

Steric, electronic and solvation effects in the co-ordination of amines by the $[\text{Fe}(\text{CN})_5(\text{OH}_2)]^{3-}$ ion†

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Equilibrium constants K for the substitution of co-ordinated H_2O in $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ by sterically hindered amines (both α and β branching, *viz.* $\text{NH}_2\text{Me-NMe}_3$ and $\text{NH}_2\text{Me-NH}_2\text{Bu}^t$) and by aniline have been determined in aqueous solution with $I = 0.1 \text{ mol dm}^{-3}$ (NaClO_4) at 25°C by UV/VIS spectrophotometry. Comparison with published data on the rates of Fe–N bond fission and their further correlation with the energetics of protonation of the free amines shows that the observed variation in $\log K$ for aliphatic amines reflects ‘solvation’ as well as more typically steric effects. Aniline differs from the aliphatic amines both in its smaller crystal-field splitting (shared by other aromatic amines) and a low value of $\log K$ comparable to that of NMe_3 .

We have previously determined equilibrium constants K in aqueous solution for the substitution of co-ordinated H_2O in the complex $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ **1** by various primary amines¹ and nitriles² in order to establish the values of a and b in the well known linear free-energy relationship (LFER) (1) and to

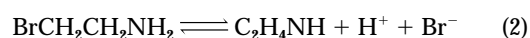
$$\log K = a \cdot \text{p}K + b \quad (1)$$

ascertain whether there are significant differences in a and/or b between the ‘soft’ low-spin d^6 iron(II) ion (able to co-ordinate CO , $\text{CH}_2=\text{CH}_2$, MeCN , R_2S , *etc.*, in competition with water)³ and the d^5 iron(III)⁴ and isoelectronic d^6 cobalt(III)⁵ ions.

Our results on the amines¹ revealed several unexpected features, in particular (i) that the LFER (1) was obeyed over 11 $\text{p}K$ units from NH_2NH_3^+ ($\text{p}K -0.9$) to NH_2Me ($\text{p}K +10.6$) with a slope $a = 0.05$ (*i.e.* essentially independent of the basicity of the amine) in contrast to the more positive values reported for other metal ions, and (ii) that NH_3 gave an anomalously low value of $\log K$ compared to that of NH_2Me . A similar value of $a \approx 0$ and low value of $\log K$ for NH_3 have also been observed in parallel experiments⁶ on the iron(II) form of the water-soluble porphyrin microperoxidase-8 [previously studied in the iron(III) form],⁴ *i.e.* these anomalies represent intrinsic features of the ‘soft’ low-spin d^6 iron(II) ion. Aymonino and co-workers⁷ have previously determined rate constants (k_r) and activation parameters for the reverse aquation of complexes of **1** with 11 aliphatic amines and with aniline. They found that the values of $\log k_r$ (including a higher value for NH_3 than for NH_2Me in agreement with our lower value of $\log K$) were relatively insensitive to the $\text{p}K$ (in agreement with our subsequent finding of $a \approx 0$) and showed that there was a correlation between the enthalpy and entropy of activation of Fe–N fission and the enthalpy and entropy of protonation of the free base, which indicated that the observed order of rate constants is strongly influenced by the energetics of transfer of the released ligand into bulk water.

The broad aim of this paper is to complete our analysis of the factors which determine the magnitude of $\log K$ for the co-ordination by complex **1** of N-containing bases which can only form σ bonds (*viz.* amines, including aniline) in order to provide the background against which to assess the co-ordination of potentially π -bonding ligands such as heterocycles. The specific aims are (a) to test whether the anilines (see ligands used in Table 1) belong to the same family as the aliphatic

amines, as judged by their d–d spectra and by the value of $\log K$ in the case of the parent aniline and (b) to investigate further the role of steric and ‘solvation’ factors in determining the magnitude of $\log K$ for the co-ordination of amines by **1** (see ligands listed in Table 1) by comparing the effects of both α branching (NH_3 to NMe_3) and β branching (NH_2Me to NH_2Bu^t) on $\log K$ with those reported by Aymonino and co-workers⁷ for $\log k_r$. No d–d bands have yet been reported for derivatives of **1** with any aniline or sterically hindered amine, though the complex with *p*-aminophenol is reported to be deep blue due to an intense charge-transfer (CT) band at 685 nm ⁹ and, in the few cases of other metal ions where aliphatic and aromatic amines have been studied together as ligands,^{10,11} they have been treated as equivalent but the data are insufficient to establish whether they belong to a single family or not. We have also (c) re-examined the co-ordination of ethyleneimine or aziridine **I** ($\text{p}K 8.0$)⁸ and 2-bromoethylamine **II** ($\text{p}K 8.5$),⁸ one of the ligands previously used to establish the validity of the LFER (1) for the amines and to determine the values of a and b ,¹ since we were previously unaware that near their $\text{p}K$ s these two amines can coexist in the slowly established equilibrium (2).^{12,†}



