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Influence of Ligand–Water Interactions on the Aquation of Pentacyano(saturated amine)ferrate(II) Ions

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Rate constants and activation parameters for the aquation of 12 saturated amines from pentacyanoamineferrate(II) in 1 M pyridine solutions are reported. While $\Delta G^{\ddagger}$ values do not correlate with $\Delta G_{\text{i}}^{\circ}$ (for the ionization of the conjugate acid) or with σ^* and E_{a} Taft's constants, an isokinetic relationship is found. For the series $(CH_3)_xNH_{3-x}$ and RNH_2, $\Delta H^{\ddagger}$ correlates with $\Delta H_{\text{i}}^{\circ}$ in water and each series shows an independent correlation of $\Delta S^{\ddagger}$ with $\Delta S_{\text{i}}^{\circ}$. These results are interpreted in terms of an adapted Caldin and Benetto's model for exchange reactions, the main contribution to the changes in activation parameters arising seemingly from the energetics of transfer of the released ligand to bulk water. This small contribution to the activation process in water is rendered observable by the remarkable insensitivity of the rate process to "inner" bonding effects.

Introduction

The release of ligands L from $[Fe(CN)_5L]^{3-}$ has been demonstrated to be a dissociative process, probably I_d.[5-7] Equations 1–3 represent the accepted interchange mechanism

$$[Fe(CN)_5L]^{3-} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + L \tag{1}$$

$$[Fe(CN)_5]^{3-} + H_2O \overset{K}{\rightleftarrows} [Fe(CN)_5H_2O]^{3-} \tag{2}$$

$$[Fe(CN)_5]^{3-} + L' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(CN)_5L']^{3-} \tag{3}$$

although equilibrium 2 might not be a separate step. Schemes 1–3 give rise to the well-known relationship between the pseudo-first-order experimental rate constant k_{exptl} and the concentration of the incoming ligand L′ featuring a saturation plateau at high L′. In this plateau, $k_{\text{exptl}} = k_{-1}$, the rate of release of L.

For L = azine, the changes in the rate of release when L is varied are mainly governed by π-bonding effects,[5] which give rise to a reversed relationship between the basicity of the ligand and k_{exptl}. For the case of amines, although various complexes have been described,[8,9] kinetic data available pertain only to the ammonia and methylamine complexes.[10] Based on these two series of data, Toma and Malin[10] have construed a LFER of the type $\log k = A + B(pK_a)$, used to estimate the magnitude of the π effects in the azine ligand series. Now, we report data on the rate of release and activation parameters of additional amines, in an effort to elucidate the effects operative in this series.

Experimental Section

Preparation of the Complexes. The complexes were prepared in solution from sodium pentacyanoamminoferrate(II), which in turn was prepared from sodium nitroprusside (Merck).[8] All chemicals were reagent grade purity. Methylamine chlorohydrate, propylamine, dimethylamine (25% solution), piperidine (Fluka), ammonia (Raudo), butylamine, cyclohexylamine (BDH), and trimethylamine (C.Erba) were used as supplied. Available ethylamine chlorohydrate was recrystallized several times from ethanol to eliminate an impurity which oxidized Fe(II). Morpholine, aniline, and ethanolamine were distilled over zinc.

