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Oxidation of organometallic complexes by water: Synthesis of diorgano(hydroxo)platinum(IV) complexes and the structure of a diorgano(aqua)platinum(IV) complex of tris(pyridin-2-yl)methanol, [PtPh$_2${(py)$_3$COH-N,N',N''}(OH$_2$)][NO$_3$]$_2$ · H$_2$O

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Abstract

The diorganoplatinum(II) complexes PtR$_2${(py)$_3$COH} (R = Me, Ph; (py)$_3$COH = tris(pyridin-2-yl)methanol) react with water in organic solvents to form diorgano(hydroxo)platinum(IV) cations [Pt(OH)R$_2${(py)$_3$COH}]$^+$, and the cation with R = Ph reacts with dilute nitric acid to form [PtPh$_2${(py)$_3$COH}(OH$_2$)]$^{2+}$. The cation in [PtPh$_2${(py)$_3$COH}(OH$_2$)] [NO$_3$]$_2$ · H$_2$O has octahedral geometry with a Pt–O bond distance of 2.04(1) Å. The higher trans influence of phenyl than aqua ligands is reflected in the Pt–N bond distances: 2.14(2) and 2.17(1) Å trans to the phenyl groups, and 1.99(2) Å trans to the aqua ligand.

1. Introduction

Organometallic compounds containing metal–carbon σ-bonds exhibit a wide range of reactivity toward water [1]. Complexes of the heavier p block metals in their higher oxidation states and some late transition metals are often stable toward water, and their aqueous solution behaviour is an important aspect of their chemistry, e.g. complexes of dimethylthallium(III), methylmercury(II), trimethyltin(IV), and dimethylgold(III). For organometallic complexes of other p block/late transition metals, reaction with water may lead to cleavage of metal–carbon σ-bonds and formation of hydrocarbons, e.g. for copper(II) and cadmium(II). Another potential reaction pathway is oxidation of the metal centre by water to form a higher oxidation state complex. There appear to be very few reports of reactions of metal–

carbon σ-bonded complexes with water to form well-characterized higher oxidation state complexes [2–7]. Except for preliminary reports of oxidation of palladium(II) complexes [5–7], they all involve platinum(II) complexes and isolation of hydroxo or aqua complexes as products, e.g. for 2,2'-bipyridyl (bpy) [3a] and pyridine (py) [4] complexes involving oxidation of platinum(II) to platinum(IV) (Scheme 1).

These reactions most likely involve oxidative addition of water to the electron-rich platinum(II) centre followed by rapid hydrolysis of the resulting unstable hydridoplatinum(IV) intermediate(s) [3a,8]. The oxidative addition step to form hydrido complexes is modelled by reactions of d^8 coordination complexes with water [9], in particular the reaction of water with [Ir(PMe$_3$)$_4$]$^+$ to form [cis-[IrH(OH)(PMe$_3$)$_4$]$^+$ [9e,f], and by reactions of d^{10} platinum(0) coordination complexes [10], e.g. the reaction of Pt(P^{i}Pr$_3$)$_2$ with water to form trans-PtH(OH)(P^{i}Pr$_3$)$_2$ [10c]. Related reactions involving oxidation of the metal centre include the reaction of the (cyclohexyne)platinum(0) complex

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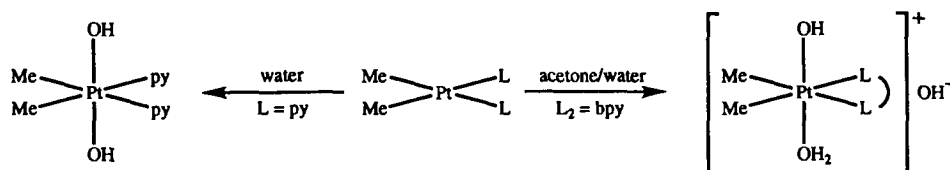
Scheme 1.

