

THERMALLY INDUCED LINKAGE ISOMERIZATION IN KCd[Fe(CN)₆]

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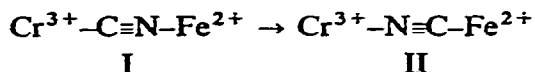
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ABSTRACT

Heating KCd[Fe(CN)₆]·5H₂O, either isothermally or in a differential scanning calorimeter, results in dehydration and linkage isomerization of the cyanides. In accord with hard-soft acid-base predictions, the product contains cyanide C-bonded to Cd²⁺. The integrated intensity of the peaks corresponding to the CN stretching vibrations indicates that two of the cyanides change bonding mode more readily than the others. Cyanide isomerization does not occur when KCd[Fe(CN)₆]·5H₂O is dehydrated at room temperature under vacuum conditions.

INTRODUCTION

On the basis of the hard-soft acid-base principle¹, it is expected that cyanide complexes containing two transition metals would contain cyanide C-bonded to the softer metal and N-bonded to the harder metal. Crystal structures show that such complexes contain cyanide bridges². If the complex is prepared so that this bonding arrangement is not present, one would expect that linkage isomerization would take place by flipping of the cyanides. The first published reports dealing with this type of linkage isomerization were those of Shriver, et al.^{2,3}. In these studies, KFe[Cr(CN)₆] was reported to isomerize to KCr[Fe(CN)₆] on heating in accord with both hard-soft and crystal field considerations. It was also found for this system that the isomerization can be followed kinetically and that the reaction



is second order in number of bonds of type I⁴, implying that the cyanides flip in pairs. For this system, the activation energy is 24 kcal mol⁻¹ and the isomerization takes place slowly even at room temperature.

Since the only system of this type which has been fully investigated is that involving KFe[Cr(CN)₆], other examples of this type of linkage isomerization have been sought. This report presents the results of studies on KCd[Fe(CN)₆].

EXPERIMENTAL

The $\text{KCd}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ was prepared by adding a solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ to a solution containing an excess of $\text{Cd}(\text{NO}_3)_2$. The solution was allowed to stir for 15 min and the solid product was removed by filtration. The product was washed with ethanol and acetone and allowed to dry in air at room temperature. The water content was established by heating samples to 140°C in the differential scanning calorimeter and determining the weight loss. Weight loss amounted to 19.50% which compares favorably with 19.86% required for the pentahydrate complex. The compound was analyzed by dissolving a sample in a minimum amount of a 1:1 mixture of conc. HNO_3 and conc. HClO_4 at the boiling point. The solution was diluted to a volume of 50 ml and an excess of 1 M NaOH added to the solution to precipitate the hydroxides of both metals. The precipitate was dried for 20 h at 260°C and the residue weighed as Fe_2O_3 and CdO. *Anal. calcd.* for $\text{KCd}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$: combined Fe, Cd, 37.1%; found, 36.4%.

Isothermal heating of samples was carried out using an oil-bath regulated to $\pm 0.2^\circ\text{C}$. Several samples in individual tubes open to the atmosphere were suspended in an aluminum holder in the oil-bath and were removed after varying times of heating. After heating, samples were made into mulls for spectral examination. Infrared spectra were taken on the mulls using a Perkin-Elmer Model 621 grating spectrophotometer. A ten-fold scale expansion was utilized to provide peaks more suitable for integrated intensity determinations. The areas of the peaks with maxima at 2155 cm^{-1} (the cyanide stretch in $\text{Cd}^{2+}-\text{N}\equiv\text{C}-\text{Fe}^{3+}$ bonds) and at 2030 cm^{-1} (the cyanide stretch in $\text{Cd}^{2+}-\text{C}\equiv\text{N}-\text{Fe}^{3+}$ bonds) were determined by integration. The total absorption of the two CN peaks remained essentially constant for all samples in a given run, indicating approximately equal extinction coefficients for the cyanide bound in either way. Thus, the peak areas were assumed to be proportional to the number of bonds of each type.

DSC studies were carried out using a Perkin-Elmer DSC-1B differential scanning calorimeter. Procedures used were similar to those previously described⁵.

RESULTS AND DISCUSSION

The infrared spectrum of $\text{KCd}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ which has not been heated shows only a single peak in the CN region at 2155 cm^{-1} in addition to the bands due to water. When samples are heated under various conditions, the peaks attributable to water disappear but a second CN absorption appears at 2030 cm^{-1} . Cyanide stretching vibrations in the $2100\text{--}2175\text{ cm}^{-1}$ region are characteristic of CN bound to a +3 metal ion while those at $2025\text{--}2095$ are characteristic of CN bound to a +2 metal ion⁶. Upon heating, $\text{KCd}[\text{Fe}(\text{CN})_6]$ undergoes a change in color from yellow orange to brownish-green. It is readily apparent that the cyanide linkages have changed from $\text{Cd}^{2+}-\text{N}\equiv\text{C}-\text{Fe}^{3+}$ to $\text{Cd}^{2+}-\text{C}\equiv\text{N}-\text{Fe}^{3+}$. Figure 1 shows the spectral changes observed for samples which have undergone various extents of linkage isomerization.

