cis-Bis(2,2′-bipyridine)bis(pyridine)ruthenium(II) Salts: a Spectroscopic and Structural Study†

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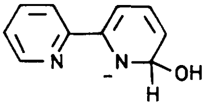
Claims that *cis*-bis(2,2′-bipyridine)bis(pyridine)ruthenium(II) salts, *cis*-$[Ru(bipy)_2(py)_2]X_2$, form covalent hydrates when treated with hydroxide ion are shown to be in error. Previously reported n.m.r. data are shown to have been incorrectly interpreted, and a full analysis of the two-dimensional ^1H n.m.r. spectra of the complex cation is presented. The crystal structure of the double salt *cis*-$[Ru(bipy)_2(py)_2][BF_4]_2 \cdot 0.5[Hpy][BF_4]$ [space group $P\bar{1}$, a = 1.018 8(2), b = 1.219 7(2), c = 1.559 2(2) nm, α = 70.82(2), β = 73.74(2), γ = 72.14(2)°, and Z = 2; R = 0.12 for 1 380 independent reflections with $|F^2| > \sigma(F^2)$] reveals all the *N*-heterocyclic rings to be conventionally aromatic.

Gillard and Hughes[1] reported in 1977, in a widely cited paper, that the salt *cis*-bis(2,2′-bipyridine)bis(pyridine)ruthenium(II) chloride, *cis*-$[Ru(bipy)_2(py)_2]Cl_2$, reacts with alkali according to equation (1), where bipy•OH represents a 'covalently hydrated' 2,2′-bipyridine, (1), in which the pseudo-base is formed by attack of hydroxide ion at the C^6 carbon atom.

$$[Ru(bipy)_2(py)_2]^{2+} + [OH]^- \rightleftharpoons [Ru(bipy{\cdot}OH)(bipy)(py)_2]^+ \quad (1)$$



(1)

Although well established for a range of organic molecules,[2] the theory of covalent hydration (or, more generally, pseudo-base formation) as applied to the complexes of simple di-imine ligands (*viz.* 2,2′-bipyridine and 1,10-phenanthroline) is extremely controversial, and the majority of the supportive experimental evidence (which has been reviewed extensively elsewhere[3–7]) is attributable to Gillard and his co-workers. In fact, very few of the claims of covalent hydration are based upon empirical observations which provide spectroscopic or structural evidence for the formation of intermediates of type (1); the majority rely upon analogy and dialectical argument. Similarly, a number of the attempts to confute Gillard's proposal have also relied upon dialectic and polemic. To quote Poincaré, 'To doubt everything or to believe everything are two equally convenient solutions; both dispense with the necessity of reflection.' A *via media* is required. Our aim, in a series of related studies, is to place the experimental observations, from which the theories derive, upon an incontrovertible basis, and hence provide a firm foundation for a critical discussion. The present investigation concerns one of the two previous reports upon the covalent hydration of pyridine complexes that are amenable to experimental study (N.B. the other report,[8] concerning $[Pt(py)_4Cl_2]^{2+}$, is the subject of a companion paper[9]); a third claim[8,10] that *trans*-$[Rh(py)_4Cl_2]^+$ has an anti-bacterial action due to its (unproven) ability to form covalent hydrates is not conducive to experimental verification.

Experimental

General Procedures.—Proton and ^{13}C n.m.r. spectra were recorded using either a Bruker WH-300 or WM-360 spectrometer. All chemical shifts are defined as positive to low field (high frequency) of the reference compound, tetramethylsilane.

Preparations.—cis-*Bis*(2,2′-*bipyridine*)*dichlororuthenium*(II) *monohydrate*.[11] Commercial ruthenium(III) chloride (7.8 g, 0.0298 mol), 2,2′-bipyridine (9.36 g, 0.06 mol), and lithium chloride (8.4 g, 0.2 mol) were heated at reflux in *N,N*-dimethylmethanamide (50 cm^3) for 5 h under dinitrogen. After this time, the original brown-black solution had become red-purple. The mixture was allowed to cool, propanone (250 cm^3) was added, and the solution cooled to 4 °C for 12 h. The black microcrystalline product was isolated by filtration, washed with water (3 × 25 cm^3) and diethyl ether (3 × 25 cm^3), and dried *in vacuo*. Yield 8.55 g (60%) (Found: C, 47.7; H, 3.35; Cl, 14.05; N, 11.1. Calc. for $C_{20}H_{18}Cl_2N_4ORu$: C, 47.8; H, 3.60; Cl, 14.1; N, 11.15%).