As before,^{1,2} the starting complex is the ion $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ **2**, which is easily prepared¹³ as the relatively stable trisodium salt and hydrolyses rapidly on dissolution in aqueous solution at $\text{pH} < 8$ to give the rather unstable **1** (**2** remains undissociated at $\text{pH} > 8$ at the concentrations normally used for UV/VIS spectrophotometry) or in 0.1 mol dm^{-3} aqueous MeCN to give the much more stable complex $[\text{Fe}(\text{CN})_5(\text{MeCN})]^{3-}$ **3**.² The complex **1** is unstable towards oxidation by traces of O_2 (controlled by deoxygenation with a stream of N_2 and the routine addition of a small amount of ascorbic acid to solutions of both **1** and **3**), dimerisation and other side-reactions (see summary in ref. 2). The greater stability of **3** and its existence as the same species over the wide range of pH from 3 (below which protonation of a co-ordinated CN^- occurs in both **1** and **3**)^{2,14} to ≥ 13 (any HO^- form of **1** is only formed at a much higher pH)¹⁵ makes it the complex of choice for studies with most ligands and almost essential for simple aliphatic amines (but not for aniline) with a high $\text{p}K \approx 10$ and a spectrum virtually indistinguishable from that observed with NH_3 (see Table 1 below).^{1,2} Conversion of the aqua into the MeCN complex

† Ligand co-ordination by the soft iron(II) ion in $[\text{Fe}(\text{CN})_5(\text{OH}_2)]^{3-}$. Part 3.¹

‡ We want to thank Dr. R. Bolton for drawing our attention to this.

Table 1 Equilibrium constants K for the substitution of co-ordinated H_2O in $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ by amines and UV/VIS spectra ($\lambda_{\text{d-d}}$) of the products

Ligand	$\text{p}K_{\text{b}}$ of free proligand ^a	pH used	$\log (K'/\text{dm}^3 \text{ mol}^{-1})$	$\lambda_{\text{d-d}}/\text{nm}$
Aniline	4.6	7.0 (10.0)	2.5 (2.6)	415
$p\text{-HOC}_6\text{H}_4\text{NH}_2$	5.5			408
$p\text{-H}_2\text{NC}_6\text{H}_4\text{NH}_2$	6.1			412
$p\text{-H}_3\text{N}^+\text{C}_6\text{H}_4\text{NH}_2$	3.3			418
NH_3^{d}	9.25	12	3.5	397
$\text{NH}_2\text{Me}^{\text{d}}$	10.6	12	4.3	398
NHMe_2	10.6	12	3.0	399
NMe_3	9.8	12	2.7 ± 0.2	402
NH_2Et	10.6	12	3.7	396
$\text{NH}_2\text{Pr}^{\text{d}}$	10.6	12	3.4 ± 0.2	398
$\text{NH}_2\text{Bu}^{\text{t}}$	10.6	12	2.3 ± 0.2	398–399

^a Ref. 8. ^b Determined using complex **3** in the presence of MeCN (see **Methods**), except for aniline. Values ± 0.1 or better except where otherwise indicated. ^c Recorded in the absence of MeCN. ^d Data from ref. 1.

does, however, incur a penalty in the apparent value of $\log K$ (see **Methods**), which makes it less suitable for studying ligands with low binding constants. A further complication is that, even after allowing for competition with co-ordinated MeCN, the addition of MeCN may affect the value of $\log K$ by some 'solvent' effect.² Aniline has therefore been studied with **1**, all the aliphatic amines with **3**.

