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Synthesis of aquanitrato(1-methyl-2,2′-bipyridin-3-yl-ium)-palladium(II) perchlorate hydrate

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Abstract

Treatment of [Pd(bpyMe–H)Cl_2]/(bpyMe–H = 1-methyl-2,2′-bipyridin-3-yl-ium) with 2 mol of $AgNO_3$ in water yields a solution of [Pd(bpyMe–H)$(H_2O)_2]^{2+}$ and NO_3^-, which on evaporation forms [Pd(bpyMe–H)$(ONO_2)_2$]. Addition of $NaClO_4$ to a solution of [Pd(bpyMe–H)$(H_2O)_2]^{2+}$ and NO_3^- yields [Pd(bpyMe–H)$(H_2O)(ONO_2)]ClO_4 \cdot H_2O$.

Introduction

Palladium(II) and platinum(II) complexes of the type $[M(L)_2Cl_2]$ (M = Pd, Pt; L = amine) hydrolyse in water to give $[M(L)_2(H_2O)Cl]^+$ and ultimately $[M(L)_2(H_2O)_2]^{2+}$. Despite this the number of well characterized crystalline aqua complexes is limited; to our knowledge the only example of a palladium(II) complex is [Pd(dmp)(bquin)$(H_2O)]ClO_4$ (dmp = 2-(dimethylaminomethyl)phenyl; bquin = benzo[*h*]quinoline) [1]. The coordination to a metal ion increases the acidity of the aqua ligand relative to pure water and hydroxy complexes can often be isolated instead. We have recently described the preparation of [Pd(terpy)(OH)]ClO_4 (terpy = 2,2′:6′,2″-terpyridine) [2].

We have been studying [3–6] the coordination chemistry of the 1-methyl-2,2′-bipyridinium ion **1** (bpyMe$^+$). As a ligand bpyMe$^+$ is similar to 2-phenylpyridine as both molecules form cyclometallated complexes readily with Pt^{II} and Pd^{II}. However, bpyMe$^+$ differs from 2-phenylpyridine in that on cyclometallation, the ligand itself is acting as a zwitterion whereas 2-phenylpyridine is negatively charged. This means that most cyclometallated compounds which contain only halides as the other ligand are neutral chloro-bridged dimers, whereas [M(bpyMe–H)Cl_2] (M = Pd, Pt) are monomers [5].

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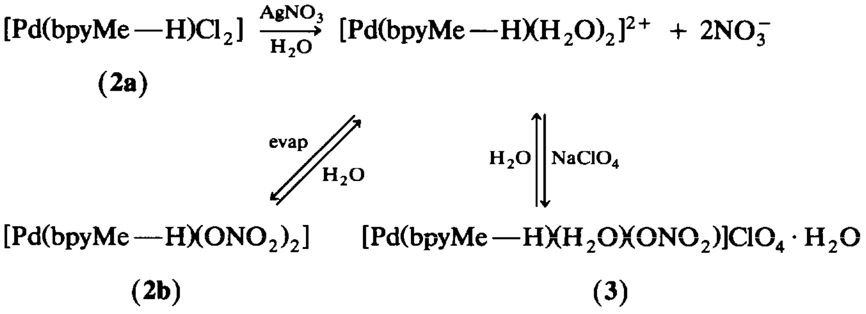
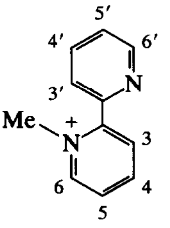


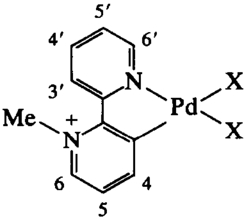
Scheme 1. Preparation and reactions of $[Pd(bpyMe\text{-}H)(H_2O)_2]^{2+}$.



