Ligand Reactivity in Iron(II) Complexes of 4′-(4‴-Pyridyl)-2,2′:6′,2″-terpyridine

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The ligand 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine (pyterpy) acts as a tridentate ligand in which the 4-pyridyl ring is not co-ordinated in the complex cation $[Fe(pyterpy)_2]^{2+}$; the non-co-ordinated ring reacts with electrophiles to give species in which the charge perturbations are localised to a '4,4′-bipyridyl' fragment.

We have been concerned for a number of years with the consequences of co-ordination to a metal centre upon the reactivity of organic ligands.[1] Spatial control of ligand conformation to produce highly organised arrays with novel topological and topographical properties has allowed the systematic synthesis of multiple-helical, knotted and catenated molecular systems. Reactivity control reliant upon the polarisation of the ligand may be reflected in enhanced rates of reaction with nucleophiles, or in totally new reaction pathways. Additional effects involving π-bonding interactions between metal and ligand centres may amplify or negate those previously described. We have made extensive studies upon kinetically inert complexes to demonstrate unequivocally these phenomena. Oligopyridine complexes of low-spin d^6 transition-metal ions have proved to be of particular application to these studies.[2] In this paper we describe studies involving the protonation and alkylation of iron(II) complexes with the novel ligand 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine (pyterpy) at nucleophilic sites spatially remote from the metal centre.

Experimental

Infrared spectra were recorded on Perkin Elmer 1710 or Philips PU9624 Fourier transform spectrophotometers, with the samples in compressed KBr discs. Proton and ^{13}C NMR spectra were recorded on Brüker WM-250 or AM400 spectrometers. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix for the FAB spectra. Electrochemical measurements were performed using an AMEL model 553 potentiostat, model 567 function generator and model 721 integrator connected to an X-Y recorder *via* an AMEL model 560/A interface. A conventional three-electrode configuration was used, with platinum bead working and auxiliary electrodes and an Ag–AgCl or Ag–Ag^+ reference. The solvent was acetonitrile distilled over P_4O_{10} immediately before use; base electrolyte was 0.1 mol dm^{-3} $[NBu_4][BF_4]$, recrystallised twice from methanol–water. Potentials are quoted *vs.* ferrocene–ferrocenium couple, and all potentials were referenced to internal ferrocene added at the end of each experiment. 2-Acetylpyridine and pyridine-4-carbaldehyde were used as supplied by Aldrich; $[Fe(H_2O)_6][BF_4]_2$ was prepared by the literature method.[3]

Preparations.—1,5-*Bis*(2-*pyridyl*)-3-(4′-*pyridyl*)*pentane*-1,5-*dione*. A solution of 2-acetylpyridine (8.4 cm^3, 0.074 mol), pyridine-4-carbaldehyde (3.0 cm^3, 0.032 mol) and sodium hydroxide (2.0 g) in water (25 cm^3) and ethanol (35 cm^3) was stirred for 1 h at room temperature. After this period water (30 cm^3) was added and a white precipitate obtained. This was collected by filtration, washed well with cold ethanol and dried *in vacuo* to give 1,5-bis(2-pyridyl)-3-(4′-pyridyl)pentane-1,5-dione as a white solid (4.5 g, 45%), m.p. 147.5–149 °C. IR (KBr): 1698s, 1600m, 1585m, 1437m, 1408m, 1358m, 1283s, 998s, 828m, 756s, 585m and 559m cm^{-1}. Mass spectrum (EI): *m/z* 331(*P*) and 225 ($P - COC_5H_4N$). NMR ($CDCl_3$): ^1H, δ 8.70 (2 H, dm, H^6), 8.52 (2 H, dd, H^c), 8.02 (2 H, dt, H^3), 7.86 (2 H, td, H^4), 7.51 (2 H, ddd, H^5), 7.37 (2 H, dd, H^6), 4.20 (1 H, qnt, $H^{4'}$) and 3.77 (4 H, ABM, $H^{3'}$); ^{13}C, δ 199.3 ($C^{2'}$), 153.6 ($C^{2/a}$), 153.0 ($C^{a/2}$), 149.8 (C^c), 148.9 (C^6), 136.9 (C^4), 127.3 (C^b), 123.2 (C^5), 121.8 (C^3), 43.2 ($C^{4'}$) and 35.4 ($C^{3'}$) (Found: C, 72.2; H, 4.95; N, 12.5. Calc. for $C_{20}H_{17}N_3O_2$: C, 72.5; H, 5.1; N, 12.7%).

