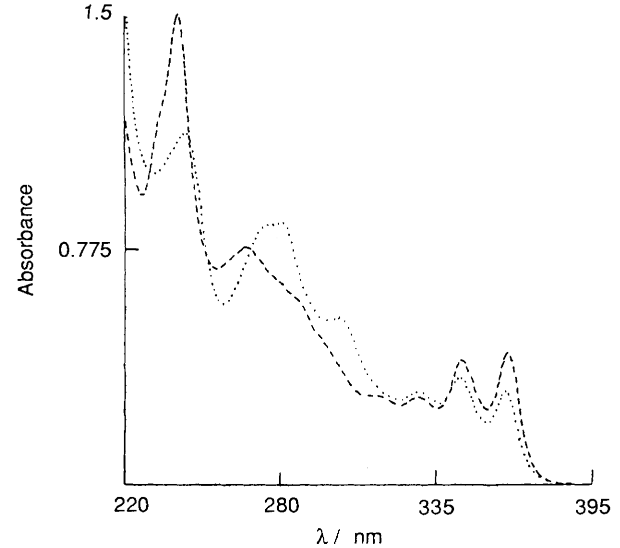

Figure 1. Electronic spectra of $[Pd(terpy)(ONO_2)]NO_3$ (2.29 × 10^{-4} mol dm^{-3}) in water (- - -) and in 2 mol dm^{-3} NaOH (· · · ·), path length 2 mm

nitric acid. Its i.r. spectrum (as a Nujol mull) shows, as expected, the presence of both co-ordinated and ionic nitrate.[16]

The molar conductivity of complex (**1**) in water (1 × 10^{-3} mol dm^{-3}) is 212 S cm^2 mol^{-1}, indicating complete hydrolysis of the co-ordinated nitrate. The electronic spectrum in water follows Beer's law in the concentration range 1 × 10^{-3}—1 × 10^{-4} mol dm^{-3}. The pH of a 0.015 mol dm^{-3} aqueous solution of the complex is 1.5. This acidity suggests equilibrium (2) to arise in solution. On evaporation of the solution to

$$[Pd(terpy)(ONO_2)]NO_3 \rightleftharpoons [Pd(terpy)(OH_2)]^{2+} \rightleftharpoons [Pd(terpy)(OH)]^+ + H^+ \quad (2)$$

dryness at room temperature complex (**1**) is reformed. Sodium perchlorate was added to the solution of $[Pd(terpy)(OH_2)]^{2+}$ in the hope of isolating either the aqua complex or a monohydroxo bridged dimer, if it is formed. After standing at room temperature for 2 d the solution furnished yellow cubes, the i.r. spectrum of which showed the presence of co-ordinated nitrate and ionic perchlorate consistent with $[Pd(terpy)(ONO_2)]ClO_4$, (**2**). We have previously isolated[8b] $[Pd(mbipy)(OH_2)(ONO_2)]ClO_4\cdot H_2O$ from a solution of $[Pd(mbipy)(ONO_2)_2]$ in water.

Of the species present in solution when $[Pd(terpy)(ONO_2)]NO_3$ is dissolved in water, it is found that the nitrato-co-ordinated complex preferentially crystallises from solution. Lock and co-workers[17] have shown that $[Pt(NH_3)_2(ONO_2)_2]$ is completely aquated in moderately concentrated solutions, whereas at higher concentrations aquation is incomplete.

The most significant changes in the absorption spectrum on addition of base to a solution of $[Pd(terpy)(OH_2)]^{2+}$ are the shift of the band at 265 nm to 275 nm (with little change in the molar absorption), and the appearance of a shoulder at 300 nm (see Table 1 and Figure 1). The absorption spectrum of both $[Pd(terpy)Cl]^+$ and the nitrato complex are identical under basic conditions.

