Co-ordination of Amines to $[Fe(CN)_5(OH_2)]^{3-}$ †

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Equilibrium constants K for the substitution of co-ordinated H_2O in the complex $[Fe(CN)_5(OH_2)]^{3-}$ by amines have been determined in 0.1 mol dm^{-3} aqueous acetonitrile solution with $I = 0.1$ mol dm^{-3} ($NaClO_4$) at 25 °C by UV/VIS spectrophotometry. The species previously assigned to the NH_2OH complex is shown to be the product of some oxidative side-reaction. In the absence of complicating factors, values of log K obey the linear free-energy relation $\log K = a\cdot pK + b$ with $a = 0.05$ and $b = 3.75$ for over 11 pK units from $NH_2NH_3^+$ (pK −0.9) to NH_2Me (pK 10.6), *i.e.* log K is virtually independent of pK. It is suggested that log K may become independent of pK where the increase in intrinsic metal–ligand bond energy with pK is balanced by the increase in the overall loss in solvation (including hydrogen-bonding) energy on co-ordination with pK. In contrast to the pattern previously found with complexes of Fe^{III} and Co^{III}, a decrease in log K (below that expected from basicity alone) is observed for glycine (attributed to coulombic repulsion between the negative charges on the ligand and complex), NH_3 and NH_2OH (both attributed to repulsion from the additional strongly held solvent molecules).

The main aim of this paper is (*i*) to establish the validity of the well known linear free-energy relation (1)[2] and the values of a

$$\log K + a\cdot pK + b \qquad (1)$$

and b for the co-ordination of amines by the iron(II) ion in the complex $[Fe(CN)_5(OH_2)]^{3-}$ **1**, and also (*ii*) to identify any factors other than steric (to be treated in a subsequent publication) which may significantly affect the value of K such as operation of the α effect (as established for NH_2NH_2 and NH_2OH with both Fe^{III} and Co^{III}),[3,4] coulombic interaction, hydrogen-bonding and other solvation effects. A major gap in the present range of 'probe' ligands available for testing the effects of basicity is the absence of amines with pK below *ca.* 5 (see Table 1 below). Bases such as the anilines are excluded because conjugation with the aromatic ring introduces effects which vitiate direct comparison with the unconjugated amines.[4,7,8] As will be seen below (*cf.* Fig. 2), the co-ordination of amines by **1** corresponds to $a \approx 0$, *i.e.* log K is virtually independent of pK. This offers the opportunity to test amines with a p$K \leqslant 1$ such as $NH_2SO_3^-$ (pK 1.0) and $NH_2NH_3^+$ (pK −0.9) which, unlike the parent NH_2NH_2, does not possess a lone pair of electrons on the unco-ordinated N atom and cannot show the so-called α effect. The uncharged cyanamide NH_2CN (pK 1.1)[5] is both protonated[9] and co-ordinated[1] to **1** *via* the nitrile N. A third aim is therefore (*iii*) to test whether a ligand such as $NH_2NH_3^+$ can provide a suitable 'probe' for basicity effects in the amine family at the low pK end. The ligands used are listed in Table 1 below, together with published pK values. The starting complex is the ion $[Fe(CN)_5(NH_3)]^{3-}$ **2** which can be prepared[10] as the stable trisodium salt but hydrolyses rapidly on dissolution in aqueous solution at pH < 8 to give the rather unstable **1** (aquation is increasingly incomplete at higher pH) or in 0.1 mol dm^{-3} aqueous MeCN to give the more stable $[Fe(CN)_5(MeCN)]^{3-}$ **3**.[1] Most values reported here for log K (corresponding to the substitution of co-ordinated H_2O in **1**) have been determined from values of log K' (for the substitution of co-ordinated MeCN in **3**) and corrected accordingly (see below). As before,[1] all proton-dependent equilibrium constants are reported as pK (including pK_c which represents protonation of a ligand), while ligand-substitution equilibrium constants are denoted by K (including K') and log K.

Experimental

Materials.—The salt $Na_3[Fe(CN)_5(NH_3)]$ was prepared by the method of Brauer.[10] Reagents and solvents were obtained as follows: MeCN (Fisons, HPLC grade, high-purity reagent); ethane-1,2-diamine (en), $NH_2OH{\cdot}HCl$, sulfamic acid and $BrCH_2CH_2NH_2{\cdot}HBr$ (all >99%, Aldrich) and glycine (98%, Aldrich); 25% w/v aqueous solution of NH_2Me (BDH); $NH_2NH_2{\cdot}H_2O$ (>99%, BDH); $NH_2CH_2CN{\cdot}HCl$ and $NH_2CH_2CH_2CN$ (both Sigma); $NH_2CH_2CF_3$ (>98%, Fluka). All were used as received after any necessary neutralisation or adjustment to the required pH.

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, with wavelength calibrated against a holmium filter. Most experiments involved *ca.* 10^{-4} mol dm^{-3} solutions of **1** or **3** (in the presence of 0.1 mol dm^{-3} MeCN). The following buffers were used: pH 3–5 (phthalate); 5–9 (phosphate); 7.5–9 (borate); 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 $NaClO_4$. All spectrophotometric titrations to determine values of K or K' were carried out in duplicate and the changes of absorbance with ligand concentration (corrected for any protonation, where necessary) analysed as before.[1] Values of log K' (for the substitution of co-ordinated MeCN in **3** by the given B) determined in 0.1 mol dm^{-3} aqueous MeCN were converted into values of log K (for the substitution of co-ordinated H_2O in **1** by the given amine B) through the use of the relationship[1] $\log K = \log K' + \log[MeCN] + 2.6$ (= the formation constant for **3**), *i.e.* $\log K = \log K' - 1.0 + 2.6 = \log K' + 1.6$.