Kinetic Experiments. In a typical kinetic experiment, a buffer solution was prepared by adding enough hydrochloric acid to the corresponding amine so that neutralization was half complete. The concentration of free amine in every case amounted to ca. 0.1 M, which was sufficiently high to form quantitatively $[Fe(CN)_5(\text{amine})]^{3-}$ from $[Fe(CN)_5NH_3]^{3-}$ (complex concentration was ca. 2×10^{-4} M); ionic strength was 1 M (NaCl). With this buffer, two reagent solutions were prepared: one with the ammonia complex and the other with the attacking ligand (pyridine); both were thermostated 15–20 min prior to mixing, thus also allowing for the complete displacement of NH_3 from the complex.[5,10,11] All reported measurements were carried out in the saturation plateau of k_{exptl} vs. pyridine (1 M solutions of pyridine). The solutions were mixed in the thermostated 1-cm optical cell of a Spectronic 600 B&L spectrophotometer. The formation of the pyridine complex was followed by measuring the increase in absorbance at 365 nm. Prior to each run, the spectra of the reactant amine complexes were obtained and compared with literature data; both λ_{max} and ϵ_{max} were coincident within experimental error.[12] For cyclohexylamine and piperidine complexes, no previous data were available; experimental values were 392, 398 (λ_{max}) and 580, 716 (ϵ_{max}), respectively. From all these spectra it could be shown that aquation of the complexes was negligible in our experimental conditions. The final absorbance value in the kinetic experiments, A_∞, was in every case in good agreement with the value expected for the quantitative formation of the pyridine complex. Temperature was measured to ±0.1 °C within the optical cell to avoid possible differences with the cell-holder temperature (control measurements showed that the difference was not negligible). The absorbance data were obtained under pseudo-first-order conditions and the plot of $\log (A_\infty - A_t)/(A_\infty - A_0)$ vs. time was rigorously linear over at least 2 half-lives (and usually up to 90% reaction). Duplicate runs were made for every single experiment. Rate constants were reproducible to within 1%, although the third significant figure quoted below is only indicative.

The activation parameters were calculated by least-squares fitting from an Eyring plot of $\log (k_{-1}/T)$ vs. $1/T$. Tabulated errors were determined by an analysis of variance about regression,[13] using Student's t values for 80% confidence limits. The temperature control was accurate enough to avoid limitation in the accuracy of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. A Diehl Combitron programmable calculator was employed in all computations.

It should be pointed out that the best values for the activation parameters quoted here for the ammonia and methylamine complexes differ from those of Toma and Malin,[10] but this may be due to the differences in composition of the medium (see below). Pyridine was the attacking ligand here, while Toma and Malin used *N*-methylpyrazinium or isonicotinamide. Also, the pH values in our experiments were near the pK_a of the amines, i.e., over two units higher than the pH used in the earlier work. In any event, the comparison of the whole set of data obtained under rigorously similar conditions provides more reliable information than the individual isolated results; thus we believe that the small changes here reported in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as L is varied are significant and can be interpreted even if comparison with data from other sources shows larger discrepancies.[14] From another perspective, the different rate of change of k with T for the various amines is real, as can be easily shown by inspection of Table I.

Results and Discussion

Table I presents a résumé of the data obtained for the different ligands. For the case of aniline, the reaction was too fast to be followed accurately with our technique, the figure given being only an estimate which is believed to be correct

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Table I. Saturation Rate Constants for the Release of Ligands L from $Fe(CN)_5L^{3-}$ at Different Temperatures

Ligand	Temp, °C	10^3k_{-1}, s^{-1}
Ammonia	10.4	1.77
	15.2	3.86
	20.0	7.68
	25.0	16.0
	28.6	25.9
Methylamine	15.0	0.67
	20.0	1.37
	24.8	2.79
	29.2	5.61
	33.6	9.39
Dimethylamine	11.0	0.78
	15.7	1.85
	20.2	3.32
	24.8	6.27
	29.5	12.9
Trimethylamine	10.9	2.23
	15.1	4.99
	20.3	9.35
	25.0	16.7
	29.6	27.8
Ethylamine	15.4	1.29
	19.9	2.65
	25.0	5.67
	29.5	10.6
	34.3	19.9
n-Propylamine	15.1	1.35
	19.6	2.79
	25.0	5.47
	29.4	11.4
	34.1	23.8
n-Butylamine	11.4	0.66
	15.3	1.39
	19.9	2.61
	25.0	5.59
	29.0	8.75
Cyclohexylamine	10.4	2.9
	15.0	5.8
	19.8	11.7
	25.0	22.7
	28.9	32.9
Piperidine	15.5	1.59
	20.5	3.22
	25.0	6.96
	29.2	10.5
	33.7	17.4
Ethanolamine	10.5	0.64
	15.1	1.57
	19.7	2.55
	25.0	5.91
	29.4	9.37
Morpholine	10.7	0.63
	15.6	1.35
	20.0	2.55
	25.0	5.2
	29.4	10.1
Aniline	25.0	ca. 100

only within 1 order of magnitude.

