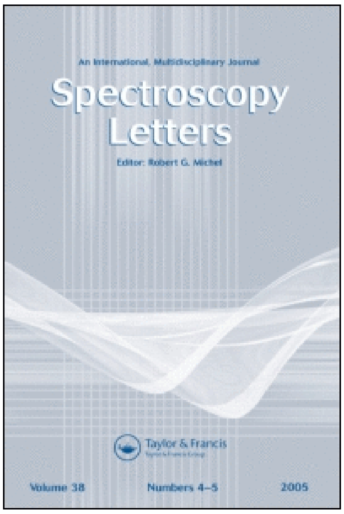

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Spectrophotometric Studies of Cyano-Bridged Complexes of the Type $[(Dien)\ M(II)\text{-}\mu\text{-}NC\text{-}Fe(III)(CN)_5]^-$

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SPECTROPHOTOMETRIC STUDIES OF CYANO–BRIDGED COMPLEXES OF THE TYPE $[(DIEN)M(II)–\mu–NC–Fe(III)(CN)_5]^-$

Keywords: Cyano–bridged complexes, Infrared spectroscopy, Electron spectroscopy

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ABSTRACT

Three kinds of new M(II)–μ–NC–iron(III) cyano–bridged complexes $[(dien)M–NC–Fe(CN)_5]^-$ (M = Ni, Co, Cu) have been synthesized and characterized by elemental analysis, IR, UV–vis spectral analysis. The formation of cyano–bridges is evident from the IR and UV–vis spectra by appearance of $\nu_{(C\equiv N)}$ shifts and changes in λ_{max} with respect to the mononuclear parent complex $[Fe(CN)_6]^{3-}$.

INTRODUCTION

Binuclear metal complexes with extended bridged structures are of current interest due to charge transfer, energy transfer and spin–exchange between metal ions[1], cyano–bridged polynuclear complexes are excellent building blocks for the construction of such devices to obtain molecules capable of accomplishing specific functions, especially for collection of electronic energy or electronic charge[2]. Dinuclear complexes with a μ–cyano ligand can be prepared by solid state heating of the previous mixed complex salts or by reaction in solution from the corresponding mononuclear ions. The first well characterized example was $[(NH_3)_5Co{-}CN{-}Co(CN)_5]$ obtained by reaction of the species $[Co(CN)_5(H_2O)]^{2-}$ and $[Co(NH_3)_5(CN)]^{2+}$ in solution[3]. Morpurgo[4] had reported the cyano–bridged complexes from $[Fe(CN)_6]^{4-}$. We reported the preparation from $[Fe(CN)_6]^{3-}$ and spectroscopic study.

EXPERIMENTAL

Materials and Methods

The cyano–bridged complexes $K[(dien)(H_2O)_2Co{-}NC{-}Fe(CN)_5]$ (**1**), $K[(dien)(H_2O)_2Ni{-}NC{-}Fe(CN)_5]$ (**2**) and $K[(dien)Cu{-}NC{-}Fe(CN)_5]$ (**3**) were prepared by the reaction of a M(II) salt, dien and $K_3[Fe(CN)_6]$ in the 1:1:1 mole ratio in aqueous solution (dien = diethylenediamine).

IR spectra were recorded on Nicolet 5DX FTIR spectrophotometer as KBr pellets. UV–vis spectra were obtained with Schimadzu UV–3100 spectrophotometer.

RESULTS AND DISCUSSION

The formation of the new cyano–bridged complexes was simplely illustrated by following equation which is a polymergation reaction between mononuclear M(II) complexes and mononuclear complex $K_3[Fe(CN)_6]$:

$$[M(dien)(H_2O)_3]^{2+} + [Fe(CN)_6]^{3-} = [(dien)(H_2O)_2M{-}NC{-}Fe(CN)_5]^{-} + H_2O$$

The formation of cyanide bridges is suggested by substitution reaction that one water molecule in the M(II) complexes is replaced by terminal nitrogen atom of cyanide in the complex anion $[Fe(CN)_6]^{3-}$.

Figure 1 shows the IR spectra of the cyano–bridged complex **3**. The IR spectrum of the mononuclear parent compound $K_3[Fe(CN)_6]$ showed a band at 2114cm^{-1}. The formation of cyanide bridges in the polynuclear complexes was confrimed by the IR spectra in the region of the stretching vibration of the cyanide ligands. The cyanide frequencies of cyano–bridged complexes and mononuclear complex $K_3[Fe(CN)_6]$ from the IR spectra are listed in Table 1. The assignments of bridging versus terminal cyanides for the polynuclear complexes are based on the comparison with $K_3[Fe(CN)_6]$.