Results

The amines studied here (together with NH_3 and NH_2CH_2CN

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† Ligand Co-ordination by the Soft Iron(II) Ion in $[Fe(CN)_5(OH_2)]^{3-}$. Part 2.[1]

Table 1 Equlibrium constants K for the substitution of co-ordinated H_2O in $[Fe^{II}(CN)_5(OH_2)]^{3-}$ by amines

Ligand[a]		pK_b[b]	pH used[c]	log K[c,d]	λ_{max}/nm of product
I	$NH_2NH_3^+$	−0.9	4.4, 5.0 (5.5)	3.7 (3.4)	403
II	$NH_2SO_3^-$	1.0	5.5	$\leqslant 0$	—
III	NH_2CH_2CN[e]	5.3	8.0 (9.0)	4.01 (3.7)	396
IV	$NH_2CH_2CF_3$	5.7	8.0 (8.0)	3.42 (3.0)	394
V	$NH_2CH_2CH_2NH_3^+$	7.3	6.5, 7.0	4.4	400
VI	$NH_2CH_2CH_2CN$	7.7	10.0	4.23	396
VII	$NH_2CH_2CH_2Br$	8.5	10.0	4.16	398
VIII	NH_3[e]	9.25	11.0 (7.5)	3.5 (4.2)	397
IX	$NH_2CH_2CO_2^-$	9.6	11.0	3.6	394
X	$NH_2CH_2CH_2NH_2$	9.9	11.0	3.9[f]	397
XI	NH_2Me	10.6	12.0	4.3	398
XII	NH_2OH				
XIII	NH_2NH_2	6.0	11.0 (7.5)	< 2.2 (2.4 ± 0.2)	*ca.* 400
		8.1	10.0	4.77[f]	398

[a] Listed in order of increasing pK but with separation of the two ligands **12** and **13** which show the α effect. [b] Values of the free base from ref. 5 except for en and Hen$^+$ from ref. 6. [c] Values in parentheses refer to aqueous solution without MeCN, others to 0.1 mol dm^{-3} aqueous MeCN. For the method of calculating log K in the presence of MeCN see the Experimental section. [d] All values of log K ± 0.1 or better except where otherwise indicated. [e] Data from ref. 1. [f] Corrected for the statistical factor by deduction of log 2 (= 0.3).

in the preceding paper)[1] and the published pK values are listed in Table 1. The least sterically hindered amide ($HCONH_2$) has also been tested, together with urea, even though amides are protonated on the O atom [see (*e*) below]. Preliminary experiments revealed the occurrence of a side-reaction with NH_2OH [see (*a*) below] and indicated that neither NH_2OH nor $NH_2SO_3^-$ could co-ordinate to **3** (*i.e.* in competition with 0.1 mol dm^{-3} MeCN). Further studies on these two ligands [see (*a*) and (*b*)] were therefore carried out with the unstable aqua complex **1**. The other ligands were studied with the more stable acetonitrile complex **3** (in 0.1 mol dm^{-3} MeCN), though values of log K for $NH_2CH_2CF_3$ and $NH_2NH_3^+$ were also determined in purely aqueous solution to confirm the previously reported trend.[1] The addition of all ligands except $NH_2SO_3^-$ produced the expected change in spectrum (*cf.* Fig. 1 of ref. 1). The spectra of the fully formed products (not obtained in the case of NH_2OH) all exhibit fairly symmetrical d–d bands with λ_{max} at 397 ± 3 nm, which are significantly different from those of the starting complex **1** or **3** yet have comparable molar absorption coefficients (*cf.* Figs. 1–2 and Table 1 in ref. 1). This leads to a convenient change in spectrum during the titration.

A study of the possible variation of the spectrum with pH revealed slight reversible changes for NH_2NH_2 (pK *ca.* 6) and en (pK *ca.* 9.5), which can both be ascribed to protonation of the co-ordinated amine; the value of this pK_c has been determined more quantitatively in the case of NH_2NH_2 [see (*c*)]. A larger change in spectrum was observed with $NH_2CH_2CH_2CN$ from λ_{max} 390 nm at higher pH to 370 nm at lower pH; as in the case of NH_2CH_2CN[1] this can be ascribed to the combined protonation and isomerisation corresponding to $Fe{-}NH_2 \cdots CN + H^+ \rightleftharpoons Fe{-}NC \cdots NH_3^+$. Other changes in spectrum associated with protonation of a co-ordinated cyanide, also characterised by a shift in λ_{max} to shorter wavelength,[1] are observed at pH $\leqslant$ 4; these have not been systematically studied. In the case of NH_2Me a further pH-dependent equilibrium was revealed by analysis of the change in absorbance with concentration of B, but had little effect on λ_{max} [see (*d*)]; as in the case of NH_3,[1] this can be ascribed to formation of an ion pair between the product and the NH_3Me^+ cation.