$Pt(\eta^2\text{-}C_6H_8)(dppe)$ with water to form the cyclohex-enylplatinum(II) complex $Pt(OH)(C_6H_9)(dppe)$ (dppe = bis(diphenylphosphino)ethane) [11].

Except for a preliminary report of the reaction of the tris(pyrazol-1-yl)borate complex $[PtMe_2\{(pz)_3BH\}]^-$ with water [6], platinum(II) reagent complexes studied to date have involved monodentate or bidentate ligands; the products have not been characterized crystallograph-ically and, for the most fully studied system (Scheme 1, L_2 = bpy), the product was difficult to fully character-ize [3a]. In view of this report, and the fundamental nature of this type of reaction and its relevance to some catalysis systems [2,9b,9d,10b,c], we have commenced a study of the interaction of water with σ-bonded organometallic compounds that are expected to be sus-ceptible to oxidation by water. Initially, we have studied diorganoplatinum(II) complexes of a typical tripodal donor ligand, tris(pyridin-2-yl)methanol [(py)₃COH]. Although this ligand was expected to yield reaction chemistry similar to that described in Scheme 1, it was hoped that it would give products that could be more readily examined because, if acting as a tridentate in a diorganoplatinum(IV) product, it permits only one site for bonding of platinum(IV) to a ligand resulting from oxidation by water, presumably a hydrido, hydroxo, or aqua group. A preliminary report of part of this work has appeared [5].

2. Results

2.1. Synthesis and characterization of complexes

The complexes $PtR_2\{(py)_3COH\}$ (R=Me, Ph) were obtained on the reaction of $[PtR_2(SEt_2)]_2$ with tris(pyridin-2-yl)methanol in acetone (R=Me) or ben-zene (R=Ph). The dimethylplatinum(II) complex is in-sufficiently soluble for NMR studies, but some of its ¹H resonances may be assigned from in situ studies of formation in $(CD_3)_2CO$, exhibiting δ(PtMe) at 0.33 ppm with ²J(HPt) = 86.8 Hz and δ(H6) for the coordi-nated pyridine rings at 8.78 ppm with ³J(HPt) = 24.5 Hz.

The platinum(IV) complex $[Pt(OH)Ph_2\{(py)_3COH\}]$-[OH] · 2H₂O (4) could be obtained on warming (approx. 50°C for 2 h) a solution of $PtPh_2\{(py)_3COH\}$ in acetone that had not been dried (Scheme 2). However, since the low solubility of $PtMe_2\{(py)_3COH\}$ prevented the facile formation of the dimethylplatinum(IV) analogue in the same manner, the synthesis of both platinum(IV) com-plexes from $[PtR_2(SEt_2)]_2$ and $(py)_3COH$ in undried acetone was developed. The complexes $[Pt(OH)\text{-}Me_2\{(py)_3COH\}][OH] · H_2O$ (3) and $[Pt(OH)Ph_2\{(py)_3\text{-}COH\}][OH] · 2H_2O$ (4) were obtained with yields of 55% (R=Me) and 85% (R=Ph). Water of hydration is included in the formulations to satisfy microanalytical data and is in accord with the tendency of this type of complex to crystallize as hydrates, exemplified by the structural analysis of $[PtPh_2\{(py)_3COH\}(OH_2)][NO_3]_2 ·$ H₂O (5) (see below). The ¹H NMR spectra of 3 and 4 exhibit similar resonances for the $(py)_3COH$ ligand, showing pyridine ring environments in 2:1 ratio, and 3 shows a single methylplatinum(IV) resonance. The spectra are similar to those reported for related cations of general formulation $[PtIR_2(L_3)]^+$ (L_3 is a neutral tripodal nitrogen donor) [12], showing δ(H6 (pyridine)) downfield from the platinum(II) analogues and with ²J(HPt) for the dimethylplatinum(IV) group (66.9 Hz) significantly less than that for the platinum(II) analogue (86.8 Hz).

