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Mössbauer Studies of Thermal Decomposition of Hexaamminecobalt(III) Hexacyanoferrate(III) and Hexaamminecobalt(III) Hexachloroferrate(III) in Air and in Nitrogen Atmosphere

Ajaib Singh BRAR,*,† Sarvjit BRAR, and Sarjit Singh SANDHU
Chemistry Department, Guru Nanak Dev University, Amritsar-143005, India

(Received January 23, 1981)

Thermal decomposition of hexaamminecobalt(III) hexacyanoferrate(III) (**1**) and hexaamminecobalt(III) hexachloroferrate(III) (**2**) in air as well as in nitrogen atmosphere was studied by using Mössbauer spectroscopy, TGA, DTA, IR spectroscopy, and magnetic susceptibility measurement. **1**, when heated in air, is stable up to 200 °C and then converted into hexacyanoferrate(II) and finally to ferrites; in inert atmosphere iron metal and carbides are formed above 400 °C. **2** in air is reduced to iron(II) species and finally to ferrites; in inert atmosphere ligand exchange takes place forming cobalt(II) chloride. A mechanism is proposed for the decompositions of **1** and **2**.

Mössbauer spectroscopy is a very helpful tool for the investigation of change in the oxidation state of intermediates.[1–3] Sanyal and Dass[4] used DTA and TGA to study thermal decomposition of iron(III) tris(oxalato)ferrate(III) tetrahydrate. Gallagher and Shurey[5] applied DTA, TGA, and the Mössbauer effect for studying thermal decomposition of europium hexacyanoferrate(III) and ammonium europium hexacyanoferrate(II). Recently, evidence has been given by Gibb[6] from Mössbauer spectroscopy for an orbitally degenerate ground state in hexaamminecobalt(III) hexacyanoferrate(III). Peev and Kurtev[7] reported that solid state decomposition of iron complexes gives ferrites, which are useful because of their semiconducting properties as well as catalytic properties. They reported a change in Mössbauer parameters with catalytic properties of ferrites. The aim of the present paper is to study thermal decomposition of hexaamminecobalt(III) hexacyanoferrate(III) and hexaamminecobalt (III) hexachloroferrate(III) and to disclose effects of ligand on thermal decomposition patterns, by using Mössbauer spectroscopy, TGA, DTA, IR spectra, and magnetic susceptibility measurements.

Experimental

Hexaamminecobalt(III) hexacyanoferrate(III) (**1**) and hexaaminecobalt(III) hexachloroferrate(III) (**2**) were prepared by the methods described in Refs. 6 and 8, respectively. For **2** a solution of hexaamminecobalt(III) trichloride (0.0016 mol) in 3.4 mol dm^{-3} HCl was treated with an aqueous solution of $FeCl_3 \cdot 6H_2O$ (0.005 mol) at 70 °C. The precipitates thus obtained were washed with ethanol and ether and dried in a vacuum desiccator. **1** was obtained as yellow needle-like crystals from a mixed aqueous solution of hexaamminecobalt(III) trichloride and potassium hexacyanoferrate(III).

IR spectra were recorded on a Mom-2000 spectrophotometer (Hungarian Optical Works) in the range 4000—700 cm^{-1} and magnetic susceptibility was measured by Gouy's method using Hg $[Co(SCN)_4]$ as calibrant. TGA and DTA thermograms were recorded in air at Chemistry Department, I.I.T., Bombay.

For thermal decomposition, **1** or **2** was heated in silica crucibles in a tubular furnace at 100, 200, 300, 400, 500, and 700 °C for 3 h in air or under a flowing nitrogen atmosphere. The nitrogen used for arranging inert atmosphere was purified by passage through copper heated at 300 °C and then through traps of anhydrous calicum chloride and potassium hydroxide. The temperature of the furnace was measured by a small chromel-alumel thermocouple connected to a portable potentiometer (Toshniwal Industries (P), Ltd., India). The sample was heated at a specified temperature for 3 h in air, or under a flowing nitrogen atmosphere. The rate of heating was kept 10 °C/min. The variation in temperature was ±5 °C. The experimental detail of our Mössbauer investigation was described in Refs. 9 and 10. Values for isomer shift were determined with reference to the natural iron.