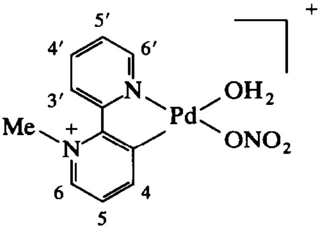
(1)

Results and discussion

Treatment of $[Pd(bpyMe\text{-}H)Cl_2]$ (**2a**) (bpyMe-H = 1-methyl-2,2′-bipyridin-3-ylium) with 2 mol of silver nitrate in water gives a pale yellow solution containing $[Pd(bpyMe\text{-}H)(H_2O)_2]^{2+}$ and nitrate (Scheme 1). Evaporation to dryness after removal of the precipitate of silver chloride yields $[Pd(bpyMe\text{-}H)(ONO_2)_2]$ (**2b**) which was recrystallised from dilute nitric acid. Addition of sodium perchlorate to the same pale yellow solution, on the other hand, gives crystals of $[Pd(bpyMe\text{-}H)(H_2O)(ONO_2)]ClO_4 \cdot H_2O$ (**3**).



(**2a**, X = Cl,
2b, X = ONO_2)



(**3**)

The coordination of the nitrate ions was confirmed by infrared spectroscopy (Table 1). Coordinated nitrate has six infrared active bands [7–9]; of these ν_3 and ν_5 are in the same region (700–800 cm^{-1}) as the four strong deformation modes of the ligand. The ν_3 mode is weak and was not observed while ν_5 is at either 714 or

Table 1
Infrared spectra of the complexes [a]

Assignment	[Pd(L)(ONO$_2$)$_2$]	[Pd(L)(H$_2$O)(ONO$_2$)]ClO$_4$·H$_2$O
ν(H$_2$O)		3570m
ν(H$_2$O)		3460s,br
δ(H$_2$O)		1675m,br
δ(H$_2$O)		1630m,br
L (ring str)	1600w	
L (ring str)	1589s	1590s
ONO$_2$ (ν_4)	1460vs	1480vs
ONO$_2$ (ν_1)	1280vs	1298vs
ONO$_2$ (ν_2)	1017s	1012s
ONO$_2$ (ν_2)	989s	
ONO$_2$ (ν_6)	817s	~ 803
L(C–H oop)	800s	803s
L(C–H oop)	785s	792s
L(C–H oop)	745s	754s
L(C–H oop)/ONO$_2$(ν_5) [b]	714s	713s
L(C–H oop)/ONO$_2$(ν_5) [b]	708s	
H$_2$O(def)		560m,br
ν(Pd–ONO$_2$)	339m	339m
	318m	
	264m	270m
ν(Pd–ONO$_2$)	239m	

[a] L = (bpyMe–H), v = very, s = strong, m = medium, br = broad, str = stretch, oop = out of plane, def = deformation. [b] See text.

708 cm^{-1}; the latter assignment is preferred. The spectrum of [Pd(bpyMe–H)(ONO$_2$)$_2$] shows considerable splitting (28 cm^{-1}) of the ν_2 band (N–O stretch) which is much larger than that observed (10 cm^{-1}) for [Pd(bpy)(ONO$_2$)$_2$] (2,2′-bipyridine) [10]. This can be attributed to the unsymmetrical nature of the (bpyMe–H) ligand since the σ-bonded carbon has a higher *trans* influence than the pyridyl nitrogen atom.

The Pd–ONO$_2$ stretching modes are assigned to the bands at 339 (*trans* to the pyridyl ring) and 239 cm^{-1} (*trans* to the cyclometallated ring), although the latter assignment is somewhat tentative. These modes are in the same region as the Pd–Cl stretching modes (333 and 256 cm^{-1}) for [Pd(bpyMe–H)Cl$_2$] [5].

The infrared spectrum (Table 1) of [Pd(bpyMe–H)(H$_2$O)(ONO$_2$)]ClO$_4$ · H$_2$O apart from water and perchlorate bands is essentially similar to that of [Pd(bpyMe–H)(ONO$_2$)$_2$], except that the ν_2 band at 1012 cm^{-1} is no longer split. The Pd–ONO$_2$ stretching mode at 339 cm^{-1} is still present, indicating that the nitrato ligand is *trans* to the pyridyl ring as in structure **3**, while the band at 239 cm^{-1} has disappeared. The Pd–OH$_2$ mode cannot be identified.