Quantitative determinations of K (and K') were carried out by spectrophotometric titration in duplicate experiments at the pH given in Table 1. The whole spectrum was scanned over the range 350–600 nm after each addition. Equilibration was rapid and reasonable-to-good isosbestic points were observed in each case [but see (*a*)]. Analysis of the changes in absorbance at a fixed wavelength (usually 397 nm) confirmed the stoichiometry of $n = 1 \pm 0.1$ and, after correction for competition with MeCN (see Experimental section), gave the values of log K listed in Table 1. Semiquantitative tests for the occurrence of en-bridged dimers by varying the concentration of complex **3** eight-fold were negative, as expected from the high accumulation of charge on any dimer. Further evidence against dimers with either en or NH_2NH_2 was the observation of good isosbestic points and the stoichiometry of $n = 1$ for the formation of both neutral and protonated forms, together with their 'instantaneous' interconversion on changing the pH. In the case of both NH_2NH_2 and en (but not their protonated forms) the listed values of log K have been corrected for the statistical factor[11–13] by deduction of log 2 (=0.3). No co-ordination was detected with $NH_2SO_3^-$ [see (*b*)] or amides [see (*e*)].

(*a*) NH_2OH.—Adding *ca.* 10^{-2} mol dm^{-3} NH_2OH to a solution of complex **3** at pH 10 led to the rapid rise of an intense band in the spectrum at *ca.* 440 nm, colouring the solution orange, when the solutions were equilibrated with air; this reaction was largely, but not completely, suppressed when solutions were well deoxygenated. Little or no co-ordination was observed under these conditions, *i.e.* in competition with MeCN as ligand, but further experiments with **1** in neutral solution showed that co-ordination could occur. The quantitative determinations of K was carried out at pH 7.5, *i.e.* below pH 8 as required fully to displace the co-ordinated NH_3 in the starting complex **2** and above the pK 6.0 for protonation of NH_2OH. Although the product clearly had λ_{max} *ca.* 400 nm and a good isosbestic point was observed at *ca.* 405 nm over the first half of the titration, the low binding constant and disruption of the isosbestic point over the latter part of the titration prevented a good end-point from being obtained. Using an end-point calculated from the spectrum of the ammine complex **2** gave values of n *ca.* 1 and log $K = 2.4 \pm 0.2$ in duplicate titrations. The possible co-ordination of NH_2OH by **3** was therefore re-examined in deoxygenated solutions at pH 11, *i.e.* in competition with 0.1 mol dm^{-3} MeCN and against the background of changes in the spectrum caused by the residual unsuppressed formation of the species with an intense band at *ca.* 440 nm. The shape of the high-energy limb of the intense charge-transfer (c.t.) band did, in fact, indicate a slight shoulder at *ca.* 400 nm, as would be expected for the $Fe{-}NH_2OH$ complex; reasonable assumptions led to an upper limit of log $K' < 0.6$ (for the substitution of co-ordinated MeCN by NH_2OH), which can be converted (see Experimental section) to give log $K < 2.2$.

(*b*) $NH_2SO_3^-$.—Similar changes in spectrum with time were shown by solutions of complex **1** in buffer pH 7, whether air-saturated or deoxygenated, when compared in the presence of

0.5 mol dm^{-3} $NaClO_4$ or $Na(O_3SNH_2)$). There was no indication, against the background of changes in the spectrum due to the decomposition of **1**, of any additional band at *ca.* 400 nm, which might provide evidence for the formation of N-co-ordinated $Fe-NH_2SO_3$, or any additional band at longer wavelength (*cf.* NH_2OH above). One can conclude that the formation constant of any N-bonded sulfamate derivative of **1** with a d–d transition in the region 390–410 nm and $\varepsilon \geqslant 400$ dm^{-3} mol^{-1} cm^{-1} must have a value of log $K < 0$.

(*c*) NH_2NH_2.—In addition to determining log K for both NH_2NH_2 and $NH_2NH_3^+$ at the pH given in Table 1, we have determined the pK_c for protonation of the co-ordinated amine by pH titration. This equilibrium is associated with a relatively small change in spectrum, involving a shift in λ_{max} from 398 above to 403 nm below the pK *ca.* 6, a decrease of $\leqslant 2\%$ in the absorbance at the band maximum and the semblance of an isosbestic point. An unbuffered and slightly alkaline solution of *ca.* 5×10^{-4} mol dm^{-3} complex **1** in the presence of 0.1 mol dm^{-3} NH_2NH_2 and 0.1 mol dm^{-3} $NaClO_4$ (making I initially 0.1 mol dm^{-3}) was titrated with $HClO_4$ and the spectrum at around 400 nm was recorded at each pH (as determined with a pH-electrode). As expected, the wavelength of λ_{max} could be recorded with smaller error than the absorbance at the given wavelength (403 nm) and, considering that the molar absorption coefficients of the two species appear to differ by less than 2%, the use of changes in λ_{max} instead of A_{403} is justified in order to reduce the errors caused by such small changes in the spectrum. Fig. 1 shows a plot of λ_{max} *vs.* pH; from the point of 50% conversion one obtains a value of pK_c = 6.3 ± 0.1. A plot of A_{403} *vs.* pH (not shown) gives pK_c = 6.1–6.4.

