

MÖSSBAUER STUDIES OF THERMAL DECOMPOSITION OF METAL(II) HEXACYANOFERRATES(II)

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(Received February 3, 1982; in revised form October 16, 1982)

The thermal decompositions of metal(II) hexacyanoferrates(II) (Co, Ni and Zn) were studied in air with Mössbauer, infrared, thermal analysis and magnetic susceptibility techniques. Dehydration is almost complete at 200° and decomposition starts at 250° in the cases of cobalt and nickel hexacyanoferrates(II), and at 300° for zinc hexacyanoferrates(II). Finally, ferrites are formed as decomposition products.

Wolski and coworkers [1] reported the formation of ferromagnetic materials by heating hexacyanoferrates(II) and hexacyanoferrates(III) with the nitrates of bivalent metals (Ba, Mg, Sr, Zn, Cd, Pb, Cu, Co and Ni). Chamberlain and coworkers [2] investigated the thermal decompositions of hexacyanoferrates(II) and ferrates(III) by using DTA and DGE. Gallagher [3] studied the formation of rare earth orthoferrites by the thermal decomposition of rare earth hexacyanoferrates(III) or cobaltcyanides. In our earlier papers, the thermal decompositions of tin(IV) [4a], zirconium(IV) [4b], thorium(IV) [4c] and metal(III) (Al, As, Sb and Bi) hexacyanoferrates(III) have been reported. Seifer and coworkers [5-7] studied the thermal decompositions of hexacyanoferrates(II) in an inert atmosphere and reported the formation of Fe₃C, C, N, Fe and metal cyanide. The aim of the present communication was to observe the effects of the metals (cobalt, nickel and zinc) on the thermal decompositions of hexacyanoferrates(II). As a continuation of our previous work, we now report results on the thermal decompositions of $M_2Fe(CN)_6 \cdot xH_2O$ ($M = Co, Ni$ and Zn) obtained with Mössbauer, infrared, thermal analysis and magnetic susceptibility measurements.

Experimental

To prepare cobalt hexacyanoferrate(II), $Co_2Fe(CN)_6 \cdot 6H_2O$, a 2 M aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ was added to a 1 M aqueous solution of potassium hexacyanoferrate(II), and the mixture was heated on a water-bath for half an hour. The precipitate thus formed was filtered off, and washed with water till free from potassium ions. The absence of potassium ion was confirmed by flame photometry. The

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precipitate was dried in an oven. In a similar way, nickel hexacyanoferrate(II) and zinc hexacyanoferrate(II) were prepared by mixing nickel nitrate or zinc nitrate with potassium hexacyanoferrate(II).

All these hexacyanoferrates(II) were heated in air at 100°, 150°, 200°, 250° and 300° for 3 hours. The samples were heated in an open crucible in a muffle furnace. The rate of heating was kept at 10 degree/min. The variation in the final temperatures was $\pm 5^\circ$.

The experimental details of the Mössbauer investigation were reported earlier [4]. For the infrared spectrum, 2% of the sample was taken and mixed with KBr and the spectrum was recorded on a MOM-2000 spectrophotometer (Hungary) in the range 4000–700 cm^{-1} . Thermal gravimetric studies were performed on a TG fabricated by FCI (India) and a DTA-02 Universal (GDR) was used for the investigation.

Results and discussion

Infrared spectra of the samples were recorded at room temperature. Cobalt hexacyanoferrate(II) showed a broad band at 3550–3200 cm^{-1} , a weak band at 1620 cm^{-1} due to OH stretching and bending of water molecules, and a strong band at 2080 cm^{-1} due to the cyanide groups. In the case of nickel hexacyanoferrate(II), the infrared bands at 3500–3200 cm^{-1} and 1620 cm^{-1} are due to water molecules, whereas a strong band at 2070 cm^{-1} is due to the cyanide groups. The infrared spectrum of zinc hexacyanoferrate(II) shows bands at 3500–3200 cm^{-1} and 1610 cm^{-1} due to OH stretching and bending of water, and a strong band at 2090 cm^{-1} due to cyanide. The Mössbauer spectra of all three hexacyanoferrate(II) display a single absorption band, as shown in Fig. 1a, b, c.

