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3- and 4-Cyanopyridine Complexes of Pentacyanoferrate(II) and Pentacyanocobaltate(III)[+][#]

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The preparation and some properties of complexes of 3- and 4-cyanopyridine with the $Fe(CN)_5^{3-}$ and $Co(CN)_5^{2-}$ groups are described. Visible, IR and NMR spectra indicate a coordination through the pyridine nitrogen.

Introduction

In this work we describe and discuss the structural properties of complexes of 3-cyanopyridine (3cypy) and 4-cyanopyridine (4cypy) with the $Fe(CN)_5^{3-}$ and $Co(CN)_5^{2-}$ moieties.

To our knowledge, only references reporting the kinetic behaviour in solution for some of these complexes are found in the literature [1, 2]. No suggestions have been made about the bonding behaviour of the bifunctional cyanopyridines in these compounds. It is therefore most interesting to determine at which of the two potential sites of coordination of cyanopyridines does the bonding to the metal center occur. Note added in proof. The nitrite-bonded unstable 3-cypy and 4-cypy complexes have been recently detected in aqueous solutions and proved to change rapidly into the stable pyridine-bonded isomers. (A. P. Szecsy, S. S. Miller and A. Haim, private communication).

In what follows, the solid salts $Na_3[Fe(CN)_5(3\text{-}cypy)]\cdot 5H_2O$, $Na_3[Fe(CN)_5(4cypy)]\cdot 10H_2O$, $K_2[Co(CN)_5(3cypy)]\cdot 1.5H_2O$ and $K_2[Co(CN)_5(4cypy)]\cdot 1.5H_2O$ will be referred to as Fe-3cypy, Fe-4cypy, Co-3cypy and Co-4cypy, respectively.

Experimental

All the chemicals used were of analytical reagent grade.

To obtain the corresponding iron complexes, $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ (prepared as in [3]) was allowed to react with a great excess of cyanopyridine in a water–methanol suspension (1:10). The mixtures were stirred at 55–60 °C during ½ to 1 hour. Filtration was made if ammino-complex remained unreacted. Cold ethanol was used as a precipitating agent for the complexes from the mother liquor. The solids were purified as before [4] and kept in a dessicator over KOH *in vacuo*.

The cobalt complexes were obtained by adding to an aqueous solution of $K_3[Co(CN)_5Cl]$ (prepared as in [5]) a great excess of ligand. The reaction mixture was heated at 50 °C during 1 to 1½ hour and then cooled and evaporated *in vacuo* at 40 °C. The excess ligand was extracted with benzene until negative test with picric acid in the washings resulted. The insoluble part was dissolved in a minimum amount of water and reprecipitated with cold ethanol. This operation was repeated until elimination of potassium chloride was achieved, as confirmed by addition of Tl(I) to the previously decanted solution. The solid so obtained was washed as before with ethanol and ether and kept in a vacuum dessicator over potassium hydroxide.

It is to be noted that the iron complexes are very hygroscopic and not very stable at room temperature; however, they can be maintained in the refrigerator unaltered for several weeks. The cobalt complexes do not present these annoying properties. Whenever possible, even with the cobalt complexes, physicochemical measurements were made with fresh samples.

Analytical, conductivity and TGA–DTA data, together with IR, UV–vis and NMR spectra were obtained as in [6].

Kinetic measurements were performed as in [7] using cyanide ion as a scavenger for the $[Fe(CN)_5]^{3-}$ ion and monitoring the absorbance changes at the

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TABLE I. Analytical and Conductivity Results for the Hydrated Alkaline-metal Salts of 3- and 4-Cyanopyridine Complexes with Pentacyanoferrate(II) and Pentacyanocobaltate(III).

Compound	%Fe or %Co		%Na or %K		%H_2O		%cypy		Λ^a (Ω^{-1} mol^{-1} cm^2)
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	
$Na_3[Fe(CN)_5(3cypy)]5H_2O$	12.5	12.0	15.4	15.3	20.0	19.0	23.2	23.0	370
$Na_3[Fe(CN)_5(4cypy)]10H_2O$	10.4	10.0	12.8	12.4	33.4	33.7	19.3	19.6	380
$K_2[Co(CN)_5(3cypy)]1.5H_2O$	14.8	15.0	19.6	19.0	6.9	7.0	26.1	25.7	252
$K_2[Co(CN)_5(4cypy)]1.5H_2O$	14.5	14.3	19.6	21.3	6.9	6.8	26.1	25.7	263

[a] Equivalent molar conductances in water ($c = 10^{-3}$ *M*). For comparison purposes, see: S. Glasstone, "An Introduction to Electrochemistry", Van Nostrand, N.Y. (1942).