The first obvious feature of our data is the small range covered by the kinetic parameters. For 11 of the 12 departing ligands, k_1 varies over a factor of 8, while $\Delta H^\ddagger$ and $\Delta S^\ddagger$ vary within a range of 3.7 kcal/mol and 10 cal/(K mol), respectively. This scarce sensitivity of the rate parameters to the donor properties of the leaving group is a remarkable feature of pentacyano(ligando)ferrate(II) systems, as also shown by pH profiles of the rate constants for the release of weakly basic ligands.[15,16] The formation rate constants k_f are also rather insensitive to the nature of the ligand, and thus it is also found that the overall stability constants of azine complexes[5] and aliphatic diamines[7,15] do not change much even when the pK_a of the ligand is amply varied.

In our series, the lack of correlation between log k_{-1} and $\Delta G_i°$ for the ionization of the conjugate acid (eq 4) is obvious

$$R_1R_2R_3NH^+(aq) \rightleftarrows R_1R_2R_3N(aq) + H^+(aq) \qquad (4)$$

from inspection of Table II, which also includes the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

In an effort to cover a wide range of $\Delta G_i°$, ligands with very diverse structure were chosen. In such a series, the possible relevance of $\Delta G_i°$ is completely swamped by other effects; thus, the most basic piperidine does not show the slowest rate, and the rate of cyclohexylamine, which is among the most basic ligands, is one of the highest. On the other hand, morpholine and ethanolamine give rise to complexes which release the ligands rather slowly in spite of their low basicities. In fact, there is no a priori reason to expect that the free energy change for the activation process for the release of L from $[Fe(CN)_5L]^{3-}$ should be related to the free energy change attending the proton release from the conjugate acid of the ligand, as it seems to occur for instance in $[Co(NH_2)L]^{3+}$ complexes (cf. ref 17), in view of the very diverse nature of the $[Fe(CN)_5]^{3-}$ and $[Co(NH_3)_5]^{3+}$ moieties. The only result arguing in favor of such a correlation is the high rate of release of aniline.

In principle, it could be possible to interpret the data in Table II on the basis of a LFER using ad hoc and comparatively large individual corrections for possible steric effects. The correlations discussed below, however, point to another line of reasoning to understand the effects operative in these reactions, namely, the consideration of solvation contributions to the activation process.

Table II. Kinetic Parameters for the Release of Aliphatic Amines and Free Energy of Ionization of Their Conjugate Acids at 25 °C

Ligand	$\Delta G_i°$,[a] kcal/mol	log 10^3k_{-1}[b]	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/(°C mol)
Ammonia	12.61	1.20	24.4 ± 0.3	15 ± 1
Methylamine	14.48	0.446	24.7 ± 0.8	13 ± 3
Dimethylamine	14.69	0.797	24.0 ± 1.0	12 ± 3
Trimethylamine	13.36	1.22	21.9 ± 1.9	7 ± 6
Ethylamine	14.50	0.754	24.9 ± 0.5	15 ± 2
n-Propylamine	14.36	0.738	25.6 ± 1.5	17 ± 5
n-Butylamine	14.46	0.747	25.3 ± 2.0	16 ± 4
Cyclohexylamine	14.52[c]	1.356	23.1 ± 0.8	11 ± 3
Piperidine	15.18	0.843	22.7 ± 1.3	7 ± 4
Ethanolamine	12.96	0.772	23.4 ± 2.0	9 ± 7
Morpholine	11.58	0.716	24.7 ± 0.5	14 ± 2
Aniline	6.27	ca. 2		

[a] Data from ref 24, unless otherwise stated. [b] At 25 °C. [c] H. K. Hall, *J. Am. Chem. Soc.*, 79, 5441 (1957).

