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Preparation and Properties of 4-Picolylamine Derivatives of Pentacyanoferrate(II): Sodium Salts of Mononuclear $[Fe(CN)_5(4\text{-picolylamine})]^{3-}$, $[Fe(CN)_5(4\text{-picolylammonium})]^{2-}$ and Binuclear, 4-Picolylamine Bridged $[Fe_2(CN)_{10}(4\text{-picolylamine})]^{6-}$

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Abstract

Mononuclear $Na_3[Fe(CN)_5(4\text{-picolylamine})]\cdot 2H_2O$, $Na_2[Fe(CN)_5(4\text{-picolylammonium})]\cdot 6H_2O$ and binuclear, 4-picolylamine bridged $Na_6[Fe_2(CN)_{10}(4\text{-picolylamine})]\cdot 5H_2O$ were prepared. Analytical data, electrophoretic runs, UV–Vis, diffuse reflectance and infrared spectra as well as ligand substitution kinetics are reported for these salts.

Introduction

As part of a study on complexes of amines and pyridines with the pentacyanoferrate(II) moiety, we have prepared the mononuclear $[Fe(CN)_5(4\text{-picam})]^{3-}$ (4-picam = 4-picolylamine), $[Fe(CN)_5(4\text{-picamH})]^{2-}$, (4-picamH = 4-picolylammonium), and the bridged binuclear $[Fe_2(CN)_{10}(4\text{-picam})]^{6-}$ complex anions. As expected, these complexes exhibit well-defined metal-to-ligand charge transfer (MLCT) absorption bands in the UV–Vis region due to electron transfer from the $t_{2g}(d_\pi)$ orbitals of low spin iron(II) to π^* orbitals of 4-picam. This electron transfer implies an additional bonding which reinforces the ligand-to-metal σ bonding and confers extra stability to the complexes. As expected from the increase of π back-donation in the binuclear complex by inductive effect of the iron nucleus of a second pentacyanoferrate(II) group, the MLCT band shifts to the red (λ_{max} = 370 nm *vs.* 365 nm in $[Fe(CN)_5(4\text{-picam})]^{3-}$) and, at the same time, its intensity increases. A batochromic shift is also observed for the mononuclear complex upon protonation [1]. The wavelength value obtained for the MLCT band of the 4-picolylammonium complex was 390 nm. The stability towards aquation of the binuclear complex is greater than for the mononuclear one in parallel with the wavelengths of the respective charge transfer bands.

Peroxodisulfate oxidizes $[Fe(CN)_5(4\text{-picam})]^{3-}$ to $[Fe(CN)_5(4\text{-cypy})]^{3-}$ (4-cypy = 4-cyanopyridine) [2] but $[Fe_2(CN)_{10}(4\text{-picam})]^{6-}$ to $[Fe_2(CN)_{10}(4\text{-picim})]^{6-}$ (4-picim = 4-picolylimine) when the oxidant is not in excess greater than three times the stoichiometric amount [3]. The bonding to two pentacyanoferrate(II) groups therefore stabilizes the imine (in fact, a terminal diimine, if the $\overset{|}{N}{=}C{-}C{=}\overset{|}{C}{-}$ aromatic group is considered as an imine) which surely is an intermediate in the oxidation of the ligand to 4-cyanopyridine in the mononuclear complex [4]. Stabilization of diimines as chelated ligands is a well-known fact (see, for example, [5]) but acting as bridging ligands is a novelty, which is not restricted to 4-picolylimine but extends also, at least, to 2-picolylimine and ethylenediimine [3a].

Experimental

Preparative

4-Picolylamine (Reilly Tar and Chemical Corporation) was used as supplied. To obtain the mononuclear complex, $Na_2[Fe(CN)_5(4\text{-picamH})]\cdot 6H_2O$, an excess of pure ligand was mixed with an aqueous solution of trisodium amminopentacyanoferrate(II) trihydrate prepared according to [6] and, after waiting for half an hour in the dark, precipitation was accomplished by adding ten volumes of ethanol at 5 °C. After an hour, the solid was collected on a sintered glass funnel and washed with ethanol and ether. Purification was carried out by dissolving the solid in a minimum amount of water containing free ligand and then precipitating it again with ethanol. The substance was stored *in vacuo* over $CaCl_2$ [7].

To obtain the deprotonated salt $Na_3[Fe(CN)_5(4\text{-picam})]\cdot 2H_2O$, the same procedure, as quoted above, was followed but deprotonating first the protonated

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anion with an equivalent of NaOH, free from carbonate.

$Na_6[Fe_2(CN)_{10}(4\text{-picam})]\cdot5H_2O$ was prepared by again dissolving $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$ in water so as to obtain a solution 0.2 M and adding the stoichiometric amount of the bridging ligand previously dissolved in a minimum amount of water. This solution was kept for 15 h at room temperature. The solvent was evaporated on a Rotavap and the solid residue dried over $CaCl_2$ [8].