Experimental

Materials

The salt $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)]$ was prepared, as previously, by the method of Brauer.¹³ Reagents were obtained as follows: NH_3 (0.880 s.g. solution), NH_2Me (30% aqueous solution), NMe_3 , aniline (all BDH); $\text{NHMe}_2 \cdot \text{HCl}$, $\text{NH}_2\text{Et} \cdot \text{HCl}$, $\text{BrCH}_2\text{CH}_2\text{NH}_2 \cdot \text{HBr}$, $\text{NH}_2\text{Pr}^{\text{t}}$, p -phenylenediamine, p -hydroxyaniline and 4-aminopyridine (all Aldrich); $\text{NH}_2\text{Bu}^{\text{t}}$ (Lancaster). Except for aniline (freshly purified before use by distillation from zinc dust) and 4-aminopyridine (recrystallised from aqueous solution), all reagents were used as received after any necessary neutralisation ($\text{NH}_2\text{Et} \cdot \text{HCl}$ and $\text{BrCH}_2\text{CH}_2\text{NH}_2 \cdot \text{HBr}$). A stock 1 mol dm^{-3} solution of ethyleneimine **I** was prepared by dissolving the required amount of **I** in over 2 mol dm^{-3} NaOH and allowing to stand for 3 h at room temperature for conversion to **I** according to equation (2) (t 20 min at 25 °C above the $\text{p}K$ of 8.0 for the pH independent rate involving the unprotonated form);¹² aliquots of this stock solution were then titrated into **1** (2 cm^3) in buffers pH 7.5 or 11 in the spectrophotometer cell. Stock solutions of **II** were prepared and stored at pH ≤ 7 and then titrated into **1** (2 cm^3) in buffers of pH 7.5 or 11.

Methods

The UV/VIS spectra were recorded and spectrophotometric titrations were carried out on a Phillips PU 8740 or 8720 spectrophotometer in cells of 1 cm pathlength thermostatted at 25 °C. Most experiments involved 2 cm^3 of a $ca. 10^{-4}$ mol dm^{-3} solution of the aqua complex **1** or the MeCN complex **3** (in the presence of 0.1 mol dm^{-3} MeCN), deoxygenated in a brisk stream of N_2 , together with $ca. 5 \times 10^{-3}$ mol dm^{-3} ascorbic acid further to protect against any leak of O_2 and reduce any Fe^{III} back to Fe^{II} . For quantitative titrations, solutions were made up to $I = 0.1$ mol dm^{-3} with NaClO_4 and a titrant added from a microsyringe. The following buffers were used:¹⁶ pH 7, dihydrogenphosphate; pH 10, borax (tetraborate); pH 11, hydrogen-carbonate; pH 12, NaOH and KCl (total $I = 0.1$ mol dm^{-3} , no NaClO_4 added). Where necessary the pH was measured with a Hanna B417 pH meter and appropriate glass electrode, standardised at pH 4.0 and 7.0 (Russell buffer tablets). The changes in absorbance recorded during the spectrophotometric titrations were used (see ref. 2) to determine values of K for the substitution of co-ordinated H_2O in **1** or K' for the substitution

of co-ordinated MeCN in **3** and the latter converted into K through use of the relationship $\log K = \log K' + \log [\text{MeCN}] + 2.6$ (formation constant for **3**), *i.e.* $\log K = \log K' - 1.0 + 2.6 = \log K' + 1.6$.

Results

Table 1 lists the amines and anilines studied here (including NH_3 and NH_2Me from previous papers in the series) and their published $\text{p}K$ values.⁸ Notes on the initial qualitative experiments and on the spectra of other derivatives are given below. For reasons explained in the Introduction, the aqua complex **1** was used for quantitative spectrophotometric titrations with aniline, the MeCN complex **3** with the amines. All titrations were carried out in duplicate at 25 °C with ionic strength $I = 0.1$ mol dm^{-3} , in the presence of a small amount of ascorbic acid to suppress any effects of oxidation by traces of O_2 , and at the pH given in Table 1 (usually $\text{pH} \geq \text{p}K + 1.4$) to ensure the proligand was mainly in the unprotonated form and to minimise any necessary corrections. After each addition of proligand the spectrum was scanned over the range 350–600 nm; equilibration was rapid, good to reasonable isosbestic points were observed (after correction for dilution where necessary), and no side-reactions occurred under the given conditions (but see ethyleneimine and the $p\text{-HO-}$ and $\text{-NH}_2\text{-C}_6\text{H}_4\text{NH}_2$ below). The absorbance corresponding to complete formation of the product was obtained indirectly by visual extrapolation in the case of $\text{NH}_2\text{Bu}^{\text{t}}$, $\text{NH}_2\text{Pr}^{\text{t}}$ and NMe_3 (*i.e.* amines with the lowest K and studied in competition with MeCN) but directly after adding an excess of reagent in all other cases. Analysis of the changes in absorbance at a fixed wavelength (usually λ_{max} of the product) confirmed the stoichiometry of $n = 1 \pm 0.1$ amine or aniline per Fe. The changes in the UV/VIS spectrum observed during the titration of **1** with the parent aniline are shown in Fig. 1 and the analysis of the changes in absorbance used to establish the values of n and $\log K$ in Fig. 2. The experimentally determined values of $\log K$, corrected for competition with MeCN when using the MeCN complex **3** by adding 1.6 to the apparent value (see **Methods**), are listed in Table 1 together with the wavelength of the d–d transition in the product. To ensure maximum formation of the products the wavelengths for the sterically hindered amines were recorded at pH 12 in the absence of MeCN and, for those with low binding constants, in the presence of very high concentration of the amine.

