Resonance-Raman and Infrared Studies of Cyanide-bridged Dimetal Complexes

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Raman and i.r. spectra have been determined in the ν(CN) region of the CN-bridged dimetal complex anions $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ and $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$. The spectra show bands at 2 130 and 2 185 cm^{-1}, respectively, which are assigned to the stretching modes of the bridging CN groups. Similar modes are assigned at 2 134 and 2 182 cm^{-1} in the spectra of the two short-lived reaction intermediates $[(NC)_5Fe^{II}(CN)Co^{III}(edta)]^{5-}$ and $[(NC)_5Fe^{III}(CN)Co^{III}(edta)]^{4-}$, respectively (edta = *NNN'N'*-ethylenediaminetetra-acetate). The terminal CN stretching modes all occur at much lower wavenumbers. ν(CN) Raman bands of the bridging group in both $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ and $[(NC)_5Fe^{II}(CN)Co^{III}(edta)]^{5-}$ show resonance enhancement associated with the absorption bands at 395 and 565 nm, respectively, indicating that these bands may be assigned to a charge-transfer transition of the type $Fe^{II} \rightarrow Co^{III}$ through the CN bridge.

In redox reactions involving metal complexes two types of mechanism are known: the so-called outer-sphere and inner-sphere types. The latter type requires the formation of a bridged activated complex or intermediate.

Hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$, reacts[1] rapidly with pentacyanocobaltate(II), $[Co(CN)_5]^{3-}$, in a nitrogen atmosphere to yield the cyanide-bridged binuclear complex $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$. This binuclear complex is stable and can be isolated as a solid. It absorbs at 395 and 325 nm with molar absorption coefficients of 700 and 900 dm^3 mol^{-1} cm^{-1}, respectively. It can be further oxidized, by iodine for example, to give the stable binuclear complex $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$. The absorption spectrum of the latter has a band with a doublet structure centred at *ca.* 410 nm and other bands occur at 325 and 300 nm with molar absorption coefficients of *ca.* 1 000, 1 200, and 1 450 dm^3 mol^{-1} cm^{-1}, respectively.

A similar reaction occurs[2,3] with ethylenediaminetetra-acetatocobaltate(II), $[Co(edta)]^{2-}$, to yield the complex intermediate anion $[(NC)_5Fe^{II}(CN)Co^{III}(edta)]^{5-}$. This intermediate (A) is short-lived and decomposes to give the final products $[Fe^{II}(CN)_6]^{4-}$ and $[Co^{III}(edta)]^{-}$. It also reacts rapidly with excess of $[Fe^{III}(CN)_6]^{3-}$ or Ce^{IV}, where Fe^{II} is oxidized to Fe^{III}, forming another intermediate, $[(NC)_5Fe^{III}(CN)Co^{III}(edta)]^{4-}$, (B). This binuclear intermediate is stable for *ca.* 1 h at 10 °C. Both (A) and (B) were detected using the electronic absorption method, where the spectrum of (A) shows bands at 520, 565, and 375 nm with molar absorption coefficients of *ca.* 750, *ca.* 800, and 375 dm^3 mol^{-1} cm^{-1}, respectively, and (B) absorbs at 550 and 410 nm (a doublet) with molar absorption coefficients of 640 and 1 200 dm^3 mol^{-1} cm^{-1}, respectively.

In this paper we report Raman, resonance-Raman, and i.r. spectra of these CN-bridged complexes. These data enable us to characterize the compounds and make an assessment of their structure and nature of bonding. Furthermore, the characterizations of the short-lived binuclear intermediate complexes are of interest in investigating the redox reaction mechanisms in solution. A preliminary communication of this work was included in a previous paper.[4]

EXPERIMENTAL

Preparation of Complexes.—$[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ *and* $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$. These complex ions were prepared according to the method of Haim and Wilmarth.[1] Iodine was used as an oxidizing agent to form the $Fe^{III}Co^{III}$ complex. The complexes were identified through their u.v.–visible absorption spectra.