Analyses

The water content of the solids was determined gravimetrically after drying over P_4O_{10} at 100 °C under reduced pressure. Iron was determined spectrophotometrically as $[Fe(o\text{-phen})_3]^{2+}$ [9, 10].

Electrophoretic Runs

The electrophoretic runs were performed at 300 V in Schleicher and Schüll 2043 paper for ten minutes. The electrolyte was an aqueous 0.1 M solution of $NaHCO_3$ and cobalt 2+ ion was used as developer.

Infrared Spectra

A Perkin-Elmer 457 spectrophotometer was used. Spectra in the 4000–250 cm^{-1} region were obtained with thin KBr disks, hand-pressed in a RIIC die.

Electronic Spectra

A Shimadzu UV-300 spectrophotometer, together with a thermostated cell support and square 1 cm silica cells, was used. Spectra were measured at room temperature in aqueous solutions and when necessary, in the presence of a buffer of pH = 10 ($NaHCO_3$–NaOH).

Diffuse Reflectance Spectra

The Integrating Sphere Attachment of the Shimadzu UV-300 spectrophotometer was used. Mixtures with MgO were prepared.

Kinetics

Ligand substitution kinetic measurements were performed spectrophotometrically at pH = 9.4 ($NaHCO_3$–NaOH), $I = 1.0$ M (NaCl), $T = 25$ °C using complex concentrations of about 3×10^{-4} M and, as a scavenger for the $[Fe(CN)_5]^{3-}$ moiety, cyanide in a 100 times greater concentration. The absorbance changes were monitored at λ_{max} of the initial complexes.

Results and Discussion

Analytical

Table I presents results (the mean of two determinations in each case) for iron and water contents. They agree with the formulae: $Na_3[Fe(CN)_5(4\text{-picam})]\cdot2H_2O$, $Na_2[Fe(CN)_5(4\text{-picamH})]\cdot6H_2O$ and $Na_6[Fe_2(CN)_{10}(4\text{-picam})]\cdot5H_2O$.

Electrophoretic Measurements

For the sake of differentiating between mononuclear and binuclear complexes, electrophoretic runs were performed. The pH (8.4) of the solution of the supporting electrolyte was just equal to the pK_a of 4-picolylamine coordinated to $[Fe(CN)_5]^{3-}$ [11]. In this condition, the mononuclear complexes travelled together, also with ferricyanide added for the sake of comparison, and went distinctly farther than the binuclear complex. Runs were performed separately with the individual complexes and with a mixture of them producing the same results.

Evidently, the smaller sizes of the mononuclear complexes make them faster than the binuclear ones, in spite of their lower charge [12].

The complexes showed high stability to hydrolysis at working conditions, as proved by the absence of additional spots in the electrophoretic paper. This is also a proof of the purity of the complexes.

Infrared Spectra

Wavenumbers, relative intensities and rough tentative assignments of absorption bands are included in Table II.

Assignments were made by comparison with spectra of the free ligand [13], free and protonated ethylenediamine [14, 15], alkylammonium halides [16], pyridine [17], and other pentacyanoferrate(II) complexes [18, 19].

A distinctive feature of the spectrum of $Na_2[Fe(CN)_5(4\text{-picamH})]\cdot6H_2O$ is the collection of bands between 2750 and 2330 cm^{-1} which confirms the existence in the complex anion of protonated 4-

TABLE I. Water and Iron Analysis

Substance	Water (%)		Iron (%)	
	Calc.	Obs.	Calc.	Obs.
$Na_3[Fe(CN)_5(4\text{-picam})]\cdot2H_2O$	9.02	9.19	14.03	14.03
$Na_2[Fe(CN)_5(4\text{-picamH})]\cdot6H_2O$	24.05	23.80	12.40	12.01
$Na_6[Fe_2(CN)_{10}(4\text{-picam})]\cdot5H_2O$	12.71	12.80	15.76	15.96

TABLE II. Infrared Spectra. Wavenumbers (Kaiser), Relative Intensities[a], and Tentative Assignments[b]

