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Equilibria in Complexes of N-Heterocycles. Part 50.[1] The Formation and Properties in Solution of the 1:1 Adducts of Bis(2,2'-bipyridine)platinum(II) and Related Ions with Hydroxide*

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Equilibrium constants are given for addition (mol ratio 1:1) of hydroxide to several palladium(II) and platinum(II) cations. $[Pt(bpy)_2]^{2+}$ (bpy: 2,2'-bipyridine) and hydroxide ion form the well-known 1:1 adduct rapidly in water; the rate is given at 25 °C by $k = 1.6 \times 10^2$ mol^{-1} dm^3 s^{-1}. The equilibrium constants for adding hydroxide to $[Pt(bpy)_2]^{2+}$ and to $[Pt(3,3'\text{-}[^2H]_2\text{-}bpy)_2]^{2+}$ are the same, but differ considerably from those for $[Pt([^2H]_8\text{-}bpy)_2]^{2+}$ and for $[Pt(6,6'\text{-}[^2H]_2\text{-}bpy)_2]^{2+}$ with hydroxide. In this reaction, the infrared spectrum (1700–900 cm^{-1}) of the cation initially $[Pt(bpy)_2]^{2+}$ in the aqueous solution shows distinct changes between pH = 7.0 and pH = 11.0, notably in the aromatic region, where the intensity of the band due to C=N at *ca.* 1600 cm^{-1} is much reduced. At pH = 7.0, the methyl groups in $[Pt(5,5'\text{-}dmbpy)_2]^{2+}$ (dmbpy: dimethyl-2,2'-bipyridine) or the 4,4'-isomer are equivalent in ^1H magnetic resonance but become inequivalent in the 1:1 adducts with hydroxide. In the presence of (–)-methylbenzylamine, both [Pt(terpy)Cl]Cl (terpy: 2,2',2''-terpyridine) and $[Pt(bpy)_2]^{2+}$ manifest a strong Pfeiffer effect, but not the 'exciton' coupling characteristic of *cis*-octahedral ions. These observations are interpreted in terms of addition of hydroxide to the bipyridine ligands.

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* We dedicate this paper to mark the eightieth birthday of Professor Smiljko Ašperger, and to acknowledge his distinguished research on the mechanisms of inorganic reactions, and his contribution to our knowledge and understanding of that field.

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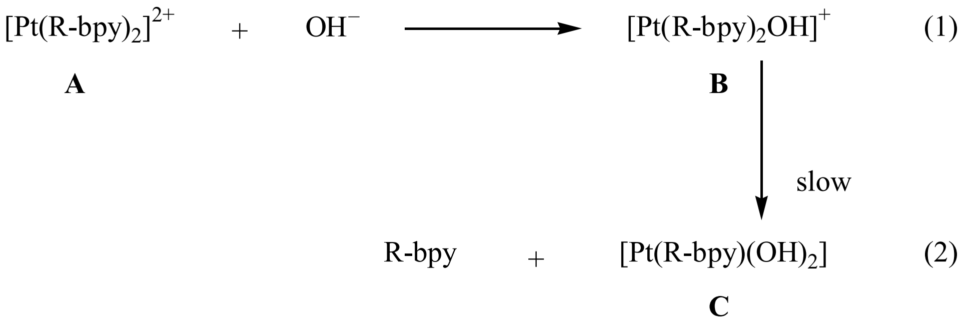
Key words: platinum(II), palladium(II), complexes with pyridine (py), 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2',2''-terpyridine (terpy), equilibrium constant with hydroxide, electronic spectra (UV-Vis, CD), NMR spectra (^{1}H, ^{13}C, ^{195}Pt), deuterium substitution, kinetic isotope effect, Pfeiffer effect, Cotton effect.

INTRODUCTION

In water, nucleophiles such as hydroxide add[2] to complex cations like **A** (Scheme 1) containing metal ions coordinated by imines (including N-heterocycles and other >C=NX systems).



$$\begin{tikzcd}[column sep=small]
\underset{\textbf{A}}{[Pt(R\text{-}bpy)_2]^{2+}} & + & OH^- \arrow[rr] & & \underset{\textbf{B}}{[Pt(R\text{-}bpy)_2OH]^+} \arrow[d, "slow"] & (1) \\
& & R\text{-}bpy & + & \underset{\textbf{C}}{[Pt(R\text{-}bpy)(OH)_2]} & (2)
\end{tikzcd}$$

Scheme 1.

Scheme 1 presents the reaction of bis(2,2'-bipyridine)platinum(II) salts with base in water. Equilibrium constants for (1), and rate constants for (1) and for the decomposition (Eq. 2) of the intermediate **B** (R = H or ^{2}H) are discussed in text. **C** undergoes dimerization and further reactions with hydroxide. These are also mentioned in the text.

Following our discovery[3] (using electronic spectra) of the equilibrium in Eq. (1) of Scheme 1, and the measurement of such properties of the aqueous system as NMR, (and its interpretation in terms of nucleophilic addition to the ligand) there has been a good deal of careful validation and extension of the facts. For instance, Mureinik and Bidani found[4] that the aqueous electronic spectrum of $[Pt(terpy)Cl]^+$ changed on adding base.* Acid caused reversal.

Wernberg measured[5] the equilibrium constants for hydroxide and other nucleophiles adding reversibly as in (1). These addends included amines,

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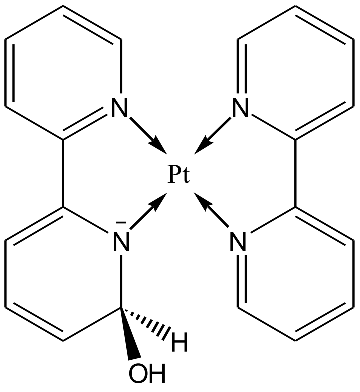
* Throughout, bpy signifies 2,2'-bipyridine, phen 1,10-phenanthroline, terpy 2,2',2''-terpyridine, and py pyridine. Abbreviation dmbpy is used for dimethyl-2,2'-bipyridine. Nu denotes a nucleophile, usually OH^- or CN^-.

thio-species (SO_3^{2-}, $S_2O_3^{2-}$, thiourea), and iodide. The spectroscopic changes between **A** and **B** were similar, regardless of the addend. Those measurements utilized a rather limited range of concentrations for the addends.

No salt of a hydroxide adduct has yet been obtained as single crystals, although ill-defined dark solids could be precipitated[6] from solutions containing the $[Pt(phen)_2]^{2+}$ ion in the presence of hydroxide. A solid of composition $[Pt(phen)_2(CN)](ClO_4)$ has been studied[7] by X-ray diffraction. Isolated from a solution obtained by adding a soluble cyanide to $[Pt(phen)_2](ClO_4)_2$, its structure was reminiscent of the only other compound[8] of ostensibly 5-coordinated platinum(II) with 1,10-phenanthroline: that had composition $[PtCl\{P(C_2H_5)_3\}_2(phen)](BF_4)$. In the cyano-species, while one phenanthroline is chelated with both its Pt–N vectors about 2.0 Å, the other forms[7] only one short bond in-plane (Pt–N, 2.0 Å). The fourth in-plane position is occupied by cyanide. The plane of the unidentate phenanthroline is perpendicular to the plane involving four co-ordinated platinum, and, as in the original case,[8] the second nitrogen atom of the rigid phenanthroline is held further from the platinum. This, in the phosphine compound, had been taken[8] as indicating a bonding interaction (»half-bonded phen«). In both cases, even if the 1,10-phenanthroline were actually unidentate, bonded through the equatorial Pt–N linkage alone, its rigid geometry ensures that its second nitrogen must be within a relatively short distance of the metal ion.

Despite this background, there has been no general agreement[2] about the structures in aqueous solution of the adducts such as **B**. The dispute is over which element (carbon or metal, in this case platinum(II) with its $5d^8$ configuration) increases in coordination number on adding hydroxide, and may be exemplified by the first such adduct discovered, **B** of Eq. (1) in Scheme 1.

