Co-ordination of Nitriles to $[Fe(CN)_5(OH_2)]^{3-}$ and Use of the Acetonitrile Complex for the Determination of Equilibrium Constants†

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Solid $Na_3[Fe(CN)_5(NH_3)]$, which hydrolyses rapidly in solution to the unstable complex $[Fe(CN)_5(OH_2)]^{3-}$ **1**, when dissolved in aqueous acetonitrile gave a solution of the much more stable complex $[Fe(CN)_5(MeCN)]^{3-}$ with log K 2.6 (25 °C, I = 0.1 mol dm^{-3}). It was shown that the use of solutions of the acetonitrile complex instead of **1** provides a general method for determining equilibrium constants for ligand substitution (directly of MeCN, hence indirectly of H_2O in **1**) under equilibrium conditions and over a wider range of pH from 3 to $\geqslant 13$. Values of log K have also been determined for other nitriles such as PhCN (3.5), $NCCH_2NH_3^+$ (3.3), $NCCH_2CO_2^-$ (2.5) and $NCNH_2$ (2.3), also for NH_3 (4.2), NH_2CH_2CN (3.7) and pyridine (3.7). The data suggest that, in the absence of complicating factors, the values of log K for nitriles show little dependence on their basicity. Comparison of present and published data on the wavelength of the first d–d transition in these and analogous complexes shows that the position of a nitrogen-containing base in the spectrochemical series depends primarily on the state of hybridisation of the donor N atom and increases in the order H_2O (443) < sp^3 N (all 400 ± 4) < sp^2 N (all 383 ± 3) < sp N (all 375 ± 2) < CN^-(325 nm).

We have been studying the co-ordination of a range of nitrogen-containing bases B (amines, azoles, azines) by the d^5 iron(III) porphyrin microperoxidase-8 (MP-8)[1–4] and the d^6 cobalt(III) corrinoid cyanocobinamide[5–7] in order to establish some of the factors which determine the magnitude of the stoichiometric equilibrium constant $K = [M\text{–}B]/[M\text{–}OH_2][B]$ for the single-step substitution of co-ordinated H_2O by B in aqueous solution and to determine the values of a and b in the well known linear free-energy relation (1).[8] [To conform with equation (1) and avoid confusion, all proton-dependent equilibrium constants (both of free bases and ligands) are reported as pK, while ligand-substitution equilibrium constants (including K', K_{obs}, $K_{W,B}$, *etc.*, as defined below) are reported as K or log K.]

$$\log K = a{\cdot}\mathrm{p}K + b \qquad (1)$$

We now wish to extend this survey to include the low-spin d^6 iron(II) ion through parallel studies on the $[Fe(CN)_5(OH_2)]^{3-}$ complex **1**, which permits the monitoring of changes in the crystal-field or d–d spectra (see Fig. 1 below), and iron(II) MP-8, where the very intense π–π^* transitions of the porphyrin, like those of the corrin ring, may reflect changes in the total electron (3d, 4s, 4p) density on the metal.[9] Iron(II) (whether in **1** or in a porphyrin complex) resembles Cu^I in being a 'soft' or class b metal ion with an unusual affinity for ligands such as CO and thioethers but is far easier to study in well defined complexes in aqueous solution than is Cu^I.[10] We are therefore interested in establishing whether the 'soft' character of Fe^{II} (and Cu^I) is associated with any unusual behaviour towards N-containing bases which might help to throw light on the origin of the 'soft' or class b character or on the unusual catalytic/enzymatic activity of iron porphyrins in *e.g.* redox reactions linking NH_2OH and NO_2^-,[11] or the recently discovered dehydration of oximes (RCH=NOH) to nitriles (RC≡N).[12] There is already some qualitative evidence that Fe^{II} differs markedly from Fe^{III} and Co^{III} in, *e.g.*, its strong affinity for unusual bases such as nitroso compounds.[13–15] We recently stated incorrectly[7] that Cu^I was the only transition metal of the first row able to co-ordinate MeCN in competition with water,[16–18] but have now found that Davies and Garafalo[19] reported in 1976 that **1** will also co-ordinate MeCN, though neither the spectrum nor the value of log K were given; co-ordination with PhCN and several other aromatic nitriles was reported in 1978.[20] In this respect Fe^{II} resembles the heavier Ru^{II}[21,22] and Os^{II}[23] as well as Cu^I, Ag^I[16,18] and Au^I.[24] In striking contrast to the values of a *ca.* 0.4 and 0.5 observed for Fe^{III}[3] and Co^{III},[7] the association constants for azines with **1** increase as the ligand basicity *decreases*, *i.e.* $a < 0$.[25] This was ascribed to compensation between a decrease in the σ-donor and increase in the π-acceptor ability of the ligand with decreasing pK, although it was pointed out that 'the important effect of ligand basicity has not yet been assessed,' which can only be done by comparison with saturated amines. In this and the accompanying paper[26] we report values of log K determined under equilibrium conditions for the co-ordination of nitriles and amines by **1**; results on iron(II) MP-8 will be reported later.

