*Journal of Thermal Analysis, Vol. 35 (1989) 2279–2290*

# THERMAL ANALYSIS OF SOME CYANO COMPOUNDS.

## Note III.[+]. The thermal behaviour of $Na_4Fe(CN)_6 \cdot 10H_2O$, $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$, $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ and $Pb_2Fe(CN)_6$

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(Received July 15, 1988)

The thermal behaviour of the title compounds in static air has been investigated by conventional thermal analysis (TG and DSC) and infrared spectroscopy of the solid residues at various temperatures.

The following points are demonstrated:

i) the presence ofan alkali metal cation (e.g. Na(I) or K(I)) appears to be a necessary, but not sufficient condition for the intermediate formation of cyanate in the oxidation of $Fe(CN)_6^{n-}$ ($n$ = 3 or 4);

ii) a multivalent cation favours a hydrolytic mechanism, with preferential evolution of HCN rather than $H_2O$;

iii) the thermally induced reduction of Cu(II) to Cu(I) occurs simultaneously with the linkage isomerism of $CN^-$, with the resultant formation of Cu(I)–$CN^-$ complexes.

The thermal behaviour of cyano compounds is complicated even as regards the variety of chemical species (cyanogen, cyanate, isocyanate, carbonate, etc.) which are related to nitrile or cyanide [1, 2], and which can be formed in thermally induced intramolecular reactions with or without the participation of the surrounding atmosphere [3, 4 and references therein].

The chemical nature of the compound (whether it is a simple, mixed or complex salt), the natures of the cations and anions, their oxidation states and probably the crystal structure too, play roles in favouring particular behaviour, in both thermodynamic and kinetic mechanisms.

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[+] This work was supported financially by the Italian MPI. It was presented in part at the "IV European Symposium on Thermal Analysis and Calorimetry", Jena (DDR), 1987, and in part at the "XV Congresso Nazionale di Termodinamica dei Complessi", Cosenza (Italy), 1988.

This research was undertaken in an attempt to clarify the oxidation mechanism in air, the first aim being to identify behaviour schemes (if they exist) which are dependent on general features (for example, the stoichiometry of the compound, the oxidation states of the components, their redox properties, the chemical affinity of the cations towards $CN^-$, etc.).

## Experimental

### *Chemicals*

$Na_4Fe(CN)_6 \cdot 10H_2O$. A commercial product was used without further purification.

$K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$. This was prepared by adding dropwise, under continuous stirring, the stoichiometric amount of a 0.1 M aqueous solution of $CuSO_4$ to 100 ml of an aqueous solution of $K_4Fe(CN)_6$(0.2 M) + $K_2SO_4$(0.5 M) [5]. The precipitate was washed 4–5 times by centrifugation with 10–20 ml of demineralized water and was then dried in desiccator at atmospheric pressure over $P_2O_5$ for 2 weeks. The sample prepared in this way turned out to be contaminated with $K_2SO_4$, as it can be seen in the IR spectrum (see Fig. 6). Further washing was not possible because of the great tendency of the compound to peptize.

$K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$. This was prepared, washed and dried in the same way as $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$, but by using $ZnSO_4$ as precipitating reactant [5].

$Pb_2Fe(CN)_6$. This was prepared by adding slowly, under stirring, 2.5 ml of a 0.1 M aqueous solution of $K_4Fe(CN)_6$ to 50 ml of a 0.01 M aqueous solution of $Pb(NO_3)_2$ [5]. The precipitate was washed and dried as for the previous complexes.

### *Thermal analysis*

Thermal analysis measurements (TG and DSC) were performed in static air with a Mettler TA 3000 apparatus. The sample holder for TG was a standard alumina crucible (No. 24193 [6]) with a single-holed lid. DSC analyses were run on samples in standard aluminium crucibles (No. 27331 [6]) whose lids were pierced with three 1 mm holes about 3 mm distant from each other.

The amounts of the samples and the heating rates are reported in the captions of the Figures.

### *Infrared spectra*

The IR spectra of the solid residues at various temperatures were recorded in nujol on a Perkin–Elmer 783 spectrometer.