TABLE 1. MÖSSBAUER PARAMETERS, ISOMER SHIFT (δ) AND QUADRUPOLE SPLITTING (Δ) OF HEXAAMMINECOBALT(III) HEXACYANOFERRATE(III) (**1**), AND HEXAAMMINECOBALT(III) HEXACHLOROFERRATE(III) (**2**) AND THEIR THERMAL DECOMPOSITION PRODUCTS

Complex		$\delta^{a)}$ or Δ/mm s^{-1} at				
		25 °C(R.T.)	200 °C in air	300 °C in air	500 °C in air	700 °C in air
$Co(NH_3)_6Fe(CN)_6$	δ	0.12±0.03	0.31±0.03	0.33±0.09	0.33±0.09	0.33±0.09
	Δ	0.35±0.03	0.75±0.03	—	—	—
				HI=492 kOe	HI=492 kOe	HI=492 kOe
$Co(NH_3)_6(FeCl_6)$	δ	0.41±0.03	0.38±0.03	0.31±0.09	0.31±0.09	0.33±0.09
	Δ	—	—	—	—	—
				HI=514 kOe	HI=506 kOe	HI=502 kOe

a) All the values of isomer shift refer to the natural iron.

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† Present address: Chemistry Department, Indian Institute of Technology, New Delhi-110016, India.

Results and Discussion

The Mössbauer spectrum of **1** (at 25 °C) indicates an isomer shift value −0.12 mm/s and a quadrupole splitting 0.35 mm/s. The relatively small value of quadrupole doublet is as expected from a distorted trigonal symmetry at the Fe site[6] (Fig. 1a). Infrared frequencies and magnetic measurements confirm the formation of **1** since they are in agreement with the values given in Refs. 11 and 12. The TGA thermogram of the complex in air does not show any weight loss up to 200 °C (Fig. 2), whereas in the DTA thermogram there is an exothermic peak at 175°C and another exothermic peak at 278 °C (Fig. 3). The Mössbauer spectrum of the sample heated at 200 °C for 15 min shows formation of hexacyanoferrate(II) as identified by a single absorption band having an isomer shift value −0.14 mm/s (Fig. 4). There is another doublet due to the parent complex and a six-line pattern associated with magnetic hyperfine splitting. The intensity of magnetic field at the nucleus is 492 kOe (1 Oe=(1000/4π) A m^{-1}), which is only slightly lower than that for normal α-Fe_2O_3. These observations reveal that on heating at this temperature a part of hexacyanoferrate(III) is reduced to hexacyanoferrate(II), while decomposition to α-Fe_2O_3 occurs concurrently.

1 was heated at 200 °C for 3 h. The Mössbauer spectrum of this sample shows a doublet (Fig. 1b) which has a quadrupole splitting of 0.79 mm/s and an isomer shift of 0.31 mm/s. These values are typical of the tervalent iron of $CoFe_2{}^{III}O_4$ in the superparamagnetic state. The value of isomer shift shows that the complex has the iron in high spin state. Mössbouer spectra of the samples thermally decomposed at 300, 500, and 700 °C in air are given in Fig. 5. The spectrum of the sample heated at 300 °C shows a six-line pattern due to magnetic hyperfine splitting which has an isomer shift value 0.33 mm/s. It also exhibits a doublet due to superparamagnetism, indicating the formation of $CoFe_2{}^{III}O_4$. The Mössbauer parameters of α-Fe_2O_3 and