The direct determination of values of log K for the co-ordination of ligands by complex **1** under equilibrium conditions is hampered by (*i*) the instability of **1** in solution involving the occurrence of several reasonably rapid, but not instantaneous, reactions such as dimerisation[27–29] which occurs even in the solid state,[29] disproportionation to give aquated Fe^{II} and $[Fe(CN)_6]^{4-}$[30] and oxidation by traces of O_2 as well as photochemical reactions (see, for example, observations and discussion in ref. 19), hence (*ii*) the impossibility of preparing a pure solid salt of the monomeric form (always contaminated with dimer),[31] (*iii*) the occurrence of other pH-dependent equilibria, and (*iv*) the existence of extensive ion pairing. Most or all published values of K for **1** have therefore been derived indirectly from the ratio of the forward to reverse rate constants ($K = k_f/k_r$) and the main interest has centred on the kinetics and mechanism of ligand substitution, which is usually studied by fast reaction techniques. The pure aqua complex **1** ionises to form the hydroxo complex, with p$K \geqslant 13$,[19] possibly as high as *ca.* 17.[32] One of the cyanides is protonated, with pK 2.6, as deduced from

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† Ligand Co-ordination by the Soft Iron(II) Ion in $[Fe(CN)_5(OH_2)]^{3-}$. Part 1.

the pH dependence of the rate of reaction with *N*-methylpyrazinium(mpyz$^+$).[33] Oxidation is usually accompanied by the appearance of a blue or greenish colour (suppressed by the addition of a low concentration of ascorbic acid[25]), which may reflect formation of the deep blue Fe^{II}Fe^{III} dimer;[34,35] it provides a useful and sensitive test for the efficiency of deoxygenation and the acceptability of the given experiment. To solve the problem of impure **1** Toma and Malin[36] introduced the now general practice of using the much more stable trisodium salt of $[Fe(CN)_5(NH_3)]^{3-}$ **2** as the starting solid instead of **1** and preparing **1** *in situ* by rapid hydrolysis of **2** on dissolution in aqueous solution ($t_{\frac{1}{2}}$ *ca.* 40 s at 25 °C).[37] However, this does not suppress any subsequent side-reactions, as required for equilibrium studies, and reduces the range of pH available for study to pH $\leqslant$ 8, above which NH_3 may remain at least partly co-ordinated (see Results section). We now find that dissolving the amine complex **2** in 0.1 mol dm^{-3} aqueous MeCN produces the complex $[Fe(CN)_5(MeCN)]^{3-}$ **3** with a d–d band distinct from that of all other families of N-containing bases and a value of log K = 2.6, which is high enough to reduce the unwanted side-reactions of **1** and to increase the range of pH available up to pH $\geqslant$ 13, yet still low enough to permit ready displacement by most other ligands of interest. This opens up the study of nitriles as ligands and provides a general method for determining values of K for **1** under equilibrium conditions, *viz.* direct determination of K for the substitution of MeCN by B, followed by correction with the previously determined value of K for the substitution of H_2O by MeCN.

The main aims of this paper, starting from the reported co-ordination of MeCN by complex **1**,[19] are (*i*) to extend our knowledge of nitriles, RCN, as ligands (R = $CH_2CO_2^-$, $CH_2NH_3^+$, NH_2 or Ph) and (*ii*) to develop a general method for determining values of K for a wide range of ligands under equilibrium conditions, based on the use of solutions of **2** in 0.1 mol dm^{-3} MeCN and employing as test ligands NH_3 (the parent amine with sp^3-hybridised N, but difficult to study because of its high pK of 9.25 and atypical behaviour, see below), NH_2CH_2CN (a much more tractable and typical amine with pK 5.3) and pyridine (py) (the parent of the well studied azine family with sp^2-hybridised N). We also wish (*iii*) to establish whether there are any definite patterns in the wavelengths of the d–d transitions (*i.e.* in the crystal-field splitting) of complexes with a wider range of N-containing bases, which might aid both in identifying complexes in solution and in understanding the nature of the metal–ligand bond.

Experimental

Materials.—The salt $Na_3[Fe(CN)_5(NH_3)]$ was prepared by the method of Brauer[38] and [mpyz]$[O_3SC_6H_4Me\text{-}p]$ by adapting the method of Bahner and Norton[39] to use *p*-$MeC_6H_4SO_3Me$ instead of methyl iodide to methylate pyrazine; satisfactory analyses were obtained. Reagents were obtained as follows: MeCN (Fisons, HPLC grade, high-purity reagent); cyanamide (Aldrich); cyanoacetic acid (Lancaster); py (BDH); $NH_2CH_2CN{\cdot}HCl$ (Sigma); pyrazole (Aldrich) and 1,2,3-triazole (Aldrich). For other azoles (used only for recording UV/VIS spectra) see ref. 4. All reagents were used as received, after any necessary neutralisation as in the case of cyanoacetic acid and the hydrochloride of aminoacetonitrile.

Methods.—The UV/VIS spectra were recorded and spectrophotometric titrations carried out on a Philips PU 8740 or 8720 spectrophotometer in cells of 1 cm pathlength thermostatted at 25 °C; for the data in Table 1 wavelengths were calibrated with a holmium filter. Most experiments involved *ca.* 10^{-4} mol dm^{-3} solutions of complex **1** or **3** except when determining log K for the complexes with py and PhCN, where the product has an intense metal-to-ligand charge-transfer (m.l.c.t.) band (ε > 10^3 dm^3 mol^{-1} cm^{-1}) and *ca.* 10^{-5} mol dm^{-3} solutions were used. The following buffers were used: pH 3–5 (phthalate), 5–9 (phosphate), and 9–12 (hydrogencarbonate). Where necessary the pH was measured with a Hanna B417 pH meter and appropriate glass electrode, standardised at pH 4.00 and 7.00 (Russell buffer tablets). For quantitative work the solutions were made up to I = 0.1 mol dm^{-3} with $NaClO_4$. To determine K from the spectrophotometric titration, the observed change in absorbance A at the wavelength of λ_{max} of either the starting complex or final product (corrected for dilution where necessary) with change in concentration of free added base B was analysed as follows. Values of log $[(A_i - A_x)/(A_x - A_\infty)]$ were plotted against log [B], where A_i, A_x and A_∞ are the values of A observed initially, at the given value of [B], and corresponding to 100% formation of product respectively. Values of A_∞ were obtained directly in all cases except for **3** with PhCN where it was obtained by graphical extrapolation. The stoichiometry of the equilibrium is given by the slope n of the plot and log K = $-$log [B] when y = 0 (see Fig. 3 below).

