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THERMAL ANALYSIS OF SOME CYANO COMPOUNDS*

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The thermal behaviour of the cyano compounds NaCN, $K_4Fe(CN)_6 \cdot 3H_2O$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$ and $K_2Hg(CN)_4$ has been investigated by using conventional thermal analysis techniques and infrared spectroscopy. The results indicate the absence of "decomplexing" reactions for all the complexes, and "internal" redox reactions for the compounds $K_3Fe(CN)_6$, $K_3Co(CN)_6$ and $K_2Hg(CN)_4$. In all the investigated cases, the formation of cyanate and carbonate is demonstrated.

In aqueous solution the cyanide ion binds to transition metal ions to form complexes of high thermodynamic stability [1–3]. Some of them are inert too and they readily give rise to heteropolynuclear complexes with variable stoichiometry, depending on the experimental conditions of formation [4–6]. Compounds such as $Ag_4Fe(CN)_6$, $KAg_3Fe(CN)_6$ and $Hg_2Fe(CN)_6$ (white) alter swiftly in air, while others, such as $K_2Zn_3[Fe(CN)_6]_2$ or $KLaFe(CN)_6$ (white), are stable for a long time. Very different behaviour is evident as regards "internal" and/or "external" reactions, depending on the nature both of the central ion of the cyano complex (inside the anion moiety of the compound) and of the counter cations [7]. On the whole, the presence of highly polarizing cations favours the oxidative decomposition of cyanide compounds [9].

Seifer [10–15] has investigated the thermal behaviour of hexacyanoferrates(II) in an inert atmosphere by using compounds where the cation moiety was constitued by "free" or at most hydrated ions. The results showed a very complicated set of endo- and exothermic effects, but the interpretation given by Seifer allows one to outline a scheme of behaviour.

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Apart from the loss of water of the hydrated compounds, two chemical events occurred constantly and for this reason they are connected to the complex anion and not to the counter cation(s). The first, endothermic, is the "decomplexing" reaction of the heteropolycomplex into its constituents ($M^{II}_2Fe^{II}(CN)_6 \xrightarrow{\text{endo}} 2\,M^{II}(CN)_2 + Fe^{II}(CN)_2$). The decomplexing temperature is always higher than 250–300° and it is strongly dependent on the metal ion. The second event is the exothermic decomposition of $Fe^{II}(CN)_6$ to cementite (Fe_3C) with evolution of nitrogen at 650–660°.

Depending on the nature of the ion in the cation moiety and on the products of the decomplexing reaction, a further set of different chemical reactions is possible.

An interesting event is the role of oxidizing counter ions (e.g. Fe(III), Cu(II)). They cause an internal exothermic redox reaction coupled with the evolution of $(CN)_2$ and concurrent flipping of Fe(II) from the anion to the cation moiety.

In air or in oxygen atmosphere, the final products are oxides or oxysalts [16–21]. However, there are reasons for supposing that the formation of the products is achieved by different mechanisms, depending on the nature of the starting compounds [22].

This work presents the results of a study on the thermal behaviour of some cyano compounds having simple compositions. It has been performed by means of thermal analysis and infrared spectroscopy.

Experimental

Chemicals. NaCN, $K_4Fe(CN)_6 \cdot 3H_2O$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$ and $K_2Hg(CN)_4$ were commercial products.

Thermal analysis. TG and DSC experiments were performed using a METTLER TA 3000 apparatus. The samples, sealed into standard aluminium pans (n° 27331 in the operating instructions of the system) with a lid having three 1 mm holes, were heated in static air at a rate of 5 deg/min.

Infrared spectroscopy. Infrared spectra of the residues of samples heated at various temperatures were recorded in nujol mulls on a Perkin–Elmer 783 spectrometer. To achieve the best reproducibility of the chemical processes recorded in TG and DSC, the samples for the IR spectra were heated up to the indicated temperatures inside the furnace of the TG system under the same experimental conditions as previously. The IR spectra were recorded immediately after the heating.