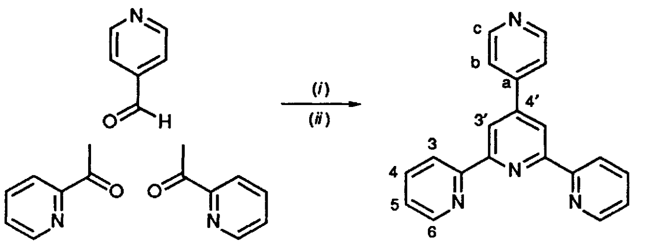
4′-(4‴-*Pyridyl*)-2,2′:6′,2″-*terpyridine*. A solution of 1,5-bis(2-pyridyl)-3-(4′-pyridyl)pentane-1,5-dione (0.400 g, 1.21 mmol) and ammonium acetate (5.00 g) in ethanol (50 cm^3) was heated to reflux for 2 h. After this period, the pale coloured solution was cooled, treated with water (50 cm^3) and reduced in volume to give an off-white precipitate which was collected by filtration. Recrystallisation from ethanol gave small white needles of 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine (0.24 g, 40%), m.p. 233–235 °C. IR (KBr): 1582s, 1565m, 1470m, 1393m, 793m and 618m cm^{-1}. Mass spectrum (EI): *m/z* 310 (*P*) and 232 ($P - C_5H_4N$). NMR ($CDCl_3$): ^1H, δ 8.765 (1 H, dd, H^c), 8.76 (1 H, s, $H^{3'}$), 8.73 (1 H, br dm, H^6), 8.68 (1 H, br d, H^3), 7.89 (1 H, td, H^4), 7.79 (1 H, dd, H^b) and 7.37 (1 H, ddd, H^5); ^{13}C, δ 155.7 ($C^{2'}$), 156.3 (C^2), 150.5 (C^c), 149.2 (C^6), 147.4 ($C^{4'}$), 145.9 (C^a), 137.0 (C^4), 124.1 (C^5), 121.7 ($C^{3/b}$), 121.3 ($C^{b/3}$) and 118.6 ($C^{3'}$) (Found: C, 77.2; H, 4.4; N, 17.9. Calc. for $C_{20}H_{14}N_4$: C, 77.4; H, 4.5; N, 18.1%).

$[Fe(pyterpy)_2][BF_4]_2$. A solution of $[Fe(H_2O)_6][BF_4]_2$ (0.20 g, 0.59 mmol) in methanol (10 cm^3) was added to a solution of pyterpy (0.366 g, 1.18 mmol) in boiling methanol (50 cm^3), and the resultant deep purple solution was heated to reflux for 10 min. After this period, the solution was allowed to cool, when $[Fe(pyterpy)_2][BF_4]_2$ precipitated as a very dark purple microcrystalline solid (0.40 g, 80%) (Found: C, 56.2; H, 3.15; N, 13.1. Calc. for $C_{40}H_{28}B_2F_8FeN_8$: C, 56.5; H, 3.3; N, 13.2%); mass spectrum (FAB) *m/z* 763 $\{Fe(pyterpy)_2(BF_4)\}$ and 676 $\{Fe(pyterpy)_2\}$. IR (KBr): 1599s, 1411m, 1085s, 1060s and 793m cm^{-1}.

$[Fe(mpyterpy)_2]I_2[BF_4]_2$ [mpyterpy = 4′-(4‴-*methylpyridinio*)-2,2′:6′,2″-*terpyridine*]. A solution of $[Fe(pyterpy)_2][BF_4]_2$ (0.10 g, 0.118 mmol) in acetonitrile (50 cm^3) was treated with MeI (2 cm^3, excess) and the solution heated to reflux for 1 h, after which period the colour had changed to a royal blue. After this period the solution was concentrated *in vacuo* to 5 cm^3 volume and treated with methanolic $[NH_4][BF_4]$. The dark blue microcrystalline product was collected by filtration to yield $[Fe(mpyterpy)_2]I_2[BF_4]_2$ (0.10 g, 75%) (Found: C, 44.7; H, 3.2; N, 9.8. Calc. for $C_{42}H_{34}B_2F_8FeI_2N_8$: C, 44.4; H, 3.0; N,

Table 1 Proton NMR data (δ)