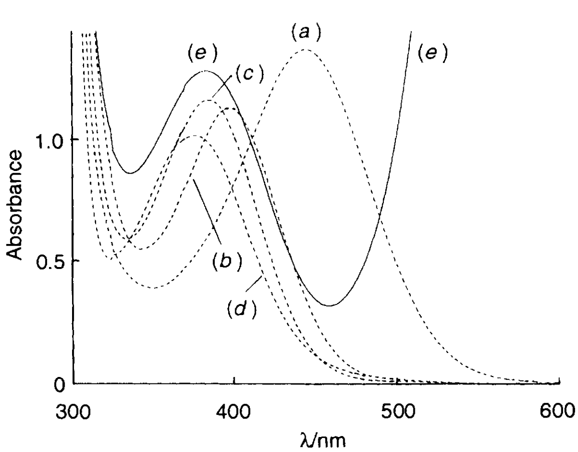

Fig. 1 Comparison of the UV/VIS spectra of *ca.* 2.5 × 10^{-3} mol dm^{-3} solutions of the complexes $[Fe(CN)_5B]^{3-}$ where B is H_2O (*a*), NH_3 (*b*), imidazole (*c*) and MeCN (*d*) and $[Fe(CN)_5B]^{2-}$ where B is mpyz$^+$ (*e*, —) where the rise in absorbance > 500 nm is caused by an intense c.t. band

Results

d–d Spectra.—We have compared the d–d spectra of the complexes $[Fe(CN)_5B]^{3-}$ where the hybridisation of the donor N atom may be sp (nitriles), sp^2 (azines and azoles) or sp^3 (amines). Their UV/VIS spectra may, however, exhibit an intense m.l.c.t. band which often hides the much weaker d–d band. The c.t. bands have been well studied with azines,[36,53–55] where λ_{max} moves progressively to longer wavelength as the electron density on the ring is decreased from 4-aminopyridine (320 nm)[54] through py (362 nm) to mpyz$^+$ (655 nm)[36] with ε in the range (4–12) × 10^3 dm^3 mol^{-1} cm^{-1}; the c.t. band moved to sufficiently low energy to reveal a free-standing d–d band only in the case of the dark blue mpyz$^+$ complex (see Fig. 1). Charge-transfer bands are also characteristic of alkyl and aryl nitroso compounds (*cf.* PhNO, λ_{max} = 528 nm),[13,14] aromatic (but not aliphatic) nitriles (*cf.* PhCN, λ_{max} = 341 nm)[20] and imidazoles with strongly electron-withdrawing substituents such as 4-NO_2[56] and 2-CHO.[57] The UV/VIS spectra of complexes with representatives of each of the four main families of N-containing bases (nitriles, azines, azoles, amines) and with H_2O are compared in Fig. 1 (all at similar concentrations, in buffer pH 7, with sufficient reagent to ensure > 98% formation). Neglecting the absorbance due to the c.t. band with mpyz$^+$, they all show a single fairly symmetrical band of similar intensity in the 350–450 nm region. Published and present data on the d–d spectra of the complexes with N-containing bases, H_2O, CN$^-$ and CO are presented in Table 1. The correct value for the unstable aqua complex (440 nm) only

Table 1 Wavelengths of d–d transitions of $[Fe^{II}(CN)_5B]$ complexes

Ligand (B)	λ/nm	ε/dm³ mol⁻¹ cm⁻¹	Ref.
OH_2	*ca.* 440		28
	442.5	≈640	40
	440	700	41
	440	≈770	19
	440	700	42
	444	660	32
	443	550	*a*
NH_3	400		43
	400		44
	405	450	45
	406		46
	398	*ca.* 450	40
	396	450	32
	397	435	*a*
NH_2Me	402		46
	397		*a*
$NH_2CH_2CH_2NH_2$	398		*a*
$NH_2CH_2CH_2NH_3^+$	402	465	47
	400		*a*
$NH_2CH_2CH_2OH$	397	470	48
NH_2CH_2CN	398		*a*
$NH_2CH_2CO_2^-$	396	450	32
Morpholine	404	550	48
NH_2NH_2	400	550	49
Imidazole	383	430	32
	383		*a*
Histidine	383	435	32
Pyrazole	385		*a*
1,2,4-Triazole	384		*a*
1,2,3-Triazole	*ca.* 385		*a*
N-Acetylimidazole	383		*a*
5-Chloro-*N*-methylimidazole	386		*a*
mpyz⁺	380		40
	383		*a*
Pyrazinecarboxylate	386[b]		40
NCMe	375	370	*a*
$NCCH_2NH_3^+$	370		*a*
$NCCH_2CO_2^-$	370		*a*
$NCNH_2$	375		*a*
CN^-	325		50
	322.5		51
	325		52
	≈325		*a*
CO	303	370	52

[a] Present results. [b] The d–d band is present as a shoulder on the c.t. band and resolved by Gaussian analysis.

became accepted during the 1970's (*cf.* 394 nm in 1976);[14] this serves to underline the problems in studying **1**. Of the ligands studied here values of ε were determined only for the complexes with H_2O, NH_3 and MeCN. Values of λ_{max} were determined at the pH used for determining log *K* for nitriles and amines (see below and ref. 26) and at pH 10 for the azoles and mpyz⁺, all in the presence of 0.1 mol dm⁻³ ligand.