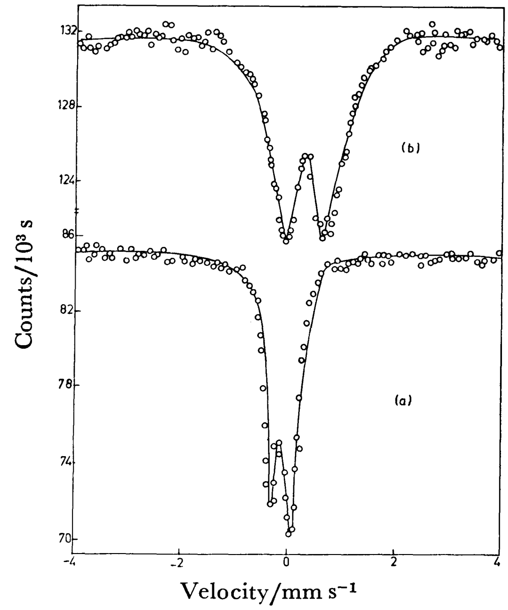

Fig. 1. (a) Mössbauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) at room temperature (25 °C). (b) Mössbauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) heated in air at 200 °C for 3 h.

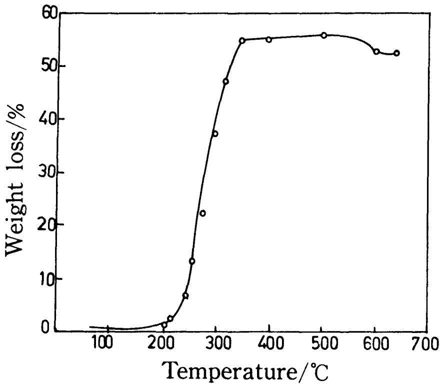

Fig. 2. TGA thermogram of hexaamminecobalt(III) hexacyanoferrate(III) in air.

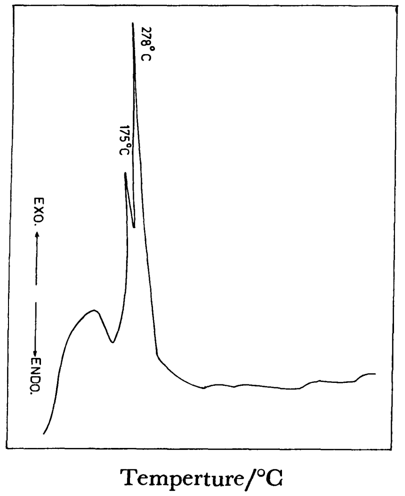

Fig. 3. DTA thermogram of hexaamminecobalt(III) hexacyanoferrate(III) in air.

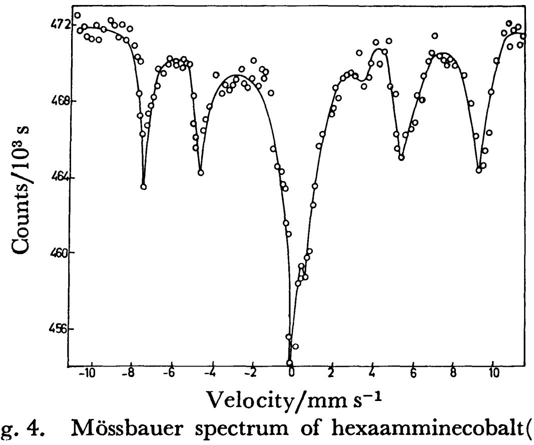

Fig. 4. Mössbauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) in air at 200 °C for 15 min.