The isomer shift values for cobalt, nickel and zinc hexacyanoferrates(II) are 0.16, 0.18 and 0.18 mm s^{-1} , respectively. These values are comparable to those in the literature [8]. Goel and Garg [9] have reported that the isomer shift decreases in going from potassium to hydrogen hexacyanoferrate(II), due to the increasing electronegativity of the cation. However, no such relation has been observed for the hexacyanoferrates(II) of cobalt(II), nickel(II) and zinc(II). This may be due to the fact that there is only a negligible difference between the electronegativities of these cations. Zinc hexacyanoferrate(II) is diamagnetic, due to the complete filling of the t_{2g} orbitals of the iron(II) ion and the d^{10} electron configuration of the zinc(II) ion. On the other hand, cobalt and nickel hexacyanoferrates(II) exhibit paramagnetic behaviour, with ψ_g values of 12.5×10^{-6} and 7.1×10^{-6} CGS, respectively. In these hexacyanoferrates(II), the cobalt and nickel are in the high-spin state, due to the weak field of the water ligand, and hence show paramagnetic behaviour. The magnetic susceptibility values are comparable to those in literature [10–12].

When heated at 100° for 3 hours in air, none of these hexacyanoferrates(II) showed any change in isomer shift or in the shape of the spectrum. The DTA curves reveal an endothermic peak at 100° in all cases, indicating the loss of uncoordinated water

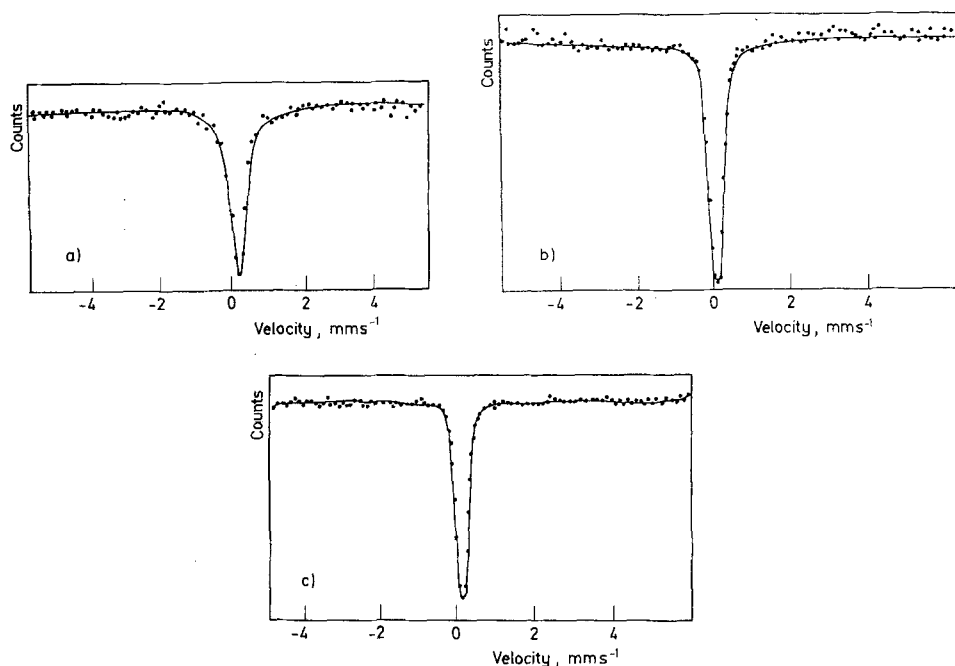


Fig. 1 (a) Mössbauer spectrum of cobalt ferrocyanide at room temperature (25°C)
 (b) Mössbauer spectrum of nickel ferrocyanide at room temperature (25°C)
 (c) Mössbauer spectrum of zinc ferrocyanide at room temperature (25°C)

molecules. The loss of weight on TG are 0.7, 8 and 1.5% for cobalt(II), nickel(II) and zinc(II) hexacyanoferrate(II), respectively, which corresponds to the removal of uncoordinated water molecules. There is no significant change in these infrared spectra, except that the intensity of the absorption band due to water shows a slight decrease as compared with that of the cyanide group. Zinc hexacyanoferrate(II) remains diamagnetic at 100°, whereas the paramagnetic characters of cobalt and nickel hexacyanoferrates(II) increase, with values of $\psi_g = 13.90 \times 10^{-6}$ and 9.34×10^{-6} CGS, respectively. The slight increases in ψ_g may be due to the loss of water molecules, which are diamagnetic in nature. From the above observation it can be concluded that dehydration starts at 100°.