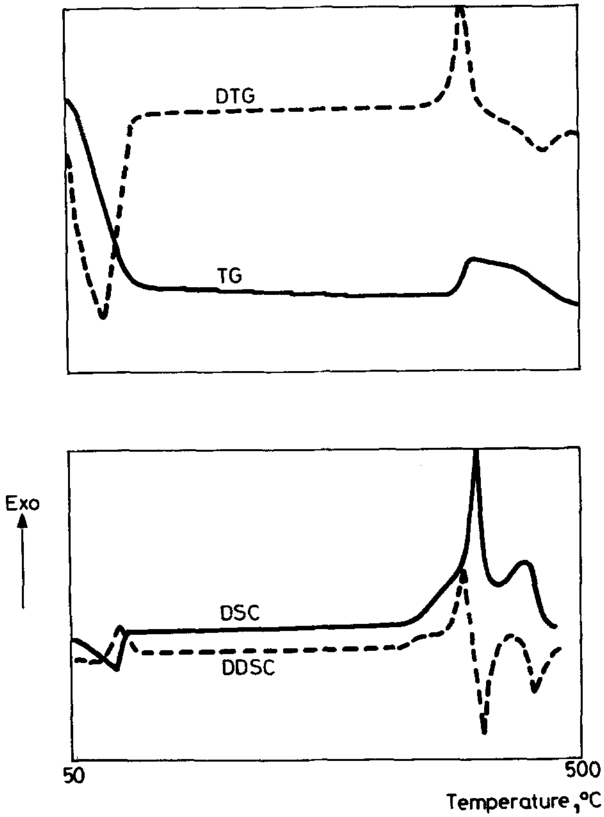
The samples for IR examinations were heated in an oven up to successive temperatures, in open air, in porcelain crucibles. At each temperature, the sample was maintained under isothermal conditions for 5 minutes. The heating temperatures were selected on the basis of the thermal analysis curves, and the isothermal heating period on the basis of preliminary experiments [3, 4].

## Results

### *Thermal analysis*

Thermal analysis curves are reported in Figs 1–4. The TG plots differ, depending on the ferrocyanide investigated.

Hydrated sodium ferrocyanide shows a negative TG step between room temperature and 100°. This is followed by a range of thermal stability up to 380°

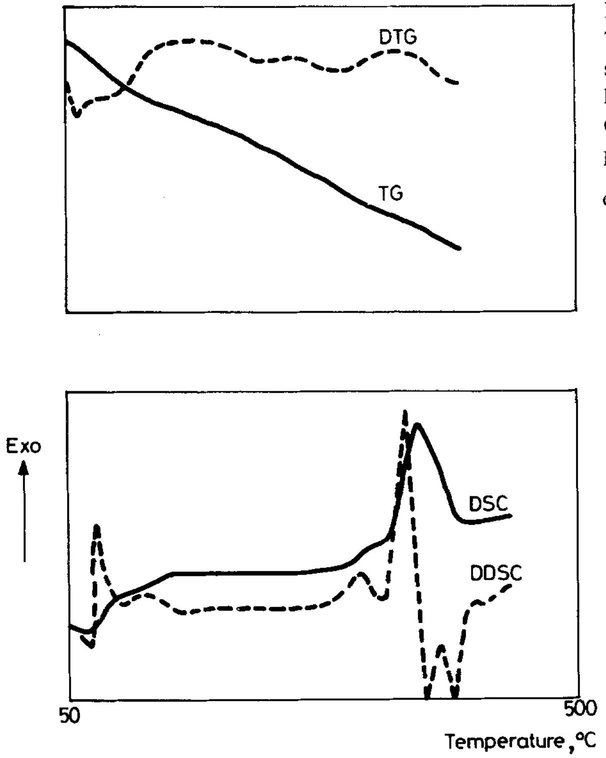


Experimental conditions:
TG
sample mass: 4.84 mg
heating rate: 10 deg $\mathrm{min}^{-1}$
Ordinate range:
primitive curve $\Delta$ mg = 2.85
derivative curve $\left[ \begin{array}{l} -0.014- \\ +0.006\ \mathrm{mg\ K^{-1}} \end{array} \right.$

DSC
2.07
20 deg $\mathrm{min}^{-1}$

$\Delta$ mW = 44
$\left[ \begin{array}{l} -0.2- \\ +0.526\ \mathrm{mW\ K^{-1}} \end{array} \right.$

**Fig. 1** TG and DSC curves (solid lines) and their derivatives (dashed lines) in static air for $Na_4Fe(CN)_6 \cdot 10H_2O$.