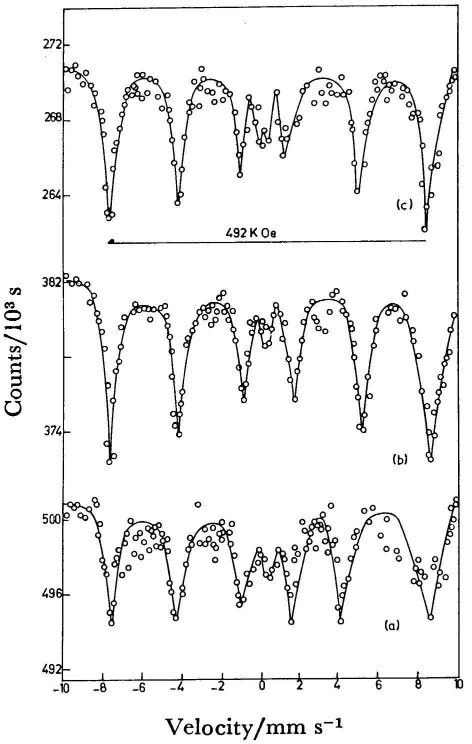

Fig. 5. (a) Mössbauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) heated in air at 300 °C for 3 h. (b) Mössbauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) heated in air at 500 °C for 3 h. (c) Mössbauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) heated in air at 700 °C for 3 h.

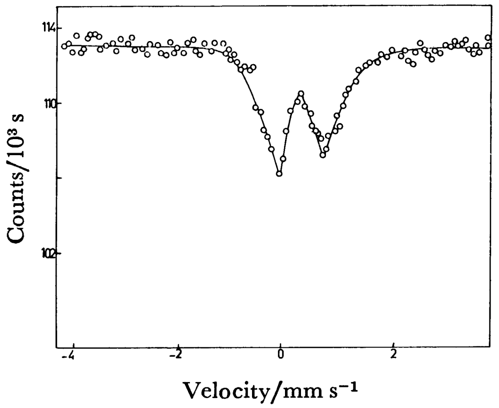

Fig. 6. Mössbauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) heated under nitrogen at 300 °C for 3 h.

$CoFe_2^{III}O_4$ are almost identical with each other at room temperature and any different sites are not resolved in ferrite, the intensity of magnetic field at the nucleus being about 510 kOe[13–15] in both the compounds. However, we assign the six-line pattern to $CoFe_2^{III}O_4$ since cobalt is available at this stage.

On further heating up to 700 °C, no remarkable change was found in the nature of this sample. The weight loss at 350 °C is 55%, which shows formation of ferrites. The DTA peak at 278 °C is considered to be due to oxidation of the complex (Fig. 3).

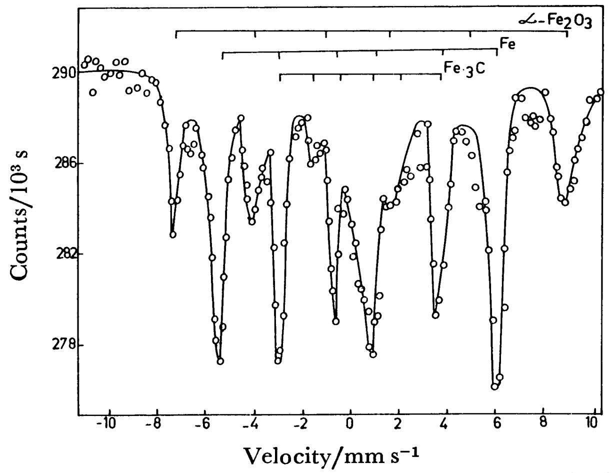

Fig. 7. Mössbabauer spectrum of hexaamminecobalt(III) hexacyanoferrate(III) heated heated under nitrogen at 400 °C for 3 h.

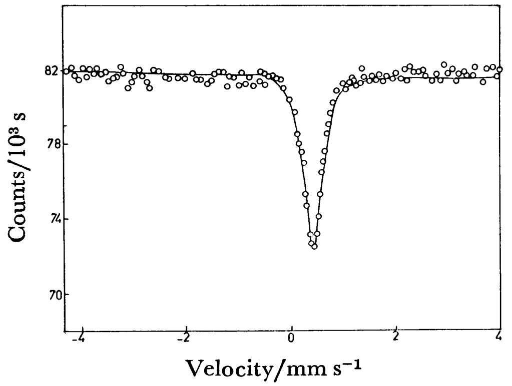

Fig. 8. Mössbauer spectrum of hexaamminecobalt(III) hexachloroferrate(III) at room temperature (25 °C).