The Mössbauer spectra of the hexacyanoferrates(II) heated at 150° do not show any change in the three cases. Thermogravimetric analysis revealed 5.5, 18.7 and 5.0% weight losses for cobalt, nickel and zinc hexacyanoferrate(II), respectively. These weight losses are due to the loss of coordinated water molecules. In the cases of cobalt and zinc hexacyanoferrates(II), the loss in weight corresponds to the removal of three more water molecules. Since two coordinated water molecules were already lost at 100°, the total loss amounts to five water molecules. Zinc hexacyanoferrate(II) is still

Table 1 Mössbauer parameters of hexacyanoferrate(II) complexes

Complex	Isomer shift, mm^{-1}	Width at half maximum, mm s^{-1}	Percentage absorption	Colour
$\text{Co}_2\text{Fe}(\text{CN})_6 \cdot 6 \text{H}_2\text{O}$	0.16 ± 0.04	0.40	16	grey green
$\text{Ni}_2\text{Fe}(\text{CN})_6 \cdot 11 \text{H}_2\text{O}$	0.18 ± 0.04	0.40	22	light green
$\text{Zn}_2\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$	0.18 ± 0.04	0.37	18	white

Table 2 Mössbauer parameters of heat treated hexacyanoferrate(II) complexes

*Complex		Temperature of treatment			
		100°	200°	250°	300°
1. $\text{Co}_2\text{Fe}_2(\text{CN})_6 \cdot 6 \text{H}_2\text{O}$	δ	0.16 ± 0.04	0.16 ± 0.04	0.27 ± 0.06	0.52 ± 0.06
	Δ	—	—	0.61 ± 0.06	—
	δ	—	—	0.94 ± 0.06	—
	HI	—	—	485 ± 6	501 ± 6
2. $\text{Ni}_2\text{Fe}(\text{CN})_6 \cdot 11 \text{H}_2\text{O}$	δ	0.18 ± 0.04	0.18 ± 0.04	0.60 ± 0.04	0.52 ± 0.06
	Δ	—	—	0.72 ± 0.04	—
	HI	—	—	—	510 ± 6
3. $\text{Zn}_2\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$	δ	0.18 ± 0.04	0.18 ± 0.04	0.18 ± 0.04	0.52 ± 0.06
	Δ	—	—	0.60 ± 0.04	—
	HI	—	—	0.42 ± 0.06	501 ± 6

*One percent complex

δ = isomer shift, mm s^{-1} ; Δ = quadrupole splitting, mm s^{-1} ; HI = magnetic field, KOe.

diamagnetic at this temperature, whereas cobalt and nickel hexacyanoferrates(II) show further increases in their ψ_g values, to 17.1×10^{-6} and 7.9×10^{-6} CGS, respectively.

Samples heated at 200° do not show any change in the Mössbauer spectrum. The infrared spectra of the samples of cobalt and zinc hexacyanoferrates(II) display very weak bands due to water as compared to the strong band of the cyanide groups. In the case of nickel hexacyanoferrate(II) the water band is absent and there is only a cyanide band at 2070 cm^{-1} . On TG, the weight loss at 200° is 10.5% for cobalt hexacyanoferrate(II), which is due to the loss of three water molecules. The weight loss for nickel hexacyanoferrate(II) is 34%, which corresponds to the loss of ten of the eleven water molecules. On TG, zinc hexacyanoferrate(II) shows a 10% weight loss, which amounts to the loss of two water molecules. Zinc hexacyanoferrate(II) remains diamagnetic at 200°, whereas the ψ_g values for cobalt and nickel hexacyanoferrate(II) are 18.4 and 8.5×10^{-6} CGS, respectively, demonstrating an increasing loss of diamagnetic water molecules.

On heating at 250°, cobalt hexacyanoferrate(II) was found to decompose completely. The Mössbauer spectrum of the sample is a six-line pattern due to nuclear Zeeman hyperfine interactions. The isomer shift is 0.21 mm s^{-1} and the magnetic field 484 KOe, along with a doublet near zero velocity having an isomer shift of 0.61 mm s^{-1} and a quadrupole splitting of 0.94 mm s^{-1} as shown in Fig. 2a.