(*d*) NH_2Me.—The co-ordination of NH_2Me by solutions of complex **3** was studied in buffered solutions at pH 9.5, 10, 11 and 12. Reasonable-to-good isosbestic points were observed in all cases and the final products all exhibited the same λ_{max}. At pH 11 and 12 the change in A_{398} (increase in the band of the $Fe-NH_2Me$ complex) showed a simple parabolic dependence on the concentration of added amine and analysis of the data gave values of $n = 1$. At pH 10 and 9.5, however, the values of A_{398} showed a sigmoidal dependence on added amine and analysis of the data gave values of n increasing from 1 to 2 (or even higher) over the course of the titration. Similar results have been observed with NH_3.[1]

(*e*) *Amides.*—Qualitative experiments with complex **1** at pH 7 (*i.e.* with no competition from NH_3 as potential ligand) provided no positive evidence for the N-co-ordination of either NH_2CHO or urea. Dissolution of the trisodium salt of **2** directly in NH_2CHO–water (1:1) (*i.e.* > 10 mol dm^{-3} NH_2CHO) produced a spectrum which, before a significant degree of decomposition of **1** had occurred, showed a slightly broader band than in water with λ_{max} at 446 nm (instead of 443 nm); this might reflect the co-ordination of NH_2CHO *via* O and/or changes in the hydrogen bonding to the CN^- and H_2O ligands. There was no evidence for any band at *ca.* 400 nm which might indicate formation of the complex with N-co-ordinated NH_2CHO, *i.e.* one can conclude that log K $\leqslant -2$ for any such complex.

Discussion

Table 1 lists the amines studied (including NH_3 and NH_2CH_2CN studied in the preceding paper)[1] and published pK values, together with our experimentally determined values of log K for the substitution of co-ordinated H_2O in complex **1** by the given amine B. All these equilibria were established rapidly and correspond to the stoichiometry of 1B per Fe. In the case of unprotonated NH_2NH_2 and en the values of log K have been corrected for the statistical factor[11] [13] by subtraction of log 2 (=0.3). Most of these values refer to a 0.1 mol dm^{-3} aqueous MeCN solution and not to a purely aqueous solution. Where comparisons have been made (see Table 1), increasing concentration of MeCN usually leads to a slight increase in log K, *e.g.* from water to 0.1 mol dm^{-3} MeCN by 0.3, 0.4 and 0.3 for NH_2CH_2CN, $NH_2CH_2CF_3$ and $NH_2NH_3^+$ respectively (see Table 1). Ammonia is anomalous (falling by *ca.* 0.6) and it appears (see Table 1) that NH_2OH may behave similarly; a possible reason is discussed below.

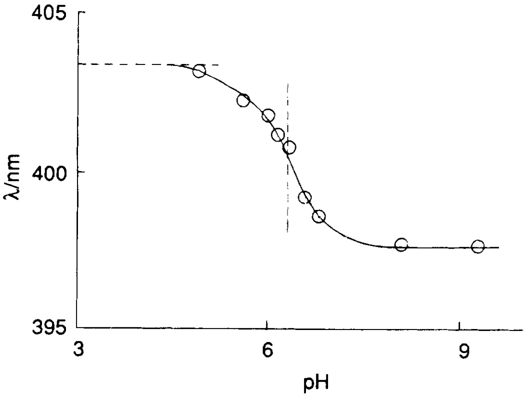

Fig. 1 Variation of λ_{max} with pH during the pH titration of a solution of the complex $[Fe(CN)_5(NH_2NH_2)]^{3-}$ to determine the pK_c (=6.3, as indicated by the vertical line) for protonation of the co-ordinated NH_2NH_2. For details see text

Several pH-dependent equilibria were observed (see Results section) in addition to protonation and displacement of B from co-ordination and protonation without displacement of a co-ordinated cyanide; these include (*a*) protonation of co-ordinated NH_2NH_2 (pK_c 6.3, see also below) and en (pK_c *ca.* 9.5), (*b*) protonation and isomerisation of co-ordinated $NH_2CH_2CH_2CN$ (as well as NH_2CH_2CN)[1] from amine to nitrile N as the donor atom, and (*c*) formation of an ion pair between $[Fe(CN)_5B]^{3+}$ and HB^+, where B is NH_2Me (as well as NH_3).[1] The pH dependence of the value of log K listed in Table 1 was tested and confirmed for three amines ($NH_2NH_3^+$, Hen^+ and NH_2Me), as indicated by the use of two pH values.

An interesting side-reaction was observed with NH_2OH. Previous workers have reported that the complex $[Fe(CN)_5(NH_2OH)]^{3-}$ is characterised by an intense absorption band at *ca.* 440 nm (ε *ca.* 4×10^3 dm^3 mol^{-1} cm^{-1})[14–16] and is formed slowly by the reaction of **1** with NH_2OH.[16] We also find a slow reaction giving an intense band at 445 nm, but the reaction can be at least partly reduced by careful exclusion of oxygen; the possibility of a residual oxygen-independent reaction cannot, however, be excluded. When this side-reaction is suppressed, a rapid equilibration with NH_2OH can be observed to give the expected complex with λ_{max} at *ca.* 400 nm but with the unexpectedly low binding constant of log K *ca.* 2.4 in aqueous solution and even less in 0.1 mol dm^{-3} MeCN (see Table 1). In view of the formation of complexes with aromatic and aliphatic nitroso compounds as ligands, which exhibit intense c.t. bands in the visible region (*cf.* PhNO, 528; MeNO, 484 nm) and can even be formed in solution by oxidation or disproportionation of the precursor hydroxylamine (*e.g.* $2PhNHOH \longrightarrow PhNO + PhNH_2 + H_2O$),[17] it seems possible that the product of the reaction between **1** and NH_2OH may contain HNO as the ligand. The analogous complex with NH_2NH_2 also shows a complicated reaction with O_2 in air-saturated solutions to give successive products with intense bands at 440 and 515 nm, which may include an iron(II) diimide (HN=NH) complex.[18]