The original suggestion was[3] that an initially aromatic carbon atom increased in coordination number, as in (1). (This was based on the related parent organic systems where nucleophiles – cyanide, sulfite, amines, carbanions, hydroxide and so on – reacted with quaternized compounds of N-heterocycles, including bpy and phen). A counter-vailing comment[9] was made that »the chemistry of this important and large group of complexes has been relegated (*sic*) to what is essentially claimed to be the organic chemistry of the ligands.« The original values[3] for K were confirmed. ^1H resonance spectra of **B** agreed quite well with prior measurements:[3] ^{13}C spectra were also measured. Those spectra were re-interpreted[9] as arising from a *cis*-bis-structure with five-coordinated platinum(II) ions or (although **B** is still diamagnetic) a related six-coordinated (*sic*) octahedral *cis*-hydroxoaquabis(2,2'-bipyridine)platinum(II) ion; **II**, Scheme 2. Because of the inequivalence of the hydroxide and the water ligands in an instant view of the preferred structure **II**, it lacked symmetry: all the NMR spectra[3,9] had indeed implied total absence of symmetry.



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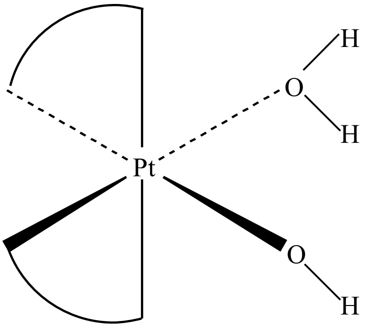


II

Scheme 2.

Two expansions of earlier work on (a)[10] *trans*-[Pt(py)$_4$Cl$_2$](NO$_3$)$_2$ and (b)[11] *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ concluded, respectively, that (a) »there were no experimental observations which could not be accounted for by classical coordination compounds«;[10] and (b) »very few claims are based upon empirical spectroscopic evidence for intermediates of type **I**«[11] (*i. e.* type **I** of the present paper). Certainly, it is impossible to distinguish between these alternative mechanisms on the basis of simple kinetic or spectroscopic results or data.

We therefore present here some experimental observations and spectroscopic evidence which are easier to reconcile with **I** rather than **II** as the actual structure of **B** and its homologues. Our additional work on these solutions involves five types of finding. Four are new: (i) the existence and nature of the Pfeiffer effect with chiral organic amines; (ii) the size of the rate constant for formation of the adduct, **B**, from [Pt(bpy)$_2$]$^{2+}$, *i.e.* with R = H;

(iii) the nature of the changes in the FTIR spectrum of aqueous solutions after additions of base, and (iv) the distinct differences in equilibrium and rate constants for addition of hydroxide to the isotopomeric ions $[Pt(^{1}H_{8}\text{-bpy})_{2}]^{2+}$ and $[Pt(^{2}H_{8}\text{-bpy})_{2}]^{2+}$: the origin of this difference has been localized (at least in large part) to the 6,6'-positions by use of selectively dideuterated isotopomeric ligands. The fifth type of finding extends our earlier measurement[3] of the ^{1}H magnetic resonance of $[Pt(5,5'\text{-dmbpy})_{2}]^{2+}$ and adds similar work on the 4,4'-dimethyl-isomer. All five methods indicate that **B** involves a modified ligand and retains a four-coordinated platinum(II) ion. We comment finally on the conflicting NMR work, on coordination numbers for platinum(II) and palladium(II), and on the rather general occurrence of hydroxide attack *via* unsaturated carbon.

This report is concerned only with aqueous solutions. In general, the reactivity of hydroxide in non-aqueous or mixed solvent is greatly enhanced. Phenomena or reactions are then often seen[2d] which are not readily accessible in water.

EXPERIMENTAL

Materials

Raney Nickel Catalyst

This was prepared by the method of Sasse and Badger.[12] A warm solution (70 °C) of potassium hydroxide (40 g) in water (150 ml) in a 500 ml round-bottomed three-necked flask was cooled in an ice-bath while nickel-aluminium alloy (31.5 g, 1:1) was added in portions. The temperature quickly reached 85–90 °C. After all the alloy had been added and the temperature had fallen to 55–60 °C, the ice-bath was replaced by a hot water bath, stirring being continued for 20–30 minutes. The catalyst was then allowed to stand from 6 to 12 hours. The supernatant was decanted and the catalyst washed with water until the washings were neutral to litmus. The catalyst requires careful handling: it was kept until use in nitrogen gas. The flask was fitted with a 100 ml dropping funnel, and then slowly evacuated (oil pump) and warmed on a water bath (100 °C) until dry (≈30 minutes).

The reactant (pyridine, picoline *etc.*) was poured from the dropping funnel carefully onto the dry catalyst. Air was excluded until the catalyst was completely covered with reactant.

2,2'-Bipyridine

The Raney nickel slurry in pyridine (100 ml) was transferred into the thimble of a Soxhlet extractor and boiling pyridine (115 °C) set to reflux through it for 48 hours. The product was isolated from unreacted pyridine by simple distillation, and purified by extraction: m.p. 69–70 °C.

Dichloro-2,2′-Bipyridineplatinum(II) [Pt(bpy)Cl$_2$] (Yellow Form)

This was prepared by the method of Morgan and Burstall,[13] by treating potassium tetrachloroplatinate(II) (0.10 g, 0.24 mmol) in hot water (150 ml) with bipyridine (0.039 g, 0.24 mmol) in dilute hydrochloric acid (2 M, 10 ml); the mixed solution was heated for about 20 minutes until the liquid became filled with the yellow product. The yield was 0.095 g. The filtrate was heated again and a further crop was obtained. The pale yellow solid was washed with ice-cold water and ice-cold ethanol and air dried.

$Pt([^1H_8]\text{-bpy})_2Cl_2$ yield: 86%. *Anal.* Calcd. for $PtC_{10}[^1H]_8N_2Cl_2$: C, 28.45; H, 1.91; N, 6.64%. Found: C, 28.7; H, 1.8; N, 6.6%.

Bis(2,2′-bipyridine)platinum(II) Nitrate Dihydrate [Pt(bpy)$_2$](NO$_3$)$_2 \cdot$ 2H$_2$O

This complex was prepared by a method analogous to that used by Morgan and Burstall[13]. The yellow dimorph of [Pt(bpy)Cl$_2$] (0.43 g, 1 mmol) in hot water (200 ml) was set to reflux with a solution of 2,2'-bipyridine (0.4 g, 2.5 mmol) in ethanol (20 ml) until most of the complex dissolved. The pale yellow filtrate was evaporated (rotary evaporator) to about 10 ml, re-filtered to remove unreacted bipyridine, then mixed with sodium nitrate 0.2 g (saturated soln.). This solution was kept for a week, giving shiny crystals, which were recrystallised from hot water (10 ml) and ethanol (5 ml): yield 0.2 g.

Anal. Calcd. for $PtC_{20}[^1H]_{16}N_6O_6H_2O$: C, 36.98; H, 2.79; N, 12.94%. Found: C, 37.1; H, 2.9; N, 12.8%.

Bis(2,2′-bipyridine)platinum(II) Iodide Dihydrate [Pt(bpy)$_2$]I$_2 \cdot$ 2H$_2$O

It was obtained by treating the preparative solution containing $[Pt(bpy)_2]^{2+}$ with aqueous potassium iodide (0.1 g): the red hair-like crystals became black on exposure to the air or washing with acetone. This phenomenon was studied by Livingstone and Wheelahan.[14] The complex decomposes above 90 °C to [Pt(bpy)I$_2$] as described by Morgan and Burstall.

Perdeutero-2,2′-bipyridine

It was made by the Raney nickel condensation of perdeuteropyridine. The isotopomeric compound $[Pt([^2H]_8\text{-bpy})_2](NO_3)_2 \cdot H_2O$ was made from it, *mutatis mutandis*, like the perproto-isotopomer.

(a) $Pt([^2H]_8\text{-bpy})_2Cl_2$ yield: 74%. *Anal.* Calcd. for $PtC_{10}[^2H]_8N_2Cl_2$: C, 27.92; H, 3.75; N, 6.51% Found: C, 27.4; H, 3.4; N, 6.7%.

(b) *Anal.* Calcd. for $PtC_{20}[^2H]_{16}N_6O_6H_2O$: C, 36.07; H, 5.21; N, 12.62%. Found: C, 36.2; H, 4.9; N, 12.4%. ^1H NMR (360 MHz, D_2O) displayed no resonances attributable to $^1H_8$-bipyridine protons.