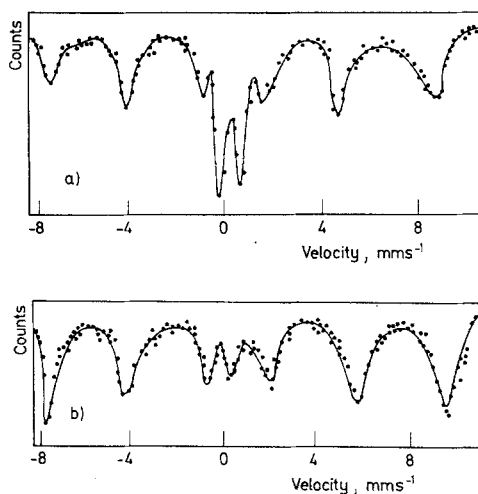


Fig. 2 (a) Mössbauer spectrum of cobalt ferrocyanide heated at 250°C
(b) Mössbauer spectrum of cobalt ferrocyanide heated at 300°C

This doublet along with the six-line pattern points to the formation of cobalt ferrite ($\text{CoFe}_2^{\text{III}}\text{O}_4$) of various particle sizes. Ferrite has a spinel structure [13]. There is a tremendous increase in magnetic susceptibility (ψ_g), which shows the formation of ferrite. The infrared spectra did not show any absorption band between 4000 and 700 cm^{-1} , thereby indicating complete decomposition of the complex at 250°. An exothermic peak at 260° on DTA may be due to a phase transformation of the ferrite. The weight loss found on TG is 12.5%, which is very small as compared to the calculated decomposition reaction. This may be due to the time factor, i.e. in TG the sample is heated at this temperature for a short time, whereas the sample was heated for 3 hours. Hence, these observations show that at 250° cobalt hexacyanoferrate(II) decomposes to form cobalt ferrite and cobalt oxide. Nickel hexacyanoferrate(II) heated at 250° displays a doublet in the Mössbauer spectrum (Fig. 3a), the peaks of the doublet having different intensities. The first peak is the resultant of the absorption band due to nickel hexacyanoferrate(II) and one band of the doublet of nickel(II) ferrite ($\text{Ni}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$). The doublet due to $\text{NiFe}_2^{\text{III}}\text{O}_4$ has an isomer shift of 0.60 mm s^{-1} and a quadrupole splitting of 0.72 mm s^{-1} . The isomer shift and quadrupole splitting values show that the iron is in oxidation state

three, in the high-spin state in a non-cubic symmetry. Kirichok and coworkers [14] have reported an isomer shift value of 0.39 mm s^{-1} (relative to natural iron) for $\text{NiFe}_2^{\text{III}}\text{O}_4$, which is close to our value. Infrared spectra of the samples show the presence of a band at 2080 cm^{-1} due to cyanide groups. ψ_g values could not be measured with our apparatus due to the superparamagnetic character of the products. DTA reveals an endothermic peak at 250° , which may be due to the loss of water molecules. The sample becomes slightly paramagnetic, with $\psi_g = 6.29 \times 10^{-6}$ CGS, which is due to the loss of water molecules and also possibly to very slight decomposition. From the above observation it can be concluded that at 250° zinc hexacyanoferrate(II) is stable, cobalt hexacyanoferrate(II) decomposes completely to give cobalt ferrite and cobalt oxide, while nickel hexacyanoferrate(II) is partially decomposed to nickel(II) ferrite and nickel oxide.