Preparation and Properties of the Aqua Complex **1** *in Solution.*—The trisodium salt of complex **2** dissolves readily in neutral aqueous solution to give initially the corresponding ammine ion (λ_{max} 397 nm) which dissociates rapidly to give the aqua complex **1** (λ_{max} 443 nm). Qualitative experiments were carried out to compare the stability of **1** in deoxygenated and air-equilibrated solutions and with and without *ca.* 10^{-3} mol dm⁻³ ascorbate at various pH and also, in connection with the next section, in the presence of 0.1 mol dm⁻³ MeCN. The following results were obtained at pH 6. In air-equilibrated solutions without ascorbate the rapid formation of **1** was followed by the fairly rapid ($t_{\frac{1}{2}}$ 5–10 min) conversion of **1** and remaining **2** into products with absorption bands at 397 and *ca.* 345 nm, which can be assigned to the formation of $[Fe(CN)_5(OH_2)]^{2-}$.[35] These reactions were suppressed and replaced by a much slower decrease in A_{443}, coupled with an increase in the near-UV region (with no distinct bands down to at least 300 nm) and an isosbestic point at 385 nm, both in deoxygenated solution without ascorbate (*ca.* 30% decrease in A_{443} in 30 min) and in the air-equilibrated solution with ascorbate (*ca.* 25% decrease in 30 min). The rate of destruction of **1** was further reduced, but not completely suppressed, in deoxygenated solutions with ascorbate added. By contrast, the presence of 0.1 mol dm⁻³ MeCN in air-equilibrated solution without ascorbate caused rapid conversion of **1** into the acetonitrile complex **3** (λ_{max} 375 nm) with no further change in the spectrum over 30 min.

Further experiments on the pH dependence of the spectra of deoxygenated solutions of complex **1** containing *ca.* 10^{-3} mol dm⁻³ ascorbate revealed the existence of two reversible pH-dependent equilibria with p*K* 2.75 ± 0.2 and *ca.* 8.5. The former is associated with an isosbestic point at *ca.* 425 nm and the formation of a new species with λ_{max} at 420 nm; considerable irreversible decomposition occurred during the pH titration. Our value agrees with the published p*K* of 2.6[33] and can be ascribed to protonation of a co-ordinated cyanide to form the CNH ligand (see Discussion section). The changes in the spectra at pH *ca.* 8.5 involve isosbestic points at 410 nm and the formation of a species with λ_{max} at 397 nm. The same isosbestic points and λ_{max} were produced by adding NH_4Cl when the solution was buffered at pH 8.5, thereby identifying the product as the ammine complex **2**, in full agreement with previous conclusions.[32] The observed pH-dependent equilibrium can therefore be written as in equation (2).

$$Fe\text{–}OH_2 + NH_4^+ \rightleftharpoons Fe\text{–}NH_3 + H_3O^+ \qquad (2)$$

Attempts to prepare solutions of complex **1** free from contamination with NH_3 by removing gaseous NH_3 with a stream of N_2 through solutions buffered at pH 10 showed that it was difficult, if not impossible (in contrast to a previous report[32]), to produce a significant change in the spectrum from that of **2** to that of **1** without the simultaneous occurrence of other changes indicating unwanted side-reactions.

Characterisation of the Acetonitrile Complex **3**.—The stoichiometry and equilibrium constant *K* for the co-ordination of MeCN by complex **1** were determined quantitatively by spectrophotometric titration of 10^{-3} mol dm⁻³ solutions of **1** with pure MeCN in duplicate experiments at both pH 5 and 7, $I = 0.1$ mol dm⁻³ ($NaClO_4$), 25 °C. Equilibration was instantaneous, excellent isosbestic points were observed at 400 nm (see Fig. 2) and analysis of the decrease in A_{440} (see Fig. 3) established a stoichiometry of 1 : 1 with $K = 3.9 \times 10^2$ and 4.1×10^2 dm³ mol⁻¹ at pH 5, 4.1×10^2 and 4.2×10^2 dm³ mol⁻¹ at pH 7, average 4.1×10^2 dm³ mol⁻¹, *i.e.* log *K* 2.6 independent of pH (see also Table 2 below). Further experiments showed (*i*) no significant difference either in A_{375} or in the general shape of the spectrum at 300–600 nm between solutions containing the same final concentrations (0.1 mol dm⁻³) of MeCN which were prepared from freshly hydrolysed solutions of **2** at pH 5 or 7 either by slow additions of MeCN over 40 min to approximate the titration conditions or by a single addition and immediate recording of the spectrum, (*ii*)

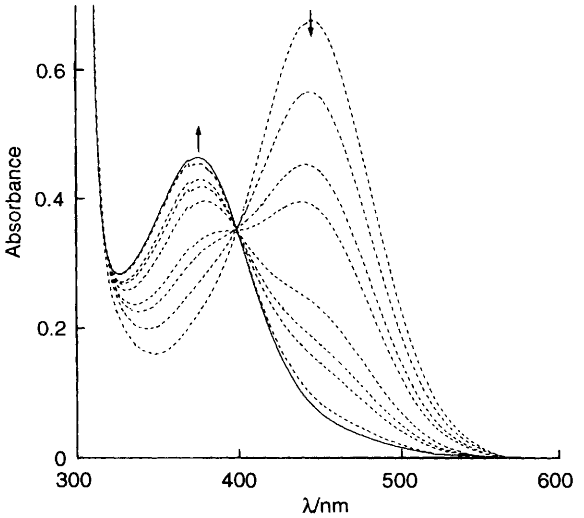

Fig. 2 Changes in the UV/VIS spectra observed during the titration of $[Fe(CN)_5(OH_2)]^{3-}$ with MeCN at pH 5