3,3'-dideuterio-2,2'-bipyridine was made by (i) permanganate oxidation of 1,10-phenanthroline to binicotinic acid (3,3'-dicarboxyl-2,2'-bipyridine); (ii) recrystallization from heavy water by first raising pD, using NaOD to cause dissolution, then lowering pD to cause reprecipitation using DCl; (iii) repeating this exchange; (iv) decarboxylation by heating in a vacuum sublimer accompanied by sublimation of the product on to the cold finger cooled by solid CO_2-acetone.

6,6'-dideuterio-2,2'-bipyridine was made by (i) $KMnO_4$ oxidation of 6,6'-dimethyl-2,2'-bipyridine to the 6,6'-dicarboxylic acid; (ii) repeated deuterium exchange in heavy water; (iii) decarboxylation and sublimation in a vacuum sublimer.

The isotopic purity of products was checked by proton NMR. For example, $[Pt([^1H]_8\text{-bpy})_2](NO_3)_2 \cdot H_2O$ shows (in D_2O) three regions of resonance, at $\delta = 7.75$, 8.35 and 8.82 ppm, with experimental intensity ratio 15.328 : 31.325 : 15.354. In $[Pt(6,6'\text{-}[^2H]_2\text{-bpy})_2](NO_3)_2 \cdot H_2O$ the corresponding spectrum showed the same chemical shifts (with altered splitting patterns) and intensities 20.800 : 44.839 : 2.661.

Measurements

Circular dichroism was measured using a Jouan Dichrographe mark V, with the constant sensitivity setting of 1×10^{-6}. Attempts to measure ^{195}Pt chemical shifts failed because of the relative insolubility of the compounds. For example, with 0.03 mmol dm^{-3} $[Pt(bpy)_2](NO_3)_2$, more or less a saturated solution, 11700 scans in the range –634 to –2634 ppm revealed no intensity.

Bis(2,2'-bipyridine)platinum(II) cation and its 5,5'-disubstituted dimethyl analogue made as solid nitrates were converted to chloride salts by anion exchange when required (as for the IR measurements in solution) or made *in situ* as described below. The rate study was done at controlled temperatures with ionic strength of 0.1 mol dm^{-3}, using *ca.* 10^{-5} mol dm^{-3} complex solutions and hydroxide solutions of concentrations from 0.05 to 0.005 mol dm^{-3}, using a stopped-flow device developed locally. Reaction was followed both at 350 nm where the optical density decreased on forming the adduct (*cf.* Fig. 1, Ref. 3) and separately at 380 nm where the optical density increased. No further change in optical density occurred when the reacted solutions were allowed to stand in the stopped flow cell for a further half hour after the rapid initial change. The derived values of k_{obs} at 350 and at 380 nm were in excellent agreement. The resulting rate law was first order in hydroxide, $k[A][OH^-]$, with k = 68 mol^{-1} dm^3 s^{-1} at 0 °C.

Equilibrium constants were measured spectrophotometrically, in the form of pH-titrations. The electronic spectra of equimolar solutions of the two isotopomeric nitrates are initially indistinguishable. On addition of hydroxide, the spectra of the equimolar isotopomeric solutions at the same pH deviate. For a given value of pH, the observed degree of change has always been greater for the $[^1H]_8$-bpy system than its $[^2H]_8$-isotopomer, at any of several wavelengths, whether the optical density rises or falls with hydroxide addition.

For the 3,3'-dideutero-complex and the perproto-isomer, the linear plots of $[A - A_i]$ / $[A_f - A]$ *vs.* $[OH^-]$ essentially coincide. For the 6,6'-pair, the nicely linear plots are quite distinct. For example, at $[OH^-] = 1.26 \times 10^{-4}$ mol dm^{-3}, the absorbance quotients are, for perproto 0.80 but for dideutero 0.41, and at 1.75×10^{-4} mol dm^{-3}, 1.09 and 0.59, respectively.

In situ *Preparation of $[Pt(bpy)_2]Cl_2$ (for IR Spectroscopy)*

A suspension of 51.0 mg (0.121 mmol) $[Pt(bpy)Cl_2]$ and 50 mg 2,2'-bipyridine in 3.4 g D_2O (density = 1.101 g/ml; thus c = 0.039 mol dm^{-3}) was stirred at about 100 °C until the complex dissolved, then extracted (4 times) with CH_2Cl_2 (this solvent had been previously stirred with D_2O) to remove excess of bpy (test with Fe^{2+}). The aqueous layer was gently warmed and purged with argon to remove CH_2Cl_2.

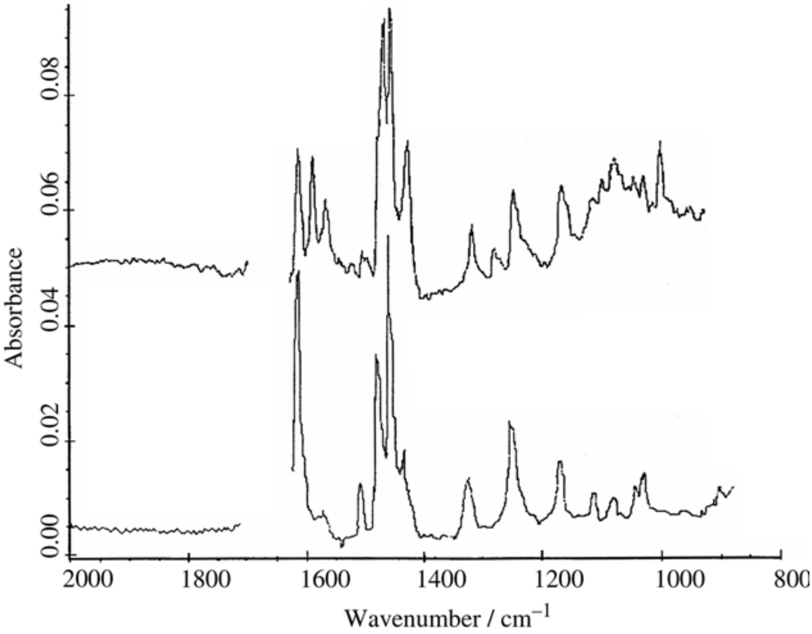


Figure 1. $[Pt(bpy)_2]Cl_2$ in water (lower) and in KOH/water (upper).

Pfeiffer Effects – Preliminary Experiments

$[Pt(bpy)_2]Cl_2$ decomposes when its solution is concentrated in vacuo. The reaction of 100 mg yellow $[Pt(bpy)Cl_2]$ and 100 mg bpy in water was used to give $[Pt(bpy)_2]Cl_2$. After evaporation at 49 °C an orange-reddish solid formed. This contained not only the desired salt but free bpy and $[Pt(bpy)Cl_2]$ as its red dimorph. (It is worth remark that all other samples of this red dimorph also arose from $[Pt(bpy)Cl_2]$ in the presence of free nitrogenous ligands). The solid was treated with CH_2Cl_2 to remove bpy and subsequently stirred with warm water. The suspension so obtained was filtered to remove the water insoluble $[Pt(bpy)Cl_2]$ and found (by UV comparison with the analogous perchlorate) to contain $[Pt(bpy)_2]Cl_2$, but no free bpy (Fe^{2+} test was negative). The solution was diluted to a reasonable optical density (0.8 at 320 nm).

Addition of (–)-α-methylbenzylamine (mba here) to such solutions caused the same changes in spectra (above 290 nm) as addition of hydroxide; those were also reversible on acidification. No observations could be made at lower wavelengths due to the absorption of the environmental compound.

The first qualitative circular dichroism (CD) measurements used only the 320 nm band: (–)-α-methylbenzylamine gave a positive Cotton effect (CE) at 319 nm, but a large excess of environmental compound was required to detect a significant CD signal.

With nicotine, a negative CE resulted which was even more difficult to detect. Strychnine (in acetonitrile) induced no CE in the 320 nm band. Despite a good deal of work on the Pfeiffer effect having depended upon cinchonine, we discontinued its use as an environmental compound here since it changes sign of CD in its own longest wavelength band upon acidification, so that any Pfeiffer effect might possibly be obscured.