The diorgano(hydroxo)platinum(IV) complexes were insufficiently crystalline for X-ray structural studies,

R = Me (1), Ph (2)   R = Me (3), Ph (4)   5
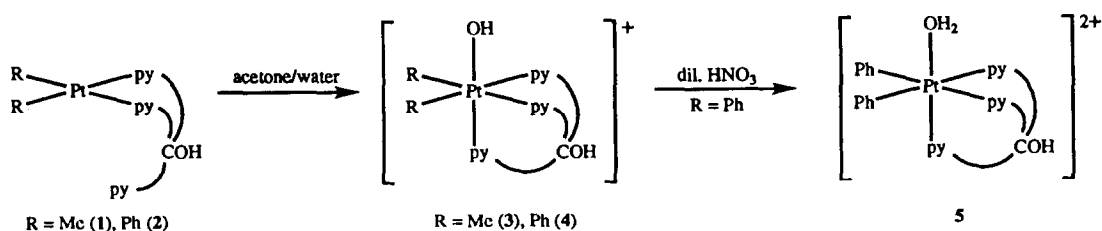
Scheme 2.

and crystalline aqua derivatives were sought by acidifying solutions of the complexes, since it has been reported that closely related Pt(OH)(OMe)Me$_2$(bpy) forms an equilibrium with [Pt(OMe)Me$_2$(bpy)(OH$_2$)]$^+$ in aqueous solution [3a]. Complex **3** decomposed on addition of a few drops of dilute nitric acid to an acetone solution, but complex **4** gave an aqua complex crystallizing as [PtPh$_2${(py)$_3$COH}(OH$_2$)][NO$_3$]$_2$ · H$_2$O (**5**). The hydroxo complexes **3** and **4** have very low solubility in (CD$_3$)$_2$CO, which is a suitable NMR solvent for the aqua complex, but it was found that a dilute solution of **4** in (CD$_3$)$_2$CO gave a spectrum for the (py)$_3$COH ligand which is different from that of the aqua complex but similar to that of both of the hydroxo complexes in CDCl$_3$.

2.2. X-ray structural study of [PtPh$_2${(py)$_3$COH}-(OH$_2$)][NO$_3$]$_2$ · H$_2$O (5)

The results of the room temperature single crystal X-ray diffraction study provide a model consistent with the stoichiometry and connectivity implied by the formulation **5** (Fig. 1), a difference map artefact being modelled as a water molecule oxygen atom. Although hydroxylic hydrogen atoms have not been located in difference maps, plausible interactions may be postulated in consequence of short oxygen · · · oxygen distances. Thus, the coordinated water molecule O(1) contacts nitrate oxygens O(12, 13, 21) at distances of 2.82(1), 2.84(2), 2.53(3) Å, while the ligand oxygen O(0) contacts the lattice water oxygen O at 2.68(3), and nitrate oxygen O(23) (1 + x, y, z) at 2.95(2) Å. The nitrate groups are ordered and planar (χ^2 0.1, 2.3). For the tripod ligand, torsion angles O–C–C(2n)–N(1n) are 177(2), −176(2), −178(2)° (n = a, b, c), with rings a', b' splayed to either side of ring c (interplanar dihedrals 61.0(8), 62.0(8)°). The platinum(IV) environment is distorted octahedral with Pt–O(1) 2.04(1) Å. The Pt–N bond distances trans to the methyl groups (2.14(2), 2.17(1) Å) are significantly longer than the Pt–N distance trans to the aqua ligand (1.99(2) Å), reflecting the greater trans influence of the methyl groups (Table 1). The intraligand angles N–Pt–N for the tripod ligand (85.6(5)–87.7(6)°) are generally smaller than the interligand angles (88.0(6)–95.7(6)°).