The molar conductance of [Pd(bpyMe–H)(ONO$_2$)$_2$] in water is 247 S cm^2 mol^{-1} (1.0 × 10^{-3} *M*) which is typical of a 2:1 electrolyte, indicating complete aquation of the nitrato ligands:

$$[\mathrm{Pd(bpyMe{-}H)(ONO_2)_2}] \xrightarrow{\mathrm{H_2O}} [\mathrm{Pd(bpyMe{-}H)(H_2O)_2}]^{2+} + 2\mathrm{NO_3^-}$$

Moreover, the resultant diaqua complex is not noticeably acidic, since any acid dissociation would result in a larger value for the molar conductance owing to the

Table 2
^{1}H NMR spectra [a]

	$(bpyMe)^+$ [b]	$[Pd(bpyMe-H)(H_2O)_2]^{2+}$ [c]	Δ (ppm) [d]
H(3)	8.15	–	–
H(4)	8.66	8.12	−0.54
H(5)	8.14	7.60	−0.54
H(6)	8.94	8.54	−0.40
H(3′)	7.84	8.45	0.61
H(4′)	8.16	8.31	0.15
H(5′)	7.73	7.72	−0.01
H(6′)	8.79	8.63	−0.16
Me	4.25	4.63	

[a] D_2O solution, $(bpyMe)^+$ = 1-methyl-2,2′-bipyridinium. [b] Coupling constants (Hz): $J_{3,4}$ 7.9, $J_{3,5} \sim 1.5$, $J_{3,6}$ –, $J_{4,5}$ 7.9, $J_{4,6}$ 1.1, $J_{5,6}$ 6.1, $J_{3'4'}$ 7.9, $J_{3'5'}$ 1.1, $J_{3'6'} \sim 1$, $J_{4'5'}$ 7.8, $J_{4'6'}$ 1.7, $J_{5'6'}$ 4.9. [c] Coupling constants (Hz): $J_{4,5}$ 8.1, $J_{4,6}$ 0.8, $J_{5,6}$ 6.1, $J_{3'4'}$ 8.3, $J_{3'5'}$ 1.2, $J_{3'6'}$ –, $J_{4'5'}$ 7.9, $J_{4'6'}$ 1.6, $J_{5'6'}$ 5.5. [d] Change in chemical shift on complex formation. Negative values indicate a shift to high field.

high ionic conductance of the H_3O^+ ion. Removal of the water reverses the reaction, while addition of perchlorate allows the intermediate complex $[Pd(bpyMe-H)(H_2O)(ONO_2)]^+$ to be isolated because of the low solubility of the perchlorate salt, although the equilibrium constant for its formation is probably small. Appleton et al. [11] have shown for the *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ system that the equilibrium constant for the formation of *cis*-$[Pt(NH_3)_2(H_2O)(ONO_2)]^+$ is 0.1.

In water $[Pd(bpyMe-H)(H_2O)(ONO_2)]ClO_4 \cdot H_2O$ also reforms $[Pd(bpyMe-H)(H_2O)_2]^{2+}$ and the proton NMR spectrum in D_2O (Fig. 1) shows seven aromatic resonances. The assignments were made beginning with the observation that H(5) is the sole doublet of doublets, followed by a consideration of spin multiplicities and coupling constants as well as by several decoupling experiments (see Tab. 2).

Upon coordination and cyclometallation of $(bpyMe)^+$ to palladium(II), there is a net upfield shift of the ring protons (Table 2) indicating a flow of electron density from the metal to the π orbitals of the aromatic rings. A similar effect was reported by Newcombe et al. [12] and Steel and Caygill [13] for cyclometallated 2-phenylpyridine complexes. However, the 3′-pyridyl hydrogen is shifted downfield by 0.61 ppm. The preferred conformation of $(bpyMe)^+$ in solution is probably with the two rings orthogonal [13]. On cyclometallation the ligand is forced into a planar structure, resulting in a van-der-Waal's interaction between H(3′) and the N-methyl group giving rise to a mutual deshielding.

