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Synthesis and Spectral Properties of Mixed Binuclear Complexes Derived from the Ion Pentacyano(4,4'-bipyridine)ferrate(II)

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New complex analogous to Prussian Blue were synthesized both in solid phase and in aqueous solution by mixing the sodium salt of pentacyano(4,4'-bipyridine)-ferrate(II) with Cu(II) and Fe(III) salts. Infrared and visible spectral data of these compounds indicate formation of a polymeric structure involving a cyanide bridge that connects the two metallic centers. Preference of cyanide over 4,4'-bipyridine bridging can be explained on the basis of its greater basicity when coordinated to a pentacyanoferrate(II) moiety.

Synthese und spektroskopische Eigenschaften gemischter zweikerniger, von Pentacyano(4,4'-bipyridin)ferrat(II) abgeleiteter Komplexe

Durch die Reaktion von Natrium-pentacyano(4,4'-bipyridin)-ferrat(II) mit Cu(II)- und Eisen(III)-Salzen entstehen neue Substanzen, die sowohl in der festen Phase wie auch in wäßriger Lösung mit Preussisch Blau verwandt sind. Die Spektren (IR und sichtbarer Bereich) zeigen die Bildung polymerer Strukturen durch Cyanidbrücken zwischen den Metallatomen. Die Bevorzugung der Cyanid-Liganden zur Brückenbildung gegenüber 4,4'-Bipyridin wird durch die höhere Basenstärke erklärt.

(Keywords: Prussian blue analogues; Cyanide bridging; Cyanoferrate complexes)

Introduction

Interest in studying binuclear complexes stems from their role in intramolecular electron transfer reactions and in phenomena related to

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colloidal chemistry[1–3]. In particular, the association of cyanoferrate complexes with Fe(III) has allowed the preparation of insoluble compounds, called Prussian Blue analogues, that can be used as inorganic pigments[4], while the reactions with Cu(II) are simple models for similar biological interactions, such as those occuring in some enzymes[5]. *Toma*[2] has studied the intervalence bands for a variety of cyanoferrate complexes, characteristic of coordination compounds with bridging ligands. In order to extend these studies and our recent findings on bridged systems[6], we have carried out a research on the synthesis and spectral properties of complexes of pentacyano(4,4′-bipyridine)ferrate(II) with Cu(II) and Fe(III) ions. We have attempted to elucidate which of the potential bidentate ligands, the cyanide group or the aromatic heterocycle 4,4′-bipyridine $[N(C_2H_2)_2C—C(C_2H_2)_2N]$ is bridging the metal centers in the above mentioned compounds.

Experimental

The used reagents were of analytical grade and tridistilled water was used throughout. The solid dihydrate sodium salt of the ion $Fe(CN)_5BP^{3-}$ (*BP* = 4,4′-bipyridine), **I**, was obtained as in Ref.[7].

Visible spectra of aqueous solutions of this complex with Cu(II) and Fe(III) were obtained by adding increasing quantities of $CuSO_4 \cdot 5\,H_2O$ and $FeCl_3 \cdot 4\,H_2O$ to a fixed quantity of **I**, in the concentration range of 10^{-4} *M*. No flocculation was observed up to a molar relation less than 1. The spectra were stable during one hour and did not change appreciably with excess *BP*. In order to obtain the solid salts, excess aqueous solutions of Cu(II) and Fe(III) ions were added to a 0.05 *M* solution of **I**. After one hour, the resulting precipitate was filtered off, washed with water, ethanol and ether and dried in a dessicator over KOH.

A Perkin-Elmer Coleman 124 spectrophotometer was used to record visible spectra from 340 to 800 nm. Infrared spectra were recorded in the range 4000–200 cm^{-1} as KBr pellets on a Perkin-Elmer 580 B IR spectrophotometer. Reflectance spectra were obtained with a Shimadzu UV-300 spectrophotometer in the range 200–800 nm using MgO as reference.

Results and Discussion

For the species studied in this work, we expected to detect intervalence electron transfer bands (IVET) from Fe(II) to Cu(II) or to Fe(III), as characteristic of Prussian Blue and other complexes with bridging ligands[2]. In this case, the IVET band is masked by the strong metal-to-ligand electron transfer band (MLCT) from a $d_{\P}$ orbital of Fe(II) to an empty $\P^*$ orbital of the ligand *BP* in the Cu(II) complex, while it appears near 800 nm in the Fe(III) complex. However, some conclusions may be drawn from the observed shifts of the MLCT bands.