The most closely related structures for d^6 metal–carbon σ-bonded organometallic complexes containing an aqua ligand appear to be the rhodium(III) complexes trans-Rh{C(O)C(Cl) = C(Cl)C(O)}Cl(OH$_2$)(PMe$_2$Ph)$_2$ [13], trans-Rh{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$-N, C, N}-Cl$_2$(OH$_2$) [14], trans-Rh{2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$-P, C, P}Cl$_2$(OH$_2$) · Me$_2$CHOH [15], and the palladium(IV) complex [Pd(CH$_2$CH$_2$CH$_2$CH$_2$){(pz)$_3$BH-N,N',N''}-(OH$_2$)] · (C$_6$F$_5$O)]$_2$ [7]. The rhodium(III) complexes containing [NCN]$^-$ and [PCP]$^-$ groups have configurations involving the aqua ligand trans to carbon, with the

aqua ligand hydrogen-bonded to chlorine (intermolecular) and propan-2-ol respectively. The dimeric palladium(IV) complex has the aqua ligand trans to nitrogen with Pd–O 2.035(4) Å, as for the present platinum(IV) complex (Pt–O = 2.04(1) Å), and the pentafluorophenolate anions act as bridges between [Pd(CH$_2$CH$_2$CH$_2$-CH$_2$){(pz)$_3$BH}(OH$_2$)]$^+$ cations by formation of two hydrogen-bonds to aqua ligands.

3. Discussion

The results reported here indicate that diorganoplatinum(II) complexes of nitrogen donor ligands may be oxidized by water under mild conditions (about 50°C) to afford hydroxoplatinum(IV) complexes in moderate to high yield. The crystallographic study of a simple aqua derivative adds support to previous studies of oxidation of organometallic complexes by water. The oxidation reactions proceed readily at ambient temperature in (CD$_3$)$_2$CO over a few hours when studied by ^{1}H NMR spectroscopy. For PtR$_2${(py)$_3$COH} complexes it would seem feasible that the oxidation reaction may be as-

Table 1
Selected bond distances and angles for [PtPh$_2${(py)$_3$COH}(OH$_2$)]-[NO$_3$]$_2$·H$_2$O (5) [a,b]

Bond distances (Å)			
Pt–C(1a')	2.01(2)	Pt–N(1a)	2.14(2)
Pt–C(1b')	2.05(2)	Pt–N(1b)	2.17(1)
Pt–O(1)	2.04(1)	Pt–N(1c)	1.99(2)

Bond angles (deg)			
C(1a')–Pt–C(1b')	95.7(6)	Pt–C(1a')–C(2a')	120(1)
C(1a')–Pt–O(1)	91.7(7)	Pt–C(1a')–C(6a')	124(1)
C(1a')–Pt–N(1a)	175.1(5)	Pt–C(1b')–C(2b')	120(1)
C(1a')–Pt–N(1b)	90.7(6)	Pt–C(1b')–C(6b')	123(2)
C(1a')–Pt–N(1c)	88.9(7)	Pt–N(1a)–C(2a)	119(1)
C(1b')–Pt–O(1)	88.0(6)	Pt–N(1a)–C(6a)	124(1)
C(1b')–Pt–N(1a)	88.1(6)	Pt–N(1b)–C(2b)	119(1)
C(1b')–Pt–N(1b)	173.4(6)	Pt–N(1b)–C(6b)	121(1)
C(1b')–Pt–N(1c)	95.2(7)	Pt–N(1c)–C(2c)	121(1)
O(1)–Pt–N(1a)	91.6(5)	Pt–N(1c)–C(6c)	119(1)
O(1)–Pt–N(1b)	90.1(5)	C(2a)–C–C(2b)	108(2)
O(1)–Pt–N(1c)	176.6(4)	C(2a)–C–C(2c)	115(1)
N(1a)–Pt–N(1b)	85.6(5)	C(2b)–C–C(2c)	110(2)
N(1a)–Pt–N(1c)	87.7(6)	O–C–C(2a)	109(2)
N(1b)–Pt–N(1c)	86.6(5)	O–C–C(2b)	105(2)
		O–C–C(2c)	110(2)