Amines

In view of the extensive previous work on the amines,^{1,2} equilibrium constants were determined only at pH 12. No attempt was made to test for the occurrence of additional equilibria involving ion-pair formation, as observed with NH_4^+ and NH_3Me^+ at $\text{pH} \leq \text{p}K$.^{1,2} Ethyleneimine **I** and 2-bromoethyl-

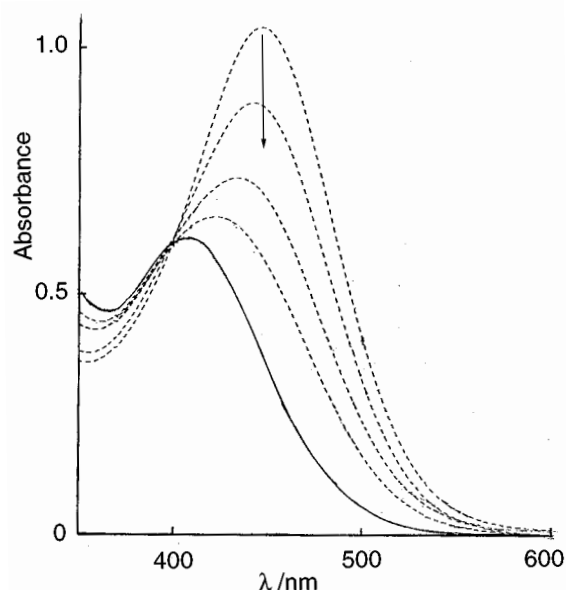


Fig. 1 Changes in the UV/VIS spectrum observed during the titration of $[\text{Fe}(\text{CN})_5(\text{OH}_2)]^{3-}$ **1** with NH_2Ph at pH 7

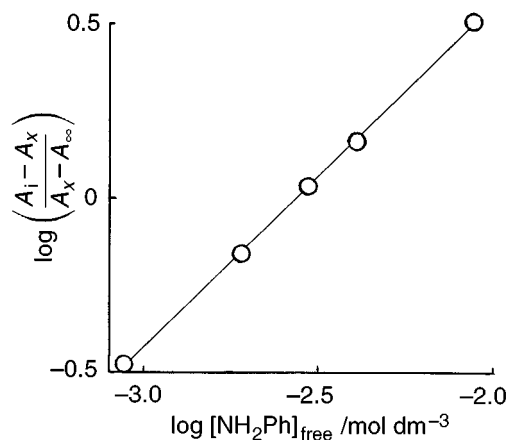


Fig. 2 Analysis of the changes in absorbance A_{445} during the spectrophotometric titration of complex **1** with NH_2Ph at pH 7 (see Fig. 1) to establish the stoichiometry (solid line corresponds to $n = 1.0$ NH_2Ph per Fe) and the value of $\log K$ ($= -\log [\text{NH}_2\text{Ph}]$ at $y = 0$)

amine **II** (for preparation see **Materials**) could be distinguished by their behaviour during titration. The titration of complex **1** with **I** at pH 11 revealed the occurrence of one or more background reactions which eventually caused the appearance of slight turbidity [presumably due to the formation of poly(ethyleneimine) polymers] as well as the formation of an amine complex with a typical λ_{max} at 396 nm. If the titration was carried out rapidly, analysis of the change in absorbance gave an apparent (and obviously spurious) value of $n > 1$. Similar anomalous behaviour, but with a far lower degree of formation, was also observed at pH 7.5. By contrast, titration with **II** both at pH 11 and 7.5 gave the expected simple $n = 1$ and a product with λ_{max} at 398 nm. It therefore appears possible to distinguish solutions which contain mainly **II** (normal behaviour with $n = 1$) from those which contain mainly **I** (abnormal behaviour with slow side-reactions and an apparent $n > 1$). This indicates that the value of $\log K$ previously reported¹ for **II** at pH 10 (4.16) with $n = 1$ does indeed refer mainly to **II**.

