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

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The thermal decomposition of metal(III) hexacyanoferrates(II) (Al, As, Sb, Bi) was studied up to 700° in air by employing Mössbauer, infrared spectroscopy and thermal analysis techniques. With the exception of the bismuth compound, the isomer shift of these hexacyanoferrates(II) increases on dehydration at 200°. Dehydration is complete at 200°, decomposition into the ferrite at 300°, and formation of α-Fe_2O_3 from aluminium and bismuth hexacyanoferrates(II) and Fe_3O_4 from antimony and arsenic hexacyanoferrates(II) at 700°.

Seifer and co-workers [1—3] have studied the thermal decomposition of hexacyanoferrates(II) using thermal and chemical analysis techniques in an inert gas atmosphere. Chamberlain and coworkers [4] investigated the thermal decomposition of hexacyanoferrates(II) and (III) and cyanonitrosylferrates by using DTA and DGE (Dynamic Gas Evolution), and reported that water was lost in the temperature range 80 to 180°, with secondary removal of cyanogen from the cyanide groups. The hexacyanoferrates (III) decomposed at lower temperatures than did the hexacyanoferrates(II). Wolski [5] studied the thermal decomposition of hexacyanoferrates(II) and reported the formation of ferromagnetic intermediates in the temperature range 200—350°. The thermal decomposition of cadmium hexacyanoferrate(II) is complete at 400°, as shown by DTA and magnetic susceptibility data, and at higher temperature CdO and $CdFe_3O_4$ are formed [6]. Zinc hexacyanoferrate(II) decomposed at 190°. Brar and coworkers reported the thermal decomposition of tin(IV) [7], zirconium(IV) [8] and thorium(IV) hexacyanoferrates(III) [9]. In the case of the thermal decomposition of tin(IV) hexacyanoferrate(II), iron(III) hexacyanoferrate(II) is formed as an intermediate, while zirconium(IV) hexacyanoferrate(II) on decomposition gives α-Fe_2O_3, and thorium(IV) hexacyanoferrate(II) yields $ThFe_2O_4$ at 300°. As a continuation of the above work, we now report studies on the thermal decomposition of $M_4^{III}[Fe^{II}(CN)_6]_3 \cdot xH_2O$ (where M = Al, As, Sb and Bi), employing Mössbauer, infrared and thermal analysis techniques. Our interest is to observe the effects of the outer trivalent cations (Al, As, Sb and Bi) on the intermediates and the products formed during the thermal decomposition.

Experimental

To prepare aluminium hexacyanoferrate(II), equimolar quantities of a solution of aluminium chloride and an aqueous solution of potassium hexacyanoferrate(II) trihydrate were mixed. The precipitate was treated with ethanol and washed with distilled water till free from potassium ions. For the preparation of the arsenic and antimony hexacyanoferrates(II), arsenic chloride or antimony chloride was added to an aqueous solution of potassium hexacyanoferrate trihydrate under acidic conditions. The precipitate was filtered off and washed with distilled water till free from impurities such as potassium ions. Bismuth hexacyanoferrate(II) was prepared by adding an aqueous solution of bismuth nitrate pentahydrate to an aqueous solution of potassium hexacyanoferrate(II) trihydrate under acidic conditions. The precipitate formed was filtered off and washed with acidic water, followed by distilled water.

The chemical analysis of carbon, hydrogen and nitrogen was done by the Chemistry Department, Calcutta University, Calcutta (India). The percentages of iron, carbon, hydrogen and nitrogen are reported in Table 1. As the hexacyanoferrates(II) are insoluble, the values of carbon, hydrogen and nitrogen are slightly different from the expected values. The percentages of iron in the hexacyanoferrates(II) were found spectrophotometrically [10].