[a] Nitrate groups: N(1)–O(11,12,13) = 1.21(2), 1.21(2), 1.23(2) Å; O(11)–N(1)–O(12,13) = 124(2), 122(2)°; O(12)–N(1)–O(13) = 115(2)°; N(2)–O(21,22,23) = 1.27(2), 1.20(2), 1.22(3) Å; O(21)–N(2)–O(22,23) = 118(2), 119(2)°; O(22)–N(2)–O(23) = 122(2)°.
[b] The pyridin-2-yl rings are planar (χ^2 range 1.9–2.3), with the Pt atom 0.06(3), 0.09(3), and 0.17(3) Å from the mean planes of rings a, b, and c respectively; the latter have dihedral angles of 43.2(6), 46.6(6), 82.6(6)° with the PtC$_2$N$_2$ plane, while those of rings a', b' are 35.2(6), 67.2(7)° (χ^2 both 1.1). For the PtC$_2$N$_2$ plane, χ^2 is 18, deviations of C(1a', b'), N(1a, b) being −0.07(2), 0.04(2), −0.05(2), 0.03(2) Å.

sisted by coordination of the third pyridine ring trans to the incoming electrophile (H^+, H_2O, H_3O^+ or larger aggregate). Coordination in this way would provide a concerted pathway to an octahedral hydridoplatinum(IV) intermediate prior to hydrolysis, and it would increase the nucleophilic character of the platinum atom in an analogous way to the proposals that axial interaction of nucleophiles assists oxidative addition of iodomethane to square planar rhodium(I) and iridium(I) complexes [16].

4. Experimental section

The reagents $[PtMe_2(SEt_2)]_2$ [17], $[PtPh_2(SEt_2)]_2$ [18], and tris(pyridin-2-yl)methanol [19] were prepared as reported. Solvents were dried and distilled, and all syntheses were carried out under nitrogen. Microanalyses were by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si.

4.1. Synthesis of complexes

4.1.1. PtMe₂{(py)₃COH} (1)

A solution of $[PtMe_2(SEt_2)]_2$ (0.100 g, 0.159 mmol) and $(py)_3COH$ (0.083 g, 0.317 mmol) in acetone (20 ml) was stirred for 3 h to give a bright yellow solution. The solvent was removed under vacuum and the yellow solid washed with diethyl ether (0.104 g, 67%). Anal. Found: C, 44.8; H, 4.2; N, 8.2. $C_{18}H_{19}N_3OPt$. Calc.: C, 44.3; H, 3.9; N, 8.6%.

4.1.2. PtPh₂{(py)₃COH} (2)

A solution of $[PtPh_2(SEt_2)]_2$ (0.088 g, 0.1 mmol) and $(py)_3COH$ (0.053 g, 0.2 mmol) in benzene (10 ml) was warmed for 5 min, at which time the reagents had dissolved and a pale yellow microcrystalline precipitate formed. The precipitate was collected and washed with benzene (5 ml) and dried in air (0.104 g, 85%). ^1H NMR ($CDCl_3$): δ 8.63 (d(b), 2, H6), 8.26 (d(b), 1, H6 (uncoord.)), 7.92 ('td', 2, H4), 7.85 ('td', 1, H4 (uncoord.)), 7.38 (m(b), 1, H3 (uncoord.)), 7.2–6.7 (m(b), 15, Ph and H3 and H5). Anal. Found: C, 54.9; H, 4.1; N, 6.4. $C_{28}H_{23}N_3OPt$ Calc.: C, 54.9; H, 3.8; N, 6.9%.

4.1.3. [Pt(OH)Me₂{(py)₃COH}][OH] · H₂O (3)

A solution of $[PtMe_2(SEt_2)]_2$ (0.100 g, 0.159 mmol) and $(py)_3COH$ (0.083 g, 0.317 mmol) in acetone (15 ml) that had not been dried was warmed for 2 h to give a clear solution from which the solvent was removed under vacuum. A white crystalline product was obtained on recrystallization from methanol–diethyl ether (0.095 g, 56%). ^1H NMR ($CDCl_3$): δ 9.07 (d(b), 1, H6 (trans OH)), 8.86 (d(b), 2, H6), 8.62 (d(b), 2, H4), 8.26 (m, 1,

H4 (trans OH)), 7.94 (m, 3, H3), 7.35 (m, 2, H5), 7.26 (m, 1, H5 (trans OH)), 1.50 ('t', $^2J_{HPt} = 66.9$ Hz, PtMe). Anal. Found: C, 40.2; H, 4.2; N, 7.5. $C_{18}H_{23}N_3O_4Pt$. Calc.: C, 40.0; H, 4.3; N, 7.8%.