Results and discussion

NaCN. The sample was clearly wet, and the TG and DSC curves (Fig. 1) show that the loss of water occurs between room temperature and 175°. The TG diagram, whose first derivative is not monotonous, and the two sharply-separated endothermic peaks in the DSC curve, indicate a two-step dehydration or two different dehydration reactions. The IR spectrum of the original sample (Fig. 2, $t = 25^\circ$) exhibits three absorptions relating to the presence of H_2O. The two bands at higher wavenumber (3800–3000 cm^{-1} and 1600 cm^{-1}) can be assigned to lattice water, while the band at 860 cm^{-1} is characteristic of water molecules strongly coordinated to the cation and to the anion (or ligand) via hydrogen-bonding

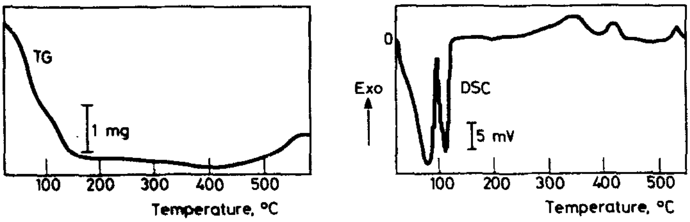

Fig. 1 Thermal analysis curves of NaCN in static air. Heating rate: 5 deg/min. Weight of the sample: 10.6 mg (TG), 5.2 mg (DSC)

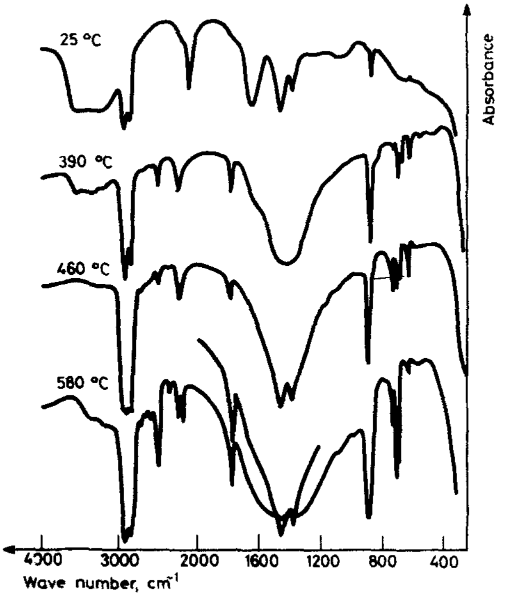

Fig. 2 Selected IR spectra of the residue of NaCN heated up to different temperatures in static air

[23–26]. Since NaCN is a hydrated salt [27], considering the shapes of the bands at 860, 1450 and 1630 cm^{-1}, which are rather superimposed bands, it is evident that the NaCN sample contains $Na_2CO_3 \cdot 10H_2O$ as impurity [28–29] and the thermal events recorded between 25° and 175° in the TG and DSC curves are due to the loss of moisture and to the dehydration of cyanide and $Na_2CO_3 \cdot 10H_2O$.

In the range 175–450° no remarkable weight changes are observed. At > 450°, the TG plot exhibits a weight gain step, while the DSC curve shows three exothermic events, which cannot be related to the presence of Na_2CO_3 [30]. The IR spectrum (Fig. 2) of the sample heated at 390° shows the complete disappearance of the band at 2080 cm^{-1}, relating to the "free" CN^-, and demonstrates that the chemical composition of the original NaCN sample has been completely altered. Strong bands are seen at 2500, 2220, 1775, 880, 700* and 630 cm^{-1} with a very large band in the interval 1900–900 cm^{-1}. The bands at 2500, 1775, 880 and 700 cm^{-1} and that in the interval 1900–900 cm^{-1} are due to the presence of anhydrous Na_2CO_3. The bands at 2220 and 630 cm^{-1} clearly indicate the presence of NaOCN in the sample, and consequently also the weak band (designated *) can be assumed to be diagnostic of this last-mentioned compound. The IR spectra of the residues at 460° and 580° show essentially the same band pattern as the one just discussed. Differences are found only in the spectrum of the residue at 580°, where the absorbance ratios for the cyanate and carbonate bands, as compared with those in the previous spectra, are changed in favour of the carbonate. Therefore, the exothermic peak centred at 540° can be ascribed to the oxidation $NaOCN \xrightarrow{exo} Na_2CO_3$, while the two previous exothermic peaks are due to the oxidation $NaCN \xrightarrow{exo} NaOCN$ and/or $NaCN \xrightarrow{exo} Na_2CO_3$, without any possibility of discrimination with the data available at present.

$K_4Fe(CN)_6 \cdot 3H_2O$. The TG curve (Fig. 3) shows a weight loss step for the whole dehydration of the salt and two positive steps starting at 340° and 390°; these correspond respectively to the endothermic and to the exothermic events in the DSC curve.