In the next stage, the samples were heated at 300° . Cobalt hexacyanoferrate(II) at this temperature gave a six-line Mössbauer spectrum due to magnetic hyperfine interactions; the value of the internal magnetic field at the nucleus is 501 KOe (Fig. 2b). The absorption band due to hexacyanoferrate(II) is absent. The internal magnetic field of 501 KOe is comparable to the value of 516 KOe reported at room temperature [13, 15, 16]. These values are comparable to those for $\alpha\text{-Fe}_2\text{O}_3$. The spectra of the ferrites and $\alpha\text{-Fe}_2\text{O}_3$ are similar in appearance. There is no absorption band in the infrared spectrum in the region $4000\text{--}700 \text{ cm}^{-1}$, which confirms the complete decomposition of cobalt hexacyanoferrate(II). The value of ψ_g increases to 2111×10^{-6} CGS, which is due to the highly paramagnetic character of the ferrites. Nickel hexacyanoferrate(II) heated at 300° gave a six-line Mössbauer spectrum due to magnetic hyperfine interactions. The value of the isomer shift was 0.52 mm s^{-1} and the internal magnetic field 518 KOe (Fig. 3b). Kirichok and coworkers [14] have reported an internal magnetic field of 505 KOe for nickel ferrite ($\text{Ni}_2^{\text{II}}\text{Fe}^{\text{III}}\text{O}_4$). In the infrared spectrum there is no absorption band in the $4000\text{--}700 \text{ cm}^{-1}$ region, and the weight loss on TG is 52%, confirming decomposition. Hence, from these observations it can be concluded that at 300° nickel ferrite is formed. Zinc hexacyanoferrate(II) heated at 300° gave a six-line Mössbauer spectrum due to magnetic hyperfine interactions, along with a doublet. The isomer shift and quadrupole splitting values of doublet set 0.60 and 0.42 mm s^{-1} , respectively. The value of the internal magnetic field is 510 KOe (Fig. 4). Evans and coworkers [17] and Robbins and coworkers [18] have reported an isomer shift of 0.36 mm s^{-1} and a quadrupole splitting of 0.35 mm s^{-1} (with respect to natural iron), which are in agreement with our values. Duncan and coworkers [19] observed this type of spectrum while studying the solid-state reaction between ZnO and Fe_2O_3 at high temperature. There is no absorption band in the infrared region ($4000\text{--}700 \text{ cm}^{-1}$), which points to the complete decomposition of zinc hexacyanoferrate(II). The sample is paramagnetic ($\psi_g = 222 \times 10^{-6}$ CGS). The weight loss on TG is 20%, which is less than that calculated from the decomposition, due to the different time of decomposition.

From all these observations it can be concluded that the temperatures of decomposition of these hexacyanoferrates(II) are different. At 250° cobalt hexacyanoferrate(II)

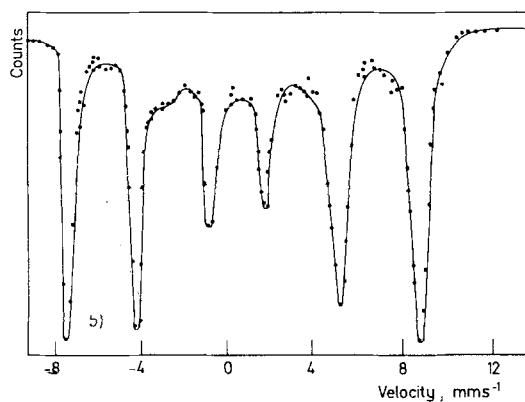
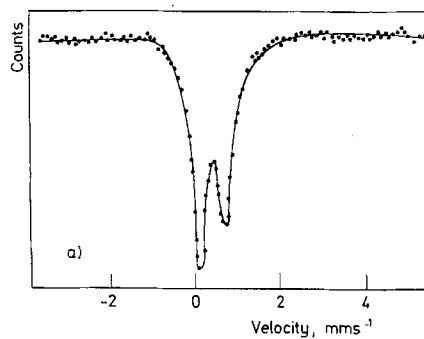


Fig. 3 (a) Mössbauer spectrum of nickel ferrocyanide heated at 250°C
 (b) Mössbauer spectrum of nickel ferrocyanide heated at 300°C