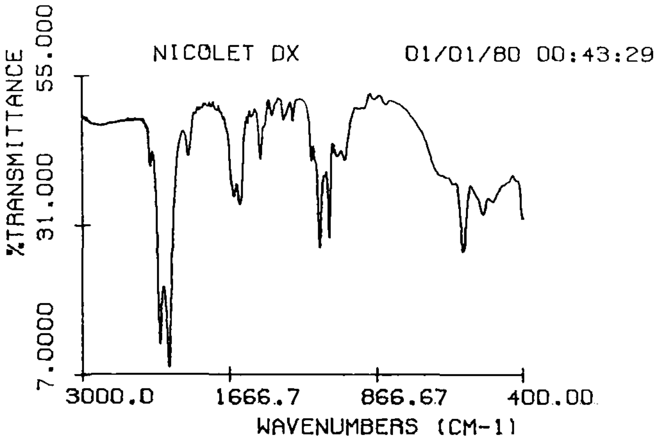

Fig.1 IR spectrum of K[(dien)Cu–NC–Fe(CN)$_5$]

Table 1 Cyanide stretching frequencies(cm^{-1}) of mononuclear and polynuclear cyano–bridged complexes

	Complex	terminal–CN band ν_{CN}	bridged–CN band ν_{CN}
	$K_3[Fe(CN)_6]$	2114	
1	$K[(H_2O)_2(dien)Co{-}NC{-}Fe(CN)_5]$	2117	2172
2	$K[(H_2O)_2(dien)Ni{-}NC{-}Fe(CN)_5]$	2108	2155
3	$K[(dien)Cu{-}NC{-}Fe(CN)_5]$	2116	2172

For the dimers based on $K_3[Fe(CN)_6]$ bridged cyanide stretching frequencies are typically observed at 35–70cm^{-1} higher than ν_{CN} of mononuclear complex $K_3[Fe(CN)_6]$. This may be explained by the simple mechanical constraint on the CN motion imposed by the presence of the second metal center M(II). (Cu(II), Co(II), Ni(II)). This effect is expected to always be present and to shift ν_{CN} to higher frequency upon bridge formation[5].

The electronic spectra data of the cyano–bridged complexes and the reference complexes are listed in Table 2. The formation of cyanide

Table 2 Electronic spectral data of complexes

Complex	λ_{max}(nm)
$K_3[Fe(CN)_6]$	420
$[Co(dien)(H_2O)_3]^{2+}$	468
$[Co(dien)-NC-Fe(CN)_5]^-$	438
$[Ni(dien)]^{2+}$	575
$[Ni(dien)-NC-Fe(CN)_5]^-$	435
$[Cu(dien)]^{2+}$	613
$[Cu(dien)-NC-Fe(CN)_5]^-$	440

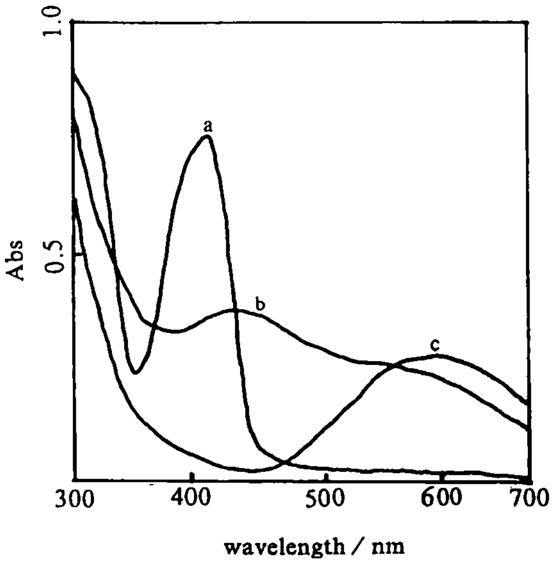

Fig.2 Electronic absorption spectra of

a) $K_3[Fe(CN)_6]$ (1×10^{-4}M)

b) $K[(dien)Cu-NC-Fe(CN)_5]$ (1.1×10^{-4}M)

c) $Cu(dien)(ClO_4)_2$ (1.5×10^{-4}M) bridges was accompanied by the appearance of a new band at 438, 435, 440 nm (Table 2), which is not a counterpart in both mononuclear complexes, is solely due to the product cyano–bridged complexes. The $K_3[Fe(CN)_6]$ complex exhibits a visible absorption with minimum energy at $\lambda_{max} = 420$ nm in aqueous solution, the complete spectrum is shown in Fig 2a. The visible band should include $d\pi(Fe) \rightarrow \pi^*(CN)$ MLCT (metal–to–ligand charge–transfer) transitions. The electronic spectrum of K[(dien)Cu–NC–Fe(CN)$_5$] in water solution is presented in Fig 2b. The band of minimum energy with respect to the mononuclear parent complex $K_3[Fe(CN)_6]$ can be explained on the basis of bridge formation.

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