Experimental conditions:

| | |
|---|---|
| TG | |
| sample mass | 1.00 mg |
| heating rate | 5 deg $\min^{-1}$ |
| Ordinate range: | |
| primitive curve | $\Delta$ mg = 2.85 |
| derivative curve | $\left[\begin{array}{l}-4.6\cdot10^{-4}-\\+1.1\cdot10^{-4}\ \text{mg K}\end{array}\right.$ |
| | DSC |
| | 5.87 mg |
| | 5 deg $\min^{-1}$ |
| | $\Delta$ mW = 61.5 |
| | $\left[\begin{array}{l}-5.34\cdot10^{-2}-\\+17.46\cdot10^{-2}\ \text{mW K}^{-1}\end{array}\right.$ |

**Fig. 2** TG and DSC curves (solid lines) and their derivatives (dashed lines) in static air for $K_2Cu_3[Fe(CN)_6]_2\cdot xH_2O$.

(only a slight negative slope is observed). From 380° to 410°, a sharp weight gain is recorded, immediately followed by the slow decomposition of the sample.

The mixed potassium-copper(II) ferrocyanide does not exhibit thermal stability. The weight of the sample decreases monotonously throughout the whole investigated temperature range, with slightly indicated negative steps (Fig. 2).

$K_2Zn_3[Fe(CN)_6]_2\cdot xH_2O$ and $Pb_2Fe(CN)_6$ similarly give steadily decreasing thermogravimetric curves, but these differ from that of $K_2Cu_3[Fe(CN)_6]_2\cdot xH_2O$. Two sharp changes are evidenced in the DTG curve (see Fig. 3, derivative curve), which correspond to a slight negative step between room temperature and 200° in the primitive plot, and to a clear-cut weight loss at $t > 200°$.

As far as $Pb_2Fe(CN)_6$ is concerned, a gradual but continuous weight loss is recorded from room temperature up to 280°. At this temperature, the sudden decomposition of the sample occurs.

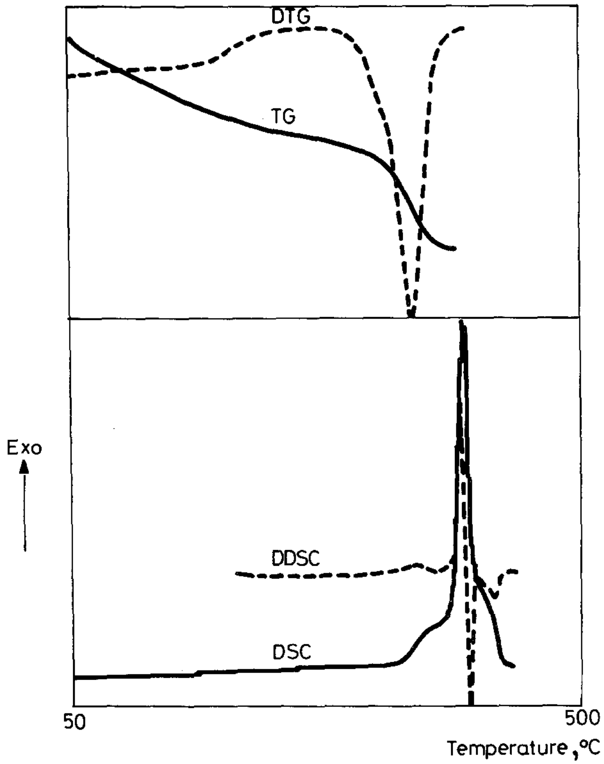
All thermal events recorded in DSC correspond to the thermogravimetric steps. The common features of the DSC plots are:

i) an endothermic event which starts almost at room temperature and ends at different temperatures for the various compounds, but always below 200° (this event is not recorded for $Pb_2Fe(CN)_6$;

ii) a very broad exothermic multiple event, always at $t > 250°$, and extending more than 150 degrees upwards.