The values of the enthalpy and entropy of activation for the whole series are also remarkably constant, for a dissociative mechanism as operative here.[5-7] This constancy, not usually found in other systems, which makes the rate not very sensitive to either the incoming or the leaving group, makes it possible to detect minor effects usually swamped out in water. As we are speaking of changes which are not very much larger than experimental uncertainties, there is always the possibility that the correlations found are only the fortitous result of random fluctuations. This is especially true for the isokinetic relationship found (see Figure 1), as in this case random changes in $\Delta H^\ddagger$ are necessarily compensated by corresponding changes in $\Delta S^\ddagger$. In general, however, it is unlikely that random changes should show the trends discussed below, which are also in agreement with other work.[15,16,18] Even in the case of the

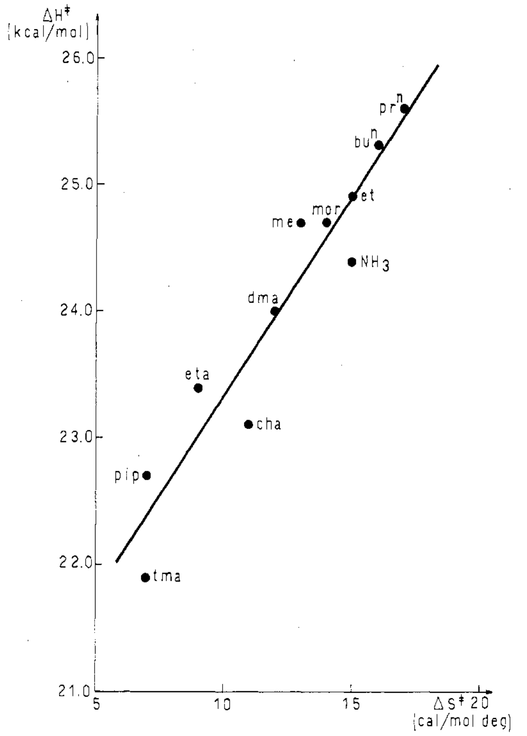

Figure 1. Isokinetic plot for amine substitution in pentacyano(amine)ferrate(II) complexes: me, methylamine; et, ethylamine; prⁿ, *n*-propylamine; buⁿ, *n*-butylamine; dma, dimethylamine; tma, trimethylamine; eta, ethanolamine; cha, cyclohexylamine; pip, piperidine.

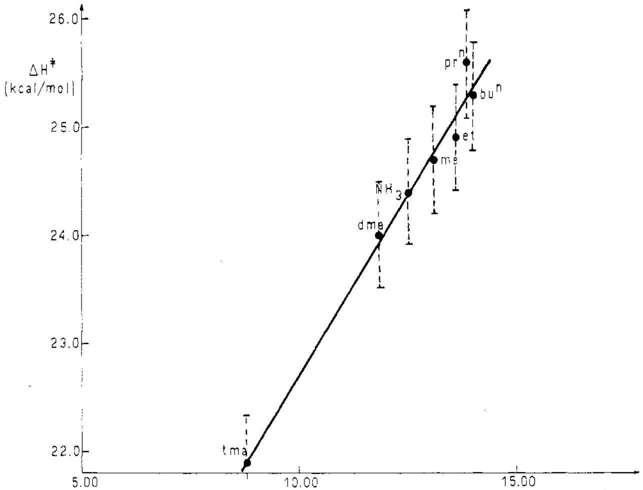

Figure 2. Enthalpy of activation for ligand substitution against enthalpy of ionization in aqueous solution for the conjugate acid of the ligand. Abscissa data are from ref 24 and error bars were calculated following ref 14.

isokinetic relationship, it is probable that it illustrates the medium effects on a set of reactions governed by a common mechanism.[19] In fact, the experimentally observed different rates of change of k_{-1} with T cannot be ascribed to random errors. The slope of Figure 1 (315 K) implies a lack of correlation between $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$, as shown by the thermodynamic relationship[20]

$$(\partial \Delta H^{\ddagger}/\partial \Delta S^{\ddagger}) = (\partial \Delta G^{\ddagger}/\partial \Delta S^{\ddagger}) + T \qquad (5)$$