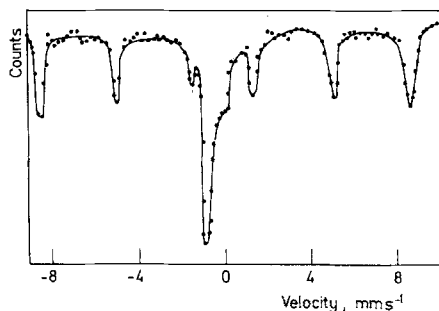
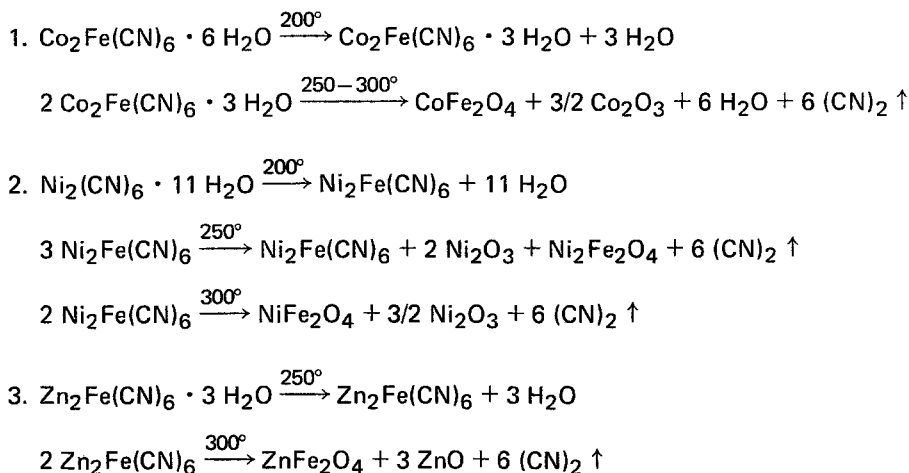


Fig. 4 Mössbauer spectrum of zinc ferrocyanide heated at 300°C

decomposed completely, while the nickel salt was partially decomposed and the zinc salt was stable. All of them are decomposed at 300°. It may be possible that cobalt(II), nickel(II) and zinc(II) first form oxides, as they are weakly bonded to the $\text{Fe}(\text{CN})_6^{4-}$ moiety, while Fe^{2+} forms strong bonds with cyanide ligands. The oxides formed may

subsequently act as catalysts to decompose $\text{Fe}(\text{CN})_6^{4-}$. This is supported by data from the earlier investigation of the decomposition of tin hexacyanoferrate(II) (4a). It was observed that at low temperature the outer tin(IV) is converted to oxide, which then acts as a catalyst to decompose $\text{Fe}(\text{CN})_6^{4-}$.

Though the actual mechanism of thermal decomposition of these hexacyanoferrates(II) may be complex, on the basis of the present studies the following pathways of decomposition may be suggested:



The weight loss found on TG in the case of cobalt hexacyanoferrate(II) at 200° is 12.3%, which is in agreement with the weight loss calculated for the decomposition step at 200° , i.e. 9.8%, while the weight loss on TG at 300° is 37%, which is lower than the weight loss at 300° due to complete decomposition (45%). In the case of nickel hexacyanoferrate(II), the weight loss on TG is 34%, which is slightly higher than that calculated for the dehydration step at 200° (37.6%), which may be due to slight decomposition. The weight loss at 300° on TG is 52% and that for complete decomposition is 54.2%. This is due to heating of the sample for 3 hours. The weight loss in the case of zinc hexacyanoferrate(II) is 10% on TG at 250° , while according to step 1 (250°) 13.6% would be expected for dehydration. For complete decomposition the calculated weight loss is 38.9%, which is higher than the 30 percent on TG; this shows that the earlier decomposition was completed at 300° on heating for 3 hours.

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Zusammenfassung — Die thermische Zersetzung von Metall(II)-hexacyanoferraten(II) (Co, Ni, Zn) in Luft wurde unter Anwendung der Mössbauer- und Infrarotspektroskopie, der thermischen Analyse und magnetischer Suszeptibilitätsmessungen untersucht. Bei 200°C ist die Dehydratisierung nahezu vollständig und die Zersetzung beginnt im Falle des Kobalt- und Nickel-hexacyanoferrats(II) bei 250°C, während die des Zink-hexacyanoferrats(II) schon bei 300°C einsetzt. Als Endprodukt der Zersetzung entstehen Ferrite.

Резюме — С помощью мёссбауэровской и инфракрасной спектроскопии, термического анализа и метода магнитной восприимчивости было изучено термическое разложение гексацианоферратов двухвалентных кобальта, никеля и цинка. Дегидратация полностью протекает при 200° а при 250° начинается разложение гексацианоферратов кобальта и никеля. Разложение же гексацианоферрата цинка начинается при 300°. Конечными продуктами разложения являются ферриты.