Anilines

Initial qualitative experiments on the two anilines reported to co-ordinate to complex **1**, viz. the parent NH_2Ph (no colour or spectrum given)⁷ and $p\text{-HOC}_6\text{H}_4\text{NH}_2$ (blue complex with an intense CT band at 685 nm)⁹ showed that the blue colour of the

latter was due to some product of aerial oxidation and that, when this was suppressed, aniline and its $p\text{-HO}$ derivative produced bands at 415 and 408 nm respectively with an absorbance similar to that of the aqua complex (see Fig. 1), indicating a d-d transition. This suggested that aromatic amines might form a family with $\lambda_{\text{max}} \approx 410$ nm distinct from the aliphatic amines with $\lambda_{\text{max}} \approx 400 \pm 4$ nm. The following aromatic amines (pK from ref. 8) were selected for further study: p -phenylenediamine, pK 3.3 and 6.1 (apparently the highest pK for any commercially available aniline); $p\text{-HOC}_6\text{H}_4\text{NH}_2$, 5.5; aniline itself, 4.6; $p\text{-CNC}_6\text{H}_4\text{NH}_2$, 1.7 (but likely, as confirmed below, to co-ordinate through the nitrile N); and the ring-protonated form of 4-aminopyridine, pK 9.2 for protonation of the pyridine N and 6 for protonation of the NH_2 group.

Like $p\text{-HOC}_6\text{H}_4\text{NH}_2$, p -phenylenediamine was very sensitive to aerial oxidation in the presence of complex **1**. The rates and products of aerial oxidation of the two anilines were compared at pH 5.5, 7, 10 and 12 in the presence of $ca. 2.5 \times 10^{-3}$ mol dm^{-3} **1**, initially deoxygenated but with no MeCN or ascorbic acid present. On shaking in air, all four solutions of each aniline rapidly produced a strong blue colour which did not further increase in intensity, suggesting the stoichiometric formation of a new complex. p -Hydroxyaniline gave the same blue colour with λ_{max} in the region 698–704 nm over the range pH 5.5–12, while p -phenylenediamine gave a more greenish blue at pH 5.5 (709) and 7 (730) and a royal blue at pH 10 (670) and 12 (666). These blue colours were discharged immediately on adding ascorbic acid to leave the weak d-d bands seen when oxidation was suppressed. In the absence of aerial oxidation, $p\text{-HOC}_6\text{H}_4\text{NH}_2$ gave the same $\lambda_{\text{max}} = 408$ nm over the range pH $ca.$ 7–13, while p -phenylenediamine showed a slight reversible pH-dependent change between $\lambda_{\text{max}} = 412$ nm at pH 7–13 and $\lambda_{\text{max}} = 418$ nm at pH 4–5, which can obviously be attributed to co-ordination of the neutral and monoprotonated forms respectively. The values of λ_{max} of these four complexes with aromatic amines (408, 412, 415 and 418, i.e. 413 ± 5 nm) are listed in Table 1. A solution of **1** reacted with 4-aminopyridine at pH 4–5 (where the pyridine N is protonated) to give an intense CT band below 400 nm and a distinct shoulder of low intensity (presumably the d-d band) at 405–415 nm. The wavelength of the CT band could not be determined more accurately as it was obscured by the rising background of the high concentration of free amine necessitated by the low formation constant. At pH 4 $p\text{-CNC}_6\text{H}_4\text{NH}_2$ also gives an intense CT band with **1** but no detectable shoulder to indicate a d-d band at $\lambda \geq 400$ nm, i.e. it probably co-ordinates *via* the nitrile N, where the expected d-d band ($ca.$ 387 nm)² would be completely hidden under the intense CT band. Neither $p\text{-CNC}_6\text{H}_4\text{NH}_2$ nor 4- $\text{H}_2\text{NC}_3\text{H}_4\text{N}$ showed any colour formation or other evidence of aerial oxidation.