The values of log K for co-ordination (except for $NH_2SO_3^-$) are plotted against the pK for protonation of the free amine in Fig. 2 (all values and numbering as in Table 1). Of the four primary amines (**III**, **VI**, **VII**, **IX**) and NH_3 (**VIII**) which together provide the 'baseline' corresponding to equation (1) for both Fe^{III} and Co^{III},[3,4] the four primary amines also show a good linear relationship with Fe^{II} which can, within experimental error, be extrapolated to low pK to include $NH_2NH_3^+$ (**I**), as shown by the solid line. Rather surprisingly, NH_3 falls significantly below the line; this is discussed below. Trifluoroethylamine (**IV**) falls on the baseline for Co^{III}, but below it for Fe^{III}, *i.e.* shows somewhat unpredictable behaviour; our present result serves to confirm that it is not suitable as a standard 'probe' ligand for assessing basicity effects and will not be discussed further. Mention should, however, be made of recent experimental and theoretical work on the solvation of protonated amines (including $NH_2CH_2CF_3$) in the gas phase.[19,20] The points for en and Hen^+ lie just below the line (by *ca.* 0.4 or, if not corrected for the statistical factor, by *ca.* 0.1) and just above it (by *ca.* 0.2) respectively. As Aymonino and co-workers[21,22] have pointed out in discussing these complexes, the suppression of basicity effects allows solvation and other effects, which are usually swamped, to be detected. If, as in the en/Hen^+ pair or glycine (Gly), the primary amine possesses a second functional group and is sufficiently flexible to form intramolecular hydrogen bonds, with or without an intervening H_2O molecule, either when free or co-ordinated, one might expect to observe anomalies in the value of log K. Although there is no direct experimental evidence for the structure of Gly in aqueous solution, some theoretical calculations suggest that it may exist predominantly in a cyclic form with H_2O acting as a bridge between the NH_2 and CO_2^- groups to form (neglecting the H atoms) a five-membered ring;[23] one could envisage analogous cyclic structures for en and Hen^+. Intramolecular hydrogen bonding involving co-ordinated en and Hen^+ has already been proposed.[6,24] It is clearly easy to suggest, but difficult to prove, possible explanations for the small deviations in log K shown by en (free base slightly stabilised by a cyclic structure?) and Hen^+ (co-ordinated form stabilised by hydrogen bonding *via* H_2O to a neighbouring cyanide?). For steric reasons neither $NH_2NH_3^+$ nor NH_2NH_2, free or co-ordinated, would be expected to show complications due to intramolecular hydrogen bonds (though NH_2NH_2 shows the α effect, see below); Fig. 2 does indeed suggest that $NH_2NH_3^+$ acts like a 'well behaved' primary amine. We conclude that the four primary amines **III**, **VI**, **VII** and **IX** and $NH_2NH_3^+$ can all be considered as suitable for use as standard probes for basicity effects in the amine series, subject to the obvious qualification in the case of $NH_2NH_3^+$ that the effects of coulombic interaction (including the formation of ion pairs) must be borne in mind and, if possible, excluded. These five ligands, indicated by filled circles in Fig. 2, show a good linear dependence of log K on pK in agreement with equation (1) for over 11 pK units with $a = +0.05$ and $b = +3.75$. Since the deviations shown by the en/Hen^+ pair towards Fe^{II} are significantly less than those shown by NH_3 and Gly, it seems likely that the former two like the latter two will act as well behaved amines towards Fe^{III}.

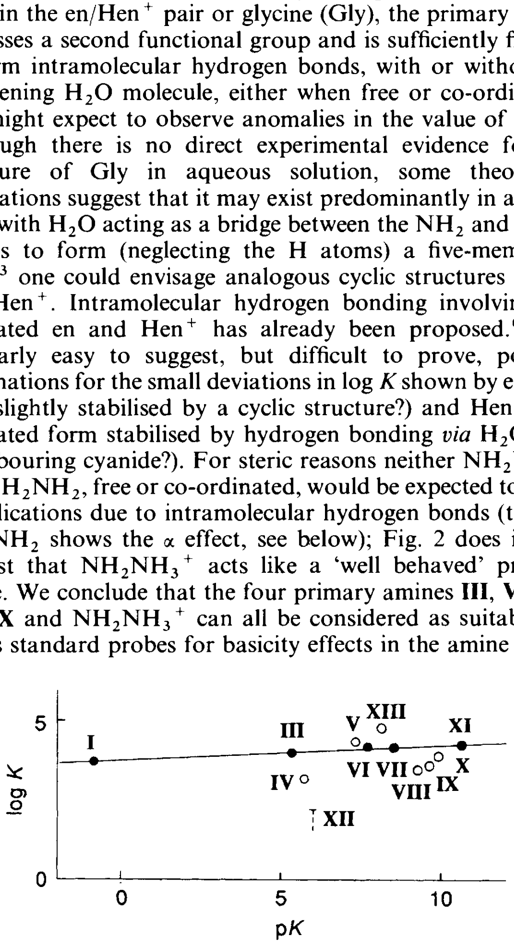

Fig. 2 Plot of log K (for co-ordination) *vs.* pK (for protonation of the free base) for amines with the $[Fe(CN)_5(OH_2)]^{3-}$ complex. Data and ligands numbered as in Table 1. The filled circles denote the five ligands used to determine the values of a and b in equation (1); the solid line corresponds to the equation log K = 0.05 pK + 3.75

Table 2 Comparison of values of a and b in equation (1) for amines as ligands to Fe^{II} in complex **1**, Fe^{III} in microperoxidase-8 and Co^{III} in cyanocobinamide, and also as hydrogen-bond acceptor towards 4-nitrophenol in 1,1,1-trichloroethane