cis-*Bis*(2,2′-*bipyridine*)*bis*(*pyridine*)*ruthenium*(II) *chloride monohydrate–methanol* (1/2). *cis*-Bis(2,2′-bipyridine)dichlororuthenium(II) monohydrate (0.5 g, 1 mmol), pyridine (2 cm^3, 25 mmol), and aqueous methanol (40 cm^3; 1:1 v/v) were heated together under reflux for 4 h. This gave a clear orange-red solution, which was then cooled and the solvent removed under reduced pressure. The resulting red solid was dissolved in a minimum amount of methanol (*ca.* 2 cm^3) and chromatographed (Sephadex LH-20, 3 × 20 cm; methanol as eluant). Two bands were observed on the column, the first red and the second brown. The red band was collected and the solvent removed *in vacuo* to yield a red powder, *cis*-$[Ru(bipy)_2(py)_2]Cl_2 \cdot H_2O \cdot 2MeOH$ (Found: C, 53.3; H, 4.75; Cl, 9.95; N, 11.7. Calc. for $C_{32}H_{36}Cl_2N_6O_3Ru$: C, 53.05; H, 5.00; Cl, 9.80; N, 11.6%). The presence and stoicheiometry of the methanol was confirmed by ^1H n.m.r. spectroscopy. The bis([$^2H_5$]pyridine) analogue was prepared by an identical route.

cis-$[Ru(bipy)_2(py)_2][ClO_4]_2$. *cis*-Bis(2,2′-bipyridine)dichlororuthenium(II) monohydrate (0.5 g, 1 mmol), pyridine

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

(1 cm^3, 12.4 mmol), and aqueous methanol (20 cm^3; 1 : 1 v/v) were heated together under reflux for 4 h. Sodium perchlorate (2 g) was added to the clear orange-red solution, and heating under reflux was continued for a further 2 h. Upon cooling, an orange-red powder, *cis*-[Ru(bipy)$_2$(py)$_2$][ClO$_4$]$_2$, separated from solution. This was collected by filtration, washed with ethanol (10 cm^3) and diethyl ether (10 cm^3), and dried *in vacuo* (Found: C, 46.5; H, 3.6; N, 10.8. Calc. for $C_{30}H_{26}Cl_2N_6O_8Ru$: C, 46.75; H, 3.40; N, 10.9%). The bis([$^2H_5$]pyridine) analogue was prepared by an identical route.

cis-[Ru(bipy)$_2$(py)$_2$][BF$_4$]$_2$·0.5[Hpy][BF$_4$]. *cis*-Bis(2,2′-bipyridine)dichlororuthenium(II) monohydrate (0.5 g, 1 mmol), pyridine (1 cm^3, 12.4 mmol), and aqueous methanol (20 cm^3; 1:1 v/v) were heated together under reflux for 3 h. Tetrafluoroboric acid (2 cm^3, 48%) was added to the clear orange-red solution, and heating under reflux was continued for 2 h. Upon cooling, orange-red plate-like crystals of *cis*-[Ru(bipy)$_2$(py)$_2$][BF$_4$]$_2$·0.5[Hpy][BF$_4$] separated from solution. These were collected by filtration, washed with ethanol (10 cm^3) and diethyl ether (10 cm^3), and dried *in vacuo* (Found: C, 46.9; H, 3.85; N, 11.15. Calc. for $C_{32.5}H_{29}B_{2.5}F_{10}N_{6.5}Ru$: C, 47.1; H, 3.55; N, 11.0%).

Determination of the Crystal Structure of cis-[Ru(bipy)$_2$(py)$_2$][BF$_4$]$_2$·0.5[Hpy][BF$_4$].—Orange-red, plate-like crystals were isolated from aqueous methanol, as described above. A crystal of dimensions 0.20 × 0.13 × 0.10 mm was used for all crystallographic measurements. These were made with nickel-filtered Cu-K_α radiation (λ = 0.154 18 nm) and an Enraf-Nonius CAD4 diffractometer.

Crystal data. $C_{32.5}H_{29}B_{2.5}F_{10}N_{6.5}Ru$, M = 1 657.43, triclinic, a = 1.018 8(2), b = 1.219 7(2), c = 1.559 2(2) nm, α = 70.82(2), β = 73.74(2), γ = 72.14(2)°, U = 1.7053 nm^3 (preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 using diffractometric setting angles for 25 reflections with $\theta \approx 22°$), Z = 2, D_c = 1.77 g cm^{-3}, $F(000)$ = 832 e$^-$, μ(Cu-K_α) = 46 cm^{-1}, space group $P\bar{1}$ (confirmed by the successful structure refinement).

Data collection and processing. The intensities for $h \pm k \pm l$ reflections with $2 < \theta < 50°$ were measured by the θ—2θ scan technique, with a scan width of $\Delta\theta = (0.80 + 0.15 \tan \theta)°$. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ, whence any reflection with an integrated intensity, I, less than its variance, $\sigma(I)$, was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.05, subject to a maximum scan time of 60 s. Two standard reflections monitored every hour showed no significant variation.

Data were corrected for Lorentz and polarization (Lp) effects, and also for absorption. After averaging any equivalent data, 1 380 independent reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{\frac{1}{2}}/\mathrm{Lp}$.

Structure solution and refinement. The structure was solved by routine heavy-atom methods. Refinement of the ruthenium and fluorine atoms with anisotropic thermal parameters was by the full-matrix least-squares method, whereas boron, nitrogen, and carbon atoms were refined with isotropic thermal parameters. It was found necessary to fix the positions of the boron atoms to achieve a satisfactory refinement.