Except for the absorption bands of H_2O, the IR spectrum at 120° is similar to the one recorded for the original sample. The residue at 340° still has well-evident bands at 2030, 585 and 420 cm^{-1}, respectively relating to νCN, νMC and δMCN of $K_4Fe(CN)_6$ [23, 26]. At the same time, the IR spectrum reveals evident signs of other compounds, which must originating (considering the thermal analysis curves) from the oxidation of the sample by air. In fact, there is a strong band at 2160 cm^{-1} and two bands at 1300 cm^{-1} and 1200 cm^{-1}, which signify unambiguously the formation of KOCN (the presence of cyanamide compounds can be excluded

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* This band is a well-resolved doublet.

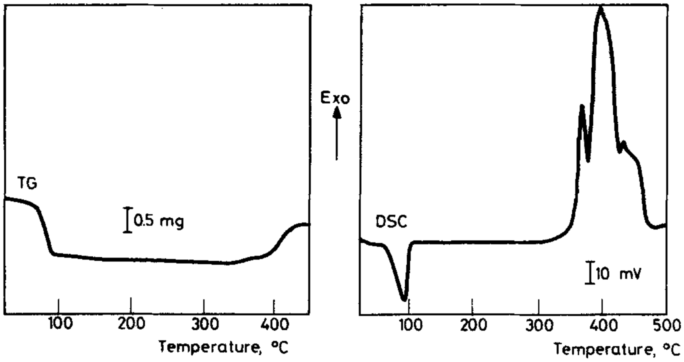

Fig. 3 Thermal analysis curves of $K_4Fe(CN)_6 \cdot 3H_2O$ in static air. Heating rate: 5 deg/min. Weight of the sample: 9.0 mg (TG), 13.5 mg (DSC)

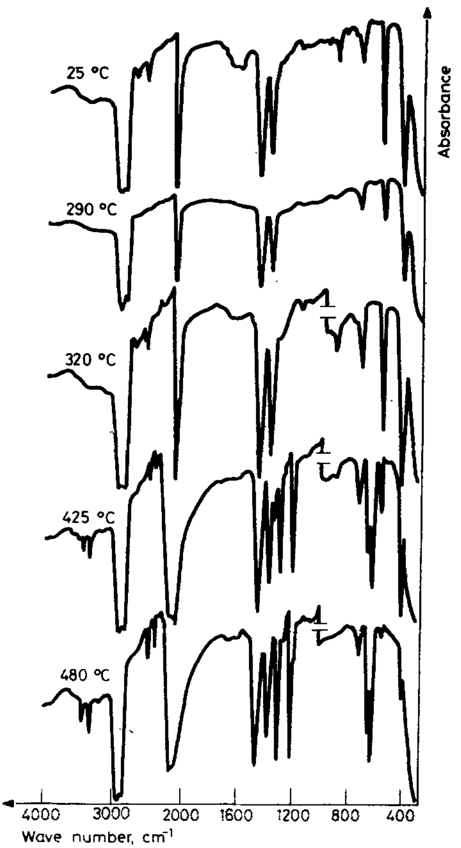

Fig. 4 Selected IR spectra of the residue of $K_4Fe(CN)_6 \cdot 3H_2O$ heated up to different temperatures

because these have a very large band in the interval 1600–2100 cm^{-1} [29], such a band clearly being absent from the spectra in Fig. 4). The presence of carbonate is shown by the large band in the interval 1500–1700 cm^{-1}. This part of the spectrum remains unaltered up to high temperature (450°). The band pattern too is unchanged, except for the ratios of the absorption intensities, which show a gradual increase, with rising temperature, of the carbonate with respect to the cyanate.

The positions of the bands relating to $K_4Fe(CN)_6$ show that the Fe(II) in the anion moiety $Fe^{II}(CN)_6$ is sufficiently protected from thermal oxidation by air.

$K_3Fe(CN)_6$. The TG curve of $K_3Fe(CN)_6$ (Fig. 5) shows a weight loss step at 350°, immediately followed by a weight gain. A linear weight loss is then observed between 425° and 500°. The DSC curve shows only exothermic effects (three in the temperature range 300–500°, with sharp distinct maxima at 360, 380 and 440°).