1 was heated under a flowing oxygen-free nitrogen atmosphere. No change was found in values for isomer shift and quadrupole splitting up to 200 °C. At 300 °C the sample gives a higher value of isomer shift 0.37 mm/s and a value of quadrupole splitting 0.63 mm/s, which may be due to ligand exchange (Fig. 6). Frequency γ(C≡N) in the infrared region shows the splitting having absorption bands at 2250 and 2125 cm^{-1}, and the band at 3200 cm^{-1} may be due to NH_3 stretching, in support of the exchange mechanism. On further heating, Mössbauer spectra show formation of iron metal, iron carbide, and a small quantity of ferrite, as shown in Fig. 7. Oxidation takes place only after the sample has been exposed to air to make the strip for recording Mössbauer spectrum. Formation of these products was confirmed also by magnetic measurements.

The Mössbauer spectrum of **2** (at 25 °C) shows a single line absorption band having an isomer shift 0.41 mm/s (with respect to the natural iron) and a line width 0.40 mm/s which indicates a cubic symmetry around the iron atoms, and the electron density is the same in all the d-orbitals of iron(III) (Fig. 8). The value of isomer shift shows that the complex is in a high spin (+3) oxidation state. Infrared frequencies

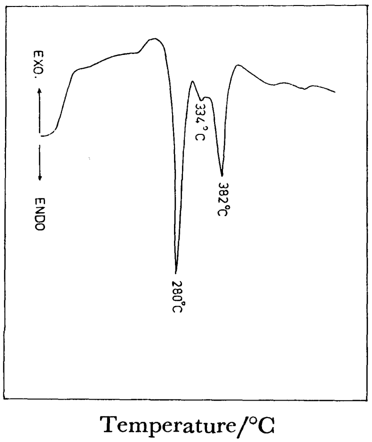

Fig. 9. DTA thermogram of hexaamminecobalt(III) hexachloroferrate(III) in air.

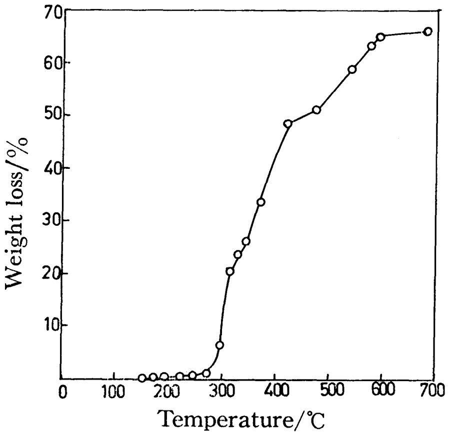

Fig. 10. TGA thermogram of hexaamminecobalt(III) hexachloroferrate(III) in air.

and ω_{eff} show formation of the above complex. The DTA thermogram shows an endothermic peak at 280 °C, very small endothermic peak at 334 °C, and a peak at 382 °C (Fig. 9). The TGA thermogram shows that there is no weight loss up to 270 °C, over which a weight loss occurs, as shown in Fig. 10. It is evident from the DTA and TGA data that this complex is stable up to 270 °C.

2 heated at 300 °C for 15 min gives a Mössbauer spectrum having an absorption band with an isomer shift 0.42 mm/s due to $FeCl_6^{3-}$ moeity and another doublet with an isomer shift 1.27 mm/s and a quadrupole splitting 1.69 mm/s due to Fe^{2+}, along with the magnetic hyperfine splitting of low intensity due to ferrite already mentioned (Fig. 11a). Thus it is clear that iron(III) is reduced to iron(II) and then oxidized to $CoFe_2^{III}O_4$.