Assignments	$[Fe(CN)_5(4\text{-picamH})]^{2-}$	$[Fe(CN)_5(4\text{-picam})]^{3-}$	$[Fe_2(CN)_{10}(4\text{-picam})]^{6-}$
$\nu(OH_2)$	3550(br,s)	3450(br,s)	3450(br,vs)
$\nu(NH_2)$	3280(sh)		
$\nu(NH_3^+)$, $\nu(CH)$, $\nu(CH_2)$	3020(m)		
	2920(m)	2920(w)	2920(w)
	2820(m)		
NH_3^+ bend. comb.	2740(m)		
	2650(m)	2650(vw)	2650(br,sh)
	2600(m)		
	2530(sh)		
	2460(sh)	2460(vw)	2460(vw)
	2330(vw)		
$\nu(CN)$	2090(s)	2090(s)	
	2050(sh)	2050(vs)	2050(vs)
	2040(vs)	2040(sh)	
$\delta(OH_2)$, $\delta(NH_2)$, $\delta(NH_3^+)$, ν(ring)	1660(sh)		
	1645(sh)		
	1625(s)	1620(s)	1620(s)
	1600(sh)		
	1560(w)	1560(w)	1560(w)
	1520(sh)		
	1510(w)	1505(m)	1505(w)
$\delta(CH_2)$	1470(vw)		
	1455(w)	1455(vw)	
	1430(m)	1430(m)	1425(w)
	1400(m)	1405(w)	
		1395(vw)	
$\omega(CH_2)$, $\tau(CH_2)$, ν(ring)	1375(sh)	1370(w)	1380(w)
	1350(w)	1350(w)	1340(w)
	1335(vw)		
	1320(sh)	1320(w)	1310(vw)
$\rho(NH_3^+)$, $\delta(CH)$, ν(ring), $\nu(CC)$, $\nu(CN)$, $\rho(NH_2)$, $\omega(NH_2)$, $\tau(NH_2)$, $\gamma(CH)$, $\rho(CH_2)$	1260(vw)	1260(vw)	
	1230(w)	1230(w)	1230(vw)
		1210(vw)	
	1155(vw)	1150(vw)	1140(vw)
	1130(vw)	1130(vw)	1125(vw)
	1125(sh)		
	1085(w)	1080(vw)	1095(vw)
	1070(vw)	1070(sh)	1065(vw)
	1055(w)	1045(vw)	
	1030(vw)	1025(vw)	1035(sh)
	1015(vw)	1005(vw)	1010(vw)
	980(vw)		
	960(vw)		960(vw)
		940(m)	
	915(w)	915(sh)	925(vw)
	905(w)		910(sh)
	895(vw)		
	880(sh)		
	840(w)	850(vw)	855(sh)
	800(w)	805(m)	810(w)
$\rho(NH_2)$, $\gamma(CH)$	640(m)	640(w)	640(m)
		615(w)	

(continued overleaf)

TABLE II *(continued)*

Assignments	$[Fe(CN)_5(4\text{-picamH})]^{2-}$	$[Fe(CN)_5(4\text{-picam})]^{3-}$	$[Fe_2(CN)_{10}(4\text{-picam})]^{6-}$
ν(FeC), ν(FeN), $L(H_2O)$, δ(CNN), δ(Fe-ring)	570(s)	570(s)	570(s)
	490(s)	495(m)	495(m)
	460(s)	440(m)	
	430(sh)	420(m)	425(m)
	400(s)	395(m)	395(m)

[a] s, strong; m, medium; w, weak, br, broad; sh, shoulder. [b] ν, stretching; δ, in plane deformation; γ, out-of-plane deformation; ω, wagging; τ, twisting; ρ, rocking; L, libration.

picolylamine [15]. In addition, the shoulder at 1520 cm^{-1} should be considered as due to a deformation band characteristic of the $R{-}NH_3^+$ group [20].

The presence of the NH_3^+ group indicates that 4-picolylamine is pyridine bonded in the mononuclear protonated complex, as expected [19] (not amine bonded as a further possibility [7]).

That the binuclear complex is 4-picolylamine bridged seems to be proved by the lack of a CN-bridged stretching band, in its spectrum, which should appear at higher wavenumber than the unbridged CN-stretchings [21] and, also, by the absence of some of the bands shown by the mononuclear unprotonated complex (1080, 940 and 805 cm^{-1}) which should be due to free NH_2 modes.

Electronic Spectra

The wavelength and molar absorptivity of the absorption peak in the spectrum of $[Fe(CN)_5(4\text{-picam})]^{3-}$ are 365 nm and 2986 M^{-1} cm^{-1}, respectively. These values are in good agreement with the corresponding values for the single peaks found in the spectra of pyridine- and 4-substituted pyridinepentacyanoferrate(II) complexes [1, 22, 23]. These bands are assignable to metal-to-ligand electron transfer [24].

Protonation of the ligand produces a red shift of the absorption band to $\lambda_m = 390$ nm and an increase of intensity ($\epsilon = 3264$ M^{-1} cm^{-1}). This red shift can be explained by the protonation of the NH_2 group which increases the π electron transfer to the ring [24] by inductive effect. This fact suggests, again, that the ligand is pyridine bonded.