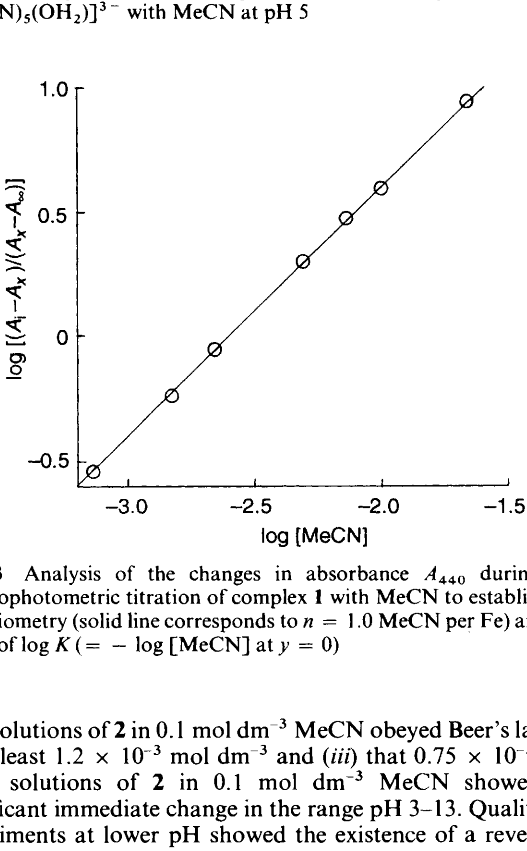

Fig. 3 Analysis of the changes in absorbance A_{440} during the spectrophotometric titration of complex **1** with MeCN to establish the stoichiometry (solid line corresponds to n = 1.0 MeCN per Fe) and the value of log K (= − log [MeCN] at y = 0)

that solutions of **2** in 0.1 mol dm^{-3} MeCN obeyed Beer's law up to at least 1.2 × 10^{-3} mol dm^{-3} and (*iii*) that 0.75 × 10^{-3} mol dm^{-3} solutions of **2** in 0.1 mol dm^{-3} MeCN showed no significant immediate change in the range pH 3–13. Qualitative experiments at lower pH showed the existence of a reversible equilibrium with pK *ca.* 2.0 involving the formation of a new species having λ_{max} = 363 nm, which can be assigned to protonation of one of the co-ordinated cyanides in **3** (see above and Discussion section). Solutions of **3** in 0.1 mol dm^{-3} MeCN at pH 6 are significantly more stable than solutions of **1** in the absence of MeCN (see above); *ca.* 10^{-3} mol dm^{-3} ascorbate was nevertheless added routinely to solutions of **3** in further experiments. Attempts to isolate **3** as a pure solid salt were unsuccessful. After dissolving **2** in deoxygenated 50% aqueous MeCN and passing a brisk stream of N_2 through the solution for 30 min to remove NH_3, the solvent was removed by rotary evaporation, using apparatus purged with N_2, to leave an olive green oil. Since solutions of **3** are pale yellow and exhibit no absorption at the low-energy end of the visible region (see Fig. 2), the green colour denotes contamination by some green or blue by-product. It proved impossible to avoid such contamination.

Other Equilibrium Constants.—Table 2 summarises the nitriles and other ligands studied here, published pK values if known, the experimental conditions used for the spectrophotometric titration (pH, concentration of MeCN) and the wavelength at which changes in the absorbance were recorded, together with λ_{max} of the product and the derived values of log K for the substitution of co-ordinated H_2O in complex **1** by the given **B**. The three non-conjugated nitriles (other than MeCN) had to be studied in the absence of MeCN because of the similarity both in λ_{max} and in log K to those of MeCN; the other four ligands were studied both in the presence and absence of MeCN. Each entry in Table 2 represents the average of at least two experiments. In all cases full spectra were recorded over the range 300–600 nm during the titration in order to check for isosbestic points (all reasonable-to-good in the case of the results reported in Table 2), rate of reaction (all virtually instantaneous) and any significant occurrence of side-reactions (experiment discarded if accompanied by the appearance of bands at 500–600 nm or if the isosbestic point was seriously disrupted). Additional experiments in the presence of NH_2CH_2CN showed the occurrence of a reversible pH-dependent change in the spectrum having pK ≈ 5 between acid and alkaline forms with λ_{max} = 375 (*i.e.* *N*$CCH_2NH_3^+$) and 398 nm (*i.e.* $NCCH_2$*N*H_2) respectively. In all cases except PhCN the end-point of the titration was attained and provided a final value (A_∞) for analysing the changes in absorbance as shown in Fig. 3; the limited solubility of PhCN prevented the end-point being reached, and a value of the end-point was therefore gauged by graphical extrapolation which corresponds to $\varepsilon \approx 5 \times 10^3$ (lit.,[20] 5.1 × 10^3 dm^3 mol^{-1} cm^{-1}). In all cases, except some of those involving NH_3 (see below), analysis of the change in absorbance established the binding of one base per Fe. In the two cases where the pH used was within 1.5 log units of a pK (*viz.* $NCCH_2NH_3^+$ at pH 4 and NH_3 at pH 10.0) the concentration of free base was corrected for partial loss or gain of a proton.