As regards the endothermic event, for $Na_4Fe(CN)_6 \cdot 10H_2O$ it is a sharp one and concludes at $t = 100°$. For $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$, it appears to be a multiple one. It is over at $t = 150°$, but DSC analysis records a continuous exothermic signal up to 250–260°. For $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$, the phenomenon is not evident possibly because of the small enthalpy change of the process and the large temperature range (from room temperature to 200°; see TG curve in Fig. 3), over which it extends uniformly.

As far as the exo transition is concerned, its structure clearly denotes the occurrence of several reactions (at least two).



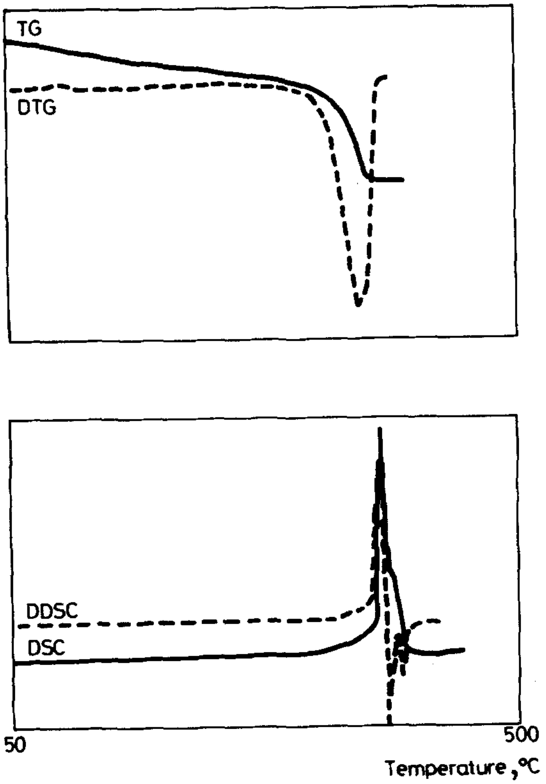
Experimental condition:
TG

| | |
|---|---|
| sample mass | 2.34 mg |
| heating rate | $5 \text{ deg min}^{-1}$ |
| Ordinate range: | |
| primitive curves | $\Delta mg = 1.49$ |
| derivative curves | $\left[\begin{array}{l}-8.65\cdot 10^{-4}-\\ +1.5\cdot 10^{-4}\text{ mg K}^{-1}\end{array}\right.$ |

DSC
5.65 mg
$5 \text{ deg min}^{-1}$

$\Delta mW = 1.45$
$\left[\begin{array}{l}-1.6-\\ +2.4\text{ mW K}^{-1}\end{array}\right.$

**Fig. 3** TG and DSC curves (solid lines) and their derivatives (dashed lines) in static air for $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_3O$.



Experimental conditions:

| | TG | DSC |
|---|---|---|
| sample mass | 2.45 mg | 3.3 mg |
| heating rate | 5 deg $\text{min}^{-1}$ | 5 deg $\text{min}^{-1}$ |
| Ordinate range: | | |
| primitive curve | $\Delta$mg = 1.49 | $\Delta$mW = 164 |
| derivative curve | $\left[\begin{array}{l} -1.1\cdot10^{-3}- \\ +1.54\cdot10^{-3}\ \text{mg K}^{-1}\end{array}\right.$ | $\left[\begin{array}{l} -0.77- \\ +1.67\ \text{mW K}^{-1}\end{array}\right.$ |

**Fig. 4** TG and DSC curves (solid lines) and their derivatives (dashed lines) in static air for $Pb_2Fe(CN)_6$.

In the diagram for $Na_4Fe(CN)_6\cdot10H_2O$ (Fig. 1, DSC curve), two resolved maxima relating to chemical phenomena with different reaction rates are clearly evident. The one at lower temperature is obviously the faster.