For thermal decomposition, the hexacyanoferrates(II) $Al_4[Fe(CN)_6]_3 \cdot 12\,H_2O$, $As_4[Fe(CN)_6]_3 \cdot 12\,H_2O$, $Sb_4[Fe(CN)_6]_3 \cdot 12\,H_2O$ and $Bi_4[Fe(CN)_6]_3 \cdot 6\,H_2O$ were heated in a silica crucible in a tubular furnace at different temperatures, i.e. 100, 200, 300, 500 and 700°. The temperature of the furnace was measured by using a chromel-alumel thermocouple connected to a portable potentiometer (Toshniwal Industries (P) Ltd., India). The samples were heated at the specified temperature

Table 1

Elemental analysis

Compound	%, Fe	%, C	%, H	%, N
I $Al_4[Fe(CN)_6]_3 \cdot 12\,H_2O$				
Calcd.	17.7	22.5	2.5	26.2
Found	16.8	21.6	1.7	27.5
II $As_4[Fe(CN)_6]_3 \cdot 12\,H_2O$				
Calcd.	14.6	18.7	2.0	21.7
Found	13.6	18.3	2.2	20.6
III $Sb_4[Fe(CN)_6]_3 \cdot 12\,H_2O$				
Calcd.	12.5	16.1	1.8	18.8
Found	12.3	17.3	2.8	19.3
IV $Bi_4[Fe(CN)_6]_3 \cdot 6\,H_2O$				
Calcd.	10.6	13.6	0.7	15.9
Found	10.3	14.8	1.0	16.8

for three hours, in all cases in air. The rate of heating was 10°/min. The variation in the final temperature was ±5°.

The experimental details of the Mössbauer investigation were reported earlier [9, 20]. For the infrared spectra, two percent of the samples was taken and mixed with KBr, and the spectra were recorded on a MOM-2000 spectrophotometer (Hungary) in the range 4000–700 cm^{-1}.

Results and discussion

The chemical compositions of the hexacyanoferrates(II) were established by determining the percentage contents of iron, carbon, hydrogen and nitrogen. The results are given in Table 1. The number of water molecules was determined from the weight loss in TG, the TG results were in complete agreement with the chemical analysis. On the basis of the above analysis, the following chemical formulae may be proposed: aluminium hexacyanoferrate(II): $Al_4[Fe(CN)_6]_3 \cdot 12\,H_2O$; arsenic hexacyanoferrate(II): $As_4[Fe(CN)_6]_3 \cdot 12\,H_2O$; antimony hexacyanoferrate(II): $Sb_4[Fe(CN)_6]_3 \cdot 12\,H_2O$; and bismuth hexacyanoferrate(II): $Bi_4[Fe(CN)_6]_3 \cdot 6\,H_2O$.

The values of the isomer shift, the line width at half maximum and the percentage absorption are given in Table 2. The Mössbauer spectra of the hexacyanoferrates(II) show a single-line absorption band at room temperature. The Mössbauer spectra of some alkali metal hexacyanoferrates and first transition metal series hexacyanoferrates have been reported [11–16]. Goel and Garg [16] have observed that as the electronegativity of the cation (K^+, Na^+, Li^+, H^+) increases, the value of the isomer shift decreases. Sandhu and coworkers [17] published Mössbauer studies on complexes of the type $M_2^{II}[Fe(CN)_6] \cdot xH_2O$ ($M = Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}$) and $M^{IV}[Fe(CN)_6] \cdot xH_2O$ ($M = Th^{4+}, Sn^{4+}, Zr^{4+}$). The isomer shift for the outer cations of valency +4 was of the order of 0.13 mm/sec, and for the cations of valency +2 was of the order of 0.18 mm/sec. From these values, they concluded that on change of the cation from Th^{4+} to Sn^{4+} or Zr^{4+}, the isomer shift was not affected. Similar results were reported for Co^{2+}, Ni^{2+}, Zn^{2+} and

Table 2

Mössbauer parameters of hexacyanoferrate(II) complexes

Complex	Isomer shift, mm/sec	Width at half maximum, mm/sec	Percentage absorption
I $Al_4[Fe(CN)_6]_3 \cdot 12\,H_2O$	0.06±0.03	0.37	10.2
II $As_4[Fe(CN)_6]_3 \cdot 12\,H_2O$	0.06±0.03	0.40	11.8
III $Sb_4[Fe(CN)_6]_3 \cdot 12\,H_2O$	0.09±0.03	0.37	20.8
IV $Bi_4[Fe(CN)_6]_3 \cdot 6\,H_2O$	0.16±0.03	0.30	9.1