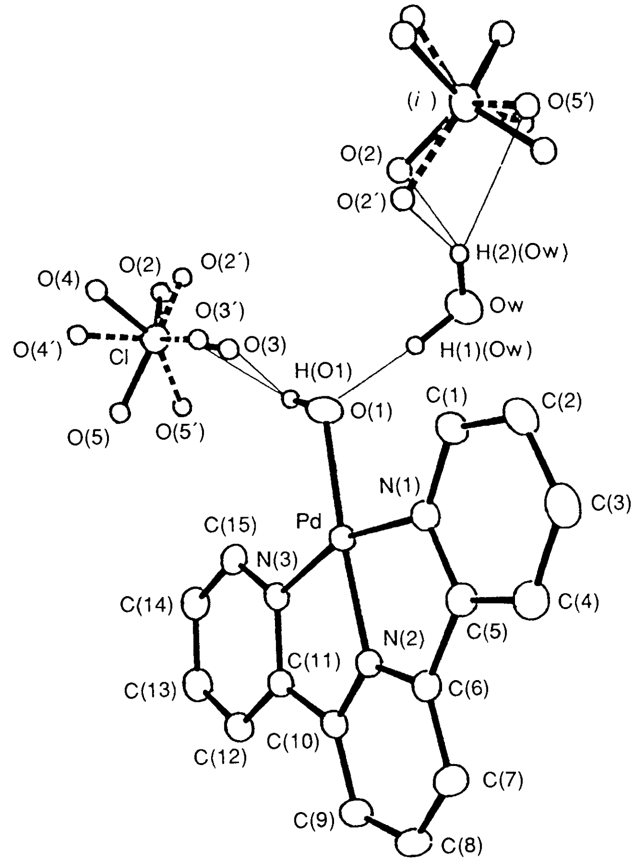

Figure 2. ORTEP diagram of $[Pd(terpy)(OH)]ClO_4\cdot H_2O$ showing the atomic numbering scheme. The ClO_4^- ions are drawn on an arbitrary scale. Fine lines denote hydrogen bonding. Symmetry relation: (i) $-\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$

When a solution of complex (**1**) containing sodium perchlorate and with the pH adjusted to 10.5 was allowed to stand at room temperature for 2 d orange needles of $[Pd(terpy)(OH)]ClO_4\cdot H_2O$ (**3**) separated. The i.r. spectrum of the compound shows sharp bands at 3 590 and 550 cm^{-1} and a medium-intensity broad band at 1 670 cm^{-1}, suggesting the presence of a hydroxyl group and a water molecule.[16b,18]

Description of the Structure of $[Pd(terpy)(OH)]ClO_4\cdot H_2O$.—The structure consists of a discrete $[Pd(terpy)(OH)]^+$ cation, a perchlorate ion, and one molecule of water of crystallisation. Interatomic bond distances and angles are given in Table 2. An ORTEP plot, together with the labelling scheme, is in Figure 2.

Table 2. Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[Pd(terpy)(OH)]ClO_4{\cdot}H_2O$

Palladium environment

Pd–O(1)	1.966(3)	Pd–N(2)	1.934(3)
Pd–N(1)	2.022(3)	Pd–N(3)	2.035(3)
O(1)–Pd–N(1)	93.9(1)	N(1)–Pd–N(2)	81.2(1)
O(1)–Pd–N(2)	174.9(1)	N(1)–Pd–N(3)	162.0(1)
O(1)–Pd–N(3)	104.1(1)	N(2)–Pd–N(3)	80.8(1)