Discussion

Table 1 lists the amines studied here and the published values of their pK values as the free base, together with our values of $\log K$ for the substitution of co-ordinated H_2O in complex **1** and the wavelength of the first d-d transition in the product. All the equilibria were established rapidly and reasonable to good isosbestic points were recorded. No further reactions were observed except in the case of ethyleneimine and of two anilines in the presence of O_2 (see below) and the stoichiometry corresponded to one base per Fe. All the experiments were carried out in at least duplicate. Conditions were found to distinguish amines **I** and **II**. Ethyleneimine **I** is characterised by the occurrence of further reactions both at pH 7.5 and 11, presumably involving polymerisation¹² and perhaps catalysed by co-ordination, while 2-bromoethylamine **II** behaved 'normally', confirming its position as one of the five amines NH_2R ($\text{R} = \text{NH}_3^+$, CH_2CN , $\text{CH}_2\text{CH}_2\text{CN}$, $\text{CH}_2\text{CH}_2\text{Br}$ or Me in order

Table 2 Comparison of equilibrium and rate constants for the co-ordination of amines by $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$

Ligand	Experimental values			'Standardised' differences ^d		
	$\log (K/\text{dm}^3 \text{ mol}^{-1})$ (1)	$3 + \log (k_{\text{r}}/\text{s}^{-1})$ (2)	$\log (k_{\text{r}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ (3)	$\Delta/\log K^*$ (4)	$\Delta/\log k_{\text{r}}^*$ (5)	$\Delta/\log k_{\text{r}}^*$ (6)
NH ₃	3.5	1.20	1.7	0.8	0.75	0
NH ₂ Me	4.3	0.45	1.75	0	0	0
NH ₂ Et	3.7	0.75	1.45	0.6	0.3	0.3
NH ₂ Pr ⁱ	3.4	1.36 ^e	1.8	0.9	0.9	0
NH ₂ Bu ^t	2.3	—	—	2.0	—	?
NH ₂ (C ₆ H ₁₁)	—	1.36	—	—	—	—
NH ₂ Ph	2.6	ca. 2	ca. 1.5	1.7	ca. 1.5	ca. 0
NH ₃	3.5	1.20	1.7	0.8	0.75	0
NH ₂ Me	4.3	0.45	1.75	0	0	0
NHMe ₂	3.0	0.80	0.8	1.3	0.35	1.0
NMe ₃	2.7	1.22	0.9	1.6	0.8	0.9

^a From Table 1. ^b From ref. 7, Table 2, where data are reported as $\log (10^3 k)$. ^c Calculated from $\log k_{\text{r}} = \log K + \log k_{\text{r}}$, i.e. (3) = (1) + (2) - 3.

^d Modulus of differences in $\log K$ (k_{r} or k_{f}) between that for the given amine and for NH₂Me. ^e Assumed equal to the value reported for cyclohexylamine in ref. 7.

of increasing $\text{p}K$) used to provide the 'baseline' for the aliphatic amines in establishing the values of $a = 0.05$ and $b = 3.75$ in the LFER (1).¹

The wavelengths of the d-d transitions listed in Table 1 show that (i) there is no significant steric effect on λ_{max} for the aliphatic amines (all still within the range of 400 ± 4 nm)² and (ii) that the aromatic amines form another family with $\lambda_{\text{max}} = 413 \pm 5$ nm, distinct from the aliphatic amines. The value of $\log K$ for the parent aniline, where no decrease due to steric distortion is expected, is significantly less (2.6) than that of primary aliphatic amines of similar $\text{p}K$ with no steric distortion such as NH₂CH₂CN (4.0)¹ and comparable to that of NMe₃ (2.7). The anilines (and perhaps all aromatic amines) therefore form a family quite distinct from the aliphatic amines, judged both by their d-d spectra and by the value of $\log K$ in the case of the parent NH₂Ph. Reasons for the decrease in basicity of the NH₂ group (compared to that observed in NH₂Me) when attached to an unsaturated C atom (as in anilines, aminopyridines, amides, cyanamide, etc.) and a corresponding increase in the basicity of another part of the molecule have been analysed in the case of the simpler ethenamine (CH₂=CHNH₂) and ethynamine (HC≡CNH₂).¹⁷ Recent experimental and theoretical work on the structure of the anilines (summarised in refs. 18 and 19) reveals a subtle dependence of the distortion and rehybridisation of the N and neighbouring C atoms on the pattern of hydrogen bonding to and from the N atom and on the nature of the ring substituents; the sum of the three bond angles around N varies from 360 (i.e. trigonal sp²) down to 338° but never reaches 328° (viz. tetrahedral sp³), giving the lone pair of electrons an s-orbital character between O and considerably less than 25%. It is therefore not surprising that $\log K$ for NH₂Ph is significantly less than those for aliphatic amines and that their d-d transitions (in nm) increase in energy in the sequence H₂O (443) < aromatic amines (413 ± 5) < aliphatic amines (400 ± 4) < five- and six-membered heterocycles (383 ± 3) < nitriles (previously given in error as 375 ± 2 , should be 372.5 ± 3) < CN⁻ (325),² which appears to follow the increase in % s (or decrease in % p) character of the ligand lone-pair orbital. The factors which may determine the magnitude of crystal-field splittings will be discussed in more detail in a later paper.