	H^6	H^5	H^4	H^3	$H^{3'}$	H^b	H^c	Other
terpy	8.70	7.34	7.86	8.63	8.46			7.97 ($H^{4'}$)
pyterpy	8.73	7.37	7.89	8.68	8.76	7.79	8.765	
$[Fe(terpy)_2][BF_4]_2$	7.06	7.06	7.88	8.46	8.91			8.67 ($H^{4'}$)
$[Fe(pyterpy)_2][BF_4]_2$	7.17	7.09	7.92	8.63	9.23	8.23	9.03	
$[Fe(mpyterpy)_2]I_2[BF_4]_2$	7.20	7.14	7.97	8.69	9.33	8.86	9.01	4.50 (Me)
$[Fe(H(pyterpy)_2]^{4+}$	7.18	7.15	7.96	8.66	9.30	8.86	9.13	



Scheme 1 (*i*) $EtOH-H_2O-NaOH$. (*ii*) $[NH_4][O_2CMe]$

9.9%). Mass spectrum (FAB): *m/z* 705 {Fe(mpyterpy)$_2$}. IR (KBr): 1642s, 1426m, 1085, 1062s, 1038 and 791m cm^{-1}.

Results and Discussion

The functionalised ligand 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine (pyterpy) was prepared from 2-acetylpyridine in two steps (Scheme 1). A solution of 2-acetylpyridine and pyridine-4-carbaldehyde was stirred in basic aqueous ethanolic solution for 1 h at room temperature. After this period either a white solid or an orange gum had been precipitated. If the orange gum were obtained, trituration with small amounts of methanol resulted in the formation of a white solid. The white solid was collected by filtration to give 1,5-bis(2-pyridyl)-3-(4′-pyridyl)pentane-1,5-dione in 45% yield. The compound exhibited a characteristic carbonyl stretching mode in its infrared spectrum at 1698 cm^{-1}. The EI mass spectrum of this diketone exhibited peaks at *m/z* 331 (*P*) and 225 (*P* − COC_5H_4N). The ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions of this diketone are fully in accord with the proposed structure.

The reaction of the diketone with an excess of ammonium acetate in ethanol in the presence of air resulted in the formation of the desired ligand pyterpy in 40% yield as a white crystalline solid. The intermediate dihydropyridine is oxidised in air during the course of the reaction to the desired pyterpy. The pyterpy ligand exhibited no carbonyl stretching modes in its IR spectrum, and a parent ion at *m/z* 310 in its EI mass spectrum. Both the ^1H (Table 1) and ^{13}C NMR spectra of solutions of pyterpy indicate that the ligand is symmetrical on the NMR time-scale. The ^{13}C NMR spectra were assigned on the basis of distortionless enhancements by polarisation transfer (DEPT) spectra, and by comparison with those of 2,2′:6′,2″-terpyridine (terpy) and 4′-phenyl-2,2′:6′,2″-terpyridine.[4] It is of note that the only significant chemical shift differences between pyterpy and the parent terpy ligand are observed at $H^{3'}$ which is shifted downfield by 0.3 ppm. This may be assigned to a combination of inductive and anisotropic π-cloud effects associated with the adjacent 4-pyridyl substituent. It is also noteworthy that the resonances of the protons on the 4-pyridyl ring (H^b δ 7.79, H^c 8.75) are almost unshifted with respect to the corresponding protons in 4,4′-bipyridine (δ 7.54 and 8.74 respectively).