The exo transitions display the same structure for all the investigated compounds, but the relative positions of their maxima and their positions on the temperature axis are different for the various compounds. The sequence of peak temperatures is invariant for the maxima:

| | |
|---|---|
| $Na_4Fe(CN)_6\cdot10H_2O$ | ($t$ = 405 and 450°) |
| $K_2Zn_3[Fe(CN)_6]_2\cdot xH_2O$ | ($t$ = 397 and 407°) |
| $Pb_2Fe(CN)_6$ | ($t$ = 390 and 395°) |
| $K_2Cu_3[Fe(CN)_6]_2\cdot xH_2O$ | ($t$ = 350 and 365°). |

### *Infrared spectra*

Figures 5–8 show selected IR spectra of the residues at various temperatures. The increased transmittance in the ranges 3100–3800 $cm^{-1}$ and 1600–1700 $cm^{-1}$ for the residue (white) formed at 150° from $Na_4Fe(CN)_6 \cdot 10H_2O$ (Fig. 5) allows the first TG step (negative, to which the endo transition corresponds) to be ascribed to the loss of crystallization water. The flatness of the spectrum indicates the loss of the whole crystallization water in one stage. At 400°, the IR spectrum reveals fundamental changes in the sample. The $Fe^{II}$–C stretching and $\delta Fe^{II}$–C–N bending bands disappear, while the C–N stretching band at 2060 $cm^{-1}$ persists, though considerably weakened. Moreover, the presence of large quantities of NaOCN (bands at 3460, 3380, 2520, 2230, 1320, 1220 and 620 $cm^{-1}$) and carbonate (large band at 1200–1700 $cm^{-1}$ and band at 880 $cm^{-1}$) is evident [7, 8]. The IR spectra for the residues at higher temperatures show an unaltered state, except for the quantitative ratios between the various band, denoting a slow oxidation of cyanate to carbonate. The colour of the residue indicates the oxidation of Fe(II) to Fe(III).

The IR spectrum (Fig. 6) of unheated $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$ reveals short-range interactions between Cu(II) and $Fe^{II}(CN)_6$ in the crystal lattice (see the broadening of the $\delta Fe^{II}$–C–N bending band and the shift of the CN band towards higher wavenumber, both as compared with the corresponding bands for hydrated sodium or potassium ferrocyanide [9]). From the structure of the absorption between 3100 and 3700 $cm^{-1}$, it can be deduced that the water is bound in different

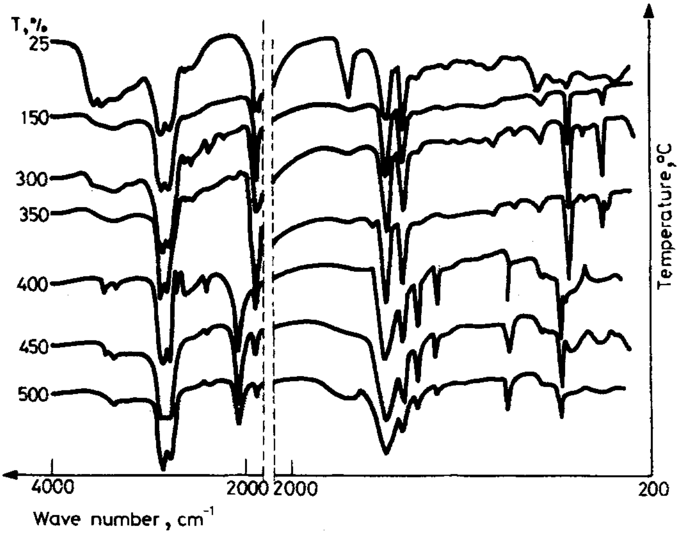


Fig. 5 Selected IR spectra of $Na_4Fe(CN)_6 \cdot 10H_2O$ and its thermolysis products at various temperatures