Hydrogen atoms were fixed at calculated idealized positions [r(CH) = 0.108 nm]. The refinement converged to R = 0.12, R' = 0.10, when the maximum shift/error was 5.3, and the weighting scheme was $w = 1/\sigma^2(F)$. The final difference map had peaks up to 0.96 e Å^{-3} near the ruthenium atom, but was elsewhere featureless.

The structure solution and refinement were performed on a PDP11/34 computer, using the Enraf-Nonius Structure Determination Package. Complex neutral-atom scattering factors[12] were used throughout. The carbon and nitrogen atoms [CN(1),

Table 1. Fractional atomic co-ordinates (×10^4 Ru, ×10^3 other atoms) for the salt *cis*-[Ru(bipy)$_2$(py)$_2$][BF$_4$]$_2$·0.5[Hpy][BF$_4$], with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Ru	635(4)	1 785(3)	2 220(2)
N(1)	3(3)	368(2)	198(2)
N(2)	−51(3)	207(2)	125(2)
N(3)	−95(3)	169(2)	334(2)
N(4)	159(3)	154(2)	324(2)
N(5)	113(3)	−3(2)	239(2)
N(6)	238(3)	194(2)	109(2)
C(1)	19(3)	427(3)	246(2)
C(2)	−39(4)	552(3)	239(2)
C(3)	−122(4)	595(3)	172(2)
C(4)	−147(4)	532(3)	127(2)
C(5)	−90(3)	408(3)	130(2)
C(6)	−106(4)	332(3)	86(2)
C(7)	−187(4)	370(3)	17(2)
C(8)	−198(4)	295(3)	−19(2)
C(9)	−146(5)	164(4)	11(3)
C(10)	−67(4)	153(3)	76(2)
C(11)	−242(4)	192(3)	338(2)
C(12)	−343(4)	207(3)	413(3)
C(13)	−312(4)	201(3)	487(3)
C(14)	−179(4)	189(3)	490(3)
C(15)	−81(4)	168(3)	410(2)
C(16)	87(4)	156(3)	409(2)
C(17)	139(4)	144(3)	484(2)
C(18)	279(4)	120(3)	474(2)
C(19)	359(4)	114(3)	389(3)
C(20)	284(4)	136(4)	321(3)
C(21)	20(4)	−66(3)	262(2)
C(22)	43(4)	−189(3)	281(3)
C(23)	176(4)	−255(3)	278(2)
C(24)	286(4)	−200(3)	254(2)
C(25)	244(4)	−78(3)	242(3)
C(26)	313(4)	268(3)	110(2)
C(27)	427(4)	289(3)	36(2)
C(28)	461(3)	230(3)	−27(2)
C(29)	388(4)	152(3)	−28(3)
C(30)	280(3)	134(3)	49(2)
CN(1)	550(4)	517(4)	416(3)
CN(2)	438(5)	491(4)	450(3)
CN(3)	387(5)	461(4)	532(3)
B(1)	332	82	750
B(2)	443	443	207
B(3)	0	500	500
F(1)	324(2)	22(2)	710(2)
F(2)	223(2)	110(2)	824(2)
F(3)	433(3)	25(3)	801(2)
F(4)	371(6)	181(3)	724(3)
F(5)	387(3)	486(3)	141(2)
F(6)	488(4)	535(2)	221(2)
F(7)	369(4)	420(4)	281(3)
F(8)	540(3)	355(3)	203(2)
F(9)	90(4)	573(4)	490(4)
F(10)	58(7)	413(5)	546(4)
F(11)	−103(6)	539(5)	566(3)
F(12)	−20(8)	487(9)	425(5)