Quantitative Pfeiffer Effect Measurement

$[Pt(bpy)_2](ClO_4)_2$ was precipitated from solutions of its chloride with potassium perchlorate and recrystallized from water as yellow needles. Some typical experiments are described in detail. All CD measurements sensitivity: 1×10^{-6}.

In water: 5.4 mg (0.00764 mmol) $[Pt(bpy)_2](ClO_4)_2$ was dissolved in 10 ml H_2O to give a stock solution with c = 0.000764 mol dm^{-1}. 10.7 mg (0.0883 mmol = 38 equiv.) of (–)-methylbenzylamine (mba) were added to 3.01 g of this solution containing 0.0023 mmol complex. At 330 nm, on the 1 cm/scale, displacement was 65 mm/$\Delta\varepsilon$ = –0.17. Adding 9.0 mg (0.0555 mmol = 24 equiv.) of nicotine to 3.01 g solution as above at 350 nm, on the 1 cm/scale, displacement was 35 mm giving $\Delta\varepsilon$ = +0.092.

$[Pt(terpy)Cl]Cl \cdot 3H_2O$: Recrystallisation from a warm, filtered, aqueous solution gave red-brown material rather than nice crystals. This appears to be rather characteristic of the compound, and is related to the existence of both red and yellow forms, probably dimorphs, which we discuss elsewhere. Here, we used »recrystallised« sample for CD measurements – 9.1 mg (0.0192 mmol) $[Pt(terpy)Cl]Cl \cdot 3H_2O$ were dissolved in 22.1 g water: thus c = 0.000825 mol dm^{-3}. To 5.49 g of this solution containing 0.00453 mmol complex was added 9.1 mg (0.0561 mmol = 12 equiv.) nicotine but no CD was induced other than environmental absorptions. Similary, to 5.94 g solution containing 0.0049 mmol complex was added 9.7 mg (0.80 mmol = 16 equiv.) (–)-methylbenzylamine.

The Pfeiffer CD induced was as follows: 470 nm: 1 cm/15 mm/$\Delta\varepsilon$ = +0.036; 436 nm: $\Delta\varepsilon$ = 0; 380 nm (region 400–360 nm): 0.2 cm/10 mm/$\Delta\varepsilon$ = –0.12; 350 nm: 0.2 cm/15 mm/$\Delta\varepsilon$ = –0.18; 345 nm: $\Delta\varepsilon$ = 0; 320 nm (about): 0.2 cm/40 mm/$\Delta\varepsilon$ = +0.5.

The reversible addition of hydroxide to this cation had been noted by Mureinik and Bidani.[4]

RESULTS AND DISCUSSION

General

K_1 (relating to the addition of Eq. (1), Scheme 1) is large (10^4–10^5), so chemical reaction (bond-change) is involved, rather than some other weaker type of association. Ion-pairing, or other outer sphere interaction, of a (2+) cation with a singly charged anion in water would not be nearly so strong. In the present system, Wernberg has reported[6] several relevant facts. For the additions of Cl^- and I^- to $[Pt(bpy)_2]^{2+}$ in water at 23 °C, he gave values for K as (respectively) < 0.2 dm^3 mol^{-1} (*sic*) (no reaction was observed, confirming the earliest report)[3] and $\log_{10} K = 2.6 \pm 0.3$. Chloride and hydroxide are more similar in ionic potential than iodide and hydroxide, so any possible ion-pairing equilibrium constant for reaction (1) is likely to have $\log_{10} K_{IP}$ no more than 2. Reaction (1) does not arise from ion-pairs. This is confirmed by the measurable rate of reaction (1) of Scheme 1. In related but octahedral systems like $[Cr(bpy)_3]^{3+}$, ion-pairs have been suggested (*sic*) to explain away the unusual feature that the rates of base hydrolysis (both thermal and photochemical) are dominated by the third order term $[Cr(bpy)^{3+}]$ $[OH^-]$.[2]

Wernberg's rather large value[5] for I^- with the present platinum compound merits comment. The property of iodide seems likely to arise from a charge/transfer transition. We confirmed[14] that the solid anhydrous salt $[Pt(bpy)_2]I_2$ is black, and its dihydrate red. (The cation itself is colourless, of course). Other quaternized systems show new spectroscopic features in the presence of iodide. For example, Kosower[15] based a scale of solvent polarity on the new charge-transfer transition of the iodide salt of *N*-benzylnicotinamide. Charge-transfer complexes are known in systems related to those here. In aprotic solvents, like cyclohexane or dmso, tertiary aliphatic amines give[16] strongly coloured charge-transfer complexes with oligo-nitro-aromatic molecules, such as 1,3,5-trinitrobenzene or tnt; such nitroaromatics are often viewed as being like N-heterocycles in their reactivity.

Similary, the complex ion tris(2,2'-bipyridine)cobalt(III) interacts[17] with bases in aqueous $LiClO_4$ (3M). Log K for these 1:1 interactions, originally taken to arise because of the formation of 1:1 outer sphere complexes,[17] were reported for NH_3, H_3CNH_2 and $H_3CCH_2NH_2$ as 0.77, 0.31 and 0.2 respectively. While we would interpret these interactions as arising from cybotactic effects of the strong salt solution, the equilibrium constants do serve to define maximal sizes of effects. However, adducts of this outer sphere type are not stable enough to account for the reaction (1) of OH^- (or indeed other nucleophiles) in our aqueous solutions. For these amines, Wernberg's values[5] for $\log_{10} K$ of addition to $[Pt(bpy)_2]^{2+}$ are 3–4.

Equilibria

The values of the equilibrium constants for reaction (1) obtained in the present work are given in Table I, and compared with some earlier and related values. For all cations of the bis-chelated type $[M(NN)(NN')]^{2+}$ where M = Pd or Pt, addition of hydroxide is favourable (K approx. 10^4). The status of a few reported values is unclear, since while some are reported as $\log_{10} K$, others are given as K with units attached (*sic*). Our own values are from very dilute solutions: $4 < pH < 11$, *i.e.* $[OH^-] < 10^{-3}$ mol dm^{-3}, and $[PtN_2^{2+}] < 10^{-3}$ mol dm^{-3}, so we take activity coefficients as 1, and our values for K are thermodynamic constants.

TABLE I

Addition of hydroxide to some palladium and platinum species; equilibrium constants in water for $[L_2M]^{n+} + OH^- = [ML_2OH]^{(n-1)+}$

M	L	*n*	log *K*	Reference
Pd	phen	2	–[a]	6
Pd	phen	2	4.04	37[b]
Pd	bpy	2	4.65	37[b]
Pd	bpy	2	4.79	37[b]
Pd	5,5'-dmbpy	2	5.8	3
Pd	4,4'-dmbpy	2	3.44	
Pd	H_2dmg[c]	0	5.5	41
Pd	[(4,5-dmbpy)$(py)_2$]	2	3.9	
Pt	5,5'-dmbpy	2	4.5	3
Pt	bpy	2	5.0	3
Pt	$[^1H]_8$-bpy	2	4.6	
Pt	$[^2H]_8$-bpy	2	4.5	
Pt	phen	2	2.5	6
Pt	4,4'-dmbpy	2	3.77	20[b]
Pt	4,5-dmbpy	2	3.7	20[b]
Pt	4-methyl-bpy	2	3.69	20b[d]
Pt	5-butyl-bpy	2	4.68	20b[d]

[a] Not measured because of rapid onward reaction.

[b] These values were obtained in the ionic medium 0.1 M K-CH_3SO_3.

[c] H_2dmg represents dimethylglyoxime, butane-2,3-dione dioxime.[41]

[d] These cations lack 2-fold symmetry between the two pyridine rings. Their bis-complexes may involve geometric isomerism, being *trans*-(centrosymmetric) or *cis*-(axial). We have not separated these isomers: the values of *K* for addition of hydroxide relate to our synthetic material, so may be a weighted composite involving both isomers.