TABLE II. Infrared Mull- and KBr-wafer Spectra.[a]

Wavenumbers and Relative Intensities						Description of Modes
3cypy	Fe-3cypy	Co-3cypy	4cypy	Fe-4cypy	Co-4cypy	
	3375 br, s	3400 br, s		3440 br, s	3444 br, s	ν_{H_2O}
3044 w		3080 w	3081 w		3190 w	ν_{CH}
		3060 w	3022 w			
2230 s	2254 m	2249 m	2241 m	2242 m	2249 vw	ν_{CN} (nitrile)
					2176 sh	ν_{CN} (cyanide)
	2040 vs	2133 vs		2050 vs	2120 vs	
					2090 sh	
					2030 vw	
		1700 sh				
	1618 br, s	1670 br, s		1618 br, m	1667 br, s	δ_{H_2O}
1582 s	1580 sh	1600 br, s	1586 s	1560 vw	1600 br, s	ν_{ring}
1557 ms		1568 sh	1537 m		1572 sh	
1468 m	1468 m	1474 m	1490 m	1484 m	1546 m	
1415 s	1411 m	1420 m	1411 m	1402 m	1400 br, m	
		1342 m				?
		1241 w				
1212 m		1215 w	1238 m	1260 m	1221 m	δ_{CH}
1204 m	1207 mw	1204 sh	1202 m	1210 w	1142 vw	
1184 m	1191 mw	1196 s				
1125 w	1108 vw	1114 m	1110 m		1114 w	
1063 w		1066 m				
1034 m		1032 w				
1020 s		998 m	1080 s	1080 vw	1059 s	ν_{ring}
972 m		975 m	1075 sh			
934 m	929 vw	927 m	985 m	1015 w	976 vw	
		830 sh				?
806 vs	807 s	814 s	825 vs	822 m	852 s	ν_{CH}, ν_{ring}, δ_{ring}, H_2O libration
779 m		742 w			834 m	
		721 w	778 vs		766 s	
695 s	688 m	687 s			671 sh	
628 s		620 w	664 w		621 sh	
557 s	571 ms	561 m	560 vs	564 m	565 br, s	Fe–C and Fe–N stretchings, FeCN, Fe N< and ligand deformations, H_2O librations *etc.*
475 m	466 m	458 w		478 vw	461 vs	
		425 sh			404 vs	
395 ms	390 vs	412 s	370 m	432 vw	370 vs	
359 m		362 m			272 vs	

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak. ν, stretching; δ in-plane deformation; γ, out-of-plane deformation.

TABLE III. Nitrile Stretching Frequencies.

Complex	ν_{CN}	$\Delta\nu_{CN}$[a]
Fe-3cypy	2254	+24
Co-3cypy	2249	+19
Fe-4cypy	2242	+ 1
Co-4cypy	2249	+ 8

[a] $\Delta\nu_{CN} = \nu_{CN}$ (complex) – ν_{CN} (free ligand).

λ_{max} of the initial complexes. Chosen experimental conditions were: t = 25.0 °C, I = 1 *M* (NaCl), [complex] = 2 × 10^{-4} *M*, [cypy] = 2 × 10^{-3} *M*, [KCN] = 0.1 *M* and pH *ca.* 10.

Results and Discussion

Analytical and Conductivity

In Table I the analytical and conductivity results for the four complexes are shown. They agree with the given formulas.

IR Spectra

The wavenumbers of the infrared absorption bands as well as their descriptions and assignments are presented in Table II for the complexes and the free ligands. Assignments are in accordance with previous work [4, 8] and with the report of Spinner [9] about the cyanopyridines.

Most interesting in the IR spectra are the shifts in the ligand bands, which can be used to elucidate the site of coordination of the cyanopyridines. In complexes of these ligands with transition metals [10–12] the bonding through the pyridine nitrogen causes an increase in the nitrile stretching wavenumber in the 2cypy and 3cypy complexes, while in those of 4cypy this value remains unchanged. Nitrile coordination also shifts this band to the blue [13]. However, in most of the complexes bonding occurs by the aromatic nitrogen, as demonstrated by the blue shifts of pyridine bands.

In complexes of cyanopyridines with pentaamminoruthenium(II), coordination takes place through the nitrile group and negative shifts in the nitrile wavenumbers are observed [14]; this last phenomenon has also been noted in similar complexes with benzonitrile and acetonitrile [15]. This lowering, although unusual, was attributed to a strong π back-bonding Ru → nitrile.

As the $Fe(CN)_5^{3-}$ and $Ru(NH_3)_5^{2+}$ moieties present strong analogies in their properties [16], coordination of cyanopyridines with $Fe(CN)_5^{3-}$ through the nitrile would also be expected. The spectral data show, however, that the reverse is true. In Table III it is seen that while the nitrile wavenumber does not change in the 4cypy complexes, it slightly increases in the 3cypy complexes.