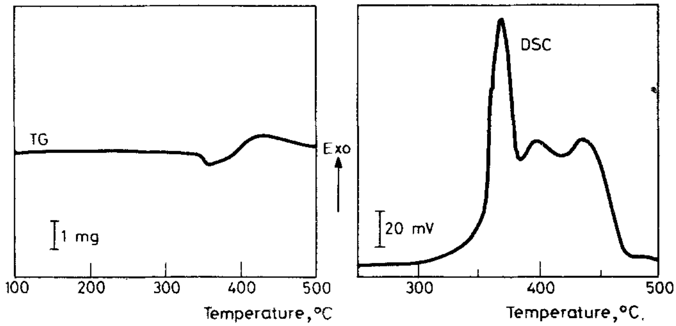

Fig. 5 Thermal analysis curves of $K_3Fe(CN)_6$ in static air. Heating rate: 5 deg/min. Weight of the sample: 31.4 mg (TG), 8.8 mg (DSC)

Hence, the change recorded in thermal analysis is characterized by various chemical events. The IR spectra (Fig. 6) show that $K_3Fe(CN)_6$ heated up to 250° does not undergo thermally-induced chemical changes. At the beginning of the weight loss step in the TG curve (which corresponds to the first exothermic event in DSC at 300°), the IR spectrum of the residue still has evident bands of $K_3Fe(CN)_6$ (2110, 505 cm^{-1}), but shows clear signs of chemical changes in progress. The irregular very strong band at 2000–2100 cm^{-1} must be noted, to which corresponds the one at 580 cm^{-1}. Both reveal the presence of $Fe^{II}(CN)_6$ in the sample. Evidently, the weight loss step in the TG curve and the first exothermic event must be ascribed to an internal redox reaction between Fe(III) and the coordinated CN^-. $Fe^{III}(CN)_6$ is still present in prevalent quantity (see band at 2105 cm^{-1}), while there is evidence of the oxidation of the coordinated cyanide. In fact, the presence of CO groups in the residue and the formation of cyanate can be noted (the large band in the interval 1700–1200 cm^{-1} and the one at 1300 cm^{-1}, respectively). The residue at 350°

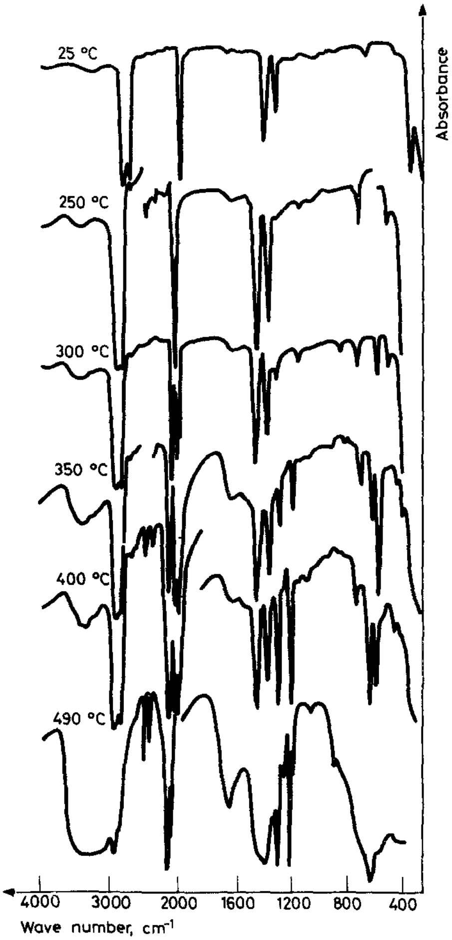

Fig. 6 Selected IR spectra of the residue of $K_3Fe(CN)_6$ heated up to different temperatures

clearly shows a different ratio of the starting compound and its products. From the absorption intensities, the samples appear to consist mainly of $Fe^{II}(CN)_6$ (bands at 2100–2000, 585 and 410 cm^{-1}), cyanate (bands at 630, 1200, 1280, 2150, 3350 and 3440 cm^{-1}) and carbonate (band in the interval 1700–1200 cm^{-1}). The sample heated at 490° does not show any cyanide content; it has been entirely transformed to cyanate and carbonate.