For the equilibrium constant, $K_H = [\mathbf{B}]/[\mathbf{A}][OH^-]$ of Eq. (1), our measured value from spectrophotometric titrations at 20 °C over a wide range of pH is log $K_H = 4.49 \pm 0.04$; at 23 °C Wernberg gives 4.11 ± 0.03,[5] though that value derived from a considerably narrower range of pH. The original value was 5.0.[3] These values relate to the complex with perproto-2,2'-bipyridine. We have also measured the smaller equilibrium constant for (1) using the isotopomer with perdeutero-2,2'-bipyridine, K_D. Log K_D is 4.40 ± 0.03. Whatever gives rise to this difference between K_H and K_D is not accompanied by exchange of C–H: there is no bond breakage at carbon; so this is not related to a primary kinetic isotope effect. Addition to carbon would simply change it from a trigonal aromatic C–H (»sp^2«) to a tetrahedral aliphatic C–H (»sp^3«), a secondary effect. While there seem to be no directly comparable values available for addition of any nucleophile to any N-heterocycle or any other aromatic, these secondary effects are usually much smaller. The ratio 1.25 found here may be of the right order for addition to carbon.

We have compared equilibrium constants for pairs of isotopomeric dideuterated ligands, at 25 °C. The values for perproto and 3,3'-dideutero-complexes are indistinguishable within experimental error; $pK_A = 4.47 \pm 0.03$ and 4.44 ± 0.03, respectively. For the 6,6'-dideutero-isotopomer, however, the value is considerably less than that for the perproto parent, determined under the same conditions at the same time $pK_A(^1H) = pK_A(^2H) - 0.21 \pm 0.04$. Perdeuteropyridine is more basic than is perprotopyridine:[18] the values of pK_A for the dissociation of $C_5H_5NH^+$ and $C_5D_5NH^+$ at 20 °C are 5.27 ± 0.01 and 5.38 ± 0.01 respectively. The corresponding values for the isotopomeric 2,2'-bipyridines as σ-donors in water are not yet known. The platinum(II) centre in $[Pt([^1H]_8\text{-bpy})_2]^{2+}$ might be electron-poor (and so have higher affinity for hydroxide ion) relative to that in $[Pt([^2H]_8\text{-bpy})_2]^{2+}$, because of the presumably greater σ-donor power of the deutero-ligand. Unfortunately, relevant measurements of stability constant are lacking. There seems to be no available comparison at all of any proto/deutero-N-heterocyclic pair of isotopomeric ligands with any metal ion. For the present, three lines of evidence speak against a marked difference in electron densities at platinum(II) in our two isotopomeric cations. First, a comparative rate study[19] of the base hydrolysis of *cis*-$[Co(en)_2(py)Cl]^{2+}$ (en: 1,2-diaminoethane) and its isotopomer with $[^2H]_5$-py was taken to show equal rates. Secondly, the electronic absorption spectra of our isotopomeric salts are indistinguishable. Likewise, the visible electronic spectra of the two isotopomeric cations *trans*-$[Rh(C_5H_5N)_4Cl_2]^+$ and *trans*-$[Rh(C_5[^2H]_5N)_4Cl_2]^+$ are identical. If the differing pK_A values of the N-heterocyclic isotopomeric ligands were to affect electron densities at the metal ion, these spectra would differ.

Finally, *pace* Table I, the equilibrium constants for addition of hydroxide to a homologous series of cations do not go with pK_A values for the parent pyridines. The simplest expression of this argument is in the relative values for 5,5'-dmbpy *vs.* bpy itself with palladium(II) ($\Delta\log K = 1.1$) as against platinum(II), where the effect goes the other way, $\Delta\log K = -0.5$.

Similarly arguing to the same end, the distinct isotopic inequality of equilibrium constants ($\Delta pK = 0.09$ at 20 °C) for the perdeutero/perproto platinum system is also large for the 6,6'-dideutero/6,6'-diproto isotopomer ($\Delta pK = 0.21 \pm 0.03$ at 25 °C) whereas the 3,3'-pair have $\Delta pK = 0$ within experimental error ($\Delta pK = 0.03 \pm 0.03$, at 25 °C).

So, we take the observed $K_H : K_D$ as more likely to arise from a secondary isotope effect inherent in nucleophile adding to an aromatic C–H. The site of addition is the 6 or 6'-carbon.

For the complex $[Pd(4,5\text{-dmbpy})(py)_2]^{2+}$, the changes in electronic spectra allow the determination of a value of equilibrium constant whereas that is not possible[20] for its platinum(II) eutrope. The observation of an isosbestic point and the reversibility (at least from weakly basic solutions) show that this is indeed an equilibrium and not hydrolysis. This example is particularly striking, because it represents the first case of such an equilibrium with hydroxide of a complex containing only one chelated bipyridine, of the type $[M(bpy)X_2]^{n+}$, where X is a unidentate ligand. All previous cases have involved either bis-bidentate ligands or tridentate terpyridine.

The equilibrium constants for the platinum compounds are all about the same, and those for the palladium compounds are, albeit smaller, likewise roughly constant.

Rates

Scheme 1 shows the hydrolysis of **A**. The overall reaction[21] from **A** to **C** is extremely slow and has the same rate law as we now find for the much faster formation of the adduct **B**, so hydrolysis proceeds through **B**, (that is, the direct pathway from **A** to final product with no intermediate is unimportant). The reaction of **A** to **B** is fully reversible with acid. An early proposal[21] that all the changes observed for **A** in basic solution arise from base hydrolysis is incorrect. As Mureinik and Bidani said[4] of their similar finding for the terpyridine compound: »This reversibility eliminates the possibility of the spectral changes being due to base hydrolysis.«

The magnitude of the rate of reaction from **A** to **B** is informative: it had been said[5] to be complete »within the time of mixing«. That is not so. The forward rate can be measured using stopped-flow techniques.

The rate constant k_1 for the forward reaction at 25 °C, 1.56×10^2 mol^{-1} dm^3 s^{-1}, while appreciable, is far too small to represent proton transfers like the suggested[9] $Pt(OH_2)^{2+}$ to $Pt(OH)^+$ (as in Eq. 3) and supports the view that a new bond is being made (from oxygen of incoming hydroxide to metal or ligand). Likewise, for the 1:1 addition of OH^- to the palladium eutrope, k_1 is 5.04×10^1 mol^{-1} dm^3 s^{-1}.

$$\begin{gathered}[\mathrm{Pt(OH_2)(bpy)_2}]^{2+} \rightleftharpoons [\mathrm{Pt(OH)(bpy)_2}]^{+} + \mathrm{H}^{+} \\ \text{or } [\mathrm{Pt(OH_2)_2(bpy)_2}]^{2+} \rightleftharpoons [\mathrm{Pt(OH)(OH_2)(bpy)_2}]^{+} + \mathrm{H}^{+}\end{gathered} \tag{3}$$

The inequality of k_H and k_D (k_H > k_D) is particularly striking. If $k_H \neq k_D$ a kinetic isotope effect (KIE) is said to exist. A normal kinetic isotope effect is a ratio k_H/k_D greater than unity; whereas if $k_H/k_D < 1$ the effect is termed inverse.

Replacement of one isotope by another in a bond which is not broken during a reaction may still cause a rate change: this effect is known as a secondary kinetic isotope effect (SKIE).

Hybridisation and crowding effects determine the α-SKIE (for substitution in the α-carbon), primarily through changes in the C_α–H (D) out-of plane bending vibrations.[22–24] Since no bond fission at the isotope atom occurs, a smaller isotope effect is observed but the perturbations of the various modes in which this effect is involved remain. In particular, the change of the stretching frequency of C–H (D) is responsible for the largest term which (according to the Bigeleisen equation)[23] may be taken as the only one of importance.[22] A change in hybridisation during the rate determing step from sp^3 to sp^2 is accompanied by a deuterium SKIE of about 1.15 (15%) for substitution on the α-carbon. In the reverse direction sp^2 to sp^3, the SKIE is inverse, around 0.9.[25]

α-Secondary kinetic isotope effects have been widely used to comment on S_N2 transition structures. In some cases, the direction of such effects is unexpected and inexplicable in terms of effects of heavy atom substitution. An example of this is reported by Isaacs and Hatcher.[26] For a change of hybridisation sp^2 to sp^3, they obtained an isotope effect of $k_H/k_D = 1.12$. This value is highly unusual: although the magnitude of the change is the expected (around 15%), its sense is opposite to that predicted. Similar results have been found here.