Initial semiquantitative titrations of complex **3** with NH_3 over the range of pH 11–4 revealed a simple parabolic dependence of A_{400} on ammonia concentration at pH 11 and 10 but a sigmoidal dependence at pH ⩽ 10. Quantitative titrations established the stoichiometry of n = 1 at pH 11 and 10 but n ⩾ 2 at pH 8 and 7. Titration of **1** with NH_3 in the absence of MeCN was carried out over the range pH 8–6.5. Complications due to undissociated **2** were observed at pH 8, a value of n = 1 was observed at pH 7.5 and over the bulk of the titration at pH 7.0, but n ≈ 2 at pH 6.5 and over the final part of the reaction at pH 7.0. There was no significant difference in the wavelength of the isosbestic points or λ_{max} of the products (all 397 nm) between the titrations corresponding to n = 1 and ≈2 either in the presence or absence of MeCN. The proton requirement for the observation of the equilibrium with n ≈ 2 indicates that the second (and perhaps even a third) molecule of reagent is bound as NH_4^+ according to the simplified equation (3); it obviously

$$\text{Fe–MeCN} + NH_3 + NH_4^+ \rightleftharpoons \text{Fe–}NH_3\cdot NH_4^+ + \text{MeCN} \quad (3)$$

forms an ion pair with, and is presumably hydrogen bonded to, the negatively charged $[Fe(CN)_5(NH_3)]^{3-}$ ion.

In view of the apparent discrepancy (see Discussion section) between our value of log K for py compared to that of PhCN (3.7 and 3.5 respectively, see Table 2) and published values deduced from kinetic data (5.5 and 3.4 respectively)[20] an additional experiment was carried out involving competition for complex **1** between py and PhCN. Charge-transfer bands of similar intensity are shown by the products of both py (362 nm, ε = 3.7 × 10^3 dm^3 mol^{-1} cm^{-1}; *cf.* our λ_{max} 368 nm, see Table 2) and PhCN (341 nm, ε = 5.1 × 10^3 dm^3 mol^{-1} cm^{-1}; *cf.* our λ_{max} 342 nm, see Table 2).[20] Addition of a stock concentration of **1** to different solutions containing 2.5 × 10^{-4} mol dm^{-3} PhCN, but with [py]:[PhCN] = 10:1, 1:1, 1:10 and 1:100, showed

Table 2 Equilibrium constants K for the substitution of co-ordinated H_2O in $[Fe^{II}(CN)_5(OH_2)]^{3-}$ by nitriles and other N-containing bases

		Experimental conditions			Product	
Ligand	pK of free base[a]	pH	[MeCN]/mol dm^{-3}	λ/nm used	λ_{max}/nm	log K[b]
$N\mathrm{CMe}$	*ca.* −10	5.0	Titrant	440	375	2.6
		7.0	Titrant	440	375	2.6
$N\mathrm{CCH_2NH_3}^+$		4.0	0	440	370	3.3
$N\mathrm{CCH_2CO_2}^-$		6.0	0	440	370	2.5
$N\mathrm{CNH_2}$	1.1	6.0	0	440	375	2.3
$N\mathrm{CPh}$		7.0	0	440	342[c]	3.5
		7.0	0.1	375	342[c]	3.9
py	5.2	7.0	0	440	368[c]	3.7
			0.05	375	368[c]	4.2
			0.1	375	368[c]	4.6
			0.2	375	368[c]	4.7
			0.3	375	368[c]	4.8
NH_3	9.25	7.0	0	440	397	4.3[d]
		7.5	0	400	397	4.2
		10.0	0.1	400	397	3.6
		11.0	0.1	400	397	3.5
$N\mathrm{H_2CH_2CN}$	5.3	9.0	0	440	398	3.7
			0.05	400	398	3.8
			0.075	400	398	3.9
			0.1	400	398	4.0
			0.2	400	398	4.0
			0.3	400	398	4.1

[a] Values from ref. 58 except for MeCN from ref. 59. [b] All values of log $K \pm 0.1$ or better except for PhCN *vs.* MeCN (± 0.2) where the end-point was estimated by graphical extrapolation. Values of log K reported in the presence of MeCN have been calculated from values of log K_{obs} by the use of equation (5). [c] Charge-transfer bands (other are d–d bands). [d] See text.

from changes in the spectrum at 300–400 nm that approximately equal concentrations of the two products were formed when the ratio was 1 : 1 (in agreement with our comparable values of log K) and not 1 : 100 (as expected if the values of log K differ by *ca.* 2).

Where the spectrophotometric titration was carried out in the presence of MeCN, the observed equilibrium constant (K_{obs}), which corresponds to the substitution of co-ordinated MeCN by the given B in the presence of a fixed concentration of MeCN ($[\mathrm{MeCN}]_{exptl}$), has been converted, first into the true stoichiometric equilibrium constant for the substitution of co-ordinated MeCN by B in the presence of 1 mol dm^{-3} MeCN and 1 mol dm^{-3} B ($K'_{\mathrm{MeCN,B}}$) through the relationship $K'_{\mathrm{MeCN,B}} = K_{obs}[\mathrm{MeCN}]_{exptl}$ and, secondly, to the equilibrium constant for the substitution of co-ordinated H_2O by B ($K_{\mathrm{W,B}}$) using the relationship (4), where $K_{\mathrm{W,MeCN}}$ is the equilibrium constant for the substitution of co-ordinated H_2O by MeCN. Since log $K_{\mathrm{W,MeCN}}$ has the value 2.6, equation (4) can be written as (5).

$$K_{\mathrm{W,B}} = K_{\mathrm{W,MeCN}}K'_{\mathrm{MeCN,B}} = K_{\mathrm{W,MeCN}}K_{obs}[\mathrm{MeCN}]_{exptl} \quad (4)$$

$$\log K_{\mathrm{W,B}} = \log K_{obs} + \log [\mathrm{MeCN}]_{exptl} + 2.6 \quad (5)$$

This will apply as long as substantially most of the starting complex is present as the acetonitrile complex; this includes the lowest concentration of MeCN entered in Table 2 (*viz.* 0.05 mol dm^{-3}). All the values of log K listed in Table 2, which have been determined in solutions containing MeCN, have been corrected in this way. There was no detectable change in λ_{max} of either the ammine complex at pH 11 or the NH_2CH_2CN complex at pH 8 in the presence or absence of 0.1 mol dm^{-3} MeCN.