$[(NC)_5Fe^{II}(CN)Co^{III}(edta)]^{5-}$ (A) *and* $[(NC)_5Fe^{III}(CN)Co^{III}(edta)]^{4-}$ (B). The unstable complex (A) was obtained and examined using the open-flow method, by mixing at equal flow rates an aqueous solution of $[Fe(CN)_6]^{3-}$ with a solution of $[Co(edta)]^{2-}$. A Unicam SP 8000 spectrometer was used to follow changes in absorption at 565 nm,[2] caused by changing the reactant concentrations, temperature, pH, ionic strength, and the total flow rate. The optimum conditions for maximizing the concentration of the intermediate (A) were found to be a solution of $[Co(edta)]^{2-}$ ten times higher in concentration than $[Fe(CN)_6]^{3-}$ {to prevent oxidation by excess of $[Fe(CN)_6]^{3-}$ of the intermediate complex formed}, mixed at a total flow rate of 100 cm^3 min^{-1} at 7 °C, pH 5, and ionic strength 0.8 mol dm^{-3}. Both pH and ionic strength were adjusted using appropriate amounts of CH_3CO_2H and $Na[O_2CCH_3]$. The detection of the complex took place 0.3 s after mixing. Under these conditions it was demonstrated that all the $[Fe(CN)_6]^{3-}$ was consumed, as judged from the absence of its strong absorption band at 415 nm.

The other complex, (B), was obtained at maximum concentration by rapid addition of Ce^{IV} to the solution of the first intermediate (A) at 7 °C. The ratio of the initial concentrations of the reactants $[Fe(CN)_6]^{3-}$, $[Co(edta)]^{2-}$, and Ce^{IV} was 1 : 1 : 3.75. Under these conditions the complex was stable for *ca.* 1 h.

Raman Spectroscopic Measurements.—These were made using a system based on the Jobin Yvon HG2 double monochromator and described elsewhere.[4,5] Spectra were obtained from the complex $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ at a concentration of 5×10^{-3} mol dm^{-3}, using a conventional rotating liquid cell spun at *ca.* 2 000 revolutions min^{-1}. The 488.0- and 457.9-nm excitations of an argon-ion laser (Coherent Radiation model 52) were used. The spectra of the other complex, $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$, at a concentration of 2×10^{-2} mol dm^{-3} were obtained using a recirculating closed-flow method to prevent decomposition in the laser beam. Only the 568.2-nm excitation of a krypton-ion laser (Spectra Physics model 171) was used due to the decomposition with shorter-wavelength excitations.

The complex intermediates (A) and (B) were examined at concentrations of 2.5×10^{-3} and 1.0×10^{-2} mol dm^{-3}, respectively, at 7 °C, using 568.2-nm excitation. The open- and closed-flow methods were used with the first and second intermediate, respectively, under the experimental conditions given earlier.

Infrared Spectroscopic Measurements.—The i.r. spectra in the cyanide region were obtained from saturated aqueous solutions of $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ and $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$ using a Perkin-Elmer model 621 spectrometer.

RESULTS AND DISCUSSION

$[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ *and* $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$.—Raman spectra in the region 1 400—2 300 cm^{-1} of the complex $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$, at a concentration of 5×10^{-3} mol dm^{-3} in aqueous solution, obtained using 457.9- and 488.0-nm excitations, are shown in Figure 1(*a*) and (*b*), respectively. In the cyanide region four bands at 2 060, 2 090, 2 130, and 2 145 cm^{-1} were observed. It is of interest that only the band at 2 130 cm^{-1} shows a resonance effect on changing the excitation wavelength from 488.0 to 457.9 nm, nearer to the absorption band at 395 nm. The intensities of the band at 2 130 cm^{-1} were measured relative to the band of water at 1 640 cm^{-1} in terms of peak heights. These values were corrected at each excitation wavelength for the absorbance of the complex, the spectral sensitivity of the instrument, and the ν^4 factor, giving corrected values of 0.95 and 2.20 for the 488.0- and 457.9-nm excitations, respectively. Infrared spectra in the cyanide region of the same complex in water show three bands at 2 045, 2 084, and 2 130 cm^{-1}.