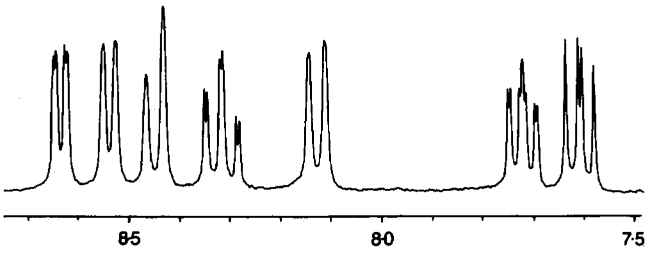


Fig. 1. ^{1}H NMR spectrum of $[Pd(bpyMe-H)(H_2O)_2]^{2+}$ in D_2O.

Conclusion

The formation of [Pd(bpyMe–H)(ONO_2)$_2$] from [Pd(bpyMe–H)(H_2O)$_2$]$^{2+}$ occurs via [Pd(bpyMe–H)(H_2O)(ONO_2)]$^+$ although Appleton et al. [11] showed that the addition of a large excess of nitrate to *cis*-[Pt(NH_3)$_2$(H_2O)$_2$]$^{2+}$ gave only a small amount of *cis*-[Pt(NH_3)$_2$(H_2O)(ONO_2)]$^{2+}$. Infrared spectroscopy shows that the aqua ligand *trans* to the pyridyl nitrogen is the first to be replaced.

Conrad and Rund [15] demonstrated in the reaction of [M(Rphen)Cl_2] (M = Pt, Pd; Rphen = substituted phenanthroline) with dithiooxamide that if π effects are kept constant, then as the σ effect increases the rate of substitution decreases with the proviso that bond-making dominates the transition state. In the formation of [Pd(bpyMe–H)(H_2O)(ONO_2)]$^+$ this implies that the aqua ligand *trans* to the pyridyl N in [Pd(bpyMe–H)(H_2O)$_2$]$^{2+}$ will be the more reactive. Similarly, reaction of [Pd(bpyMe–H)Cl_2] with pyridine (py) yields as the first product [Pd(bpyMe–H)(py)Cl]$^+$ in which the pyridine is *trans* to the pyridyl N [16].

Experimental

Infrared spectra were recorded (4000–200 cm^{-1}) on a Perkin-Elmer 983 spectrophotometer using both nujol and hexachlorobutadiene mulls (CsI plates) and cesium halide discs. The proton NMR spectra were recorded on a Bruker WM250 Fourier transform spectrometer. Conductance measurements in water were measured at 25°C with a Beckman RC-18A conductivity bridge. C, H, N analyses were carried out by the Interuniversity Microanalytical Services, Ecole Nationale Supèrieure de Chimie de Toulouse. [Pd(bpyMe–H)Cl_2] (**2a**) was prepared by the method previously described [5].

Preparation of the complexes

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with the necessary precautions [17].

[Pd(bpyMe–H)(ONO_2)$_2$] (2b). $AgNO_3$ (0.523 g; 3.07 mmol) was added to a stirred suspension of [Pd(bpyMe–H)Cl_2] (**1**) (0.537 g, 1.54 mmol) in water (40 ml). AgCl precipitated immediately. The mixture was stirred for 10 min and the AgCl removed by centrifugation. A few drops of concentrated nitric acid were added to the pale yellow solution which was then evaporated to dryness. The compound was recrystallised from dilute nitric acid (pH ≈ 1); yield 65%. Anal. Found: C, 33.1; H, 2.5; N, 14.0. $C_{11}H_{10}N_4O_6Pd$ calc.: C, 33.0; H, 2.5; N, 14.0%.

[Pd(bpyMe–H)(H_2O)(ONO_2)]$ClO_4 \cdot H_2O$ (3). [Pd(bpyMe–H)(ONO_2)$_2$] (**2b**) (0.20 g; 0.50 mmol) was dissolved in a minimum amount of water to give a lemon-yellow solution. A concentrated solution of sodium perchlorate was added to the point of incipient turbidity. The solution was left for 3 days at ambient temperature whereupon yellow-orange cubes of the product **3** separated. The cubes (70%) were isolated, washed with water, ethanol and ether and dried *in vacuo*. Anal. Found: C, 27.7; H, 2.8; N, 8.8. $C_{11}H_{14}ClN_3O_9Pd$ calc.: C, 27.9; H, 3.0; N, 8.9%.

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