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Alkyl 4-Pyridinecarboxylate Complexes of Pentacyanoferrate(II)

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The preparation and spectral and kinetic properties of new complexes of pentacyanoferrate(II) coordinated to methyl and ethyl 4-pyridinecarboxylates are described. Ester substitution by solvent water seems to compete effectively with the alkaline or acid ester hydrolysis due to a remarkable metal inhibition of the latter reaction.

(Keywords: Ester hydrolysis; Kinetics of substitution; Spectral properties)

Alkyl-4-pyridincarboxylat-Komplexe von Pentacyanoferrat(II)

Darstellung, spektroskopische und kinetische Eigenschaften von neuen Komplexen von Pentacyanoferrat(II) mit Methyl- und Ethyl-4-pyridincarboxylaten werden beschrieben. Die Substitution mittels Lösungsmittel—Wasser scheint sehr effektiv mit der basischen und sauren Hydrolyse zu konkurrieren, wobei letztere eine bemerkenswerte Metall-Inhibition zeigt.

Introduction

The kinetics of coordinated ligand reactions without cleavage of the metal-ligand bond is a topic of current interest[1]. Metal centers play a fundamental role in catalysing hydrolysis reactions[2–4], thus suggesting an explanation for enzymatic activity. To the best of our knowledge, no previous studies on metal promotion have been made on pentacyano(ligand)ferrate(II) complexes. Therefore, we have undertaken a study of the effect of coordination to the $Fe(CN)_5^{3-}$ moiety on the

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hydrolysis of alkyl 4-pyridinecarboxylates. In order to interprete the obtained results, spectral properties and kinetics of substitution of the new complexes were also investigated.

Experimental

The complexes of pentacyanoferrate(II) with methyl and ethyl isonicotinates were prepared as sodium salts by a method similar to that previously described for other pentacyanoferrate(II) complexes[5], with some modifications. Excess pure ligand was mixed with an aqueous solution of trisodium pentacyanoammineferrate(II) trihydrate and after waiting for half an hour, precipitation was accomplished by adding an ether—ethanol mixture (1 : 1). The new compounds were collected on a sintered-glass filter, washed with ethanol and ether, and then stored *in vacuo* under KOH. Purification was carried out by dissolving in a minimum amount of water and then precipitating with ethanol—ether.

IR spectra of solid samples were recorded on a Perkin-Elmer 457 IR spectrophotometer, as KBr disks in the range 4000-250 cm^{-1}. UV-visible spectra of aqueous solutions (prepared with a slight excess of free ligand to prevent aquation) were obtained by using a Perkin-Elmer Coleman 124 spectrophotometer. Water content of the samples was obtained by adding excess pyridine and comparing the final constant absorbance data at λ_{max} with already published values[5].

Kinetic measurements were done in the thermostatted cell-holder of a Spekol ZVEK5 visible spectrophotometer. Final concentrations were: [complex] = $2 \cdot 10^{-4} M$, [*py*] = $0.1 M$, [free isonicotinate] = $2 \cdot 10^{-3} M$, [I] = $1 M$ (NaCl). *pH* was *ca.* 11 and $t = 25.0 \pm 0.1\,°C$. Triplicate runs were made at $\lambda = 362$ nm, maximum of the pentacyanopyridineferrate(II) ion[5]. *Guggenheim*'s method[6] was employed to evaluate the rate constants with an estimated error of 5%. A similar procedure was followed to study the effect of added tetramethylammonium bromide.

For studying alkaline hydrolysis, standard volumetric, conductimetric, titrimetric and spectrophotometric techniques[6] were used. Variable concentrations of NaOH and ethyl complex in aqueous solutions were employed in the range 0.01-0.1 M. Acid hydrolysis was followed by adding HCl up to 0.01 M to a freshly prepared aqueous solution of the ethyl complex and recording spectral changes on a Beckman DBG UV-vis spectrophotometer. Degassed bidistilled water was used throughout.