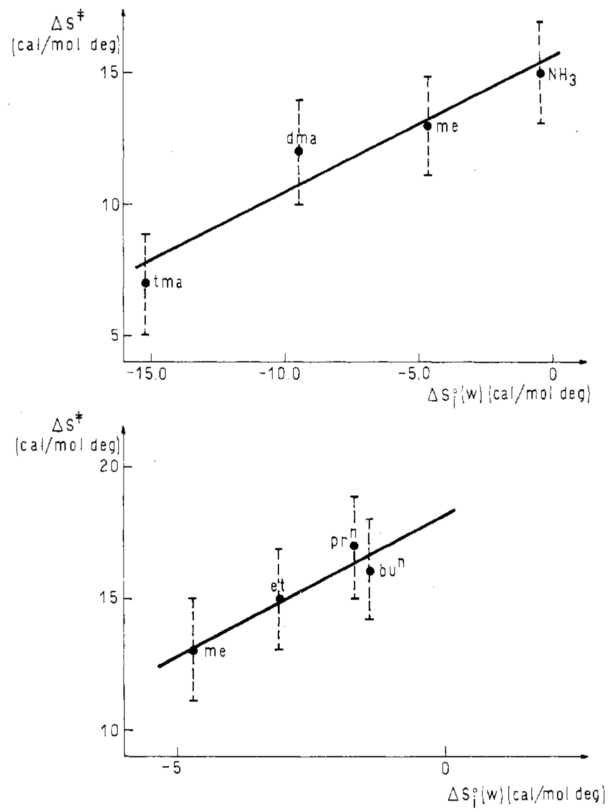

Figure 3. Entropy of activation for ligand substitution against entropy of ionization in aqueous solution for the conjugate acid of the ligand. Abscissa data are from ref 24.

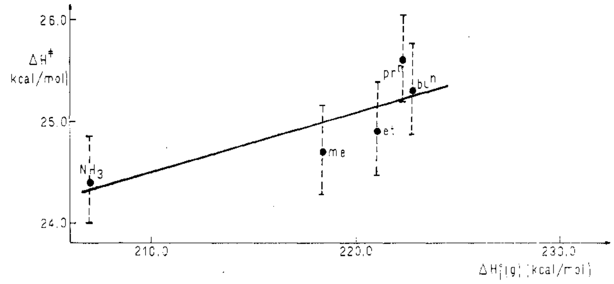

Figure 4. Enthalpy of activation for ligand substitution against enthalpy of ionization in gaseous phase for the conjugate acid of the ligand. Abscissa data are from ref 23.

That solvent effects govern the changes in the energetics of aquation is borne out by inspection of the data of two series of closely related ligands: $(CH_3)_xNH_{3-x}$ (x = 0–3) and RNH_2 (R = Me, Et, *n*-Pr, *n*-Bu). Even within these series, no correlation is found between log k_{-1} and ΔG_i° or Taft's substituent constants (σ^*, E_s).[21] This is not surprising, as the trends in the basicity of the aliphatic amines in solution are known to be "anomalous" and do not lend themselves to be interpreted on the basis of any single effect.[22] On the other hand, there is a good correlation between $\Delta H^{\ddagger}$ and ΔH_i° and, even more important, there are two independent correlations between $\Delta S^{\ddagger}$ and ΔS_i°, one for each series (see Figures 2 and 3).

The energetics of ionization of substituted ammonium ions in solution has been subjected to a detailed analysis and resolved into the contribution of gas-phase ionization and the solvation of the ions and neutral molecules. Thus, $\Delta H^{\ddagger}$ correlates with ΔH_i° (gas phase)[23] as far as this latter magnitude is related to ΔH_i° (solution), i.e., only for the series RNH_2, while secondary and tertiary amines, $(CH_3)_2NH$ and $(CH_3)_3N$, do not fit the line (see Figure 4). The slope ($\partial \Delta H^{\ddagger}/\partial \Delta H_i^{\circ}$ (gas phase)) = 0.06 points to the low sensitivity of the kinetic process to the "inner" effects already mentioned and the deviation of $(CH_3)_2NH$ and $(CH_3)_3N$ can easily be

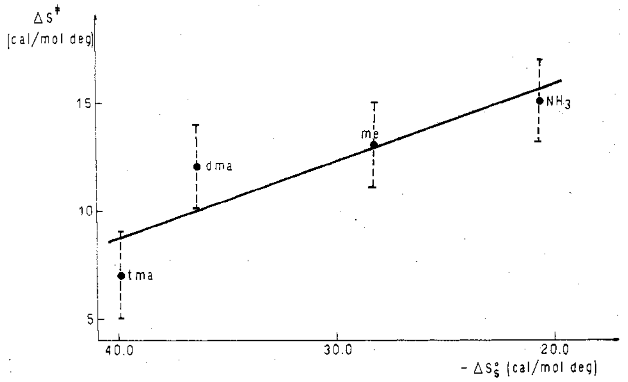

Figure 5. Entropy of activation for ligand substitution against entropy of solution for the free ligand. Abscissa data are from ref 22.