2,2′:6′,2″-Terpyridine

N(1)–C(1)	1.334(5)	C(8)–C(9)	1.380(6)
C(1)–C(2)	1.385(6)	C(9)–C(10)	1.378(6)
C(2)–C(3)	1.373(7)	C(10)–N(2)	1.350(5)
C(3)–C(4)	1.383(7)	C(10)–C(11)	1.477(6)
C(4)–C(5)	1.381(6)	N(3)–C(11)	1.375(5)
C(5)–N(1)	1.365(5)	C(11)–C(12)	1.386(6)
C(5)–C(6)	1.482(6)	C(12)–C(13)	1.384(7)
N(2)–C(6)	1.342(5)	C(13)–C(14)	1.377(7)
C(6)–C(7)	1.379(6)	C(14)–C(15)	1.383(6)
C(7)–C(8)	1.385(6)	C(15)–N(3)	1.345(5)
Pd–N(1)–C(1)	127.1(3)	C(6)–C(7)–C(8)	118.4(4)
Pd–N(1)–C(5)	113.0(2)	C(7)–C(8)–C(9)	121.3(4)
C(1)–N(1)–C(5)	119.8(3)	C(8)–C(9)–C(10)	118.5(4)
N(1)–C(1)–C(2)	121.7(4)	C(9)–C(10)–N(2)	119.3(4)
C(1)–C(2)–C(3)	118.9(4)	C(9)–C(10)–C(11)	128.3(4)
C(2)–C(3)–C(4)	119.8(4)	N(2)–C(10)–C(11)	112.4(8)
C(3)–C(4)–C(5)	119.2(4)	Pd–N(3)–C(11)	112.9(2)
C(4)–C(5)–N(1)	120.5(4)	Pd–N(3)–C(15)	127.9(3)
C(4)–C(5)–C(6)	124.5(4)	C(11)–N(3)–C(15)	119.2(3)
N(1)–C(5)–C(6)	114.9(3)	N(3)–C(11)–C(10)	115.0(3)
Pd–N(2)–C(6)	118.2(3)	N(3)–C(11)–C(12)	120.8(4)
Pd–N(2)–C(10)	118.8(3)	C(10)–C(11)–C(12)	124.2(4)
C(6)–N(2)–C(10)	123.0(3)	C(11)–C(12)–C(13)	119.1(4)
N(2)–C(6)–C(5)	112.7(3)	C(12)–C(13)–C(14)	119.8(4)
N(2)–C(6)–C(7)	119.5(4)	C(13)–C(14)–C(15)	119.3(4)
C(5)–C(6)–C(7)	127.8(4)	C(14)–C(15)–N(3)	121.8(4)

The geometry around the palladium is distorted square planar, with the terpy co-ordinating as a terdentate ligand and with the fourth position occupied by a hydroxide group. There is little deviation of the atoms around the co-ordination plane. Due to the constraints imposed on the terpyridine on co-ordination,[19] the bite angles N–Pd–N are reduced to 81.2(1) and 80.8(1)°, with consequent 'opening up' of O(1)–Pd–N(3) [104.1(1)°] and O(1)–Pd–N(1) [93.9(1)°]. Angles smaller than the theoretical 90° expected for a square-planar complex have been observed for other platinum and palladium complexes of tridentate N-donor ligands.[20] The dihedral angles between the co-ordination plane and the pyridine planes are 2.3, 2.9, and 2.9°. The angle between the pyridine rings containing N(1) and N(2) is small (1.6°), but between pyridine rings containing N(2) and N(3) the dihedral angle is somewhat larger at 4.5°.

The Pd–O(1) distance is 1.966(3) which is considerably shorter than the Pd–O bond length observed for aqua complexes[8b,21] {2.132(3) for $[Pd(mbipy)(OH_2)(ONO_2)]^+$, and 2.20(1) Å for $[Pd(dmp)(bquin)(OH_2)]^+$}. In comparison, the Pt–O distance[22] in $[Pt(NH_3)_2(OH_2)(mcyt)]^{2+}$ is not excessively long (2.052 Å) and there is only a minor shortening of this bond on deprotonation to form the corresponding hydroxo complex (2.027 Å).

The Pd–N(2) distance to the central pyridine ring [1.934(3) Å] is shorter than those to the other two nitrogen atoms of terpy [2.022(3) and 2.035(3) Å]. These distances are comparable to the values observed for $[Pd(terpy)Cl]Cl{\cdot}2H_2O$.[23]

The crystal packing is reinforced by a hydrogen-bonding network, with strong hydrogen bonds between the oxygen of the hydroxo ligand and the water molecule, Ow···O(1) 2.698(5), H(1)(Ow)···O(1) 1.74(4) Å, Ow–H(1)(Ow)···O(1) 170(5)°, and weak hydrogen bonding between the hydroxy group and the perchlorate ion, O(1)···O(3) 3.03(2) and O(1)···O(3′) 2.97(2) Å. Further, there are weak hydrogen bonds between the molecule of water of crystallisation and the perchlorate ion. Hence the hydrogen-bonding requirement postulated by Lock and co-workers[9] for a terminal hydroxo group to accept protons to form strong hydrogen bonds has been satisfied.