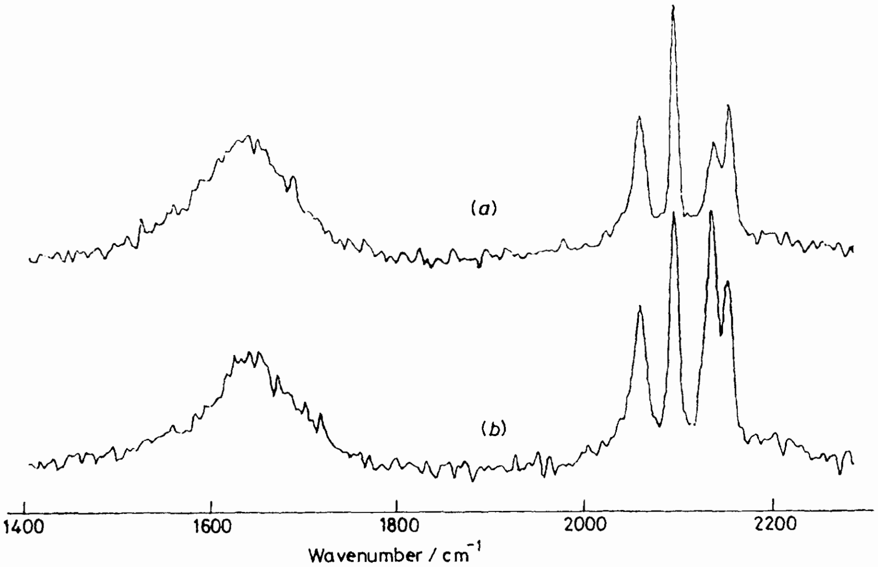


FIGURE 1 Raman spectra of 5×10^{-3} mol dm^{-3} $[(NC)_5Fe(CN)Co(CN)_5]^{6-}$ using 457.9- (*a*) and 488.0-nm (*b*) excitations

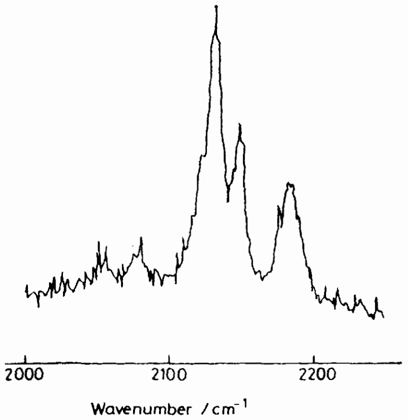
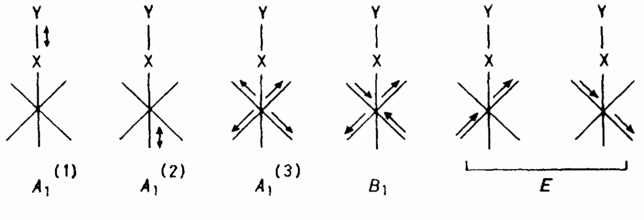


FIGURE 2 Raman spectrum in the ν(CN) region of $[(NC)_5Fe(CN)Co(CN)_5]^{5-}$ using 568.2-nm excitation

The Raman spectrum of the other complex, $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$, shows bands at 2 060, 2 090, 2 132, 2 147, and 2 187 cm^{-1}, as shown in Figure 2. The i.r. spectrum in the cyanide region of the same complex in water shows bands at 2 045, 2 081, 2 115, 2 130, and 2 183 cm^{-1}.

Based on the local C_{4v} symmetry of the $M(CN)_5(XY)$ part of the binuclear complex, where M is the metal ion and XY represents the bridging cyanide group, the CN stretching modes may be depicted as below.



The symmetric stretching mode of the bridging cyanide groups was assigned at 2 130 and 2 185 cm^{-1} in $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ and $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$, respectively. The increase of ν(CN) with oxidation state of the associated metal is normal. This assignment is also consistent with the wavenumber increase of ν(CN) on bridging, as discussed later. The bands at 2 090 and 2 145 cm^{-1} were assigned to the totally symmetric stretching $A_1^{(3)}$ modes of the equatorial cyanide groups in the $Fe^{II}(CN)_5$ and $Co^{III}(CN)_5$ local units, respectively, for the $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ complex, and at 2 130 and 2 147 cm^{-1} for the $Fe^{III}(CN)_5$ and $Co^{III}(CN)_5$ local units, respectively, for the $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$ complex. These assignments are consistent with the reported values for this mode in the mononuclear complexes $K_4[Fe^{II}(CN)_6]$, $K_3[Fe^{III}(CN)_6]$, and $K_3[Co^{III}(CN)_6]$.[6] The depolarized Raman band at 2 060 cm^{-1} may confidently be assigned to the B_1 asymmetric ν(CN) mode of the equatorial cyanide groups in the $Fe^{II}(CN)_5$ local unit. The i.r. spectrum contains a very strong broad band peaking at 2 045 cm^{-1}, which is asymmetric and appears to include a component at 2 060 cm^{-1}. Such a band was not detected in the spectrum of the $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$ complex. The i.r. band at 2 045 cm^{-1} may be due to an E-type mode, but the above assignments do not account for all the expected number of modes in both complexes, which might be due either to the fact that the missing bands are too weak to be observed or that they are coincident with other bands.