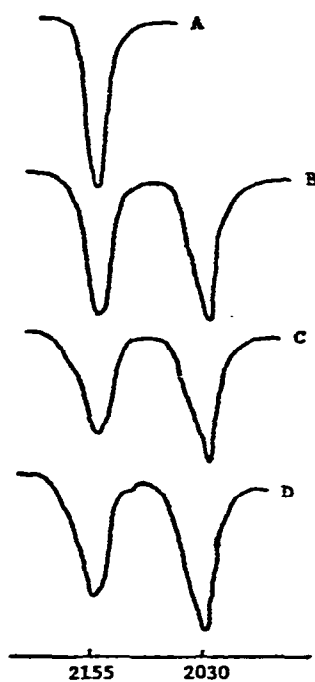


Fig. 1. Infrared spectra of $\text{KCd}[\text{Fe}(\text{CN})_6]$. Curve A is for the unheated complex and curves B, C, and D are for the complex heated at 150°C for 10, 45, and 100 min., respectively.

TABLE 1

BOND RATIO (2030 cm^{-1} peak area/ 2155 cm^{-1} peak area)

Temperature ($^\circ\text{C}$)	Heating time (min)	Bond ratio
110	30	0.54
110	60	0.74
110	90	0.79
110	120	0.92
110	150	0.97
110	180	1.00
110	210	1.11
110	240	1.17
120	15	0.44
120	30	0.72
120	45	0.76
120	60	0.78
120	90	0.98
120	120	1.05
120	150	1.28
120	180	1.57
150	10	1.01
150	20	1.02
150	30	1.16
150	45	1.18
150	100	1.30
150	210	1.43

Table 1 shows the ratio of the area of the band at 2030 cm^{-1} ($\text{Cd}^{2+}-\text{C}\equiv\text{N}-\text{Fe}^{3+}$ linkages) to that at 2155 cm^{-1} ($\text{Cd}^{2+}-\text{N}\equiv\text{C}-\text{Fe}^{3+}$ linkages) for samples removed after various heating times. The ratio of the integrated intensities was taken as the ratio of the number of bonds of the two types. Attempts to study the kinetics of the cyanide linkage isomerization were not entirely successful in that linear plots of the bond ratio vs. time were not found. The runs at 110 and 120°C gave satisfactory linear plots for samples removed after about 30–45 min. The run at 150°C is inconclusive owing to more extensive decomposition of the complex at the longer heating times.

One curious aspect of the results obtained in this study is that while the ratio of the two CN bands increases rapidly at first, it does not continue at the same rate. In the case of $\text{KFe}[\text{Cr}(\text{CN})_6]$, the CN band corresponding to $\text{Cr}^{3+}-\text{C}\equiv\text{N}-\text{Fe}^{2+}$ linkages entirely disappears on heating at 100°C for a few minutes⁴ and the change in bond ratio is linear. However, in the present case, the runs at 110 and 120°C give a very rapid increase in bond ratio to a value of about 0.5. This value corresponds to the inversion of two of the six cyanide groups per complex. Clearly, the first two cyanides invert rapidly, but the others much more slowly. After the isomerization of two cyanide groups, the linear portions of the bond ratio plots for these runs enable an estimation of the activation energy to be made and the value is about 33 kcal mol^{-1} .

The DSC curves obtained for $\text{KCd}[\text{Fe}(\text{CN})_6]\cdot 5\text{H}_2\text{O}$ show a dehydration endotherm in the range 75 – 125°C . The attendant mass loss corresponds closely to the expected value for complete dehydration. However, before the dehydration is complete, an exothermic transition occurs. Infrared spectra of samples removed during the endothermic dehydration process show that some isomerization has occurred because absorption bands are found at both 2155 and 2030 cm^{-1} . The exothermic DSC peak corresponds to additional linkage isomerization. The dehydration and isomerization processes are not cleanly separable so that separate ΔH values could not be determined. Heating to higher temperatures in the DSC gives extensive degradation of the complex with total mass losses of 30–35%.

Because of the rapid isomerization during dehydration in the first few minutes of isothermal heating and the characteristics of the DSC curves, it was first thought that the initial dehydration itself might be responsible for the isomerization. There is ample evidence to show that both geometrical isomerization⁷ and racemization^{8,9} can occur in the solid state by an aquation–anation mechanism. To determine if such a mechanism might be involved in this case, a sample of the original $\text{KCd}[\text{Fe}(\text{CN})_6]\cdot 5\text{H}_2\text{O}$ was partially dehydrated under high vacuum at room temperature. An infrared spectrum of this material shows only one CN band at 2155 cm^{-1} , indicating that isomerization has not occurred. It does not appear, therefore, that the linkage isomerization is a necessary consequence of dehydration as in the case of $\text{K}_4[\text{Ni}(\text{NO}_2)_6]\cdot \text{H}_2\text{O}$ (refs. 10, 11).

Infrared spectra of samples of $\text{KFe}[\text{Cr}(\text{CN})_6]$ which have been allowed to stand at room temperature show that linkage isomerization occurs under these conditions⁴. However, $\text{KCd}[\text{Fe}(\text{CN})_6]$ which has been allowed to stand for several

months under these conditions still shows only the CN band at 2155 cm^{-1} , indicating that it does not isomerize at room temperature.

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