There are few data available by way of direct comparison of isotopic measurements on N-heterocycles coordinated to metals. Measurements[19] on the base hydrolysis of *cis*-$[\mathrm{CoCl(en)_2([^1H_5]\text{-}py)}]^{2+}$ against *cis*-$[\mathrm{CoCl(en)_2([^2H_5]\text{-}py)}]^{2+}$ were not very conclusive. Most studies are for organic systems, and seem to include no nucleophilic aromatic substitution of any kind, carbocyclic or N-heterocyclic.

NMR – Results and Interpretation

For $[\mathrm{Pt(5,5'\text{-}dmby)_2}]^{2+}$ in neutral heavy water, there is one aliphatic signal (δ = 2.63 ppm)[3] corresponding to the 12 protons of the four equivalent methyl groups. However, we now find that, on adding base ([Pt] : [OH⁻] =

2 : 1), half of this intensity is replaced by a new 1 : 2 : 1 signal at rather higher field (δ = 2.50, 2.41, 2.25 ppm) which, in an excess of base, remains as the only spectrum and is therefore the spectrum of the adduct (Wernberg used this argument – in respect of electronic spectra – in his measurements[5] of K for equilibrium (1) and similar nucleophilic additions). This confirms and extends our original finding,[3] and shows that (on the timescale of proton resonance) the adduct lacks symmetry (even 2-fold). It is asymmetric, rather than dissymmetric. Further, the spectrum of this 1 : 1 adduct measured at 100 and at 200 MHz is the same. The breadth of the central signal (δ = 2.41 ppm), with intensity double that of the wings, may imply the presence of the two almost equivalent methyl groups (R_3 and R_4), as in structure (**I**) for R = CH_3, to add to the obviously distinct R_1 (δ = 2.50 ppm) and R_2 (δ = 2.25 ppm). This spectrum is not consistent with the methyl compound having the same structure about platinum as that advanced[9] for **B** (R = H) on the basis of ^{13}C and ^{1}H NMR spectra.

It might be argued that all that these NMR spectra show is that new compounds are formed upon the addition of hydroxide: that interpretation could say that three new compounds with equivalent methyl groups are formed. However, if that were really happening, than the intensity ratios of the newly split methyl signals would not be simple, except by chance. Very similar results are obtained for positional isomers. For example, in the successive spectra for the bis-4,4'-dimethylbipyridineplatinum(II) cation on addition of hydroxide, the four methyl groups, initially equivalent, again become inequivalent.

An early study[27] of the proton NMR spectra of $[Pt(bpy)_2]^{2+}$ and its 5,5'-dimethyl homologue commented on the deceptive simplicity of some spectra. Some observed spectra show effects, which could arise from rapid chemical exchange. We have indeed occasionally seen marked modifications (line broadenings and even apparent disappearance of signals) by exchange effects in similar systems. However, the effect of adding base to $[Pt(5,5'\text{-dmbpy})_2]^{2+}$ rules that out under our present conditions. At intermediate ratios of base to complex, both spectra (for **A**' and for **B**') are quite distinctly seen. Exchange is slow on this time scale. Again, substitution of the hydrogens at positions 5 and 5' by methyl might just conceivably alter solvation energies or related factors in such a way that the structure of the intermediate **B** for R = H differs from that for its homologue **B**' where R = 5-CH_3. However, the equilibrium constants[3] for these two additions are so similar (R = H, pK_a = 9.0; R = 5-CH_3, pK_a = 9.5) that structural conclusions from one system may safely be transferred to the other. The same remark applies, *mutatis mutandis*, to the 4,4'-system.

The observed proton resonance spectrum in base for the 5,5' (but not for the 4,4'-) system could, in principle, arise from the accidental overlap of 2 doublets: however, the coupling constants then required (*viz. ca.* 18 and 32 Hz) are too large for the system C(H)–C(CH_3) of an aromatic ring. So the NMR spectrum demonstrates the inequivalence of the four methyl groups (originally 5,5'-) on the proton resonance timescale.

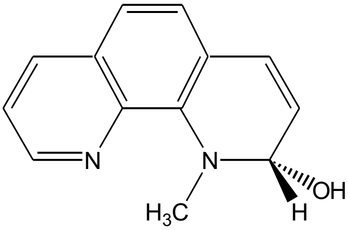
Electronic Spectra
(Including Circular Dichroism)

On passing from **A** to **B** (R = H), the electronic spectrum changes markedly. There is a decrease in intensity from **A** to **B** at *ca.* 250 and 260 (sh) and at 320 and 340 (sh) nm. The molar extinction coefficient at 320 nm is roughly proportional to the number of bipyridine ligands. Between **A** and **B**, it is about halved, suggesting that one ligand in **B** is not simple bipyridine (*e.g.* for $[Pd(4,5\text{-dmbpy})_2]^{2+}$, ε_{320} (× 10^{-4}) at pH = 7 is 2.6 but at pH = 12 is 1.6). When **A** goes to **B**, there is a rise in intensity at *ca.* 220, at *ca.* 270 and clearly at *ca.* 390 nm.

For octahedral or five coordinated *cis*-bis(bipyridine) species like **II**, belonging to point groups of C_2 and C_1 symmetry, the long-axis polarised transitions of the bipyridine ligands couple,[28] giving very strong absorption at about 34 000 cm^{-1}. In complex ions *cis*-$[M(bpy)_2X_2]^{n+}$, this is commonly the strongest band in the observed isotropic spectrum. These strong in-phase and out-of-phase coupled transitions are called »exciton« bands by coordination chemists, although the name is usually reserved by spectroscopists for a solid state effect. Such an obvious »exciton« band is certainly not generated in **B**.

The observation of a Pfeiffer effect for the solutions containing the cationic adduct and uncharged (–)-methylbenzylamine is noteworthy. It does not arise from ion-pairing, since there is no possible chiral ion-pair present. Speaking even more strongly against an origin based on cationic charge is the fact that there is no Pfeiffer effect in the absence of hydroxide. That is, the doubly charged ion **A** of Scheme 1 shows no chiral interaction with the benzylamine, whereas the singly charged **B** does.

The strongest Cotton effect is at 320 nm, which proves that an asymmetric chromophore is absorbing in that position. The new Cotton effect generating the Pfeiffer effect arises from electronic transition(s) within the structure of **B**, made asymmetric by interaction with the environment compound. This transition is not at *ca.* 270 nm: we are not dealing with an exciton band. The present situation, the generation of a new asymmetric centre in an originally flat molecule (here a chelated ligand), is akin to that[29] in the *N*-methyl-1,10-phenanthrolinium ion, which, on addition of natural strychnine as an environment compound, gave a very large Pfeiffer effect. That was attributed to the generation of new chiral centres in the flat factor by the addition of hydroxide forming the pseudo base shown in **III**, Scheme 3.



III

Scheme 3.

The present observations of the Cotton effects could stem from either of two modes of interaction of the environment compound (methylbenzylamine, mba) with **A**. That may be indirect, through the amine acting as a base, giving hydroxide, which forms **B**, whose new asymmetric carbon atom (as in **III**) is established stereoselectively by hydrogen-bonding to mba. It may be direct: the amine may well act as a nucleophile. Such additions by amines to coordinated N-heterocycles are described in other systems. Indeed, in the present system, the 1:1 additions of NH_3, H_3CNH_2, $(H_3C)_2NH$, and piperidine to $[Pt(bpy)_2]^{2+}$ in water occurred[5] with values of log K 3.32, 3.18, 3.02 and 3.65, respectively.

We studied the salt [Pt(terpy)Cl]Cl as a Pfeiffer compound. Mureinik and Bidani had already shown[4] that it reversibly adds hydroxide. With (+)-methylbenzylamine, it shows a large circular dichroism (Pfeiffer effect), which can hardly arise from dissymmetry at platinum. We take it that the Pfeiffer CD stems from the (+)-methylbenzylamine generating one enantiomer of the newly formed asymmetric carbon atom or selecting one hand of the initially racemic pseudo-base rather than the other.

It is particularly noteworthy that the »new« electronic absorption bands of **B** (*e.g.* those above 400 nm) shown strong Cotton effects: it is the novel structural feature of the hydroxide adduct which gives rise to the dissymmetry.