4.1.4. [Pt(OH)Ph₂{(py)₃COH}][OH] · 2H₂O (4)

A solution of $[PtPh_2(SEt_2)]_2$ (0.112 g, 0.13 mmol) and $(py)_3COH$ (0.068 g, 0.26 mmol) in acetone (20 ml) that had not been dried was warmed until the acetone refluxed (about 5 min) and the pale yellow solution was refluxed for a further 10 min. The volume was reduced by rotary evaporation to about 10 ml; on standing overnight a colourless crystalline precipitate formed. The product was collected and dried in a vacuum (0.13

Table 2
Non-hydrogen atom coordinates and isotropic thermal parameters ($Å^2$) for $[PtPh_2\{(py)_3COH\}(OH_2)][NO_3]_2 \cdot H_2O$ (5)

Atom	x	y	z	U_{eq}
Pt	0.09568(6)	0.25864(3)	0.33121(4)	0.0322(3)
O(1)	0.071(1)	0.3420(5)	0.4021(7)	0.037(7)
C(1a')	−0.064(2)	0.1952(8)	0.295(1)	0.03(1)
C(2a')	−0.045(2)	0.117(1)	0.324(1)	0.05(1)
C(3a')	−0.147(2)	0.0696(9)	0.308(2)	0.06(2)
C(4a')	−0.278(2)	0.102(1)	0.256(1)	0.06(2)
C(5a')	−0.304(2)	0.178(1)	0.224(1)	0.05(1)
C(6a')	−0.200(2)	0.2249(9)	0.242(1)	0.04(1)
C(1b')	−0.025(1)	0.3263(9)	0.200(1)	0.04(1)
C(2b')	−0.008(2)	0.3220(9)	0.128(1)	0.05(1)
C(3b')	−0.082(2)	0.373(1)	0.043(1)	0.06(1)
C(4b')	−0.170(2)	0.429(1)	0.030(2)	0.07(2)
C(5b')	−0.182(2)	0.4343(9)	0.102(1)	0.05(1)
C(6b')	−0.113(2)	0.3860(9)	0.184(1)	0.05(1)
N(1a)	0.276(1)	0.3170(7)	0.3749(9)	0.037(9)
C(2a)	0.394(2)	0.2742(9)	0.420(1)	0.04(1)
C(3a)	0.516(2)	0.3046(9)	0.452(1)	0.05(1)
C(4a)	0.518(2)	0.386(1)	0.441(1)	0.05(1)
C(5a)	0.402(2)	0.4321(9)	0.400(1)	0.05(1)
C(6a)	0.283(2)	0.3941(9)	0.368(1)	0.04(1)
N(1b)	0.243(1)	0.1969(7)	0.4776(9)	0.041(9)
C(2b)	0.365(2)	0.1706(9)	0.507(1)	0.04(1)
C(3b)	0.459(2)	0.133(1)	0.597(1)	0.06(1)
C(4b)	0.441(2)	0.125(1)	0.665(1)	0.07(1)
C(5b)	0.317(2)	0.152(1)	0.638(1)	0.06(1)
C(6b)	0.218(2)	0.1891(9)	0.542(1)	0.05(1)
N(1c)	0.129(1)	0.1745(7)	0.2701(9)	0.037(8)
C(2c)	0.256(2)	0.1449(8)	0.322(1)	0.04(1)
C(3c)	0.280(2)	0.085(1)	0.285(2)	0.06(2)
C(4c)	0.170(2)	0.0478(9)	0.194(2)	0.06(2)
C(5c)	0.036(2)	0.0771(9)	0.138(1)	0.05(1)
C(6c)	0.017(2)	0.142(1)	0.178(1)	0.05(1)
C	0.380(2)	0.1843(9)	0.427(1)	0.05(1)
O	0.507(1)	0.1477(6)	0.4701(8)	0.047(9)
N(1)	0.343(2)	0.434(1)	0.608(1)	0.06(1)
O(11)	0.430(1)	0.4697(8)	0.688(1)	0.09(1)
O(12)	0.334(2)	0.3634(8)	0.604(1)	0.10(2)
O(13)	0.255(2)	0.468(1)	0.525(1)	0.12(1)
N(2)	−0.182(2)	0.3278(9)	0.405(1)	0.06(1)
O(21)	−0.056(1)	0.3049(7)	0.4630(9)	0.067(9)
O(22)	−0.223(1)	0.3752(7)	0.338(1)	0.08(1)
O(23)	−0.254(1)	0.3063(8)	0.423(1)	0.08(1)
O(0)	0.535(1)	0.1810(8)	0.333(1)	0.08(1)