We have found that the reported⁹ blue complex of **1** with *p*-aminophenol **III** is, in fact, a product of aerial oxidation and that *p*-phenylenediamine **IV** behaves similarly to give another intense blue complex but that when oxidation is prevented, the expected simple co-ordination of **III** and **IV** is observed. It is known that the yellow iron(II) tetracyanide containing *o*-phenylenediamine as a bidentate ligand also reacts rapidly with O₂ to give an intensely blue product possessing *o*-benzo-

quinone diimine as the ligand²⁰ and that the pentaamine aqua and/or chloro complexes of the heavier d⁶ ruthenium(II) ion co-ordinate **III** and **IV** (also other aromatic diamines) as monodenate ligands which are readily oxidised by O₂ to intensely coloured products with *p*-benzoquinone imine and diimine as ligands respectively;²¹ we assume analogous reactions and products with **1**. The ready formation of intensely coloured products of aerial oxidation has therefore been observed for complexes of **1** with NH₂NH₂²² and NH₂OH¹ (probably with the parent HN=NH and HN=O as ligands) as well as **III** and **IV** (i.e. the quinone analogues); cf. also the intensely coloured complexes with RNO (R = aryl) and RNO.²³ The reduced iron(II) and ruthenium(II) ions show an unusual ability to catalyse such aerial oxidations; the driving force appears to be the remarkable stability of the oxidised form of the ligand when co-ordinated to these reduced low-spin d⁶ ions.²¹ It is interesting that an intense CT band is also observed for the complex of **1** with the monoprotonated (on the pyridine N) form of 4-aminopyridine, which indicates that metal to ligand CT does not require that the ligand donor atom is part of an unsaturated group.

All the aliphatic amines listed in Table 1 exhibit similar $\text{p}K$ values when free and elicit similar λ_{max} when co-ordinated; they provide a good series with which to assess steric, solvation and other effects. Aymonino and co-workers⁷ reported rate constants (here denoted by k_{r}) for the reverse aquation of complexes of **1** with various amines, which can be related to our values of $\log K$ by $K = k_{\text{r}}/k_{\text{f}}$ or $\log K = \log k_{\text{r}} - \log k_{\text{f}}$. Our values of $\log K$, together with their values of $\log k_{\text{r}}$ and the derived values of $\log k_{\text{f}}$, are given in Table 2. In order to highlight the similarities and differences, however, we also refer all sets of data to that of NH₂Me as the 'standard' and tabulate the modulus of the differences in $\log K$ (k_{r} or k_{f}) between that of the given amine and of NH₂Me. Three points can be made.

(1) The overall decrease in $\log K$ from NH₂Me to NMe₃ (viz. 1.6) and to NH₂Bu^t (2.0), due to α - and β -branching respectively, is far less than that observed with the iron(III) porphyrin microperoxidase-8 (ca. 4 and >3.5 respectively),²⁴ let alone the cobalt(III) corrinoid aquacobalamin (≥ 5 for both);²⁵ even the large, 'soft' and two-co-ordinated MeHg⁺ ion is more sensitive to the effects of α -branching (2.5)²⁶ but, like the d¹⁰ Ag⁺,²⁷ is insensitive to β branching (0.05). It would appear that for derivatives of complex **1** some factor counteracts the decrease in $\log K$ expected from α and β branching.