ascribed to hydration effects.[23]

The entropy correlations (Figure 3) are in good agreement with this idea; the changes in the series $(CH_3)_xNH_{3-x}$ seem to be governed by the contribution from the hydration of the free amine, as shown by Figure 5, where we plot $\Delta S^{\ddagger}$ against $\Delta S_s{}^{\circ}$ for the process

$$(CH_3)_xNH_{3-x}(g) + H_2O(l) \rightarrow (CH_3)_xNH_{3-x}(aq) \qquad (6)$$

This is in agreement with previous reports[22] which attribute the changes in $\Delta S_i{}^{\circ}$ to the changes in $\Delta S_s{}^{\circ}$. The more heavily substituted amines are better structure forming in water, thus accounting for the corresponding lower $\Delta S^{\ddagger}$ values.

For the RNH_2 series, an explanation can be offered by analogy with the changes attending the ionization of carboxylic acids: the negative charge of the anions hinders the rotations of the aliphatic chains and the $\Delta S^{\ddagger}$ for the release of the ligands shows an increased contribution from rotational entropy as the chain gets longer (cf. ref 24).

Summing up, all the data fit well into a dissociative (I_d or D) scheme corrected to take into account the model for ligand interchange proposed by Caldin and Benetto.[19] According to this model, in substitution reactions the energetics of the process involving the transfer of the released ligand to bulk solvent affects the activation free energy; in the reactions studied by Caldin and Benetto the composition of the solvent was changed, giving rise to changes in the energetics of the "quasicondensation" process of a solvent molecule; in our case, in the $(CH_3)_xNH_{3-x}$ series it is the nature of the ligand transferred to bulk solvent (which in this case is not pure water but 1 M pyridine solution) that changes. The availability of data for phase transfer (gas → solution) makes it possible to show the close similarity between both processes. When longer chain ligands are involved, it is of course expected that the difference in solvation when coordinated and in bulk must decrease as the chain gets longer (i.e., the far end of the coordinated chain "dips" into solvent), and the main contribution to the changes detected arises from the increased freedom of rotation when the ligand L is released from the negatively charged moiety.

It is also worthwhile pointing out that while data for k_{-1} obtained from the saturation plateau by scavenging of $[Fe(CN)_5]^{3-}(aq)$ with various ligands might be directly comparable, Caldin and Benetto's model implies that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ should be sensitive to changes in the "structure-stiffening" or "loosening" properties of the scavenger.

Finally, it must be emphasized that while good correlations can be found independently for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, the small difference between the slopes of Figures 2 and 3 gives rise to random changes in $\Delta G^{\ddagger}$, for which therefore no apparent correlation is found with $\Delta G_i{}^{\circ}$; a different situation was found in the case of Ni(II)-substituted pyridine complexes,[25] and it is probable that log k_{-1} and log K_i for $[Fe(CN)_5(azines)]^{n-}$ could also show some correlation if π-bonding effects were not present (cf. ref 10).

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Registry No. $[Fe(CN)_5(NH_3)]^{3-}$, 13717-31-2; $[Fe(CN)_5(me)]^{3-}$, 20774-55-4; $[Fe(CN)_5(dma)]^{3-}$, 63883-53-4; $[Fe(CN)_5(tma)]^{3-}$, 63848-43-1; $[Fe(CN)_5(et)]^{3-}$, 20774-56-5; $[Fe(CN)_5(pr^n)]^{3-}$, 21107-53-9; $[Fe(CN)_5(bu^n)]^{3-}$, 20774-58-7; $[Fe(CN)_5(cha)]^{3-}$, 63848-44-2; $[Fe(CN)_5(pip)]^{3-}$, 63848-45-3; $[Fe(CN)_5(eta)]^{3-}$, 36732-84-0; $[Fe(CN)_5(mor)]^{3-}$, 36732-46-4; $[Fe(CN)_5(aniline)]^{3-}$, 63848-46-4.

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