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Preparation and some Properties of 3-, and 4-Cyanopyridinepentacyanoferrate(III)

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Sodium 3-, and 4-cyanopyridinepentacyanoferrate(III) as the trihydrate and monohydrate respectively have been obtained by oxidation with bromine water of the corresponding ferrate(II). Analytical data, UV-visible and infrared spectra are reported for these salts.

Introduction

Some time ago we reported the preparation and properties of solid 3- and 4-cyanopyridine complexes with the pentacyanoferrate(II) and pentacyanocobaltate(III) moieties [1–3], and we also advanced results on the corresponding pentacyanoferrate(III) complexes [1]. Now we wish to report fully on these complexes as the hydrated sodium salts: $Na_2[Fe(CN)_5(3\text{-cypy})]\cdot 3H_2O$ and $Na_2[Fe(CN)_5(4\text{-cypy})]\cdot H_2O$ (cypy = cyanopyridine), respectively.

Experimental

The corresponding Fe(II) complexes, prepared as in [2], were oxidized [1, 4] in 0.5 *M* ice-cooled aqueous solutions with an excess of bromine water added dropwise with continuous stirring. The resultant solutions were concentrated in a rotatory evaporator at room temperature until thick slurries were obtained, which were dissolved with the minimum amount of ethanol and then precipitated with ether. The products were dissolved again in ethanol and reprecipitated with ether. They were kept in a desiccator over calcium chloride.

The purified products were analyzed for iron as before [2]; TGA-DTA data were also obtained as reported earlier [2], as were infrared and UV-visible spectra.

Results

The solids are yellow and rather prone to spontaneous reduction (in this sense the behaviour is rather unpredictable). Good samples could be kept unaltered in the ice box for relatively long periods of time. However, only fresh, well-behaved samples were used for chemical analyses, TGA-DTA and spectra.

Chemical Analyses

The best samples gave the following results (in parentheses: Calcd. %): $Na_2[Fe(CN)_5(3\text{-cypy})]\cdot 3H_2O$; Fe: 12.8(13.52); $Na_2[Fe(CN)_5(4\text{-cypy})]\cdot H_2O$; Fe: 13.8(14.32).

TGA-DTA

Results are gathered together in Table I. The internal redox process leading to the assumed cyanogen evolution occurs in $Na_2[Fe(CN)_5(4\text{-cypy})]\cdot H_2O$ as practically the same temperature as in $Na_2[Fe(CN)_5py]\cdot 3H_2O$ (py = pyridine) [4], while in $Na_2[Fe(CN)_5(3\text{-cypy})]\cdot 3H_2O$ it takes place surprisingly at *ca.* 100 °C higher. The thermal redox process can go spontaneously at room temperature as stated before.

Infrared Spectra

Wavenumbers and intensities as well as tentative assignments (*cf.* [2]) are presented in Table II. Lack of C–N stretching bands from $[Fe(CN)_5]^{3-}$ precludes spontaneous reduction in the samples.

The spectra closely resemble those of the corresponding Co(III) complexes and show the expected shifts in comparison with the Fe(II) spectra [2] due to the differences in the oxidation state of iron and the concomitant differences in σ and π metal-to-ligand bonding [*cf.* 4].

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TABLE I. DTA-peak Temperatures (°C) and Weight-losses (%) (in brackets: measured and calculated values, respectively).

$Na_2[Fe(CN)_5(3\text{-cypy})]\cdot 3H_2O$	$Na_2[Fe(CN)_5(4\text{-cypy})]\cdot H_2O$	Assumed volatile products
70, 85(13.6, 13.9)	40 (5.3, 5.1)	H_2O
281 (6.8, 6.7)	170 }(33.0, 36.6)	$(CN)_2$
314 (24.0, 26.7)	190 }	cypy

TABLE II. Infrared Spectra: Wavenumbers (cm^{-1}) and Relative Intensities.[a]

$Na_2[Fe(CN)_5(3\text{-cypy})]\cdot 3H_2O$	$Na_2[Fe(CN)_5(4\text{-cypy})]\cdot H_2O$	Assignment
3082 vw		ν_{CH}
3064 vw		
2250 s	2255 w	ν_{CN} (nitrile)
2126 vs	2121 vs	ν_{CN}
1606 s	1612 sh	ν_{ring}
	1600 sh	ν_{ring}
	1546 w	ν_{ring}
1474 w	1492 m	ν_{ring}
1418 s	1412 vs	ν_{ring}
1213 m	1228 m	δ_{CH}
	1213 m	
1196 s	1193 w	
1129 m		
1111 m		
1066 m	1061 m	ν_{ring}
1052 w	1025 w	
990 vw	970 vw	ν_{ring}
968 w		
933 w		
821 vs	837 vs	ν_{CH}, δ_{ring}
	782 w	ν_{ring}, H_2O libration
689 vs		
658 w		
557 s	567 vs	ν_{FeCl}, δ_{FeCN}
497 sh		δ_{FeN}, δ_{ligand}
457 sh		H_2O libration, etc.
398 vs	402 vs	
354 sh		

[a] vs: very strong, s: strong, m: medium; w: weak, vw: very weak.