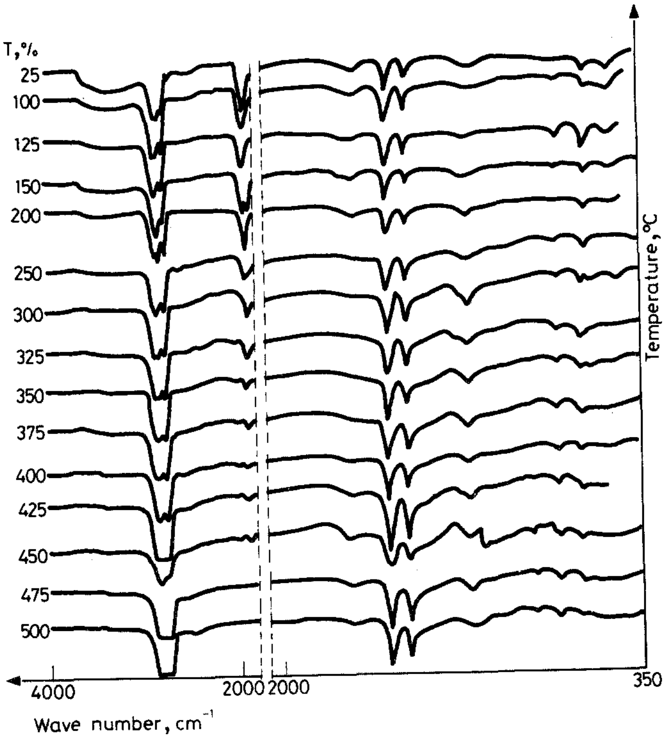


**Fig. 6** Selected IR spectra of $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$ and its thermolysis products at various temperatures

ways (at least two) in the crystal lattice. The IR spectra of the residues at 200° show the presence of water in the samples and the CN stretching band systematically moves towards lower wavenumbers (from 2100 cm$^{-1}$ for the unheated sample, it moves to 2070 cm$^{-1}$ for the residue at 250°). From this temperature, the band remains centred at 2070 cm$^{-1}$, but gradually decreases in intensity. From 200° to 375°, the Fe$^{II}$–C stretching band gradually decreases and simultaneously a new band increases at 715 cm$^{-1}$. A small band centred at 2170 cm$^{-1}$ is recorded for the residues at 325° and 350°. The formation of carbonate begins at 200°, as confirmed by the effervescence when the sample is treated with HCl solution.

For the mixed potassium-zinc(II) ferrocyanide, the IR spectra do not show any change in the sample between room temperature and 350° (confirmed by the unaltered white colour of the sample). They reveal alterations only from 375° (the colour turns to pale-brown), showing:

i) loss of the crystallization water;

ii) alteration of the structure of the CN stretching band, but whose maximum remains centred at 2080 cm$^{-1}$;

iii) a small absorption between 1300 and 1700 cm$^{-1}$ for the incipient formation of carbonates;

iiii) disappearance of the $\delta$Fe$^{II}$–C–N bending band at 580 cm$^{-1}$.

The residues at higher temperatures show a gradual decrease in the band at 2080 cm$^{-1}$ up to its complete disappearance, and simultaneously an increase in the presence of carbonates (bands at 1300–1700 cm$^{-1}$ and 880 cm$^{-1}$) [7, 8, 10].

As far as $Pb_2Fe(CN)_6$ is concerned, the IR spectra remain unaltered up to 375°, but the colour of the sample clearly changes (from white at room temperature to green-blue at 200°, and finally to pale-brown). Between 375° and 400°, the $Fe^{II}(CN)_6$ is completely transformed.