Discussion

UV/VIS Spectra.—The pentacyanides of interest here and the hexacyanide all show d-d bands in the range 300–450 nm with similar ε 400–700 dm^3 mol^{-1} cm^{-1} (see Table 1 and Fig. 1), unless obscured by an intense m.l.c.t. band (as with most azines). The data show, first, that amongst the N-containing bases the position of the ligand in the spectrochemical series depends mainly on the state of hybridisation of the donor N atom and increases regularly in the order H_2O (443 nm) < sp^3 N (all 400 ± 4 nm) < sp^2 N (all 383 ± 3 nm) < sp N (all 375 ± 2 nm) < CN^- (325 nm) and, secondly, that when B is H_2O or NH_3 and several values of λ and A from different workers can be compared, there is greater variation than might have been expected (reflecting differences in ion-pair formation?, see below). This regularity makes it easy to identify the donor atom (italicised) in $N\mathrm{CNH_2}$ and $\mathrm{NCCH_2}N\mathrm{H_2}$ as well as $N\mathrm{CCH_2NH_3}^+$, and to distinguish between $C\mathrm{NH}$ (expected to fall between CN^- and CO) and the isomeric $N\mathrm{CH}$ (expected to be similar to NCMe) as the product of protonation of co-ordinated CN^-. The reversible protonation of both complexes **1** and **3** was accompanied by a shift in λ_{max} to higher energy (*i.e.* formation of $C\mathrm{NH}$). The $C\mathrm{NH}$ ligand has been established by X-ray analysis in the $[Fe^{II}(CNH)_6]^{2+}$ complex,[60] formed by full protonation of the hexacyanide, and in the isoelectronic d^6 $[Cr(CO)_5(CNH)]$.[61]

Ligand-substitution Equilibria.—Dissolution of the solid amine complex **2** in aqueous solutions of pH 5–8 rapidly gives the relatively unstable yellow aqua complex **1** with an apparent pK of *ca.* 8.5 (under our conditions) corresponding to equilibrium (2), while dissolving **2** directly in aqueous MeCN gives the significantly more stable acetonitrile complex **3**, which has been thoroughly characterised (see Results section, Table 2 and Figs. 2 and 3) as the 1 : 1 complex with a pH-independent value of log K 2.6 and a spectrum which remains unchanged up to pH ⩾ 13 and down to 3. We were, however, unable to prepare complex **3** as a pure solid. We can therefore use spectrophotometric titration with complex **3** in 0.1 mol dm^{-3} aqueous MeCN solution (I = 0.1 mol dm^{-3} 25 °C) as a general method for determining values of K' for the substitution of co-ordinated MeCN by a given B, which can be corrected (see Results section) for the equilibrium between co-ordinated H_2O and MeCN to give the required K for substitution of co-ordinated H_2O by B. This method fails where the product has λ_{max} too close to that of complex **3** (*i.e.* other non-aromatic nitriles, see Table 1) or a value of *K* equal to or less than that of MeCN itself (*e.g.* other non-aromatic nitriles, see Table 2, and NH_2OH);[26] in these cases the equilibria were studied directly with the less-stable aqua complex **1**. The ligands studied and the values of log *K* determined (directly or indirectly *via K'*) are given in Table 2. With the exception of NH_3 below its p*K* (see below), all equilibria correspond to the co-ordination of 1 B per Fe.

The data of Table 2 show the general ability of complex **1** to co-ordinate nitriles in aqueous solution, irrespective of charge or basicity. There are, unfortunately, few p*K* values known for nitriles; that for cyanamide NH_2CN (on the nitrile N)[62] has been determined experimentally as 1.1,[58] while that of MeCN has been estimated as *ca.* −10.[59] Judging from these two neutral nitriles alone, therefore, it would appear that log *K* for the co-ordination of nitriles by **1** shows little dependence on basicity, *i.e.* equation (1) has values of $a \approx 0$ and *b ca.* 2.3. Although the co-ordination of MeCN and aromatic nitriles such as PhCN is well known (*e.g.* with Ru^{II}),[21,22] there are only a few reports of the co-ordination as a simple nitrile of cyanoacetate (with W^0,[63] Ru^{II},[21] Cu^I [64]) and cyanamide (with W^0 [65] and Re^I [66,67]) and apparently none with $NCCH_2NH_3^+$. The parent HC*N* ligand has been identified by NMR spectroscopy in the complex $[Ag(NCH)_2]^+$ formed in liquid HF.[68,69] It will be shown later that the iron(II) ion in the porphyrin MP-8 shows similar behaviour towards nitriles,[70] *i.e.* the unexpected affinity for nitriles in competition with water is characteristic of low-spin Fe^{II}.

Ion Pairing and Other Outer-sphere Interactions.—We have found that increasing the acetonitrile concentration increases the apparent value of *K* for complex **1** towards both py and NH_2CH_2CN with an overall increase in log *K* (see Table 2) of *ca.* 0.9 for the former and *ca.* 0.3 for the latter; the increase becomes relatively small above 0.1 mol dm^{-3} MeCN, hence the use of this concentration for the indirect determination of values of log *K*. Similar increases in log *K* by 0.4, 0.4 and 0.3 respectively were observed for PhCN (see Table 2), $NH_2CH_2CF_3$ and $NH_2NH_3^+$.[26] Since further work on the co-ordination of amines and other N-containing bases will be carried out mainly under the standard conditions of 0.1 mol dm^{-3} MeCN, the values of log *K* determined here for the nitriles in the absence of MeCN will be increased by 0.4 to give 'corrected' values for comparison later with others determined in the presence of MeCN. Ammonia is anomalous in that the value of log *K* falls by *ca.* 0.6 in the presence of MeCN; for a possible explanation see ref. 26. These changes in log *K* may be connected with the unexpected minimum in the enthalpy of water–MeCN mixing around 0.02 mole fraction MeCN (*ca.* 1 mol dm^{-3}), which has been ascribed to hydrogen bonding between H_2O and MeCN.[71,72]