The reaction of pyterpy with $[Fe(H_2O)_6][BF_4]_2$ in methanol results in the formation of an intensely purple solution, from which the complex $[Fe(pyterpy)_2][BF_4]_2$ is obtained as small analytically pure purple crystals. The FAB mass spectrum of this complex exhibits a parent ion at *m/z* 763 ([Fe(pyterpy)$_2$][BF$_4$]) and a daughter peak at *m/z* 676 ([Fe(pyterpy)$_2$]). The electronic spectrum of an acetonitrile solution of the purple complex exhibits an metal-to-ligand charge-transfer (m.l.c.t.) band at 569 nm (ε 24 500 $dm^3 mol^{-1} cm^{-1}$), together with ligand-based $\pi^* \longleftarrow \pi$ or $\pi^* \longleftarrow n$ transitions at 245, 276, 284 and 324 nm. The complex is redox active and the cyclic voltammogram of an MeCN solution exhibits a single fully reversible iron(II)–iron(III) oxidation process at +0.801 V ($[NBu_4][PF_6]$ supporting electrolyte, Ag–AgCl or Ag–Ag^+ pseudo-reference electrodes, potentials *versus* ferrocene–ferrocenium). These data may be compared with those for $[Fe(terpy)_2]^{2+}$ salts, which exhibit an m.l.c.t. band with λ_{max} 552 nm (ε 11 900 $dm^3 mol^{-1} cm^{-1}$)[5] and $E_{\frac{1}{2}}$ +0.77 V. The more positive potential for the oxidation, combined with the higher energy m.l.c.t. band, of the pyterpy complex suggests that with pyterpy either the iron(II) state is additionally stabilised, or the iron(III) state is destabilised. This is in accord with the pyterpy ligand being a better π acceptor than terpy. These data are consistent with the formation of a complex in which the two pyterpy ligands are acting as tridentate chelating ligands to a six-co-ordinate iron centre. The electrochemical reversibility strongly suggests that the iron(III) complex possesses a similar geometry. The cyclic voltammogram of a solution of $[Fe(pyterpy)_2][BF_4]_2$ also exhibits two reversible ligand-based reductions at −1.932 and −2.083 V (*cf.* −1.65 and −1.85 V for $[Fe(terpy)_2]^{2+}$). Again, the more positive potentials for the reduction of the pyterpy complex indicate that the ligand is a better π acceptor than is terpy.

The ^1H NMR spectrum of a CD_3CN solution of $[Fe(pyterpy)_2][BF_4]_2$ is shown in Fig. 1(*a*). The spectrum is relatively sharp and well resolved, and illustrates the high symmetry of the iron(II) complex on the ^1H NMR time-scale. The spectrum was unambiguously assigned on the basis of decoupling and nuclear Overhauser effect (NOE) experiments and by comparison with the spectrum of $[Fe(terpy)_2]^{2+}$. The observation of an NOE between $H^{3'}$ and H^b (of the same sign as that between $H^{3'}$ and H^3) unambiguously allows the AA′BB′ pattern for H^b and H^c to be assigned. The terminal rings of each ligand in the $[Fe(pyterpy)_2]^{2+}$ cation are clearly in very similar environments to the terminal rings in the $[Fe(terpy)_2]^{2+}$ cation with negligible differences in co-ordination shifts Δδ (= $\delta_{complex} - \delta_{ligand}$, Table 2). The use of co-ordination shifts is more reliable in comparisons of this type than the direct comparison of chemical shift. It is of particular interest that the co-ordination shifts associated with $H^{3'}$ ($\Delta\delta_{terpy}$ +0.45 ppm, $\Delta\delta_{pyterpy}$ +0.47 ppm) are similar. This strongly suggests that the electronic changes occurring within the ligand upon co-ordination to the metal are similar with the two ligands, which in turn indicates that there are no significant changes in the configuration of the non-co-ordinated pyridine ring upon adoption of the terdentate mode. Although we have no solid-state structural data for these complexes, analogy with studies on 4′-phenyl substituted ligands suggest that the interplanar angles between the central ring of the terpy and the 4-pyridyl substituent will be in the range 5–20°.[4,6]

Upon adding acid to methanol or acetonitrile solutions of $[Fe(pyterpy)_2]^{2+}$ a colour change from purple to blue occurred. This corresponds to the formation of a complex in which the co-ordinated ligand is protonated at the free 4-pyridyl group,

Table 2 Co-ordination shifts Δδ

	H^6	H^5	H^4	H^3	$H^{3'}$	H^b	H^c	Other
terpy [a]	−1.64	−0.28	+0.02	−0.17	+0.45			+0.70 ($H^{4'}$)
pyterpy [a]	−1.56	−0.28	+0.03	−0.05	+0.47	+0.44	+0.265	
mpyterpy [b]	+0.03	+0.05	+0.05	+0.06	+0.10	+0.63	−0.02	
Hpyterpy [b]	+0.01	+0.01	+0.04	+0.03	+0.07	+0.63	+0.10	

[a] $\Delta\delta = \delta_{complex} - \delta_{ligand}$. [b] $\Delta\delta = \delta_{complex} - \delta_{pyterpy\ complex}$.