$K_3Co(CN)_6$. The TG curve of $K_3Co(CN)_6$ (Fig. 7) shows the beginning of a weight loss step at 350°, immediately followed by the decomposition of the sample in several steps, starting at 400°. In the same temperature range (350–500°), the DSC curve records a strong exothermic event (t_{max} = 430°), which is superimposed on

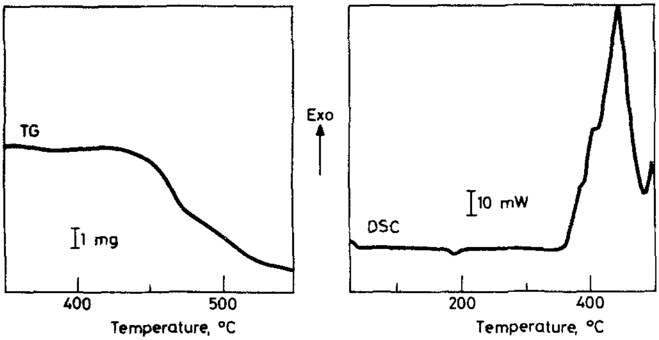

Fig. 7 Thermal analysis curves of $K_3Co(CN)_6$ in static air. Heating rate: 5 deg/min. Weight of the sample: 25.2 mg (TG), 17 mg (DSC)

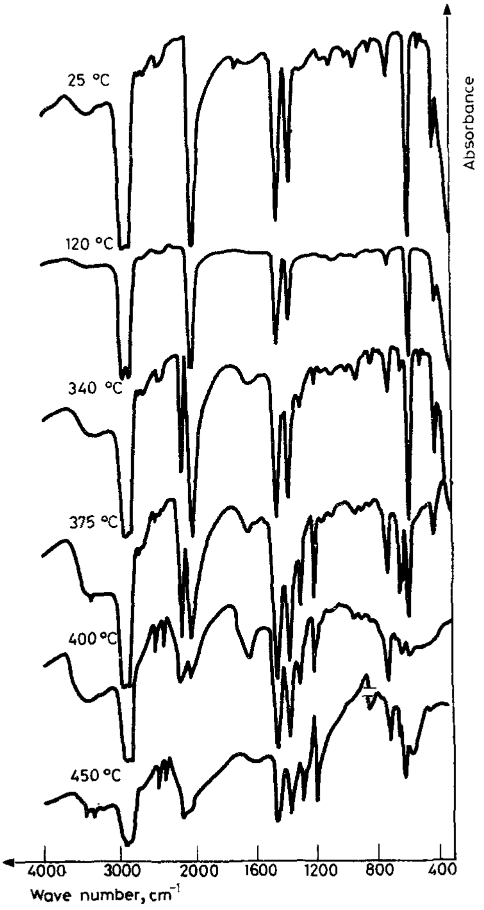

Fig. 8 Selected IR spectra of the residue of $K_3Co(CN)_6$ heated up to different temperatures

other, less intense thermal events. In the IR spectra, the characteristic bands $K_3Co(CN)_6$ (2120, 560 and 410 cm^{-1}) [23, 25, 26] remain unchanged up to 320°. The residue at 425° shows the bands of cyanate (3350, 3440, 2500, 2400, 1280, 1200 and 630 cm^{-1}), while the formation of carbonate is less evident than for the previous compounds. The sample still contains a high percentage of $K_3Co(CN)_6$, as demonstrated by the two absorption bands at 560 and 410 cm^{-1}, buth the structure of the band in the interval 2000–2200 cm^{-1} is deeply altered. It appears particularly large if compared with the one for the original sample, and has a tail towards low wavenumbers. Due to the presence of cyanate (identified by the other infrared absorptions), this band is certainly to be assigned to the νCN of the cyanate, at 2100–2200 cm^{-1}. Moreover, the lengthened form towards low wavenumbers indicates [8, 31, 32] (also on the analogy of $Fe^{II}(CN)_6$ and $Fe^{III}(CN)_6$) the presence of cyano complexes of Co(II), derived from the internal reduction of Co(III) by the coordinated cyanide. Such a hypothesis is supported by two further points:

1 The exothermic event, which indicates that the chemical process is not a mere thermal decomposition.

2 The recording of a band at 650 cm^{-1} (Fig. 8, at 425°), the intensity of which increases as the intensities of those at 410 and 510 cm^{-1} decrease. This band at 650 cm^{-1} can be ascribed to $\nu Co^{II}CN$. In fact, it is centred about 90 cm^{-1} higher with respect to the band relating to $\nu Co^{III}CN$ (it is known that the strength of the M—CN bond increases as the oxidation number of the central metal ion decreases, and for the couple $Fe^{III}(CN)_6/Fe^{II}(CN)_6$ a positive shift of about 70–80 cm^{-1} has been observed [23, 25, 26, 32].