(2) The unexpected order NH₃ < NH₂Me > NH₂Et has been observed for $\log K$ by us, for $\log k_{\text{r}}$ (in inverse order) by Aymonino and co-workers⁷ and for the volume of activation for Fe-N fission by Reddy and van Eldik²⁸ (cf. ΔV^\ddagger 16, 24 and 16 cm³ mol⁻¹ for NH₃, NH₂Me and NH₂Et respectively), i.e. the

different observables appear to reflect the same underlying change.

(3) The observed variations in $\log K$ caused by β branching (including NH_2Ph) are due almost entirely to changes in $\log k_f$ (rate of Fe–N fission) but α branching (NHMe_2 , NMe_3) appears to cause an additional decrease in $\log k_f$ (rate of Fe–N formation) by ca. 1.

Aymonino and co-workers⁷ have shown a correlation between the enthalpy of activation for Fe–N bond fission and the enthalpy of protonation of the free amine in solution and also between the two entropies (but with separate correlations for α and β branching). The differences in the energies of protonation have, in turn, been explained in terms of the gas-phase proton affinities and solvation energies. They concluded that the main contribution to the changes in activation parameters arises from 'the energetics of transfer of the released ligand to bulk water'. The same conclusion obviously applies to the variations in $\log K$ reported here and similar arguments may explain the previously noted effects of added MeCN on the magnitude of $\log K$ (e.g. increased by 0.7 for NH_3 , decreased by 0.3 for $\text{NH}_2\text{CH}_2\text{CN}$ by 0.1 mol dm⁻³ MeCN). Reddy and van Eldik²⁸ further concluded from their high-pressure studies with five amines that 'the extent of bond breakage in the transition state may vary with the nature of the leaving group' and that the low rate of Fe–N fission and large volume of activation observed for NH_2Me indicated a late transition state for this amine. The use of ligands with polar substituents (*cf.* the amines and nitriles already studied with complex **1**)^{1,2} will introduce further 'solvation' effects and mention should be made of the use of the volume changes on proton ionisation of amines and carboxylic acids to explore the effects of electrostriction and changes in the hydration sheath of the hydrophobic CH_2 groups.^{29–31} results include the findings that NH_3^+ causes a large decrease in the volume of the hydrocarbon hydration sphere while CO_2^- causes a smaller increase and that the effects of electrostatic interaction between two NH_3^+ groups can be detected even when separated by a $(\text{CH}_2)_{11}$ chain. Furthermore, a comparison of the two $\text{p}K$ values of the diamines $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ with $n=2$ –10 showed that the statistically expected difference of 0.6 (= $\log 4$) between the upper and lower $\text{p}K$ was reached only for $n \geq 8$, while a comparison of the UV/VIS spectra of the protonated and unprotonated forms of the complexes $[\text{Co}^{\text{III}}(\text{NH}_3)_5\{\text{NH}_2(\text{CH}_2)_n\text{NH}_2\}]^{3+}$ also showed effects up to at least $n=8$ which could be ascribed to intramolecular hydrogen bonding between the co-ordinated Co– NH_2R and the terminal unprotonated NH_2 .³² The strong hydrogen-bonding tendency of co-ordinated CN^- (see summary in ref. 33) provides further scope for intramolecular hydrogen bonding. It appears that, when the normally dominant effects of basicity are nullified (*i.e.* when $a \approx 0$), other effects may intrude and upset the patterns of equilibrium and rate constants otherwise expected on the grounds of basicity (*cf.* the anomalously low value of $\log K$ for NH_3 compared to that of NH_2Me).¹ steric effects (as discussed here) or through operation of the α effect (as noted previously for NH_2NH_2 and NH_2OH).¹ Conversely, kinetic and equilibrium studies on complexes of **1** with substituted amines and on the effects of ion pairing and solvent composition could provide a wealth of information on such additional effects in purely aqueous solution. Using six solvents ranging in polarity from water to toluene, we have also examined the effect of solvent polarity on the co-ordination of substituted pyridines by a five-co-ordinate cobalt(III) corrinoid.³⁴

The underlying basic patterns shown by the aliphatic and aromatic amines, where co-ordination cannot involve π bond-

ing, provide the necessary background against which to assess the patterns shown by heterocyclic and other ligands where π bonding is possible.

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