Electronic Spectra

Aqueous solutions of the complex salts gave the spectra features in Table III. The spectra are quite similar to the $[Fe(CN)_5py]^{2-}$ spectrum [4], especially in the high wavenumber region where the first two bands have nearly the same wavenumbers and intensities (for $[Fe(CN)_5py]^{2-}$ CN → M: 415 nm (12), d → d: 368 nm (9.3) [4]). It is to be noted that quite recently Brisset and Biquard [5] have reported for $[Fe(CN)_5(3\text{-cypy})]^{2-}$ a band at 383/392 nm differing from the present results. Differences are greater in the next spectral region where a shoulder at 314 nm [13] in the spectrum of $[Fe(CN)_5py]^{2-}$ was assigned to a py → Fe charge transfer [4] and no feature was observed for $[Fe(CN)_5(3\text{-cypy})]^{2-}$. Also, no bands have been observed in the spectra of the corresponding Co(III) complexes in this region [1, 2]. In the case of $[Fe(CN)_5(4\text{-cypy})]^{2-}$ there is in

TABLE III. Electronic Spectra in Aqueous Solutions: Wavelengths (nm), Intensities[a] and Assignments[b].

	CN → M	d → d	M → cypy	cypy → M	$\pi \rightarrow \pi^*$ [c]
$[Fe(CN)_5(3\text{-cypy})]^{2-}$	412(11)	366(10)		298(22)	246(11)
$[Fe(CN)_5(4\text{-cypy})]^{2-}$	420(11)	360(13)	325(60)	276(49)	220(210)

[a] In brackets: apparent molar absorptivities in $10^{-2} \cdot l \cdot mol^{-1} \cdot cm^{-1}$ units. [b] *cf.* [4]. [c] Intraligand (cypy) $\pi \rightarrow \pi^*$ transitions (see text).

this region a more intense and definite band at a longer wavelength (325 nm), suggesting that it could be due to the Fe → 4-cypy charge transfer which in the $[Fe(CN)_5(4\text{-cypy})]^{3-}$ spectrum appears at 476 nm (55) [1, 2]. The difference in wavelengths should be ascribed to the different oxidation states of iron in both complexes. In any case, this charge transfer is enhanced by the conjugative effect exerted by the nitrile substituent in the *para*-position of the pyridine ring. The additional polarization brought about by this effect could explain the displacement of the band assigned to the cypy → Fe charge transfer towards shorter wavelengths (276 nm) in comparison with $[Fe(CN)_5(3\text{-cypy})]^{2-}$ (298 nm) and $[Fe(CN)_5py]^{2-}$ (314 nm [4]). The decreasing intensities of these bands (49, 22 and 13 [4], respectively) seem to confirm that the cyanide ligand is involved in this transition, its intensity effect being greater when in the more remote position (*para*). The mere inductive effect of the cyanide substituent is seen in $[Fe(CN)_5(3\text{-cypy})]^{2-}$. These tentative assignments leave no features for the d–d transition assigned to the shoulder found at 281 nm (21) in the $[Fe(CN)_5py]^{2-}$ spectrum [4] (this assignment, as well as the others proposed for $[Fe(CN)_5py]^{2-}$ [4], was suggested by results reported in [6]). This leaves for intraligand (cypy) $\pi \rightarrow \pi^*$ transitions the bands found at 246 nm and 220 nm in the $[Fe(CN)_5(3\text{-cypy})]^{2-}$ and $[Fe(CN)_5(4\text{-cypy})]^{2-}$ spectra, respectively, and for metal-to-ligands charge transfers, bands peaking out of the range of our spectrophotometer. The tail of such a band surely increases the apparent intensity of the band at 220 nm in the $[Fe(CN)_5(4\text{-cypy})]^{2-}$ spectrum. In the $[Fe(CN)_5py]^{2-}$ spectrum [4] a shoulder at 252 nm (47) was assigned to a $\pi \rightarrow \pi^*$ (pyridine) transition. This again puts the three complexes in the same spectral order as above (py > 3-cypy > 4-cypy) according now to the wavelengths of ligand (not cyanide) $\pi \rightarrow \pi^*$ transitions. It must be noted that present assignments are somewhat different with respect to those formerly proposed [1] but in any case always on a speculative basis.

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