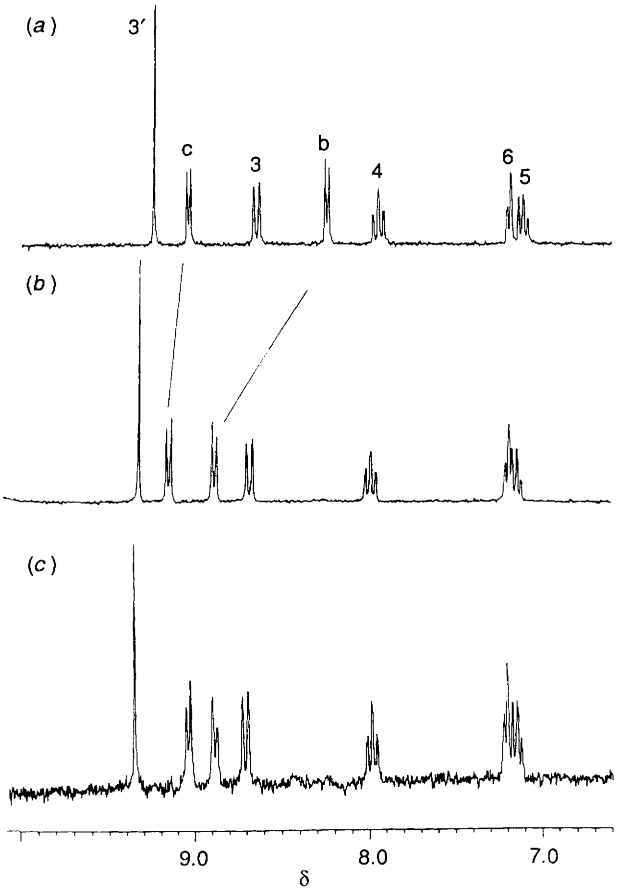


Fig. 1 250 MHz ^1H NMR spectrum of CD_3CN solutions of (*a*) $[Fe(pyterpy)_2]^{2+}$, (*b*) $[Fe(Hpyterpy)_2)_2]^{4+}$ and (*c*) $[Fe(mpyterpy)_2]^{4+}$

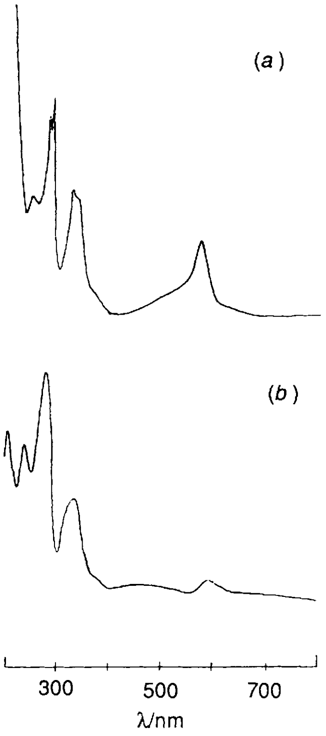


Fig. 2 Electronic spectra of (*a*) $[Fe(pyterpy)_2]^{2+}$ and (*b*) $[Fe(Hpyterpy)_2]^{4+}$ in methanolic solution. Absorption coefficient of the 569 nm band in $[Fe(pyterpy)_2]^{2+}$ is 24 500 dm³ mol⁻¹ cm⁻¹

$[Fe(Hpyterpy)_2]^{4+}$, and the colour change is associated with a shift in the m.l.c.t. band (in MeCN solution) from 569 nm in $[Fe(pyterpy)_2]^{2+}$ to 594 nm in $[Fe(Hpyterpy)_2]^{4+}$. Shifts also occur within the ligand-based $\pi^* \longleftarrow \pi$ or $\pi^* \longleftarrow n$ transitions which are observed at 239, 282(broad) and 334 nm (Fig. 2). The shift of the m.l.c.t. band to lower energy is compatible with the lowering in energy of the π^* levels of the ligand upon protonation. Systematic shifts in the electronic spectrum occurred upon titration of solutions of $[Fe(pyterpy)_2]^{2+}$ salts with acid. A single protonation process with an approximate pK_a of 2.9 ± 0.2 is observed in 2:1 aqueous methanol. We believe that this represents protonation of both non-co-ordinated pyridyl groups at the same pK_a, and have observed no other protonation process with large excesses of acid.