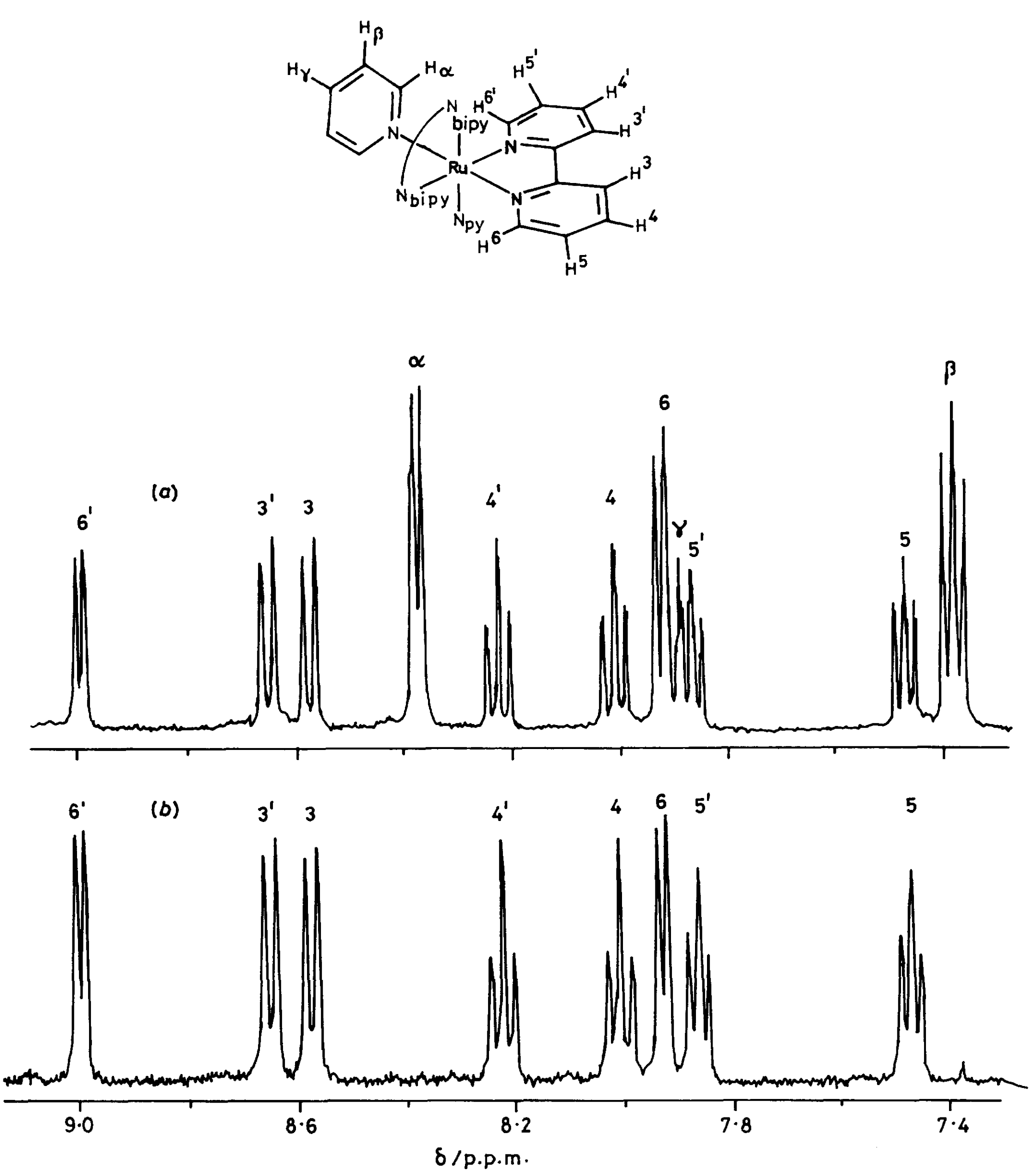

Figure 1. The ^1H n.m.r. spectra (360 MHz) of (*a*) $[Ru(bipy)_2(py)_2]^{2+}$ and (*b*) $[Ru(bipy)_2(C_5D_5N)_2]^{2+}$ in $(CD_3)_2SO$

CN(2), and CN(3)] of the pyridinium cation were disordered, and were assigned an average scattering factor. One of the tetrafluoroborate anions, $[B(3)F(9)F(10)F(11)F(12)]^-$, lies on an inversion centre and is disordered, with an occupancy of 0.5. The final fractional atomic co-ordinates are listed in Table 1.

Results and Discussion

Complex Synthesis.—The synthesis of $[Ru(bipy)_2(py)_2]^{2+}$ salts has been described by Dwyer *et al.*[13] and Meyer and co-workers,[14] and the preparations described here follow the well known synthetic principals for this type of complex.[15]

Interpretation of the ^1H *N.M.R. Spectrum of* $[Ru(bipy)_2(py)_2]^{2+}$.—The ^1H n.m.r. spectrum of $[Ru(bipy)_2(py)_2][ClO_4]_2$ in $(CD_3)_2SO$ is illustrated in Figure 1, where it is compared with that of $[Ru(bipy)_2(C_5D_5N)_2][ClO_4]_2$. The chloride salts were also studied, and the results were found to be independent of the nature of the anion. The signals due to the H_α, H_β, and H_γ protons of the co-ordinated pyridine are immediately identifiable by comparing the two spectra, and occur at δ 8.381, 7.381, and 7.911 p.p.m. respectively (H_α, of course, resonating at the lowest field), with $^3J(H_\alpha H_\beta) = 5.2$, $^3J(H_\beta H_\gamma) = 7.8$, and $^4J(H_\alpha H_\gamma) = 1$ Hz. This leaves eight signals identifiable with the bipyridine protons, one set of four (defined as 3′-H, 4′-H, 5′-H, and 6′-H) associated with the rings *trans* to another bipyridine ring, the other set of four (defined as 3-H, 4-H, 5-H, and 6-H) associated with the bipyridine rings *trans* to pyridine (see Figure 1, inset). By comparison with assignments previously reported for $[Ru(bipy)_2Cl_2]$,[16] $[Ru(bipy)_2(H_2NCH_2CH_2NH_2)]^{2+}$,[17] and $[Ru(4,4'Me_2\text{-bipy})_2(NH_3)_2]^{2+}$ (4,4′Me$_2$-bipy = 4,4′-dimethyl-2,2′-bipyridine),[18] the 6′-H protons [which should appear as a doublet split by $J(H^{5'}H^{6'})$] are expected to appear at lowest field. Thus, the doublet at 8.999 p.p.m. [$^3J(H^{5'}H^{6'}) = 5.7$, $^4J(H^{4'}H^{6'}) = 1.0$ Hz] is immediately identifiable with 6′-H. This resonates at a much lower field than the 6,6′ protons in $[Ru(bipy)_3]^{2+}$ as it is not rigidly located above the plane of an aromatic ring; the pyridine, as revealed in the crystal structure (see below), is free to rotate about the RuN bond. The doublet due to 6-H, however, is clearly visible (in the spectrum of the $[^2H_5]$ pyridine analogue) at 7.930 p.p.m. [$^3J(H^5H^6) = 5.5$ Hz], some 1 p.p.m. to higher field, and close to the resonances of the