Infra-red Spectra of Solutions

The changes (Figure 1) in that part of the infrared spectrum which we are able to study in aqueous media (we used both H_2O and D_2O) are in the regions associated both with aromatic vibrations and with C–O modes. They are consistent with a structure like **I**, but not with an unchanged bipyridine framework as in **II**. The infrared spectrum of chelated 2,2'-bipyridine is little affected by the nature of the complex in which it resides, *i.e.* by changes in the stereochemistry of the complex or the presence of other ligands, whatever its nature, and alters in a major way only when the aromatic ligand itself is altered.

The IR spectra of all complexes of *N,N'*-chelated 2,2'-bipyridine in aqueous solution, are, from 1600–4000 cm^{-1}, essentially similar and like that of **A**, $[Pt(bpy)_2]^{2+}$. There is, in all cases, little absorption between 1600 and 1480 cm^{-1}.

Most strikingly, the IR spectrum of the solid hydrated nitrate and of its aqueous solution at pH = 6 are extremely similar, so much so that they might be thought to show that the 4-coordinated structure of the cation in the solid (confirmed here)[20a] is maintained on dissolution. However, the essential constancy of the spectrum of chelated 2,2'-bipyridine, whatever its actual environment, cuts both ways. The observed similarity of these two spectra proves no more than that the ligand is 2,2'-bipyridine, but it does prove that.

By the same token, the change (Figure 1) in the vibrational spectrum of the solute on forming the adduct with hydroxide strongly implies a major change in the nature of at least one organic ligand.

The changes with pH of the IR spectrum of aqueous solutions of $[Pt(bpy)_2]X_2$ were very similar for $X^- = Cl^-$ or NO_3^-. For the nitrate, the very broad and strong absorption due to ν_2 of the nitrate ion itself (centred at about 1360 cm^{-1}) obscures a wide range of energies, so most of our work on solutions relates to the chloride. A mere loss of proton, as in an acid dissociation of some aquaplatinum(II) species, Eq. (3), would not suffice to explain the major changes we find, since even major changes of geometry of ancillary ligand hardly affect the infrared spectrum of *N,N'*-chelated 2,2'-bipyridine.

Similarly, an addition of hydroxide to 4-coordinated platinum(II), giving a 5-coordinated hydroxo-species or 6-coordinated hydroxo-aqua cation (whatever its magnetism) would have little effect on the IR of the bipyridine.

At pH = 11, the spectrum is due to the cation **B**: it differs sharply from that of **A**. In particular, the band at 1615 cm^{-1} in **A** roughly halves in intensity, being replaced by new strong absorption at 1575 cm^{-1} and 1530 cm^{-1}, where **A** (Figure 1) and other derivates of chelated 2,2'-bipyridine show no absorptions. Similarly, while the absorption at 1450 cm^{-1} remains about constant in strength from **A** to **B**, the absorption at 1510 weakens, while those at 1440 and 1475 cm^{-1} become stronger. Major new bands also occur in **B** at about 1080 cm^{-1} and at about 1000 cm^{-1}. These last may perhaps be associated with vibrations of a new C–O moiety. Further, we used solutions in heavy water, adding sodium deuteroxide, to observe the region where absorption occurs from aromatic CH deformations (800–1000 cm^{-1}). As shown in the Figure, there is no very striking change, though a strong band at 900 cm^{-1} in the solution at pD = 6 is greatly reduced at pD = 10. This may represent a modification of the CH framework. A pair of bands at 1035 and 1050 cm^{-1} becomes weaker.

Comment on Discrepancies in NMR Interpretations

We now comment on the apparent conflict between two magnetic resonance studies. The earliest NMR measurements[3,27] on salts $[Pt(bpy)_2]X_2$, including those of a methylated homologue (amplified here) were interpreted in terms of addition to ligands. A later study[9] on $[Pt(bpy)_2]^{2+}$ utilized not only proton resonance but ^{13}C as well. Those later and more extensive results on the unsubstituted parent **A** and **B** were interpreted[9] in terms of addition to the platinum(II) central ion. The measurements agreed well where there was direct overlap (*i.e.* in the ^1H spectra of parent $[Pt(bpy)_2]^{2+}$ salts): it is the interpretations that differ.

Several points remove the ostensible rigour of argument in the later study:[9]

(i) The NMR spectra of $[Pt(bpy)_2(OH)]^+$ were interpreted in terms of a totally asymmetric structure, shown as **II**, *cis*-$[Pt(bpy)_2(H_2O)(OH)]^+$. The »extra« proton in this would in fact show rapid chemical exchange in basic solution, and generate an effective C_2 symmetry on the ^1H NMR timescale.

(ii) The favoured formulation[9] is six coordinate: there seem to be[30] no known model six-coordinated compounds of platinum(II) nor indeed of any other ion with the electronic configuration $5d^8$: they would be paramagnetic. Six coordinated eutropes containing nickel(II), $3d^8$, are indeed paramagnetic. **B** is in fact diamagnetic.

(iii) The coordination number of platinum(II) (in the proposed structures of **B**) is 5 or 6. Close precedents are rare. In labile complexes like those of copper(II), there are no doubt intermediates with coordination number 5. Indeed, the crystal structure[31] of $[Cu(bpy)_3](ClO_4)_2$ shows that – at any one time – five only of the six nitrogen atoms are bound to the copper ion (with $202 < Cu–N < 222$ pm: the sixth Cu–N is 247 pm).

Kinetically inert systems, however, like those here involving platinum(II) are quite different: the $N \rightarrow Pt$ bonds cannot be making and breaking at all rapidly. Indeed, the overall rate of hydrolysis, where these bonds do break, is very slow ($k \approx 10^{-7}$ s^{-1}) so the four Pt–N bonds of **A** are intact in **B**. Increase of coordination number at Pt(II) beyond 4 is rare (and generally leads in aqueous solution to substitution, *via* a rate law $k[PtX_4][Nu]$).

Even for $4d^8$ ions like Pd^{II}, 5 or 6 coordinated complexes are rare, and (for example Ref. 32) have not been observed in solvent extraction of palladium. The relatively few well characterized compounds involve »noninnocent« ligands as in $[Pt(SnCl_3)_5]^{3-}$ or the dichloro-olefin-bis-hydrazine compounds studied[33] by Panunzi and his school. Typical examples collected by Handler, Peringer and Müller[34] involved chiefly phosphine ligands, in such species[34a] as $[Pt\{P(OMe)_3\}_5]^{2+}$ or $[Pt\{P(Et)_3\}_4H]^+$ (and a compound with a

PtP_4Hg core is known).[34b] The phosphine ligands are terdentate in several examples.

The nearest type of compound to ours seems to be those of the hindered 2,9-dimethyl-1,10-phenanthroline (dmphen), where $[Pt(\eta^2\text{-}C_2H_4)Cl(dmphen)]$ has[35] a trigonal bipyramidal environment for platinum.

(iv) Features in the observed NMR spectra[3,9] reveal that the ostensibly rigorous arguments used to support structure **II** are questionable. Unassigned broad but minor resonances underlie the sharp assigned chemical shifts. They are particularly obvious in Fig. 1b of Ref. 3. We have again seen just such features in the spectra of solutions containing mixtures of **A** and **B** for methyl-substituted complexes: we believe them to arise from interchange of proton sites at rates comparable with proton relaxation times. The property is quite distinct from the proton chemical exchange with D_2O also observed in the activated methyl groups of complexed 4-methyl- or 4,4'-dimethyl-bpy. There is no rapid proton exchange with D_2O in aqueous $[Pt(phen)_2]^{2+}$ (Ref. 6) or $[Pt(bpy)_2]^{2+}$.