Experimental

Infrared spectra were recorded (4 000—200 cm^{-1}) on a Perkin-Elmer 983 spectrophotometer using Nujol mulls, electronic spectra on a Varian Cary 2300 spectrophotometer at room temperature. Conductance measurements in water were made at 25 °C with a Philips GM 4249 conductivity bridge. The C, H, and N analyses were carried out by the Interuniversity Microanalytical Services, Ecole Nationale Supérieure de Chimie de Toulouse. 2,2′:6′,2″-Terpyridine was purchased from Sigma Chimie S.A.R.L. and palladium salts from Johnson Matthey. The complex $[Pd(terpy)Cl]Cl{\cdot}2H_2O$ was prepared following the method of Morgan and Burstall.[24]

Synthesis.—$[Pd(terpy)(ONO_2)]NO_3{\cdot}H_2O$. (*i*) *From palladium nitrate*. 2,2′:6′,2″-Terpyridine (0.167 g, 0.72 mmol) was added to a solution of $Pd(NO_3)_2$ (0.157 g, 0.68 mmol) in dilute nitric acid (20 cm^3). The mixture was heated under reflux for 1 h and allowed to stand at room temperature for 4 h. The black residue was removed by centrifugation and the yellow supernatant concentrated to half the volume from which yellow crystals of the product separated. The complex was isolated, washed with acetone, and dried *in vacuo*. A second fraction of the product was obtained from the filtrate after several days. Total yield 65%.

(*ii*) *From* $[Pd(terpy)Cl]Cl{\cdot}2H_2O$. Silver nitrate (0.084 g, 0.49 mmol) dissolved in water (1 cm^3) was added dropwise to a stirred solution of $[Pd(terpy)Cl]Cl{\cdot}2H_2O$ (0.110 g, 0.25 mmol) in water (15 cm^3). Some white precipitate separated, and further AgCl was formed when a few drops of concentrated nitric acid were added. The mixture was stirred with slight warming for 30 min and AgCl removed by centrifugation. The yellow supernatant was evaporated to dryness on a rotary evaporator (45 °C) and the pale yellow solid washed with acetone and diethyl ether. The compound was recrystallised from dilute nitric acid. Total yield 50% (Found: C, 37.5; H, 2.6; N, 14.6. $C_{15}H_{13}N_5O_7Pd$ requires C, 37.4; H, 2.7; N, 14.5%). I.r.: co-ordinated nitrate, ν_4 1 500, ν_1 1 270, and ν_2 990; ionic nitrate, ν_3 1 350, and ν_2 820 cm^{-1}.

$[Pd(terpy)(OH)]ClO_4{\cdot}H_2O$. The pH of a solution of $[Pd(terpy)(ONO_2)]NO_3$ (0.071 g, 0.15 mmol) in water (10 cm^3) was increased to 10.5 by addition of NaOH (2 mol dm^{-3}). A concentrated solution of $NaClO_4$ was then added to the resulting orange solution which furnished orange-yellow needles of the hydroxo complex after 2 d. The needles were collected, washed with cold water, and dried *in vacuo*. Yield 70% (Found: C, 37.8; H, 2.9; N, 8.9. $C_{15}H_{14}ClN_3O_6Pd$ requires C, 37.9; H, 3.0; N, 8.9%).

X-Ray Crystal Structure Determination of $[Pd(terpy)(OH)]ClO_4{\cdot}H_2O$.—*Crystal data*. $C_{15}H_{14}ClN_3O_6Pd$, $M = 474.1$, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $a = 8.044\,1(8)$, $b = 16.974(1)$, $c = 12.191(1)$ Å, $\beta = 94.34(1)°$, $U = 1\,659.8(5)$ Å^3, $Z = 4$, $D_c = 1.897$ g cm^{-3}, $F(000) = 944$, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, $\mu = 13.0$ cm^{-1}, $T = 293$ K.