Results

The new complexes were characterized by their IR and visible spectra. IR bands for trisodium pentacyano(ethyl 4-pyridinecarboxylate)ferrate(II) dihydrate appeared at 2050 cm^{-1} (ν_{CN}), 1725 cm^{-1} (ν_{CO}), 1413 cm^{-1} (ν_{ring}), 1285 and 1130 cm^{-1} (δ_{CH}) and 573 cm^{-1} (δ_{Fe-CN}). Similar bands were observed for the methyl complex at 2050, 1715, 1413, 1295, 1128 and 572 cm^{-1}.

Visible absorption bands showed maxima at $\lambda = 450 \pm 2$ nm

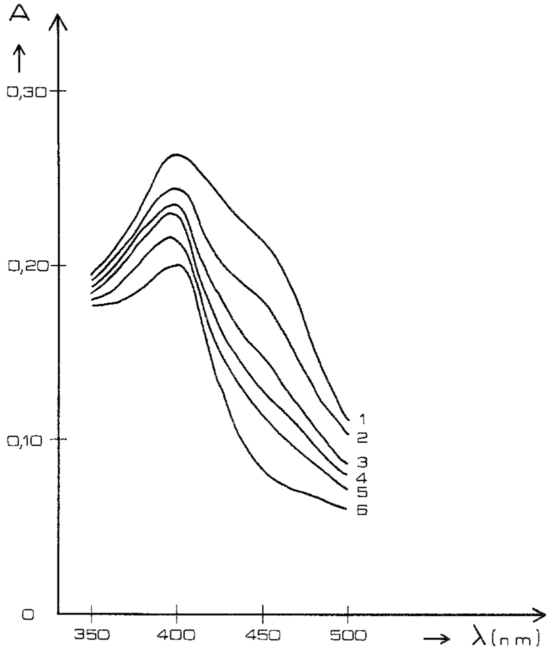

Fig. 1. Effect of added HCl on the spectral properties of the pentacyano(ethyl isonicotinate)ferrate(II) ion. [HCl] = 0.01 *M*, [complex] = $1 \cdot 10^{-4}$ *M*, [I] = 1 *M*. Curves 1 to 6 correspond to 3, 7, 11, 16, 22, and 42 min respectively

Table 1. *Comparison between values of the energy of charge transference,* E_{CT}*, and the rate constants for the dissociation of* L, k_{-L} *(at 298 K) for complexes of the type* $Fe(CN)_5L^{3-}$

L	E_{CT} (kcal)	$10^4 k_{-L}$ (s^{-1})	Ref.
4-aminopyridine	31.3	25	9
4-methylpyridine	28.1	11.5	5
pyridine	27.6	11.0	5
isonicotineamide	23.0	7.3	5
methyl isonicotinate	21.9	6.7	this work
ethyl isonicotinate	22.2	5.7	this work
4-cyanopyridine	21.0	5.0	7
N-methylpyrazinium	15.1	2.8	5

($\log \varepsilon = 3.5$) and at $\lambda = 456 \pm 2$ nm ($\log \varepsilon = 3.6$) for the ethyl and methyl complexes respectively.

Table 1 shows the observed rate constants for the substitution of alkyl isonicotinates by pyridine in the corresponding pentacyanoferrates(II) under pseudo-first order conditions ($k_{\text{obs}} = k_{-L}$, the rate constant for the release of ligand L, see Ref. [5]). Rate constant values for similar systems together with their maximum visible absorption data are included in Table 1 for comparison purposes.

In Table 2, salt effects are shown for the ethyl complex. The limiting rate constant k_{-L} increases with the concentration of added $[NMe_4]Br$.

No significant changes in volume, conductivity, λ_{max} or volume of titrant were observed up to one hour after mixing variable amounts of the ethyl complex and NaOH. The effect of added HCl on the absorption spectra is shown in Fig. 1. A shift of $\Delta\nu = 2.8$ kcal was observed after adding HCl ($c = 10^{-2}\,M$) followed by a steady decrease in the intensity of the absorption maximum.