6,6′ protons found for $[Ru(bipy)_3]^{2+}$.[19] This upfield shift of 6-H with respect to 6′-H is due to the diamagnetic anisotropic effect of the adjacent bipy ring.[18] The remaining two doublets in the spectrum (8.657 and 8.579 p.p.m.) must then be due to 3′-H and 3-H (logically, but not necessarily, respectively). Appropriate decoupling experiments established the two high-field triplets (7.867 and 7.469 p.p.m.) to be due to 5′-H and 5-H, and the two low-field triplets (8.224 and 8.010 p.p.m.) to be due to 4′-H and 4-H. The remaining important coupling constants are $^3J(H^{3'}H^{4'})$ = 7.9, $^4J(H^{3'}H^{5'})$ = 0.4, $^3J(H^{4'}H^{5'})$ = 7.6, $^3J(H^3H^4)$ = 7.9, $^4J(H^3H^5)$ = 0.5, and $^3J(H^4H^5)$ = 7.6 Hz.

The only uncertainty in the above assignment is the implicit, and quite reasonable, assumption that the protons (n') of the bipy ring *trans* to the bipy ring resonate consistently at lower field than those (n) of the bipy rings *trans* to pyridine. This was investigated by a correlated two-dimensional n.m.r. experiment,[20] the results of which are summarized in Figure 2. This unambiguously establishes the connectivities which prove this postulate to be correct.

Effect of Base upon the ^{1}H *N.M.R. Spectrum of* $[Ru(bipy)_2(py)_2]^{2+}$.—The original report[1] of the effect of added alkali upon the ^{1}H n.m.r. spectrum of $[Ru(bipy)_2(py)_2]^{2+}$ was based upon low-field (apparently 100 MHz) observations (see Figure 3). These were interpreted as follows: 'The signal (indicated by asterisks) assigned to H^6 is most affected, which indicates that the adduct has the hydroxide ion at C^6. In this position the

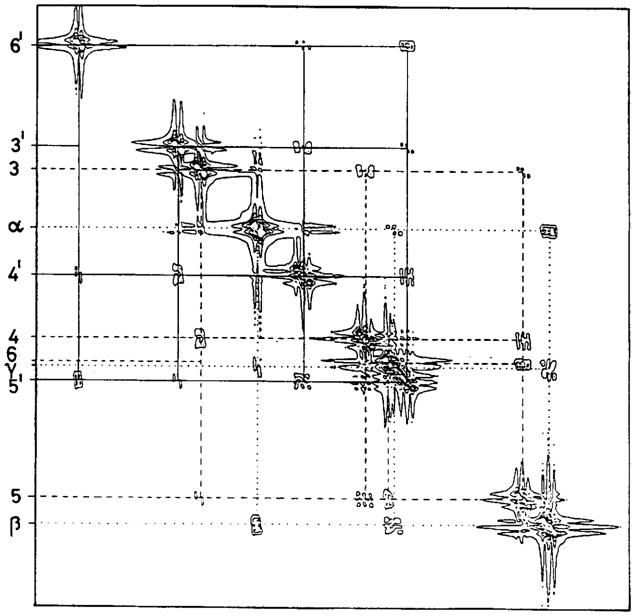

Figure 2. The correlated two-dimensional n.m.r. spectrum of $[Ru(bipy)_2(py)_2]^{2+}$ in $(CD_3)_2SO$