The single absorption band at 370 nm in the spectrum of the binuclear complex also shows a red shift and a more important increase of intensity than in the case of the protonated complex ($\epsilon = 4694$ M^{-1} cm^{-1}). The high intensity of the band and the wavelength shift confirms that the bridge is of Fe–L–Fe type rather than Fe–CN–Fe because intensity enhancement is not observed in the latter cases [8, 21] and the wavelength shifts are to the blue.

Diffuse Reflectance Spectra

The position of the bands in the diffuse reflectance electronic spectra are, respectively, 380 nm for the mononuclear non-protonated complex, 388 nm for the binuclear complex and 394 nm for the protonated mononuclear complex. The three spectra exhibit a shoulder at 518 nm.

The shifts of the MLCT bands in solution compared with bands in the reflectance spectra of the mixtures with MgO should be ascribed to solvatochromic effects [25].

Ligand Substitution Kinetics

To ensure pseudo first-order conditions in the kinetics of the substitution of cyanide for 4-picam in $[Fe(CN)_5(4\text{-picam})]^{3-}$, a 10^{-3} M concentration of the leaving ligand was added purposely to the reacting solution. The value found for the first-order rate constant is $(7.8 \pm 0.2) \times 10^{-4}$ s^{-1} [11] which fits in the correlation existing between rate constant and backbonding interaction, as measured by the position of the MLCT band (when λ_m increases k_{-L} decreases [1]) (see Table III).

The affinity of pyridine for $[Fe(CN)_5]^{3-}$ is about five times higher than the affinity of ethylenediamine as measured by the first-order rate constants for the corresponding ligand substitution reactions ($k_{-1}(py) = 11.0 \times 10^{-4}$ s^{-1} [1] and $k_{-1}(en) = 51.5 \times 10^{-4}$ s^{-1} [26]). In the case of 4-picolylamine, where

TABLE III. Electronic Absorption Maxima and First-order Rate Constants for Ligand Exchange in $[Fe(CN)_5L]^{3-}$

L in $[Fe(CN)_5L]^{3-}$	$\bar{\nu}_{max}$ (kKaiser)	$k_{-1} \times 10^4$ (s^{-1})	Reference
4-picoline	28.1	11.5	1
pyridine	27.6	11.0	1
4-picolylamine	27.4	7.8	This work
isonicotinamide	23.0	7.3	1
pyrazine	22.2	4.2	1

$k_{-1} = (7.8 \pm 0.2) \times 10^{-4}$ s^{-1}, the isomer present at equilibrium should be, therefore, pyridine bonded (in agreement with results of the electronic and IR spectra discussed above).

The kinetics of ligand substitution of 4-picamH was measured at pH = 7 (KH_2PO_4–NaOH). Ligand substitution rate was found to be $(9.5 \pm 0.1) \times 10^{-4}$ s^{-1} (at 25 °C and $I = 1.00$ M (NaCl) [11]). The difference with the rate constant for the unprotonated ligand could be explained by solvation effects [27].

The correlation existing between λ_m and k_{-L} for neutral and anionic ligands [28] fails when complexes of the same ligand in different protonation states are compared. For cationic ligands, little is known about the reactivity of the pentacyanoiron(II) complexes. However a correlation can be established between N-methylpyrazinium ($\lambda_m = 662$ nm, $k_{-L} = 2.8 \times 10^{-4}$ s^{-1} [1]) and 4-picamH ($\lambda_m = 390$ nm, $k_{-L} = (9.5 \pm 0.1) \times 10^{-4}$ s^{-1}).

The kinetics of substitution of cyanide for 4-picam in the binuclear complex was also followed, spectrophotometrically, under the same conditions as for $[Fe(CN)_5(4\text{-picam})]^{3-}$ but with the addition of ascorbic acid to the solutions and bubbling deoxygenated nitrogen through them. When oxygen was present in the solution, a new band appeared at 476 nm whose intensity increased during the first minutes of the reaction and then decreased and disappeared. This band may be due to $[Fe(CN)_5(4\text{-cypy})]^{3-}$ [19] produced by terminal oxidation of 4-picolylamine in $[Fe_2(CN)_{10}(4\text{-picam})]^{6-}$ followed by partial hydrolysis.

The experimental rate constant in anaerobic conditions is $(6.3 \pm 0.2) \times 10^{-4}$ s^{-1}, smaller than the value found for the mononuclear complex (see above). This observation does not agree with the expected differences in bonding, as discussed above, between the two active centers of 4-picolylamine and the pentacyanoferrate(II) moiety, making the N(aliphatic)–Fe bond the most labile. A kinetic effect related to the relative differences in sizes between leaving ligands in the mononuclear complex (4-picam) and the binuclear one ($[Fe(CN)_5(4\text{-picam})]^{3-}$), as compared with size of voids of structured solvent water, could explain the smaller dissociation rate constant for the last complex [29].

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