System	a	b	Ref.
Ligand to Co^{III}	0.58	−2.6	3
Ligand to Fe^{III}	0.43	−0.5	4
Hydrogen-bond acceptor	0.37	−1.1	28
Ligand to Fe^{II}	0.05	+3.75	This work

Hydrazine (**XIII**) shows an enhanced value of log K which, as in the case of complexes of Fe^{III} and Co^{III}, can be ascribed to operation of the α effect (see below). By contrast, anomalously low values are shown by NH_2OH (which should also exhibit the α effect) and Gly as well as by NH_3 and $NH_2SO_3^-$. Our combined results are discussed in terms of (*i*) basicity effects, the values of a, and the range of amines available with low pK, (*ii*) coulombic and other interactions which may decrease the value of log K below the baseline, and (*iii*) the α effect which may increase the value of log K.

(*i*) *Basicity Effects and the Value of* a.—The value of $a \approx 0$ for the amines is not unexpected. Aymonino and co-workers[21,22] have pointed out that the rate constants for ligand substitution involving complex **1** show little dependence on the basicity of the amine, although only a very narrow range of pK was available for study, and any basicity effects were generally swamped by other effects. They also deduced an apparent value of pK_c *ca.* 10 (*cf.* our pK_c *ca.* 9.5) for the protonation of co-ordinated en from the pH dependence of the rate constant k_r, compared to a pK of 9.9 for free en (or 9.6 after correction for the statistical factor).[24] We have shown that values of pK_c in principle (*e.g.* where complexes with both forms of the ligand fall on the baseline) can be used to calculate the value of a by means of equation (2), used in conjunction with values of pK_a

$$a = (\mathrm{p}K_a - \mathrm{p}K_c)/(\mathrm{p}K_a - \mathrm{p}K_b) \qquad (2)$$

and pK_b (here equated with the first and second stages of protonation of free en).[25] It is clear that the near identity of pK_c with pK_a in this case will give the numerator a relatively small (or even negative) value, which will automatically lead to $a \approx 0$. Our results using amines spanning a range of 11 pK units fully and more quantitatively support Aymonino's conclusion.[21,22] Initial experiments indicate that the iron(II) ion in microperoxidase-8 (MP-8) shows values of a *ca.* 0 and b *ca.* +3 comparable to those of **1**,[26] *i.e.* such values are not peculiar to Fe^{II} in the specific environment of **1**. An apparent value of pK_c = 9.7 was also deduced for the analogous ruthenium(II) complex $[Ru(CN)_5(en)]^{3-}$ from the pH dependence of the rate constant k_r for the displacement of en by pyrazine;[27] this would also give $a < 0$.

The values of a and b obtained here are compared in Table 2 with the analogous results for the binding of amines as ligands to the iron(III) porphyrin microperoxidase-8 and the cobalt(III) corrinoid cyanocobinamide and as hydrogen-bond acceptor towards 4-nitrophenol in 1,1,1-trichloroethane. The Fe^{II} therefore shows significant differences from Fe^{III} and Co^{III} in both the very low value of $a \approx 0$ and the unusually high value of b. A possible explanation for a value of $a \approx 0$ is suggested by the parallels already noted[3,29] between the behaviour of amines (and other N-containing bases) as ligands and as hydrogen-bond acceptors (see Table 2). If, as observed, the free energy of hydrogen-bond formation to the free base **B** increases linearly with pK, then it seems likely that that part of the total solvation (including hydrogen-bond) energy of the free base which is lost on co-ordination will also increase linearly with pK (with slope z). If the equilibrium for ligand substitution is now rewritten schematically as in equation (3), where the further interactions

$$\mathrm{M{-}OH_2 + B\cdots HOH \rightleftharpoons M{-}B + H_2O\cdots HOH} \qquad (3)$$

of the four species with the solvent are ignored for simplicity, then it can be seen more clearly that the observed dependence of log K on pK (which is represented by a) will reflect the difference between the increase in the intrinsic metal–ligand (M–B) bond energy with the pK of B (slope y) and the increase in loss of solvation energy (represented by B $\cdots$ HOH) with pK (slope z), *i.e.* $a = y - z$. The value of b in equation (1), which does not vary with the pK of B, will therefore be determined mainly by the properties of the species M–OH_2, while $H_2O \cdots HOH$ remains a constant. Irrespective of other possible factors such as π bonding, the value of a may therefore become zero or even negative when $y < z$, *i.e.* when the effective Lewis acidity of the metal ion becomes equal to, or less than, that of the hydrogen bond in water. Possible reasons for the variation in b will be discussed later in the light of results related to the *trans* effect in cobalt(III) corrinoids.

We have been particularly interested in extending the study of basicity effects in the amine series below pK 5 (*viz.* that of NH_2CH_2CN), using amines with strongly electronegative substituents that are readily available and preferably possess some or all of the following characteristics: reasonably soluble and stable in aqueous solution, known pK, no steric hindrance and not part of a conjugated system (as in the anilines) where other effects intrude.[4,7,8] Commercially available amines (with pK in parentheses)[5] include: cyanamide NH_2CN (1.0), but protonated on the nitrile N;[9] amides such as NH_2CHO (0.1) and NH_2COMe (0.0), but all are protonated mainly or entirely on the O atom;[30–32] the charged sulfamate $NH_2SO_3^-$ (1.0) and hydrazinium ion $NH_2NH_3^+$ (−0.9). A theoretical analysis of ethynamine $HC{\equiv}C{-}NH_2$ to explain the marked decrease in nitrogen basicity and preferred protonation on C, which is obviously relevant to the isoelectronic $N{\equiv}C{-}NH_2$, has been published.[33] We have tested NH_2CN (but co-ordinated to complex **1** through the nitrile N),[1] $NH_2SO_3^-$, urea and NH_2CHO (no detectable formation of the characteristic d–d band at *ca.* 400 nm). We have, however, shown that $NH_2NH_3^+$ does co-ordinate to **1** and can be an acceptable 'probe' for basicity effects (see also below).