TABLE IV. DTA data for the Release of Water and Cyanopyridines[a].

Species	Peak Temperatures (°C) and Description (DTA)	Products
Fe-3cypy	75 s, endo	H_2O
	189 m, endo	3cypy
Fe-4cypy	49 s, 64 s, 114 w, endo	H_2O
	184 m, endo	4cypy
Co-3cypy	56 s, endo	H_2O
	280 m, endo	3cypy
Co-4cypy	70 s, br, endo	H_2O
	256 m, endo	4cypy

Peak description: s = strong; m = medium; w = weak; br = broad

[a] For TGA data, see Table I.

The ring stretching bands of the cyanopyridines in the region 1400 to 1600 cm^{-1} appear at higher energies in the cobalt complexes than in the free ligand, and this confirms an electron donation of the pyridine nitrogen to the Co(III) nucleus [11]. The same bands do not shift at all in the iron complexes but this may be due to the greater π back-donation of iron as compared to cobalt. The in-plane deformation modes near 1200 cm^{-1} also change to the blue in the iron complexes; for other bands, the shifts are not so evident.

Anyway, it seems safe to deduce that bonding of cyanopyridines to the $M(CN)_5^{n-}$ moieties here considered occurs through the ring nitrogen. This fact is further substantiated by the failure in preparing the corresponding complexes with benzonitrile and acetonitrile. The difference in behaviour of the iron complexes as compared to the ruthenium ones may be due to the different charges of the moieties coordinated to the cyanopyridines. In other complexes already reported of iron with strong π acceptors such as dimethylglioxime [17], the bonding to 4cypy was also suggested to take place by the pyridine nitrogen.

TGA–DTA

DTA results are presented in Table IV. The corresponding changes in weight have been presented in Table I. It is noteworthy that the iron complexes lose the cyanopyridines at temperatures slightly lower than the temperature at which pyridine is evolved from $[Fe(CN)_5py]^{3-}$ (~200 °C, [18]), hinting again a bonding through the ring nitrogen. For the cobalt complexes, pyridine and the cyanopyridines are released at temperatures (py ~300 °C) which are 50 to 100 °C higher than those for the iron complexes. This explains the observed lower stability of the iron complexes with respect to the cobalt ones at room temperature; it also proves the preponderance of σ-bonding over π-bonding.

TABLE V. Electronic Spectra.

Species	λ_{max} (nm)	ϵ_{max} ($l\ mol^{-1}\ cm^{-1}$)	pH	Assignment
Fe-3cypy	413	3432	8	$d_\pi(Fe) \rightarrow \pi^*$ (3cypy)
	383	2923	2	
Fe-4cypy	476	5481	8	$d_\pi(Fe) \rightarrow \pi^*$ (4cypy)
	437	3768	2	
Co-3cypy	355	260	7	$^1A_1 \rightarrow {}^1E_a$
	355	252	2	
	278	1570	7	$\pi \rightarrow \pi^*$, $d_\pi(Co) \rightarrow \pi^*$(3cypy)
	214	19955	7	$d_\pi(Co) \rightarrow \pi^*$(CN)
Co-4cypy	352	255	7	$^1A_1 \rightarrow {}^1E_a$
	353	249	2	
	264	4608	7	$\pi \rightarrow \pi^*$, $d_\pi(Co) \rightarrow \pi^*$(4cypy)
	212	20161	7	$d_\pi(Co) \rightarrow \pi^*$ (CN)

Electronic Spectra

The electronic bands and their assignments for the four complexes are shown in Table V. Fe-3cypy and Fe-4cypy present strong absorptions at 413 and 476 nm respectively resulting from a charge transfer t_{2g} (Fe) → π^* (cypy) (*cf.* [4, 16]). The λ_{max} and ϵ_{max} values fit very well in the sequence builded by Toma and Malin [16] for complexes of the pentacyanoferrate(II) moiety with substituted pyridines. The ordering of the complexes on the basis of increasing band energies (Fe-4cypy < Fe-3cypy < Fe-py) reflects a decreasing order of π-backdonation which in turn agrees with the nitrile group being a powerful electron-withdrawing substituent, more effective in position 4 than in position 3. A nitrile-coordination would shift this band 50–100 nm below the actually observed values (*cf.* [14]). Besides, the shifts of the band maxima to greater frequencies and the decrease in absorptivities produced when the pH is diminished (see Table V) are consistent with the trend observed for other pentacyano(substituted pyridine)ferrates(II) and can be interpreted by the protonation of the cyanides bonded to iron [16]. No changes with pH are observed for the pentacyanocobaltates as due to the poor back-bonding ability of the cobalt nucleus.