The Mössbauer spectrum of the sample heated at 300 °C for 3 h in air shows a six-line pattern having a value of isomer shift 0.21 mm/s, as shown in Fig. 11b. The intensity of the magnetic field is 514 kOe, which agrees well with that of $CoFe_2O_4$. There was no observable change found in the spectra of the samples heated up to 700 °C (Figs. 11b and c). The magnetic moment of the sample at room temperature is 5.9 BM ($\psi_g=32.7\times10^{-6}$). The ψ_g values of the samples at 200 and 300 °C are 37.6×10^{-6} and 51.61×10^{-6} cgs, respectively. The samples heated at 400, 500, and 700 °C are highly paramagnetic and are attracted towards the magnet. The IR spectrum of the sample heated at 300 °C shows a peak at 3100—3300 cm^{-1} due to ν(N–H), a peak at 1600 cm^{-1} due to δ_{asy}(N–H), and a peak at 1400 cm^{-1} δ_{sym}(N–H), which shows the presence of ammonia at this temperature. Thus it is shown that the parent complex is present in the mixture along with the ferrites. There is, however, no absorption band in the range 4000—700 cm^{-1} with the samples heated at higher temperatures, which shows complete decomposition of the complex into ferrites. This is supported by magnetic susceptibility data. DTA and TGA thermograms also show elimination of ammonia and the chloride group by giving endothermic peaks at 334 and 382 °C. The samples for Mössbauer measurement were first heated at 300 °C and then at a higher constant temperature for 3 h, so that decomposition products were formed at a little lower temperature than expected in DTA and TGA. The weight loss is also in agreement with the formation of ferrites.

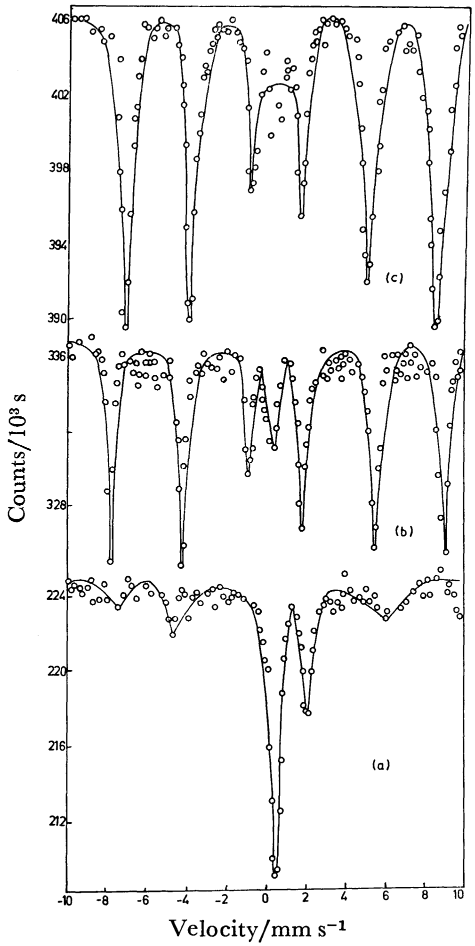

Fig. 11. (a) Mössbauer spectrum of hexaamminecobalt(III) hexachloroferrate(III) heated in air at 300 °C for 15 min. (b) Mössbauer spectrum of hexaamminecobalt(III) hexachloroferrate(III) heated in air at 300 °C for 3 h. (c) Mössbauer spectrum of hexaamminecobalt(III) hexachloroferrate(III) heated in air at 700 °C for 3 h.

In the case of **2** in inert atmosphere, the sample was found stable up to 300 °C. On further heating, for example, up to 400 °C, ligand exchange takes place. Even with the maximum care to avoid the samples from being exposed to air, they got fully oxidized when taken out of the furnace to make the strip for Mössbauer spectral recording. A chemical analysis of these pinkish products shows presence of cobalt(II) chloride, which is highly hygroscopic, absorbs water from air, and oxidizes the sample quickly. This is why the spectrum of the sample heated at 500 °C in inert atmosphere shows a ferrite pattern (Since we had no arrangement for recording Mössbauer spectra with sample kept in the furnace in nitrogen atmosphere, the experimental information obtainable was limited to what has been given above.).