For completeness, several other amines with electronegative substituents should be mentioned. A value of pK_a 6.7 has been calculated for the unstable carbamic acid;[34] although the structure was written as NH_2CO_2H, there appears to be no reason to exclude the zwitterionic form. The unstable nitramide NH_2NO_2 also has pK_a 6.5;[35] a study of its acid-catalysed decomposition suggested the intermediate formation of a species such as $HN{=}N(OH)_2^+$ with a very low pK_b (< 0).[36] Salts of the NH_3F^+ ion have been prepared; their solutions in MeCN allow some formation of NH_2F but the salts are readily decomposed by moisture.[37] Rather surprisingly, the relatively stable aminomalononitrile $NH_2CH(CN)_2$, which is of interest because of its possible role in prebiotic evolution,[38] has pK_b 6.5,[39] *i.e.* it is even more basic than NH_2CH_2CN (5.3),[5] as is $NH_2CH_2SO_3^-$ (5.75).[5] There appear to be no non-conjugated amines available to fill the gap in pK between NH_2CH_2CN (+5) and $NH_2NH_3^+$ (−1).

(*ii*) *Coulombic and Other Interactions.*—Further insight into the factors which cause deviations in log K from the baseline in Fig. 2 may be obtained by comparison with published values of the forward and reverse rate constants (second-order k_f and first-order k_r), where available (see Table 3). To a first approximation the value of k_f is independent of the nature of the incoming ligand (though appreciably lower for anionic ligands, see Gly in Table 3), while the magnitude of k_r depends strongly on the nature of the outgoing ligand and varies inversely with the magnitude of the equilibrium constant. No value of k_f has been reported for NH_2Me which, by comparison with NH_3 and en, is here taken to be 350 dm^3 mol^{-1} s^{-1}. The data of Table 3 allow one to see whether the decrease in log K by 0.6–0.7 (*i.e.* in K *ca.* 5 dm^3 mol^{-1}) from that for NH_2Me (4.3) to those observed for $NH_2NH_3^+$ (3.7), Gly (3.6), and NH_3 (3.5) is caused by changes in the values of k_f and/or k_r. The ion $NH_2NH_3^+$ provides a useful check because the decrease in log K is, according to our interpretation of Fig. 2, simply the result of the decrease in basicity and should therefore be reflected mainly in an increase in k_r with little change in k_f as is observed. The hydrazinium ion therefore behaves like a primary amine with pK −1 and extrapolation of the baseline to include this ligand is justified. Glycine and NH_3 provide a contrast where the decrease in log K is reflected in a decrease in k_f (Gly) and an increase in k_r (NH_3) respectively. The low value of k_f for Gly has been attributed to coulombic repulsion of the anionic Gly[41,42] and the decrease in K can therefore be explained in the same way. It is, therefore, surprising that log K for $NCCH_2CO_2^-$ (2.5) differs so little from that of NCMe (2.6);[1] a possible explanation is that the proposed cyclic structure of Gly[23] serves to hold the negative charge of the CO_2^- group close to N in the incoming ligand, while the linear $NCCH_2^-$ group holds it sufficiently far away to have a negligible effect on k_f. The increase in k_r for NH_3 is the same as that reported (by the same authors) for NMe_3 (*viz.* 17 × 10^{-3} s^{-1}),[21] which suggests that the ammine complex is destabilised by some increased strain and/or decreased bonding compared to the complexes of primary amines. We tentatively suggest that this may be related to the larger number and/or different arrangement of H_2O molecules associated with the three N–H bonds of the Fe–NH_3 group (with C_{3v} symmetry) compared to the two N–H bonds of the Fe–NH_2R group (C_{2v}) and the greater difficulty of accommodation against the planar $Fe(CN)_4$ group of C_{4v} symmetry. The observed difference in k_r, and our proposed difference in solvent interaction, between NH_3 and primary amines may be related to the observed difference in effect of adding 0.1 mol dm^{-3} MeCN, which decreases log K for NH_3 but increases log K for NH_2CH_2CN (also pyridine and PhCN);[1] it appears that NH_2OH may behave like NH_3 (see Table 1). This, in turn, suggests that the further decrease in log K observed for NH_2OH (see Table 1), which completely obscures any possible increase due to the α effect (see below), may also be related to the greater solvation and hence repulsion expected for OH compared to NH_2 and Me. The ligand $NH_2SO_3^-$ (log $K \leqslant 0$) clearly suffers severe depression from the combined effects of negative charge (*cf.* Gly), considerable solvation of the sulfonate group (*cf.* NH_2OH) and/or steric hindrance from a bulky substituent.

Table 3 Rate constants for the reaction of complex **1** with various amines (published data, conditions vary). Parentheses denote values determined indirectly

Amine	k_f/dm^3 mol^{-1} s^{-1}	10^3k_r/s^{-1}	Ref.
NH_2Me	(350)*	2.8	21
$NH_2CH_2CH_2NH_2$	(330)	5.6	24
$NH_2NH_3^+$	(250)	50	40
$NH_2CH_2CO_2^-$	28	2.7	41
NH_3	365	16	21, 42
NH_2NH_2	(400)	1.6	40

* By comparison with NH_3 and en (see text).