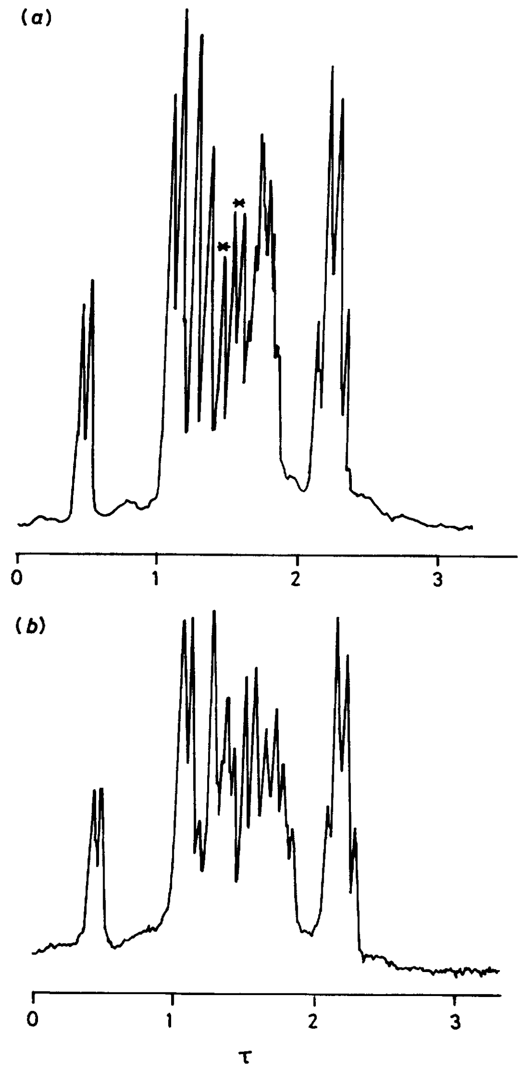

Figure 3. The ^{1}H n.m.r. spectra of $[Ru(bipy)_2(py)_2]^{2+}$ (a) in neutral water and (b) in the presence of added alkali, reproduced from ref. 1. The asterisks mark the doublet assigned to H^6

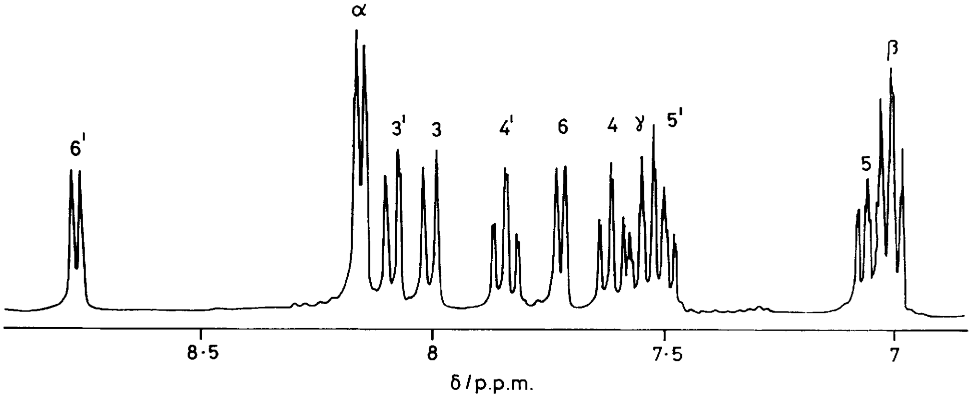

Figure 4. The ^{1}H n.m.r. spectrum (300 MHz) of $[Ru(bipy)_2(py)_2]^{2+}$ in the presence of added $[OH]^-$

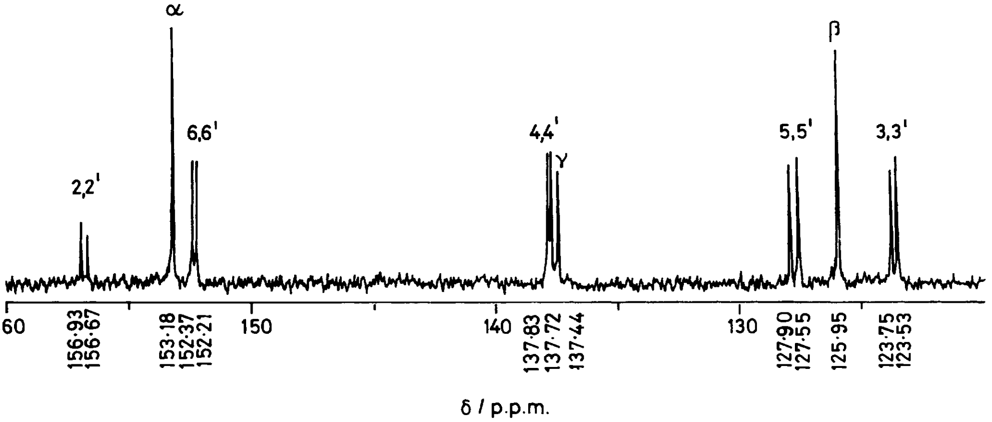

Figure 5. The ^{13}C n.m.r. spectrum (360 MHz) of $[Ru(bipy)_2(py)_2]^{2+}$ in $(CD_3)_2SO$