Co-3cypy and Co-4cypy exhibit weak bands at 355 and 352 nm respectively which can be adscribed to a d–d transition of the $^1A_1 \rightarrow {}^1E_a$ type. The λ_{max} and ϵ_{max} values nearly coincide with those for the pyridine complex [4] and so the three ligands can be placed between NH_3 and NCS^- in the spectrochemical series [19].

Strong absorptions in the UV are due to charge transfer Me → CN^- and intraligand $\pi \rightarrow \pi^*$ bands.

PMR Spectra

Proton chemical shifts for the complexes in D_2O and literature values for the cyanopyridines in dimethylsulfoxide are shown in Table VI.

The α-protons in the iron complexes are displaced downfield when compared to the free ligands, while an upfield shift is observed for the β- and γ-protons. A general agreement with previous results for pyridine and other pentacyano(substituted pyridine)-ferrates is found [4, 20]. It is to be noted, however, that the pyridine α-protons in $[Fe(CN)_5py]^{3-}$ are not shifted with respect to the free ligand when

TABLE VI. PMR Spectra. $\delta(^1H)$ in ppm, Relative to DSS.

	3cypy[a]	Fe-3cypy	Co-3cypy	4cypy[a]	Fe-4cypy	Co-4cypy
α-protons	9.22 9.09	9.32 9.20	9.20 9.06	9.05	9.20	9.04
β-protons	7.81	7.40	7.75	8.00	7.45	7.81
γ-protons	8.47	8.07	8.36			

[a] Taken from W. Brügel, *Z. Elektrochem.*, *66*, 159 (1962).

referring to a cyclohexane solution of pyridine [4] instead of a water solution [20]. Our discussion is therefore restrained to the β-protons and the results in Table VI seem to confirm once again a coordination through the ring nitrogen.

The shifts of the β-protons for the iron salts are higher than the corresponding shift in the pyridine complex and lower than in the methylpirazinium ($MePz^+$) complex. The data thus disclose an increasing order of π-backdonation:

$$\text{Fe-py} < \text{Fe-3cypy} < \text{Fe-4cypy} < \text{FeMePz}^+,$$

a trend also reflected by the energy of the charge transfer bands, as shown in Table VII. Stronger π-backbonding produces a higher "shielding" effect [20] and so greater $\Delta\delta$ values are observed when the electron-withdrawing power of the pyridine ring is enhanced.

TABLE VII. Correlation between Absorption Maxima in the Visible and Proton Chemical Shifts for $[Fe(CN)_5L]^{3-}$ Complexes.

L	λ_{max} (nm)	$\Delta\delta$ (ppm)^a	Ref.
py	362	0.19	4
3cypy	413	0.41	this work
4cypy	476	0.55	this work
$MePz^+$	655	1.15	16, 20

$^a\Delta\delta = \delta$(β-protons in free ligand) $- \delta$(β-protons in complex).

Upfield shifts were also found for the β- and γ-protons in the cobalt complexes, but of magnitudes lower than for the iron complexes. However, in pentacyanopyridinecobaltate(III) [4] the β- as well as the γ-protons suffer downfield shifts. The difference with the cyanopyridine complexes might be adscribed to the lower basicity and better π-acceptor properties conferred to the pyridine ring by the cyano substituent.

Ligand Exchange Kinetics

If the visible spectral data are correlated with the rate constants for the release of cyanopyridines from the $[Fe(CN)_5]^{3-}$ moiety, the following order of limiting rate constants is expected:

$$k_{py} > k_{3cypy} > k_{4cypy}$$

Results presented in Table VIII show a different trend ($k_{3cypy} > k_{py} > k_{4cypy}$). The values of the limiting pseudo-first-order rate constants k_{3cypy} and k_{py} agree with results obtained by other authors ([1] and ref. of Table VIII).

TABLE VIII. Rate Constants for the Release of L from $[Fe(CN)_5L]^{3-}$.

L	10^3 k_{-L} (sec^{-1})	Ref.
3cypy	2.5	this work, 1
py	1.1	a
4cypy	0.5	this work^b

^{a}Taken from A. D. James and R. S. Murray, *J. Chem. Soc. Dalton,* 1530 (1975). ^{b}Note added in proof: a value of 1.02×10^{-3} sec^{-1} has been recently found by A. P. Szecsy, S. S. Millar and A. Haim (private communication).

The unexpectedly high rate constant for the release of 3cypy as compared with py could be accounted for by steric crowding of the nitrile group with the adjacent cyanides bonded to iron. A solvation effect, however, may not be discarded as was actually put into evidence for other pentacyano(ligand)ferrates [21].

We conclude from the analysis of DTA, IR, UV–vis and NMR results that the proposed bonding mode is correct.

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