The intensities of signals for **B** (R = H) including these unexplained broad ones were said[9] to resemble those of salts of *cis*-$[Rh(bpy)_2Cl_2]^+$, **D**. The proton spectra of **D** do indeed also manifest such small broad features. The argument based on that resemblance must be rejected. The complex **D** was taken as a well understood unreactive Werner-complex species with rigid C_2 symmetry, a model for such species as **II** ($X = Y = Cl^-$). On the contrary, like many N-heterocyclic compounds of rhodium(III), aqueous solutions of **D** are by no means simple, and should not be used as a model for **II**. **D** is quite unlike *cis*-$[Rh(en)_2Cl_2]^+$, **E**, (where en = 1,2-diaminoethane) which is in truth a standard unreactive compound. For example, on removal of di-oxygen from its aqueous solution, **D** racemizes remarkably quickly; **E** does not. This implies the operation of some redox-catalyzed processes even in ostensibly simple aqueous solutions of the simple salts of **D**. Similarly, selective chemical isotope exchange is said to occur in heavy water for hydrogens of 2,2'-bipyridine coordinated to rhodium(III). Despite the known crystal and molecular structure[36] of the di-hydrated salt, *cis*-$[Rh(bpy)_2Cl_2]Cl \cdot 2H_2O$, made by the reaction in ostensibly non-aqueous (*sic*) conditions of bipyridine with $[RhCl(\eta^2\text{-}PC)(\eta^2\text{-}OCCl)]$, **D** in solution is too ill-understood to serve as a model to underpin arguments on other systems. The relationship taken[9] to exist between **D** and **B** is illusory.

(v) In many systems involving N-heterocyclic chelates, half-lives of nucleophilic addition or substitution are comparable with nuclear relaxation times. This is true of the present systems, where $t_{1/2}$ for hydroxide addition is about 10^{-3} s. This feature may vitiate first-order arguments based on chemical shifts alone. Consequently, in our work on properties in solution, we have preferred vibrational and electronic (or CD) spectra, where response times are many orders of magnitude shorter than those of nucleophilic addition.

Coordination Numbers

There are several 5-coordinated structures proposed for ammines of platinum(II) and palladium(II), but – so far as we can see – almost entirely among these complex compounds of chelating N-heterocycles. $[Pd(phen)(OH)_3]^-$ was said to exist, on the basis[37] of titrations. Although this early example has been queried,[38] several mixed compounds of platinum(II) and palladium(II) containing both hydroxide and N-heterocyclic chelators have subsequently been formulated as containing 5-coordinated metal ions. These are closely related to the present bis-species and include $[M_2L_2(OH)_3]^+$, **G**,[38] made as in Eq. (4) and said to have the μ,μ',μ''-trihydroxo-bridged structure, with two 5-coordinated metal ions.

$$\underset{(\mathbf{F})}{[LPt(OH)_2PtL]^{2+}} + OH^- = \underset{(\mathbf{G})}{[LPt(OH)_2PtL \cdot OH]^+} \qquad (4)$$

The equilibrium constant for the nucleophilic addition of Eq. (4)

$$K = [\mathbf{G}] / [\mathbf{F}][OH^-]$$

is[38] about 10^8, *i.e.* comparable with other values in Table I. The possible structures of **G** again exemplify isomerism between 5-coordinated platinum or 4-coordinated carbon. The ^{195}Pt chemical shifts of **F** and of **G** are –1340 and –1318 (referred to Na_2PtCl_6), respectively, whereas the monomeric $[Pt(bpy)(OH)_2]$, **C**, shows[38b] its single chemical shift at the very different value of –1776. That might suggest that the environments of the platinum(II) ions in **F** and in **G** are closely similar, *i.e.* 4-coordinate in both, leaving the »extra« hydroxide in **G** to go on to a ligand *via* a C(OH) link, or possibly, preserving the identity of both platinum ions, forming a structure $[\{Pt(bpy \cdot OH)(OH_2)\}_2(\mu\text{-}OH)]^+$. The strong similarity between the reversible (electronic) spectroscopic changes of **F** to **G** (*i.e.* reaction 4) and of **A** to **B** (reaction 1) encourages belief that the underlying cause is the same. Even the wavelengths of the two sets of isosbestic points coincide.

Similarly, the changes in electronic spectra during the reaction (1), either with Pt or its eutrope Pd are very much alike. That is also the case for other nucleophiles with platinum (palladium has yet to be studied in that connection).

CONCLUSION

The differing equilibrium constants for isotopomers, the slow formation of the stable adduct, the inequivalence even on the slower NMR time-scale of the four methyl substituents in basic solutions of the 5,5'- or 4,4'-dimethylbipyridine complexes, the changes in the electronic spectrum (particularly the Pfeiffer effect), and the modification of the vibrations of the aromatic framework are more consistent with the addition of hydroxide to the quaternized (coordinated) aromatic ligand as in **I**, than with addition to the metal ion as in **II**.

The present findings of marked selective effects among isotopomers of the platinum(II) systems with hydroxide have been extended to other complexes and nucleophiles. The detailed results will be given elsewhere. In summary, large kinetic isotope effects also occur for the systems $[Fe([^1H_8]\text{-bpy})_3]^{2+}$ and its $[^2H]_8$-isotopomer with both hydroxide[39] and cyanide. No such effects were observed for equilibria involving: $[Pd(bpy)_2]^{2+}$ with hydroxide; $[Pt(bpy)_2]^{2+}$ with cyanide or thiourea.

Isomerism arising from differing locations of a proton on a fixed molecular framework is tautomerism. A related isomerism arising from two possible locations for a hydroxide ion occurs in several contexts. Such isomerism, where the two possible locations are covalent bond as against ionic solvated hydroxide, has had several independent names (pseudo-base, Meisenheimer adduct, carbinol). Cases of isomerism like the present one, where the hydroxide ion may be covalently bound at two distinct elements (here Pt or C) have no name.

This nucleophilic addition to coordinated imine is an example of a reaction of general importance. The concept[2c] that coordination *via* nitrogen of N-heterocycles and other ligands containing >C=N (such as imines, oximes, Schiff bases and so on) is like quaternization of the same ligand concerts many facts. The concept leads to chemistry related (or, *pace* others,[9] »relegated«) to the organic chemistry of the ligands: the carbon may be activated in many ways, organic or inorganic. Burgess and Hubbard recently surveyed[40] nucleophilic substitution into spin-paired iron(II) complexes of di-imines, where good evidence for several additions to the ligands is available.

In metal metabolism, unsaturated N-ligands are extremely common, so the biochemical significance of these covalent products of solvolysis is high.

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SAŽETAK

Ravnoteže u kompleksima N-heterociklâ. 50. Nastajanje i svojstva 1:1 adukata hidroksidnog iona s bis(2,2'-bipiridin)platinom(II) i srodnim ionima u otopinama

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Određene su ravnotežne konstante za adiciju (u množinskom odnosu 1:1) ionâ OH^- za katione paladija(II) i platine(II). Reakcija $[Pt(bpy)_2]^{2+}$ s OH^- je brza: $k = 1,6 \times 10^2$ $dm^3\ mol^{-1}\ s^{-1}$. Ravnotežne konstante za adiciju OH^- na $[Pt(bpy)_2]^{2+}$ i $[Pt(3,3'-[^2H]_2-bpy)_2]^{2+}$ međusobno se ne razlikuju, ali su različite od onih za adiciju OH^- na $[Pt([^2H]_8-bpy)_2]^{2+}$ i $[Pt(6,6'-[^2H]_2-bpy)_2]^{2+}$.

Tijekom te reakcije, IR spektar (1700–900 cm^{-1}) početno prisutnoga $[Pt(bpy)_2]^{2+}$ u vodenoj otopini uočljivo se mijenja u rasponu $7 < pH < 11$, osobito u aromatskom

području, gdje se znatno smanjuje intenzitet vrpce C=N (*cca.* 1600 cm^{-1}). Iz spektara ^{1}H NMR pri pH = 7 vidi se da su vodikovi atomi dviju metilnih skupina u [Pt(5,5'-dmbpy)$_2$]$^{2+}$ i [Pt(4,4'-dmbpy)$_2$]$^{2+}$ (dmbpy: dimetil-2,2'-bipiridin) ekvivalentni, ali tomu nije tako u 1 : 1 aduktima tih spojeva s OH$^-$. U prisutnosti (–)-metilbenzilamina, i [Pt(terpy)Cl]Cl i [Pt(bpy)$_2$]$^{2+}$ očituju jak Pfeifferov učinak, ali ne i ekscitonsko sprezanje karakteristično za *cis*-oktaedarske ione. Ta se opažanja tumače adicijom hidroksidnog iona na bipiridinski ligand.