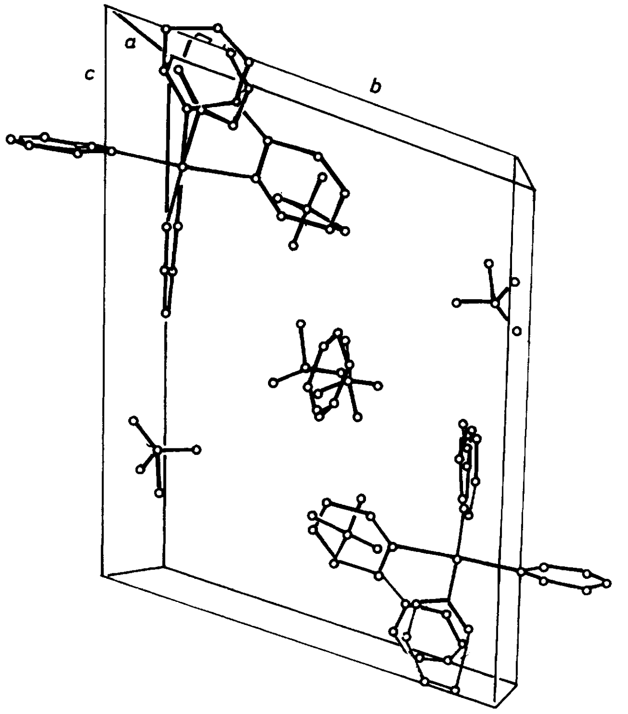

Figure 6. The unit cell of *cis*-$[Ru(bipy)_2(py)_2][BF_4]_2$·$0.5[Hpy][BF_4]$

hydroxide ion may subsequently displace pyridine in a concerted fashion.' This is the sole piece of evidence quoted that supports the formation of a covalent hydrate in this system, and is clearly worthy of further examination. Figure 4 illustrates the effects of added $[OH]^-$ upon the 300-MHz ^1H n.m.r. spectrum of $[Ru(bipy)_2(py)_2]^{2+}$. The assignments are unambiguous, and follow those discussed above. The relative positions of the H^6 and H_α protons remain essentially unchanged, and Table 2 shows the proton shifts relative to H^6. Since the shift of H^6 is also upfield, it is immediately clear that, contrary to Gillard's contention (see above), H^6 is the *least* affected proton in the cation. We have previously noted[19] the acidity of the 3,3′ protons of $[Ru(bipy)_3]^{2+}$ (results recently independently confirmed by other workers[7,21]) and of the 3,3′,5′,3″ protons of $[Ru(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine),[22] and so it was not unexpected to find that the chemical shifts of the 3,3′ protons of $[Ru(bipy)_2(py)_2]^{2+}$ were by far the most sensitive to the addition of base. Examination of a three-dimensional model of the complex shows that the protons on the periphery of the

Table 2. The shifts, $\Delta\delta$, of the protons of $[Ru(bipy)_2(py)_2]^{2+}$ upon the addition of base, measured relative to H^6

Proton	Δδ*/p.p.m.	Proton	Δδ*/p.p.m.
H_α	+0.008	$H^{3'}$	+0.302
H_β	+0.13	$H^{4'}$	+0.136
H_γ	+0.14	$H^{5'}$	+0.141
H^3	+0.298	$H^{6'}$	+0.027
H^4	+0.125		
H^5	+0.186		
H^6	+0.000		

* Positive shifts are to higher field.

Table 3. Selected intramolecular distances (nm) and angles (°) for the salt *cis*-$[Ru(bipy)_2(py)_2][BF_4]_2$·$0.5[Hpy][BF_4]$, with e.s.d.s in parentheses

Ru–N(1)	0.213(2)	Ru–N(2)	0.204(3)
Ru–N(3)	0.201(2)	Ru–N(4)	0.199(3)
Ru–N(5)	0.206(3)	Ru–N(6)	0.213(2)
N(1)–C(1)	0.126(5)	N(1)–C(5)	0.148(5)
N(2)–C(6)	0.143(4)	N(2)–C(10)	0.124(6)
N(3)–C(11)	0.143(5)	N(3)–C(15)	0.122(5)
N(4)–C(16)	0.132(4)	N(4)–C(20)	0.122(5)
N(5)–C(21)	0.129(5)	N(5)–C(25)	0.137(4)
N(6)–C(26)	0.136(5)	N(6)–C(30)	0.127(4)
C(5)–C(6)	0.138(6)	C(15)–C(16)	0.168(5)
C–C(bipy)	0.125(6)— 0.148(5)	C–C(py)	0.132(6)— 0.140(5)
H(4) ··· H(7)*	0.255	H(14) ··· H(17)	0.188
N(1)–Ru–N(2)	85(1)	N(1)–Ru–N(3)	88(1)
N(1)–Ru–N(4)	94(1)	N(1)–Ru–N(5)	176(1)
N(1)–Ru–N(6)	90(1)	N(2)–Ru–N(3)	98(1)
N(2)–Ru–N(4)	175(1)	N(2)–Ru–N(5)	91(1)
N(2)–Ru–N(6)	86(1)	N(3)–Ru–N(4)	77(1)
N(3)–Ru–N(5)	92(1)	N(3)–Ru–N(6)	176(1)
N(4)–Ru–N(5)	90(1)	N(4)–Ru–N(6)	99(1)
N(5)–Ru–N(6)	90(1)		
Ru–N(1)–C(5)	104(2)	Ru–N(1)–C(1)	127(2)
Ru–N(2)–C(6)	112(3)	Ru–N(2)–C(10)	139(2)
Ru–N(3)–C(15)	122(3)	Ru–N(3)–C(11)	128(2)
Ru–N(4)–C(16)	122(2)	Ru–N(4)–C(20)	129(3)
C(1)–N(1)–C(5)	128(2)	C(6)–N(2)–C(10)	107(3)
C(11)–N(3)–C(15)	108(3)	C(16)–N(4)–C(20)	109(3)
Ru–N–C(py)	113(2)— 126(3)	C–N–C(py)	109(3), 121(3)

* Hydrogen atoms are assigned labels of the carbon atoms to which they are bonded.