## Conclusions

The differences in behaviour of the various cyano compounds are evident. Those compounds which contain alkali metal ions (for example, NaCN, potassium ferro- and ferricyanide, sodium ferro- and mixed potassium-lanthanide ferrocyanide) give rise to the formation of cyanate [3, 4], while this species is not formed

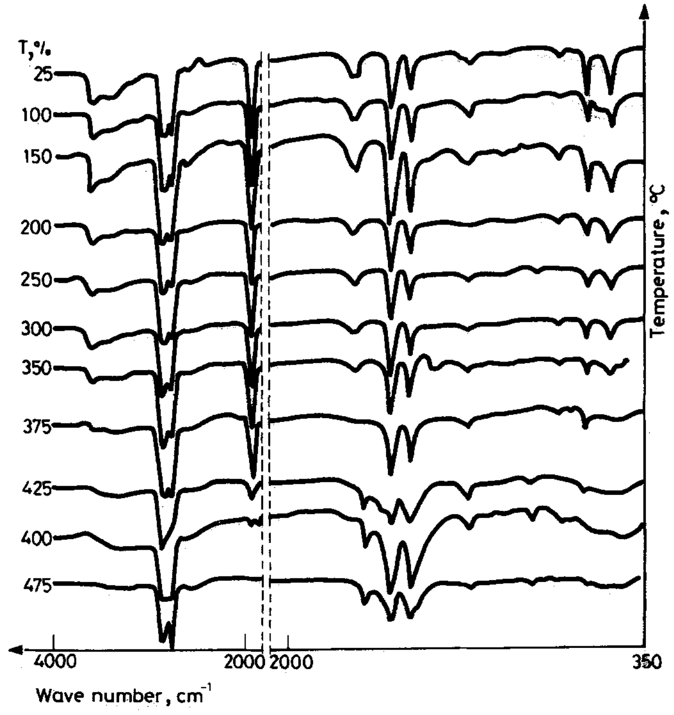


Fig. 7 Selected IR spectra of $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ and its thermolysis products at various temperatures

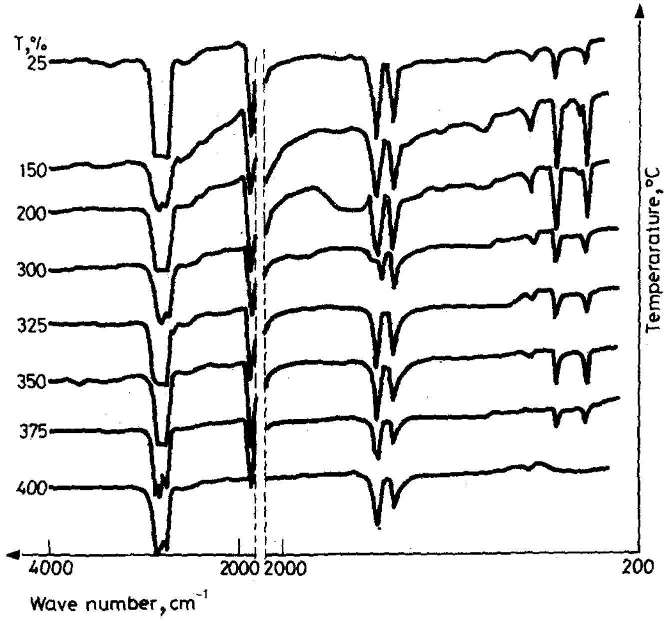


Fig. 8 Selected IR spectra of $Pb_2Fe(CN)_6$ and its thermolysis products at various temperatures

from $Pb_2Fe(CN)_6$. The presence of alkali metal ions therefore appears to be a necessary condition for the formation of $NCO^-$ in thermally induced reactions between cyano compounds and atmospheric oxygen. $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$ and $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ are expections. In fact, the IR spectra of their heating residues do not show bands indicative of the presence of $NCO^-$, notwithstanding the fact that they contain alkali metal ion in an equivalent quantity to that in $KLnFe(CN)_6$ (Ln = lanthanide ion). (In both cases, one valence of $Fe^{II}(CN)_6$ is counterbalanced by one K(I).) It can be assumed that the presence of an alkali metal ion is a necessary, but not sufficient condition for the formation of $NCO^-$. This also depends on its ready stabilization (in respect of further oxidation*), which can occur when the alkali metal ion and the cyanate-generating anion are in suitable positions in the lattice.