We have also found that, although only one NH_3 reacts with complex **1** at pH 7.5 and with **3** at pH 10 and 11, a second molecule of base is bound below these pH values with no obvious effect on the wavelength of the d–d band; NH_2Me behaves similarly.[26] Although the pH dependence has not been quantitatively established, these results indicate that the second molecule of base is bound as the NH_4^+ ion and we conclude that the NH_4^+ cation forms an ion pair with the negatively charged amminepentacyanide complex **2** according to equilibrium (3). It has been noted[73] that the trisodium salt of **2** may easily be contaminated by the disodium ammonium salt, *i.e.* the proposed ion pair occurs in the solid state; we have, in fact, noticed that the carbon and nitrogen analyses sometimes indicate an N : C ratio higher than that expected for pure **2** as the trisodium salt.

Ion-pair formation in solution has been quantitatively established, and differentiated from an ionic strength effect, between the cation K^+ and the two hexacyanides $[Fe^{II}(CN)_6]^{4-}$ (log *K* 2.3,[74] 2.37,[50] 2.35[75]) and $[Fe^{III}(CN)_6]^{3-}$ (log *K* 1.2)[76] in aqueous solution; ion-pair formation between NH_4^+ and the former has also been noted.[50]

Comparison of Equilibrium and Rate Constants.—Finally, we compare our values of log *K* obtained under equilibrium conditions with published values derived from the ratio of forward to reverse rate constants ($K = k_f/k_r$) for the reactions of complex **1** as shown without charges in equilibrium (6) where

$$[(NC)_5Fe{-}OH_2] + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [(NC)_5Fe{-}B] + H_2O \qquad (6)$$

k_f is the second-order forward rate constant and k_r the first-order reverse rate constant. Although the value of k_f can be determined directly from the reaction of **1** with B, that of k_r is determined indirectly from the rate of displacement of B by a more strongly bound base B' (often the charged $mpyz^+$). In apparently all cases studied so far, saturation is observed with increasing concentration of B', the limiting rate is taken to be k_r, and the mechanism is taken to be D (dissociative) or I (interchange); see, for example, references and discussion in ref. 32. Saturation kinetics due to formation of an outer-sphere complex with **1** have been established in a few cases;[77,78] *cf.* also the evidence for outer-sphere interaction between the d^6 $[Ru^{II}(NH_3)_5(OH_2)]^{2+}$ complex and both $mpyz^+$ [79] and 2,6-dimethylpyridine[21] and the very recent evidence for saturation kinetics and outer-sphere intermediates in ligand-substitution reactions of d^6 cobalt(III) corrinoids.[80,81] It has been shown that increasing the concentration of $LiClO_4$ can have a marked effect on the rate constants for the reaction of **1** with charged ligands (k_f for $mpyz^+$ falls from 2410 to 560 dm^3 mol^{-1} s^{-1} in 0.1 and 1.0 mol dm^{-3} $LiClO_4$ respectively)[37] and it has been suggested that differences between rate constants determined in the presence of lithium and sodium salts may reflect differences in ion-pairing.[19] Anomalous and unexplained kinetics have also been reported in the reactions of **1** (prepared by the dissolution of **2**) when carried out below pH 8 and above a certain concentration of complex.[19] In the protonation of the hexacyanide to give the $[Fe(CN)_5(CNH)]^{3-}$ complex, Legros[82] found that the pH dependence of the rate of hydrolysis of the hexacyanide in the presence of PhNO gave an apparent p*K* of 6.15 which, as she pointed out, was 'very appreciably' and inexplicably higher (by ⩾2 p*K* units) than the p*K* determined for protonation of a co-ordinated cyanide under equilibrium conditions.[83–88] Amongst the ligands in Table 2, comparisons can be made for NH_3, py, and PhCN. Values of log *K* for NH_3 have been reported as 3.8 ± 0.2 [from *K* for the analogous iron(III) complex, together with the Fe^{II}–Fe^{III} redox couple, conditions various][42] and 4.3 ($I = 0.1$ mol dm^{-3}, from rate constants at pH 8–9),[32] *cf.* our comparable value of 4.2 (see Table 2), also *ca.* 4.7 at 0 °C ($I = 0.05$ mol dm^{-3}, pH 8–11, equilibrium assayed using the different rates of reaction with nitrosobenzene).[44] The values of log *K* determined kinetically (and by the same authors) for py (*K* 3.31×10^5 dm^3 mol^{-1} or log *K* 5.5) and PhCN (*K* 2.35×10^3 dm^3 mol^{-1} or log *K* 3.4)[20] can be compared with our values of 3.7 and 3.5 respectively (in the absence of MeCN); the values for PhCN are in good agreement, while those for py differ by *ca.* 2 units. It is hoped that further work may serve to identify the main causes of these interesting differences between directly and indirectly (*i.e.* kinetically) determined equilibrium constants, first reported over 30 years ago.[82] One might, for example, expect ion-pair formation to have a more pronounced effect on rates than on overall equilibria because of their charge-compensating effects in the transition state for ligand substitution. The role of ion pairing and other outer-sphere interactions in the kinetics and mechanism of ligand substitution of these highly charged complexes has yet to be elucidated. Our aim is to determine a range of equilibrium constants under 'standard' equilibrium conditions, where the criterion of validity is the emergence of self-consistent and meaningful patterns (*cf.* the amines).[26]

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