Table 2. *Salt effects on the kinetics of ligand exchange in the pentacyano(ethyl isonicotinate)ferrate(II) complex at 298 K*

Salt	c (M)	$10^4 k_{-L}$ (s^{-1})
NaCl	1.0	5.7
$[NMe_4]Br$	0.5	6.6
$[NMe_4]Br$	1.0	7.5

Discussion

IR spectra.—The identity of the $Fe(CN)_5^{3-}$ moiety is evidenced by its characteristic bands at 2050 and 573 (2) cm^{-1} (Ref. [8]). Coordination through the pyridine nitrogen can be deduced from observed blue shifts for pyridine bands when compared to free ligand. Carbonyl stretching frequencies remain unaltered for both complexes, as observed already in the IR spectrum of trisodium pentacyano(isonicotinohydrazide)ferrate(II) hexahydrate[8].

Visible spectra.—The visible absorption spectra resemble those of other pentacyanoferrate(II) complexes[5, 8], thus confirming the formation of the new compounds. The bands can be assigned to a charge transference from a d_π orbital of Fe(II) to a π^* orbital of alkyl isonicotinate. The positions of band maxima allow us to include these ligands between isonicotineamide and 4-pyridylpyridinium in a spectrochemical series of increasing π backbonding from the $Fe(CN)_5^{3-}$ group to the aromatic ligand[5].

Kinetic data.—As shown in Table 1, the rate constants for the dissociation of ethyl and methyl isonicotinates fall in the expected range, between $1 \cdot 10^{-3}\,s^{-1}$ and $5 \cdot 10^{-4}\,s^{-1}$, as could be inferred from the values of the energy of band transference, E_{CT}. *Toma* and *Malin*[5] found a correlation between $\lambda_{\max}$ and k_{-L} for pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles which follows the π acceptor properties of the releasing ligands. In this case, the values of k_{-L} (see Table 1) seem to reflect a lesser amount of π backbonding for the methyl complex when compared to the ethyl complex, in agreement with a smaller value of *Hammett*'s σ_p (cf. [9]). The value of $\lambda_{\max}$ for the methyl complex is somewhat higher but, as they are almost equal within the experimental error, we cannot infer a real inversion of the expected order.

Solvation effects must be taken into account when studying the effect of added $[\mathrm{N}Me_4]\mathrm{Br}$. Indeed, as shown in Table 2, the increase in the rate constant with increasing concentration of inert salt is similar to that observed for the release of pyrrolidine from the pentacyano(pyrrolidine)ferrate(II) ion[10]. The "reinforcement" of water structure by an alkylammonium ion makes energy requeriments for reordering water molecules less demanding and this results in a smaller value of $\Delta G^{\neq}$, although the effect seems to be more dramatic for an aliphatic ligand where π bonding is not operative (cf. [10]).

Ester hydrolysis.—Basic hydrolysis of coordinated ethyl isonicotinate could not be observed up to one hour. For the free ligand, the reaction would have proceeded to completion during this period. Indeed, the half-life for the hydroxide ion catalyzed hydrolysis of 4-ethylpyridinecarboxylate is almost 6 min at 25 °C when $[\mathrm{OH}^-] = 0.01\,M$ in 70% ethanol—water[11]. Basic hydrolysis is considerably faster in water[12]. The remarkable observed metal inhibition must be due not only to electrostatic repulsion between the anionic complex and OH^- but also to the electron donating properties of the $\mathrm{Fe(CN)}_5^{3-}$ moiety which makes the carbonyl carbon less electrophilic and so less susceptible to nucleophilic attack.

Addition of acid produces a shift in $\lambda_{\max}$ to smaller values (see Fig. 1). The observed $\Delta\nu_{\max}$ coincides with that reported for the pentacyanopyrazineferrate(II) ion[5] (its $\lambda_{\max}$ being 452 nm) and can be adscribed to the protonation of coordinated cyanide. The rate of decrease in $\varepsilon_{\max}$ that occurs afterwards is of the order of magnitude of the rate of ligand aquation, somewhat increased by acid. That acidic ligand hydrolysis does not compete effectively with ligand release must be attributed to coordination which removes electron density from the ester.

Conclusions.—While ligand substitution in pentacyanoferrate(II) complexes of alkyl isonicotinates shows the influence of π backbonding and solvation effects, the stability conferred to these ligands when bonded to a strong π donor such as $Fe(CN)_5^{3-}$ results in an unusual example of metal inhibition of the hydrolysis of coordinated esters.

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