$K_2Hg(CN)_4$. The TG behaviour of this compounds is very simple. It exhibits a sharp, vertical weight loss at 400° (Fig. 9). At the same time, a large exothermic peak

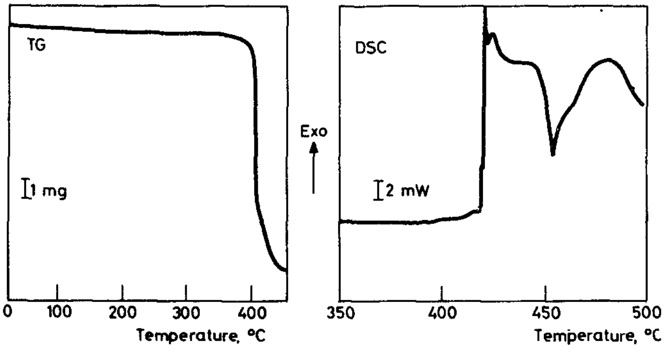

Fig. 9 Thermal analysis curves of $K_2Hg(CN)_4$ in static air. Heating rate: 5 deg/min. Weight of the sample: 20.5 mg (TG), 10 mg (DSC)

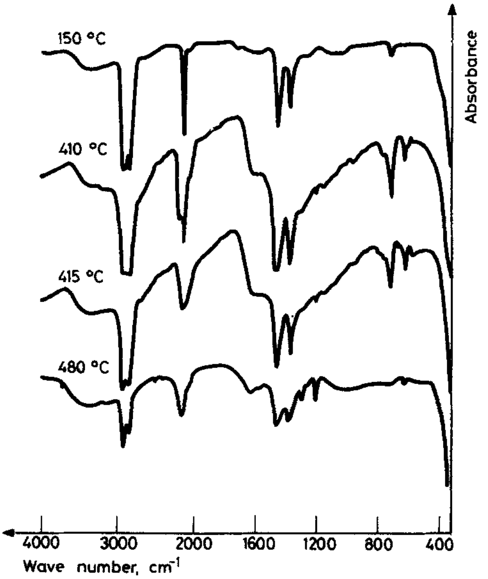

Fig. 10 Selected IR spectra of the residue of $K_2Hg(CN)_4$ heated up to different temperatures

is recorded in the DSC curve. The IR spectra of the residues at 410, 415 and 480° show the large band of carbonate, traces of cyanate and broadening of the νCN band, for which what was previously said for $K_3Co(CN)_6$ still holds.

Conclusions

The heating of the compounds studied here up to 500° leads to the formation of carbonate and cyanate in different percentages, depending on the heating temperature and on the original compound. For the cyanide complexes, it must be stressed that endothermic effects were never recorded and consequently "decomplexing" reactions and also the formation of cyanamide derivatives can be excluded for the complexes examined in this research.

The external oxidation, by air, of the coordinated ligand and an internal redox reaction coupled with weight loss and probable evolution of $(CN)_2$ [10–15, 18] are observed when the redox properties of the central metal ion in the anion moiety allow this. This process is clearly evident in the cases of $K_3Fe(CN)_6$ and $K_3Co(CN)_6$ and it can also be presumed for $K_2Hg(CN)_4$.

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Zusammenfassung — Das thermische Verhalten der Cyanoverbindungen NaCN, $K_4Fe(CN)_6 \cdot 3H_2O$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$ und $K_2Hg(CN)_4$ wurde mittels konventioneller thermischer Analysentechniken und Infrarotspektroskopie untersucht. Die Ergebnisse deuten darauf hin, daß bei allen Komplexen keine „Dekomplexierungs"-Reaktionen verlaufen und bei den Verbindungen $K_3Fe(CN)_6$, $K_3Co(CN)_6$ und $K_2Hg(CN)_4$ „interne" Redoxreaktionen vor sich gehen. In allen untersuchten Fällen werden Cyanat und Carbonat gebildet.

Резюме — Используя обычeные термоаналитические методы и ИК спектроскопию, было изучено термическое поведение цианосоединений NaCN, $K_4Fe(CN)_6 \cdot 3H_2O$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$ и $K_2Hg(CN)_4$. Полученные результаты служат доказательством отсутствия для всех комплексов реакций «декомплексирования» и отсутствие «внутренних» окислительно-восстановительных реакций для соединений $K_3Fe(CN)_6$, $K_3Co(CN)_6$ и $K_2Hg(CN)_4$. Разложение всех исследованных соединений протекает с образованием цианата и карбоната.