The variable relative position of NH_3 and NH_2Me is surprising. For both Fe^{III} and Co^{III} these ligands lay, within reasonable limits, on the same 'baseline' with a = 0.43 and 0.58 respectively, *i.e.* log K was greater for NH_2Me.[3,4] For co-ordination by the iron(II) complex log K is again greater for NH_2Me than NH_3, but we now know that a is *ca.* 0 and the lower value of NH_3 is unrelated to its lower pK; when NH_3 and NH_2Me were the only two amines which were compared the difference in values of k_r was correlated with the difference in pK.[43] In their studies on the co-ordination of NH_3 and NH_2Me by the ruthenium-(II) and -(III) pentaammines Yeh and Taube[44] found that NH_3 gave an equilibrium constant 10 times greater than that of NH_2Me with Ru^{II} and 10^2 greater with Ru^{III}; they ascribed this to shielding by the alkyl group of the interaction between the metal ion and the solvent. These differences between NH_3 and NH_2Me serve to emphasise the importance of studying a range of amines with varying pK in order to establish a realistic baseline and provide a pointer to the source of any anomaly.

(*iii*) *The* α *Effect*.—Hydrazine is the only ligand which gives a value of log K (4.8 after correction for the statistical factor) which is significantly higher than that of the baseline at the same pK (*viz.* 4.2). This increase in log K can probably be ascribed to operation of the so-called α effect, which has been shown to cause a significant increase in values of log K (above the baseline) for both NH_2NH_2 and NH_2OH (as well as pyridazine) with both Fe^{III} and Co^{III}.[3,4] The $[Fe(CN)_5(NH_2NH_2)]^{3-}$ complex and its protonated form have previously been studied by Olabe and Gentil[40] who suggested, but without an adequate baseline for comparison, that the Fe–NH_2NH_2 complex might be slightly stabilised by the α effect; our results support their conclusions. It would appear that any possible increase in log K for NH_2OH due to the α effect is swamped by other, undefined 'solvation' effects of the type discussed above; an analogous, but smaller, reduction in any increase due to the α effect might be expected for NH_2NH_2. Additional studies [*e.g.* with the iron(II) porphyrin] are clearly required in order to provide further evidence on the factors involved and their relative importance.

Hydrazine offers the most readily available 'α-effective' ligand which can be converted by simple protonation into a form ($NH_2NH_3^+$) which cannot display the α effect. The additional stabilisation of co-ordinated NH_2NH_2 over H_2O and over $NH_2NH_3^+$ will therefore cause both an increase in log K over that expected from the baseline and a decrease in pK_c below that expected from equation (2). This equation can be rewritten in the form $pK_a - pK_c = a(pK_a - pK_b)$ to show that when $a \approx 0$, as is the case here, pK_c should almost coincide with pK_a, as is observed with the en complex (see above). A significantly greater value of the difference ($pK_a - pK_c$) for NH_2NH_2 compared to that for the en complex would then indicate operation of the α effect in the hydrazine complex. Olabe and Gentil[40] obtained a value of $pK_c = 6.2$ from the pH dependence of k_r for the displacement of NH_2NH_2, *cf.* our value of 6.3 (see Results section). They noted that the difference ($pK_a - pK_c$), using values uncorrected for the statistical factor, was greater for the NH_2NH_2 than for the en complex, but concluded merely that 'lack of sensitivity to ligand basicity (as with en) is perhaps not a general phenomenon in the aqueous chemistry (of **1**), as was previously suggested.' Our present results indicate that a lack of sensitivity to basicity (reflecting the value of a *ca.* 0) is a general phenomenon in this family of complexes and that NH_2NH_2 provides an exception specifically because protonation is coupled with loss of the α effect which stabilises only the unprotonated form of the complex.

Conclusion

The results presented here (*a*) indicate that $NH_2NH_3^+$ can act as a 'well behaved' amine ligand with pK −1, which considerably extends the range of available 'probes' for basicity effects in the amine series, (*b*) demonstrate the validity of the linear free-energy relation (1) for complexes of **1** with amines having $a = 0.05$ and $b = 3.75$ over 11 pK units and, in contrast to the pattern observed with complexes of Fe^{III} and Co^{III}, (*c*) reveal a significant decrease in log K below that expected from basicity alone for NH_3 and NH_2OH (by *ca.* 0.7 and 1.2 respectively). They explain certain apparent anomalies in the literature such as the low pK_c for the NH_2NH_2 complex and the slow formation of a highly coloured complex with NH_2OH. We have suggested a possible explanation for the value of $a \approx 0$ and will discuss possible explanations for the marked variation in b later. We have termed these linear free-energy relations represented by equation (1) the structural members which form the grid of log K values resulting from the interplay between the basicity (and other properties) of the ligand and the Lewis acidity (and other properties) of the metal ion.[3] The underlying significance of the values of a and b, and the importance of understanding the factors which determine their magnitude, are further emphasised here by the remarkable span of linearity observed for the amines and by the striking differences in a and b from those previously found for complexes of Fe^{III} and Co^{III}. Our present results provide a firm foundation of σ-only effects, and the first case where the virtual absence of basicity effects (*i.e.* $a \approx 0$) has been conclusively established for any metal ion. They can now be used as the basis for assessing the possible role of π bonding in iron(II) complexes with azines and azoles.

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