It is of interest to note that the ν(CN) modes of the bridging cyanide groups, $A_1^{(1)}$, in both $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ and $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$ complexes were assigned much higher wavenumbers than those for the terminal ν(CN), $A_1^{(3)}$ mode. The increase is of the order of 45 and 55 cm^{-1} for the two complexes. This shift may be understood in terms of the nature of the Co–N(bridging CN) interaction. Electron withdrawal from the lowest filled antibonding CN $\sigma_s{}^*$ molecular orbital may be considered [7] as resulting in increased C–N bond order and hence its vibrational wavenumber.

On the basis of the vibrational frequency of the bridging group in the complex $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ and the resonance effect observed for this band using excitation near the absorption band at 395 nm, as explained earlier, we may assign this absorption band to a charge-transfer transition of the type $Fe^{II} \rightarrow Co^{III}$ through the CN bridge. However, the corresponding band with a doublet structure centred at 410 nm in the spectrum of the $[(NC)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$ complex is characteristic of the $Fe^{III}(CN)_5$ part of the molecule {$K_3[Fe^{III}(CN)_6]$ shows an absorption band with doublet structure centred at *ca.* 415 nm}.

$[(NC)_5Fe^{II}(CN)Co^{III}(edta)]^{5-}$ (A) *and* $[(NC)_5Fe^{III}(CN)Co^{III}(edta)]^{4-}$ (B).—Raman spectra in the cyanide regions for the complex-ion intermediates (A) and (B) in aqueous solutions with concentrations of 2.5×10^{-3} and 1.0×10^{-2} mol dm^{-3} respectively, obtained using 568.2-nm excitation, are shown in Figure 3. Bands at 2 134 and 2 080 cm^{-1} are observed for the first complex, and at 2 182 and 2 132 cm^{-1} for the second. The individual bands for each complex were assigned to the stretching mode of the bridging CN group and the symmetric stretching mode of equatorial CN groups, respectively. The increase of ν(CN) on bridging is expected, as explained in the previous section. The ν(CN) of the bridging group in complex (A) has a much higher band intensity than the stretching mode of the terminal CN groups. The 568.2-nm excitation falls within the absorption band at 565 nm and this selective intensity enhancement is attributed to a resonance effect. Therefore, we assign the band at 565 nm to a charge-transfer transition of the type $Fe^{II} \rightarrow Co^{III}$ through the CN bridge. The other nearby absorption bands at 520 and 550 nm in the spectra of the $Fe^{II}Co^{III}$ and $Fe^{III}Co^{III}$ complexes, respectively, may be related to the Co^{III}(edta) part of both compounds {$K[Co^{III}(edta)]$ absorbs at 540 nm}. However, the corresponding $Fe^{II} \rightarrow Co^{III}$ transition for the complex ion $[(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-}$ was assigned at higher energy (395 nm). This suggests that the five cyanide groups co-ordinated to Co^{III} cause a greater increase in the charge density on cobalt than that produced by the edta.

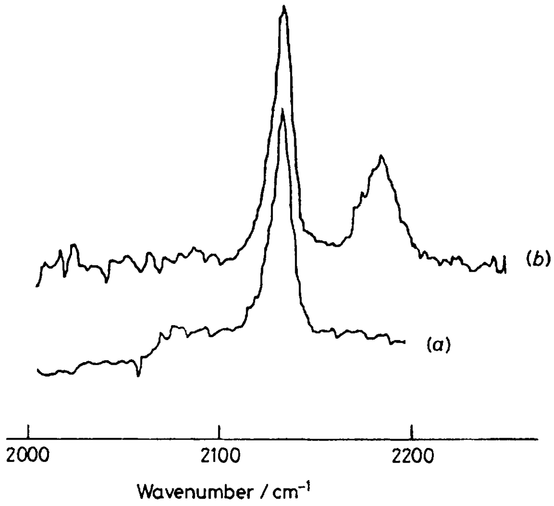


FIGURE 3 Raman spectra of (*a*) $[(NC)_5Fe(CN)Co(edta)]^{5-}$ and (*b*) $[(NC)_5Fe(CN)Co(edta)]^{4-}$ using 568.2-nm excitation

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REFERENCES

[1] A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, 1961, **83**, 509.

[2] D. H. Huchital and R. G. Wilkins, *Inorg. Chem.*, 1967, **6**, 1022.

[3] A. W. Adamson and E. Gonick, *Inorg. Chem.*, 1963, **2**, 129.

[4] R. E. Hester and E. M. Nour, *Indian J. Pure Appl. Phys.*, 1978, **16**, 167.

[5] E. E. Ernstbrunner, R. B. Girling, W. E. L. Grossman, and R. E. Hester, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1977.

[6] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, London, 1967, ch. 3.

[7] B. I. Swanson, *Inorg. Chem.*, 1976, **15**, 253.