g, 85%), ^{1}H NMR ((CD$_3$)$_2$CO): δ 9.20 (d(b), 1, H6 (trans OH)), 8.96 (d(b), 2, H6), 8.23 (m(b), 1, H4 (trans OH)), 8.01 (m, 5, H3 and H4), 7.37 (m(b), 1, H5 (trans OH)), 7.25 (m(b), 2, H5), 7.2–7.0 (m, 10, Ph). Anal. Found: C, 48.5; H, 4.2; N, 6.4. C$_{28}$H$_{29}$N$_3$O$_5$Pt. Calc.: C, 49.3; H, 4.3; N, 6.2%.

4.1.5. [PtPh$_2${(py)$_3$COH}(OH$_2$)][NO$_3$]$_2$·H$_2$O (5)

The complex [Pt(OH)Ph$_2${(py)$_3$COH}][OH] · H$_2$O (0.078 g, 0.12 mmol) was warmed in acetone (10 ml) until it dissolved. A few drops of 2 M nitric acid were added and the solution refluxed for 10 min. Acetone was removed by rotary evaporation to give a viscous liquid which was extracted with dichloromethane (3 × 10 ml). The dichloromethane extract was dried over MgSO$_4$ and filtered. The volume reduced to 5 ml and hexane added until the solution became cloudy, and crystals of the product subsequently formed (0.058 g, 64%). ^{1}H NMR ((CD$_3$)$_2$CO): δ 8.81 (dd, 1, H6 (trans OH$_2$)), 8.65 (dd, 2, H6), 8.54 ('td', 1, H4 (trans OH$_2$)), 8.30 ('td', 2, H4), 8.23 (dd, 2, H3), 8.14 (dd, 1, H3 (trans OH$_2$)), 7.68 (m, 1, H5 (trans OH$_2$)), 7.58 (m, 2, H5), 7.16 and 7.05 (m, 10, Ph). Anal. Found: C, 42.6; H, 3.5; N, 9.7. C$_{28}$H$_{27}$N$_5$O$_9$Pt. Calc.: C, 43.5; H, 3.5; N, 9.1%.