From the above investigations it is clear that patterns of decomposition and products formed depend on ligands and atmospheres employed, as expected. For both the complexes the temperature of decomposition in air is lower than in inert atmosphere. The temperature of decomposition for **1** is comparable to the temperature of thermal decomposition for alkali metal hexacyanoferrate(III). But the temperature of decomposition for **2** is higher than those for hexacyanoferrate(III) complexes. **1** is reduced to ferrate(II) around 200 °C and on further heating to higher temperatures ferrites are formed in air, whereas iron metal and carbides are formed in inert atmosphere. In the case of **2**, on the other hand, the products formed under inert atmosphere are readily oxidizable and hygroscopic, absorb moisture and oxygen from air, and get oxidized partially to ferrites. In earlier investigations,[16] in a preparation of cobalt oxides from carbonates in vacuum, cobalt oxides prepared at 300 °C were observed to take oxygen from air and to change in color from grey to black. This type of oxidation of cobalt also results in formation of ferrites. Ligand exchange takes place at 300 °C forming cobalt(II) chloride, which was confirmed from its violet pink color and by chemical analysis. The products when exposed to air absorbed water from air, and iron and cobalt are oxidized to ferrites. This may be due to the high surface reactivity of small particles of the powdered iron and cobalt metals (The ferrites and mixed oxides formed by the decomposition of the abovementioned complexes are useful in industry because of their semiconducting as well as catalytic activities.).

Although the mechanism of solid state decomposition is complex, the present information furnished from Mössbauer, infrared, and magnetic measurements, differential thermal analysis, and thermogravimetric analysis, allows us to deduce the following paths of decomposition in air for **1** and **2**:

$$4[\mathrm{Co(NH_3)_6}][\mathrm{Fe(CN)_6}] \xrightarrow[15\,\mathrm{min}]{200\,^\circ\mathrm{C}} [\mathrm{Co(NH_3)_6}]_4[\mathrm{Fe(CN)_6}]_3$$
$$+ {}^1/_2\mathrm{Fe_2O_3} + 3(\mathrm{CN})_2,$$

$$[\mathrm{Co(NH_3)_6}]_4[\mathrm{Fe(CN)_6}]_3 + {}^1/_2\mathrm{Fe_2O_3} \xrightarrow[\mathrm{air}]{350\,^\circ\mathrm{C}} \mathrm{Co_2O_3}$$
$$+ 2\mathrm{CoFe_2{}^{III}O_4} + 9(\mathrm{CN})_2 + 24\mathrm{NH_3},$$

$$2[\mathrm{Co(NH_3)_6}][\mathrm{FeCl_6}] \xrightarrow[15\,\mathrm{min}]{300\,^\circ\mathrm{C}} 2[\mathrm{Co^{II}(NH_3)_6}][\mathrm{Fe^{II}Cl_4}] + 2\mathrm{Cl_2},$$

$$2[\mathrm{Co(NH_3)_6}][\mathrm{Fe^{II}Cl_4}] \xrightarrow[\mathrm{air}]{400\,^\circ\mathrm{C}} \mathrm{CoFe_2{}^{III}O_4} + {}^1/_2\mathrm{Co_2O_3}$$
$$+ 12\mathrm{NH_3} + 4\mathrm{Cl_2}.$$

The percentage weight loss calculated for the decomposition of **1** effected by 15 min heating at 200 °C is 9%, corresponding to 2% weight loss in TGA. The higher value of weight loss is due to the heating time being longer than in TGA. The weight loss for the second step is 57.2% which is in agreement with the TGA value (55%) for decomposition. In the case of **2** the weight loss calculated for the first step is 15% which is higher than the TGA value (10%) due to longer heating time. The weight loss calculated for the second step is 63% which is in agreement with the TGA value (65%) for the thermal decomposition. The temperature of decomposition is higher in the case of **2**, which indicates that the ligand has a great effect on the thermal stability of the complex.

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