Fig. 1 shows the visible spectra of aqueous solutions containing 1 ·

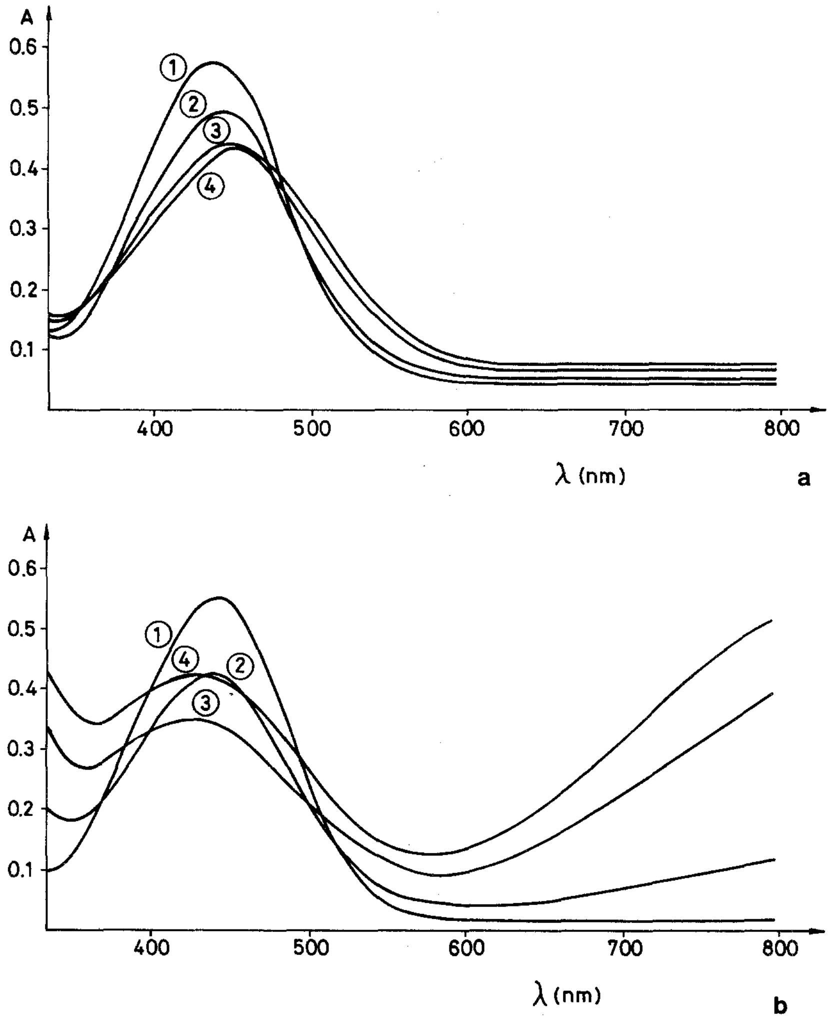

Fig. 1. Visible spectra of aqueous solutions containing $1\cdot10^{-4}$ *M* of $Fe(CN)_5$ BP^{3-}: (a) with increasing quantities of Cu(II) ions, (1) 0 *M*, (2), $0.5\cdot10^{-4}$ *M*, (3) $1.2\cdot10^{-4}$ *M*, (4) $1.5\cdot10^{-4}$ *M*, and (b) with Fe(III) ions, (1) 0 *M*, (2) $0.5\cdot10^{-4}$ *M*, (3) $1.2\cdot10^{-4}$ *M*, (4) $1.5\cdot10^{-4}$ *M*

10^{-4} *M* of **I** with increasing concentrations of Cu(II) (a) and Fe(III) (b). A small bathochromic shift with intensity loss is observed for the MLCT band of the binuclear species formed by association of **I** with Cu(II), while an hypsochromic shift, also with intensity loss, is observed for the same band corresponding to association of **I** with Fe(III).