As far as the endo transition and the negative step are concerned, the IR spectra demonstrate that they originate from different chemical phenomena. $Na_4Fe(CN)_6 \cdot 10H_2O$ clearly loses its crystallization water (in agreement with the

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* Cyanate is not the final product (the one with the highest oxidation state) of the oxidation of the nitrile group in air; rather it is an intermediate, probably in the first stage, of higher oxygenated compounds (carbonate).

behaviour of hydrated potassium ferrocyanide [3]), whilst the presence of the divalent cations in $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$ and $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ favours the preferential elimination of HCN via a hydrolytic mechanism, as for the rare earth mixed ferrocyanides [4].

$K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$ is a very interesting case. It has already been mentioned that its thermogravimetric plot decreases uniformly over the whole temperature range, and the DSC curve records a continuous exothermic heat flux.

From the general trend of the IR spectra of cyano complexes [9–18], it can be deduced that the CN stretching frequencies increase with the ratio of the valence of the central ion and the number of coordinated $CN^-$ ions.

The thermal elimination of cyanide groups corresponds to an increase in this ratio, so that a positive shift (towards higher wavenumbers) of the CN band must be foreseen. In contrast, the experimentally observed shift is in the opposite direction. It follows that in the solid sample a chemical reaction (reactions) occurs, leading to a product in which the ratio of the valence of the central ion to the number of coordinated groups is lower than 1:3 (the case for $Fe^{II}(CN)_6$). Because of the chemical affinity of Cu(I) towards $CN^-$ and the short-range interaction between Cu(II) and the anion $Fe^{II}(CN)_6$ in the mixed potassium-copper(II) ferrocyanide [9], the experimentally observed data can be explained in terms of an intramolecular redox reaction, leading to the formation of Cu(I)-cyano complexes and the simultaneous elimination of cyanogen (this reaction has been hypothesized previously [19], but not sufficiently demonstrated). The maximum of the new CN stretching band at 2076 $cm^{-1}$ indicates the presence of $Cu^{I}(CN)_4$ in the solid sample.

Because of the complete disappearance of the $Fe^{II}$–C stretching bands, this reaction involves the ferrocyanide complexes quantitatively. The band at 2170 $cm^{-1}$, which appears later, indicates the successive formation of $Cu^{I}$–CN [9].

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The author is gratefully indebted to A. Bonetti who kindly performed thermal analysis measurements in his laboratory.

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**Zusammenfassung** — Die thermischen Eigenschaften von folgenden Komplexen wurden untersucht: $Na_4Fe(CN)_6 \cdot 10H_2O$, $K_2Cu_3[Fe(CN)_6]_2 \cdot xH_2O$, $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ und $Pb_2Fe(CN)_6$. Folgendes wird verdeutlicht: i) die Gegenwart eines Alkalimetallkations (z. B. Na(I) oder K(I)) scheint eine notwendige, aber nicht ausreichende Bedingung für die Bildung von intermediärem Zyanat bei der Oxydation von $Fe(CN)_6^{n-}$ (mit $n = 3$ oder 4) zu sein; ii) ein multivalentes Kation begünstigt einen hydrolytischen Mechanismus, bei dem eher HCN als $H_2O$ gebildet wird; iii) parallel zur thermisch induzierten Reduktion von Cu(II) zu Cu(I) findet auch die Bindungsisomerisierung von $CN^-$ statt, wodurch es zur Bildung von Cu(I)–$CN^-$ Komplexen kommt.

**Резюме** — Представлены следующие особенности термического поведения некоторых цианосоединений: а) присутствие каких-либо щелочных катионов (напр. натрия или калия) должно быть неоходимым, но недостаточным условием образования цианата, как промежуточного продукта, при окислении $Fe(CN)_6^{n-}$ с $n = 3$ или 4, б) многовалентных катион способствует гидролитическому механизму с предпочтительным выделением скорее HCN, чем $H_2O$ и в) термически наведенное восстановление двухвалентной меди до одновалентной происходит одновременно с изомерией связи $CN^-$, что приводит к образованию комплексов Cu(I)–$CN^-$.