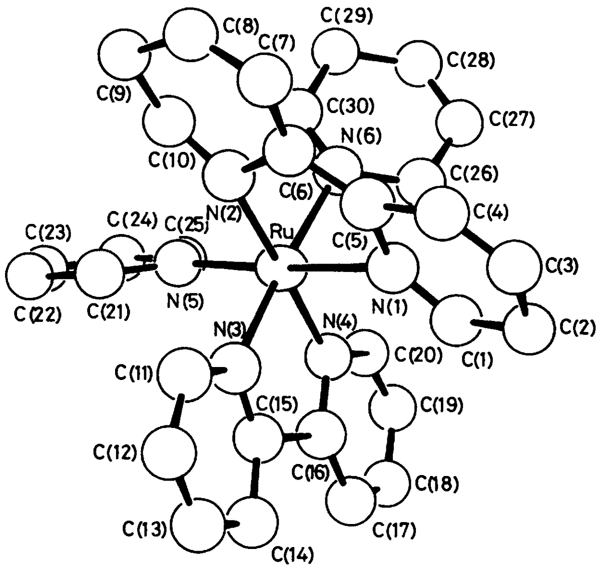

Figure 7. The structure of the ruthenium-containing cation in *cis*-$[Ru(bipy)_2(py)_2][BF_4]_2{\cdot}0.5[Hpy][BF_4]$

molecule (*i.e.* those likely to be influenced most by solvent interactions) are those which are most affected by the addition of base, and those 'within' the molecule (*viz.* H^6, $H^{6'}$, and H_α) are the least affected. Using the principle of Ockham's razor, it is clear that the observed effects of base upon the ^1H n.m.r. spectrum of $[Ru(bipy)_2(py)_2]^{2+}$ should be interpreted in terms of classical outer-sphere solvent interactions, and that it is not necessary to invoke the covalent hydration hypothesis. Moreover, the experimental observations would not support a structure of type (**1**), even if it were believed that the observations were not totally in accord with classical theory.

The ^{13}C *N.M.R. Spectrum of* $[Ru(bipy)_2(py)_2]^{2+}$.—The ^{13}C n.m.r. spectrum of $[Ru(bipy)_2(py)_2]^{2+}$ in $(CD_3)_2SO$ is illustrated in Figure 5. Thirteen signals, corresponding to the thirteen chemically different carbon atoms, are observed in the region conventionally associated with heterocyclic carbon atoms. No signals were observed at $\delta < 100$ p.p.m., the region associated with 'covalently hydrated' carbon atoms.[4] There is no significant change in this spectrum when base is added; in particular, no new signal at $\delta < 100$ p.p.m. appears.

The Structure of cis-$[Ru(bipy)_2(py)_2][BF_4]_2{\cdot}0.5[Hpy][BF_4]$.—The crystal structure of *cis*-$[Ru(bipy)_2(py)_2][BF_4]_2{\cdot}0.5[Hpy][BF_4]$ confirmed that 1 mol of pyridinium tetrafluoroborate (detected analytically) had co-crystallized with 2 mol of the ruthenium salt. The unit cell is illustrated in Figure 6: the carbon and nitrogen atoms of the pyridinium cation, and the position of its associated tetrafluoroborate anion, were disordered, but there was no evidence for the presence of occluded water. The structure of the ruthenium-containing cation is illustrated in Figure 7, and selected bond lengths and bond angles are detailed in Table 3. The mean ruthenium–nitrogen bond length of the bipyridine ligand, $\bar{r}(RuN)_{bipy}$, is 0.204(6) nm {*cf.* $\bar{r}(RuN)_{bipy} = 0.2056$ nm for $[Ru(bipy)_3][PF_6]_2$},[23] whereas the mean ruthenium–nitrogen bond length for the pyridine ligand, $\bar{r}(RuN)_{py}$, is 0.210(5) nm {*cf.* $\bar{r}(RuN)_{py} = 0.212$ nm for $[Ru(py)_6][BF_4]_2$;[24] $r(RuN)_{py} = 0.2097$ nm for *trans*-$[Ru(phen)_2(py)_2][PF_6]_2$[25] (phen = 1,10-phenanthroline)}. The bipyridine ligands show little sign of strain or distortion. The dihedral angles between the rings containing N(1) and N(2), and N(3) and N(4), are 7 and 5°, respectively, whereas the dihedral angle between the planes of the pyridine rings is 60°. The angles C(2)C(5)C(6), C(5)C(6)C(9), C(12)C(15)C(16), and C(15)C(16)C(19) have values of 174, 175, 174, and 170°, respectively, again showing little evidence for a bowing strain. Given the value of the discrepancy index (high because of the presence of the disordered anion), no abnormal distortion, unusual bond lengths, or strained bond angles were observed for the co-ordinated ligands, for the pyridinium cation, or for the tetrafluoroborate anions.

The most important feature of the structure determination is its normality, each of the co-ordinated *N*-heterocyclic rings being conventionally aromatic. There is a total absence of any water in the structure. It should be stressed, however, that these crystals were grown from *acidic* solution, and there are no claims (nor expectation) that this structure relates to the arguments concerning covalent hydration.

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