Table 3. Fractional atomic co-ordinates with e.s.d.s *

Atom *	*x*	*y*	*z*
Pd	0.711 59(4)	0.469 23(2)	0.501 49(2)
O(1)	0.659 6(4)	0.373 7(2)	0.583 4(3)
H(O1)	0.709(7)	0.370(4)	0.658(2)
N(1)	0.578 3(4)	0.434 9(2)	0.362 4(3)
N(2)	0.755 0(4)	0.558 5(2)	0.409 3(3)
N(3)	0.861 2(4)	0.532 8(2)	0.610 7(3)
C(1)	0.489 8(5)	0.368 9(2)	0.347 0(4)
C(2)	0.407 2(5)	0.350 9(3)	0.246 3(4)
C(3)	0.417 3(6)	0.402 6(3)	0.160 4(4)
C(4)	0.507 3(5)	0.471 6(3)	0.176 0(4)
C(5)	0.587 5(5)	0.487 0(2)	0.277 8(3)
C(6)	0.688 8(5)	0.558 3(2)	0.304 9(3)
C(7)	0.722 2(6)	0.619 9(3)	0.236 2(4)
C(8)	0.825 7(6)	0.679 8(3)	0.277 5(4)
C(9)	0.892 5(6)	0.679 0(3)	0.385 2(4)
C(10)	0.854 2(5)	0.616 9(2)	0.451 6(3)
C(11)	0.910 2(5)	0.603 4(2)	0.568 2(3)
C(12)	1.004 7(5)	0.656 5(3)	0.633 1(4)
C(13)	1.050 2(6)	0.637 4(3)	0.741 6(4)
C(14)	1.003 3(5)	0.566 0(3)	0.783 1(4)
C(15)	0.908 8(5)	0.514 8(3)	0.715 8(3)
Cl	0.777 2(2)	0.354 64(7)	0.928 99(9)
O(2)	0.846(3)	0.299(1)	0.998(1)
O(3)	0.787(2)	0.337(1)	0.818(1)
O(4)	0.598(1)	0.351 5(6)	0.949 5(9)
O(5)	0.826(2)	0.432 4(5)	0.951 4(7)
O(2′)	0.842(5)	0.276(2)	0.975(3)
O(3′)	0.703(3)	0.348(2)	0.824(2)
O(4′)	0.685(3)	0.390(2)	0.995(1)
O(5′)	0.948(2)	0.392(1)	0.928(1)
Ow	0.725 5(5)	0.230 1(2)	0.502 4(4)
H(1)(Ow)	0.715(8)	0.282(2)	0.535(5)
H(2)(Ow)	0.620(4)	0.203(3)	0.497(5)

* Occupancy factors are 0.60 for O(2), O(3), O(4), and O(5) and 0.40 for O(2′), O(3′), O(4′), and O(5′).

Data collection and processing. A yellow plate crystal of dimensions 0.450 × 0.125 × 0.075 mm was centred on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The unit-cell dimensions were determined from the setting angles of 25 reflections in the range $12.2 < \theta < 14.5°$. A data set of 3 248 reflections ($1.5 < \theta < 26°$, $h, k, \pm l$) was recorded as described previously[25] by the ω—2θ scan mode (ω scan width $0.80 + 0.35 \tan\theta$, ω scan speed 1.1—8.2° min^{-1}). The intensities of three standard reflections monitored every 2 h showed no significant variation during data collection. Data reflections were corrected for Lorentz and polarisation effects[26] and for empirical absorption[27] (maximum, minimum transmission factors 1.00, 0.95). Equivalent reflections ($0kl$ and $0k\bar{l}$) were merged ($R_{av.}$ = 0.016). 2 502 Reflections with $F_o^2 > 3\sigma(F_o^2)$ were considered to be 'observed' and used for the structure solution and least-squares refinement.

Structure determination. The structure was solved by the heavy-atom method. After locating the Pd atom by a Patterson map, subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps using SHELX[28] enabled all the non-hydrogen atoms in the structure to be located. Oxygen atoms of the perchlorate anion were disordered. All other parameters being fixed, their occupancy factors over two sites were refined to 0.60 and 0.40 respectively. These values then being kept fixed, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on a Fourier difference map. Those bonded to O(1) and Ow were allowed to vary with a common isotropic thermal parameter, U = 0.10(1) Å^2. The other H atoms were introduced in calculations with constrained geometry (C–H 0.97 Å) with a variable isotropic thermal parameter, U = 0.055(4) Å^2. Neutral atom scattering factors were used, those for non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[29] Unit weights were applied and gave satisfactory weight analysis. In the last full-matrix least-squares refinement cycle, maximum shift was equal to 0.5 times the estimated standard deviation (disordered O parameter) and the final R value was 0.025 (R' 0.029). A final Fourier difference map showed a maximum residual electron density of 0.3 e Å^{-3}. All calculations were performed on a VAX-11/730 DEC computer. Atomic co-ordinates are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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