Attempts to isolate the protonated complex in the solid state were unsuccessful, and resulted in the regeneration of the purple parent compound, although the species is formed quantitatively in solution. The electrochemical behaviour of a blue acetonitrile solution of the protonated complex also differs from that of the parent cation. The iron(II)–iron(III) process moves to more positive potential, and is observed as a fully reversible wave at +0.870 V *versus* ferrocene–ferrocenium in the cyclic voltammogram. This shift reflects the additional destabilisation of the iron(III) state with the introduction of positive charge onto the ligand. In the presence of acid, all ligand reductive processes are obscured by proton reduction.

The ^1H NMR spectrum of the protonated complex cation $[Fe(Hpyterpy)_2]^{4+}$ was readily obtained by the addition of a drop of CF_3CO_2D to a CD_3CN solution of $[Fe(pyterpy)_2][BF_4]_2$, and this is presented in Fig. 1(*b*). The chemical shifts for this species are presented in Table 1, and the protonation shifts $\Delta\delta$ $(= \delta_{protonated\ complex} - \delta_{parent\ complex})$ in Table 2. The assignment of the resonances to H^b and H^c are unambiguous, and have been made on the basis of NOE experiments. A number of features are immediately noted. The terminal pyridine rings are essentially unperturbed by protonation, and all of the changes in charge density are associated with the central '4,4′-bipyridine' functionality. Most surprisingly, the major shift (+0.63 ppm) is associated with H^b and not with H^c, the proton adjacent to the site of protonation. This is in accord with the known protonation behaviour of pyridine and 4,4′-bipyridine in D_2O.[7] The downfield shift of H^b is much larger than that for $H^{3'}$. In order further to investigate the origins of these effects, we also prepared the *N*-methylated complex.

The reaction of $[Fe(pyterpy)_2][BF_4]_2$ with an excess of methyl iodide in acetonitrile results in the formation of an intense blue solution, from which a blue solid with a composition corresponding to $[Fe(mpyterpy)_2]I_2[BF_4]_2$ may be obtained. This complex is diamagnetic, and contains low-spin iron(II) cations. The ligand has been methylated upon the nitrogen of the non-co-ordinated pyridyl ring. The electronic spectrum of a (blue) solution of this complex in acetonitrile exhibits an m.l.c.t. band at 595 nm (ε 25 700 dm^3 mol^{-1} cm^{-1}). This is comparable to the corresponding band at 594 nm in $[Fe(Hpyterpy)_2]^{4+}$. The shift of the band to lower energy in each case corresponds to the lowering of the π^* levels upon increasing the charge on the ligand. Again, there are shifts associated with the ligand-based $\pi^* \longleftarrow \pi$ or $\pi^* \longleftarrow n$ transitions at 247, 278, 286 and 330 nm. The electrochemical behaviour of an acetonitrile solution of the complex $[Fe(mpyterpy)_2]I_2[BF_4]_2$ closely resembles that of the protonated species $[Fe(Hpyterpy)_2]^{4+}$. The iron(II)–iron(III) oxidation process is observed as a fully reversible wave at +0.850 V *versus* ferrocene–ferrocenium in the cyclic voltammogram. Ligand-based reductions are considerably more facile than those for the cation $[Fe(pyterpy)_2]^{2+}$, and are observed at −1.08 and −1.54 V (*cf.* −1.93 and −2.08 V).

The ^1H NMR spectrum of a solution of this complex is presented in Fig. 1(*c*) and Table 1, and the methylation shifts in Table 2. Again, the assignments of H^b and H^c are unambiguous (on the basis of NOE experiments). The similarity in behaviour of the methylated and protonated complexes is marked. The terminal pyridyl rings experience essentially no changes in either case. The protonation and methylation shifts associated with the central '4,4′-bipyridine' unit are essentially identical. We believe that two factors are involved in the shifts associated with H^b and $H^{3'}$. The first is a purely electronic one, which results in charge build-up on the non-co-ordinated pyridyl ring. Molecular-orbital calculations on model systems confirm that protonation at this site results in a considerable degree of charge localisation upon this ring. The second effect involves rotation about the interannular bond between the two rings of the '4,4′-bipyridine' unit. This will result in changes in the anisotropic shielding and deshielding of H^b and $H^{3'}$, but cannot easily be quantified. We have been unsuccessful in obtaining any X-ray quality crystals of the complexes to investigate directly the conformation of the two rings.

We have shown that after co-ordination to a metal the ligand pyterpy still acts as an electrophile. We are currently investigating the potential of ligands of this type for the preparation of one-dimensional materials in which reversible conformational changes about interannular bonds allow control over metal–metal interactions.

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