4.2. X-ray structure determination

Crystals of [PtPh$_2${(py)$_3$COH}(OH$_2$)][NO$_3$]$_2$ · H$_2$O (5) were obtained on dissolution in acetone followed by diffusion of diethyl ether vapor into the solution. A unique data set for complex 5 was measured at 295 K to $2\theta_{max} = 50°$ using an Enraf–Nonius CAD-4 diffractometer fitted with a monochromatic Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) source and operating in conventional 2θ–θ scan mode. A total of 4958 independent reflections were obtained, 2835 with $I > 3\sigma(I)$ being considered observed and used in the full matrix least squares refinement after analytical absorption correction, and solution of the structure by vector methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at estimated values. Residuals R and R_w on F at convergence were 0.052 and 0.051; statistical weights derived from $\sigma^2(I)$ $= \sigma^2(I_{diff}) + 0.0004\ \sigma^4(I_{diff})$ were employed. Neutral atom complex scattering factors were used [20]; computation used the XTAL 3.2 program system implemented by Hall [21]. Crystal data, coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, and the geometries of the complex are given in Tables 1 and 2, and a view of the complex is shown in Fig. 1. Crystal data: [PtPh$_2${(py)$_3$COH}(OH$_2$)][NO$_3$]$_2$ ·
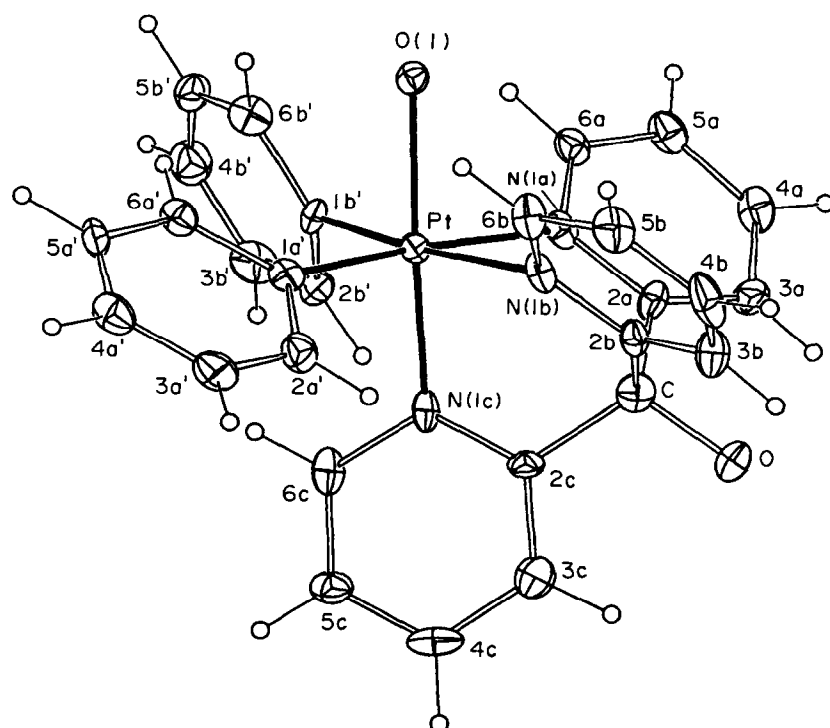
Fig. 1. The molecular structure [PtPh$_2${(py)$_3$COH}(OH$_2$)][NO$_3$]$_2$ · H$_2$O (5). Thermal ellipsoids (20%) are shown for the non-hydrogen atoms. Hydrogen atoms (constrained at estimated positions) are shown for phenyl and pyridin-2-yl rings and have been given an arbitrary radius of 0.1 Å.

H_2O, $C_{28}H_{27}N_5O_9Pt$, $M_r = 772.7$, monoclinic, space group $P2_1/c$, $a = 12.810(6)$, $b = 17.088(7)$, $c = 17.292(3)$ Å, $\beta = 131.91(2)°$, $Z = 4$, $U = 2817(2)Å^3$, $D_c = 1.82$ g cm^{-3}, $F(000) = 1520$, $\mu = 50.5$ cm^{-1}, $A^*_{min,max} = 1.18$, 1.45, crystal size $= 0.38 \times 0.066 \times 0.035$ mm^3.

4.2.1. Abnormal features and variations in procedure

Limited, rather weak data from a small specimen sustained meaningful full anisotropic thermal parameter refinement for all non-hydrogen atoms but did not permit location of hydrogen atoms confidently throughout. A difference map artefact was modelled congenially as a fully populated oxygen atom, presumed to be water.

Lists of thermal parameters, hydrogen atom coordinates, and a complete lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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