Table 1. *Maximum wavelengths and extinction coefficients for the* MLCT *bands of binuclear complexes formed by association of* $Fe(CN)_5BP^{3-}$ (**I**) *and M*

Complex	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})	Reference
I	432	$5.6 \cdot 10^3$	8
I + $Fe(CN)_5^{3-}$	452	$13 \cdot 10^3$	8
I + $Co(NH_3)_5^{3+}$	505	$6 \cdot 10^3$	1
I + $Ru(NH_3)_5^{2+}$	497	—	10
I + $Rh(NH_3)_5^{3+}$	481	$5.4 \cdot 10^3$	9
I + $Co(CN)_5^{2-}$	454	$5.7 \cdot 10^3$	9
I + Cu(II)	455	$\sim 4.3 \cdot 10^3$	this work
I + Fe(III)	425	$\sim 4.1 \cdot 10^3$	this work

It is well known that electron acceptors coordinating to the remote N of *BP* in $Fe(CN)_5BP^{3-}$ ion cause a shift to greater wavelengths of the MLCT band[1], as indicated in Table 1. These bathochromic changes are of considerable magnitude (varying from 20 to 70 nm) and, at the same time, an intensity gain is observed[8]. On the other hand, protonation of cyanide groups leads to a shift to lower wavelengths with simultaneous intensity loss, because of the greater degree of ¶ backbonding from Fe(II) to protonated cyanide[7].

Besides, lack of isosbestic points in Fig. 1 indicate complex equilibria, possibly involving both types of association. However, by taking the above mentioned facts into account, we can deduce that a cyanide bridge is connecting complex **I** with Fe(III), while an association through both *BP* and CN^- seems to be operative in the complex of **I** with Cu(II). In this latter case, the intensity loss and the small bathochromic shift (ca. 20 nm) points to greater proportion of cyanide bridges.

Data from reflectance spectra for both binuclear complexes show that the broad MLCT bands are shifted to lower wavelengths with respect to the monomer complex **I**, thus evidencing formation of a cyanide bridge between both metallic centers in solid phase.

The obtained solid compounds were non-crystalline and insoluble in water. They could be identified as $Cu_3[Fe(CN)_5BP]_2 \cdot xH_2O$ and $Fe[Fe(CN)_5BP] \cdot xH_2O$ by analyses of their visible and IR spectra. They have not been reported previously in the literature. Chemical analyses were not carried out due to problems existing in the analyses of cyanide complexes[11]. Preparations were carried out in a similar way to that of *Fluck* et al.[4], so that the proposed formulas should be correct. These compounds are Prussian Blue analogues, must be polymeric in view of their insolubility and often contain 8–14 molecules of water per formula

Table 2. IR *spectra of 4,4'-bipyridine dihydrate* (A), $Na_3[Fe(CN)_5BP] \cdot 2\,H_2O$ (B), $Cu_3[Fe(CN)_5BP]_2 \cdot xH_2O$ (C), *and* $Fe[Fe(CN)_5BP] \cdot xH_2O$ (D)[a]

A	B	C	D	Assignments
	3 565	3 550		ν_{H_2O}
3 420 vs	3 445 s, br	3 440 s, br	3 400 s, br	
3 250 vs	3 273	3 300	3 200	
3 050 w				ν_{CH}
	2 093 sh	2 150 sh	2 120 sh	ν_{CN}
	2 048 vs	2 090 vs, br	2 060 vs, br	
1 690 vw	1 637 m	1 660 m	1 640 m	δ_{H_2O}
1 650 vw				
1 600 vs	1 605 w	1 610 m	1 613 m	ν_{ring}
1 545 w	1 534 vw	1 535 vw	1 537 vw	
1 490 vw	1 488 w	1 488 w	1 492 w	
1 415 m	1 410 w	1 415 w	1 410 w	
	1 388 vw			
1 325 vw	1 325 vw	1 325 vw	1 325 vw	
1 225 s	1 224 vw	1 223 vw	1 224 w	δ_{CH}
1 100 vw		1 190 vw	1 135 vw	
		1 100 m	1 125 vw	
1 080 w	1 073 vw	1 065 w	1 065 w	
1 045 vw	1 020 vw	1 020 vw	1 023 vw	ν_{ring}
990 m		953 w	927 vw	
	825 w	898 w		
810 vs	804 w	815 w	815 w	γ_{CH}
		765 vw		ν_{ring}
740 vw	730 vw	725 w	725 w	
635 m		640 w	637 w	δ_{ring}
615 m	615 vw	620 w		
	578 w	585 w	584 w	δ(FeCN) + ν(FeC) + δ(FeCNM) + *BP* vibr.
575 w	505 vw	525 sh	517 m	
510 w	430 vw	480 m	480 m	
370 w	403 vw	400 vw	400 vw	

[a] Wavenumbers are in cm^{-1}.

Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, ν = stretching, δ = in-plane bending, γ = out-of-plane bending.

unit[12]. Table 2 shows IR spectral data for both complexes; data corresponding to the free ligand *BP* and of the monomer complex **I** (also not previously reported) have been included for comparison purposes. Reported data are mean values of different samples. The obtained reproducibility error was $\pm 3\,cm^{-1}$. The proposed assignments are tentative and have been made on the basis of previous works[4, 13—15].

In the region of cyanide stretchings, very broad bands are observed in the binuclear complexes of **I** with Cu(II) and Fe(III), which are shifted to higher wavenumbers with respect to the mononuclear species. This is a first evidence of a polymeric structure, with cyanide bridges, similar to Prussian Blues[4, 13, 16]. Indeed, ν(CN) increases with the oxidation state of the metal about 45–55 cm^{-1} because of electron drain from the occupied antiligant orbital σ_s^* of CN$^-$ [17, 19]. Two different frequencies corresponding to terminal and bridging cyanides are usually observed in similar systems[20]. As shown in Table 2, shoulders appear at 2 150 and 2 120 cm^{-1} for the Cu(II) and Fe(III) binuclear complexes respectively, which can be assigned to bridging cyanide stretchings. The strong bands centered at 2 090 and 2 060 cm^{-1} for the same complexes can be assigned to terminal cyanide stretchings. In a recent work[6], we found that bands at 2 115 and 2 055 cm^{-1} for the complex $Na_6[Fe(CN)_5(4\text{-}cypy)]_2 \cdot 3\,H_2O$ (4-*cypy* = 4-cyanopyridine) should be attributed to bridging and terminal cyanide stretchings, respectively. The broadening of the cyanide stretchings band must be due to the overlapping of various ν(CN) bands, as already observed[21] in cyanide bridged complexes formed by Cu(II) complexes and $Fe(CN)_6^{4-}$.

Bands due to *BP* vibrations are very altered in intensities but slightly changed in wavenumbers, when comparing the coordinated ligand to the free one (see Table 2). A similar behaviour was observed in other complexes of *BP*[15]. New bands appear in the binuclear complexes, probably because of lowering of the ligand symmetry. Moreover, bands assigned to ring vibrations of *BP* are not shifted, within experimental error, in the Cu(II) and Fe(III) salts of **I** with respect to the sodium salt of **I**, thus confirming that CN$^-$ and not *BP* is bridging the metallic centers in the solid compounds.

Shifts to higher wavenumbers are observed for bands due to ν_{FeC} and δ_{FeCN} in the 600–400 cm^{-1} zone, when going from the sodium salt to the Cu(II) and Fe(III) complexes. Possibly, the Fe—C bond is strengthened when forming these latter salts[4].

From visible and infrared spectral data we deduce a tridimensional structure for the solid complexes under study, with an ambidentate coordination for CN$^-$, leading to the four-atom sequence M—C$\equiv$N—M' (with M = Fe^{II} and M' = Cu^{II} or Fe^{III}). A small electron delocalization is expected[12].

Preference for formation of cyanide bridges can be explained not only on a statistical basis but also by considering that *BP* complexed to $Fe(CN)_5^{3-}$ must be much less basic than free *BP*, because the cyanide groups complete for electrons causing a decrease of electron density in the aromatic ring. As already noted in a similar complex with pyrazine[11], the pK_a of an aromatic ligand coordinated to the $Fe(CN)_5^{3-}$ moiety decreases nearly 10 times, so that a value between 0.3 and 0.4 is expected for the pK_a

of bonded *BP*. On the other hand, basicity of a coordinated cyanide is an order of magnitude greater; its pK_a being[7] near 2.

We then conclude that a cyanide bridge is connecting the metallic centers in the new solid complexes studied, because coordinated CN^- is nearly 50 times more basic than coordinated *BP*. A *BP* bridge occurs when the second metallic group is a strong ¶-donor, such as $Fe(CN)_5^{3-}$ or $Ru(NH_3)_5^{2+}$[8,10]. Cu(II) and Fe(III) are weak ¶-donors to Fe(II), so that σ-bonding effects must be considered. The bridged complexes described in this work can be precursors in electron transfer reactions.

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