Fe^{2+}. Fanning and Monaghan [18] recently gave the isomer shift and quadrupole splitting values of alkali metal-substituted hexacyanoferrates(II) and hexacyanoferrate(III). The isomer shift was correlated with the size of the cation in the lattice in the case of the hexacyanoferrates(II), which showed that the electronegativity of the outer cation was influencing the isomer shift. The isomer shift is a measure of the *s*-electron density of the Mössbauer atom in the low-spin complexes. Raj and Puri [19] observed the effects of the cations (Na^+, K^+, Rb^+, Cs^+) in the tetrahedral alkali metal dithioferrates(III) on the isomer shift. The increasing electronegativity of the cation decreases the 4*s* electron density at the iron nucleus, thereby increasing the isomer shift. Brar and Randhawa [20] reported the variation of the isomer shift in the alkali metal trisoxalatoferrate(III) complexes. The isomer shift value is more affected by the electronegativity of the cation in the case of high-spin rather than low-spin complexes. The isomer shift values for $M_4[Fe(CN)_6]_3 \cdot xH_2O$ (where M = Al, As, Sb, Bi) are the same within the experimental error, with the exception of bismuth hexacyanoferrate(II). Thus, no effect of the change of the cation on the isomer shift value is observed in general. This may be due to the same electronegativity of the outer cations. The effect of the size of the outer cation does not influence the isomer shift either. The value of the isomer shift of bismuth hexacyanoferrate(II) is higher, possible due to the lower number of water molecules.

The infrared spectra of these hexacyanoferrates were recorded with the following results: $Al_4[Fe(CN)_6]_3 \cdot 12\,H_2O$: absorption bands in the region 3200–3400 cm^{-1} and at 1600 cm^{-1} due to water molecules; an absorption band at 2180 cm^{-1} due to C≡N stretching. $As_4[Fe(CN)_6]_3 \cdot 12\,H_2O$: absorption bands in the region 3200–3400 cm^{-1} and at 1600 cm^{-1} due to water molecules; an absorption band at 2200 cm^{-1} due to C≡N streching. $Sb_4[Fe(CN)_6]_3 \cdot 12\,H_2O$: absorption bands in the region 3200–3400 cm^{-1} and at 1600 cm^{-1} due to water molecules; an absorption band at 2125 cm^{-1} due to C≡N stretching. $Bi_4[Fe(CN)_6]_3 \cdot 6\,H_2O$: absorption bands in the region 3200–3400 cm^{-1} and at 1600 cm^{-1} due to water molecules; an absorption band at 2100 cm^{-1} due to C≡N stretching. Mössbauer, infrared, magnetic susceptibility, TG and chemical analysis confirmed the formation of the above-mentioned hexacyanoferrates.

The hexacyanoferrates were denoted as follows. At room temperature: were labelled as: aluminium hexacyanoferrate(II) $Al_4[Fe(CN)_6]_3 \cdot 12\,H_2O$ (I); arsenic hexacyanoferrate(II) $As_4[Fe(CN)_6]_3 \cdot 12\,H_2O$ (II); antimony hexacyanoferrate(II) $Sb_4[Fe(CN)_6]_3 \cdot 12\,H_2O$ (III); and bismuth hexacyanoferrate(II) $Bi_4[Fe(CN)_6]_3 \cdot 6\,H_2O$ (IV). The samples heated at 100°: (Ia, IIa, IIIa, IVa); those heated at 200°: (Ib, IIb, IIIb, IVb); those heated at 300° (Ic, IIc, IIIc, IVc); those heated at 500°: (Id, IId, IIId, IVd); those heated at 700°: (Ie, IIe, IIIe, IVe), respectively. The Mössbauer parameters are given in Table 3. The Mössbauer spectra of the samples heated at 100° show a single absorption band, and the isomer shift values are Ia = 0.16 mm/sec, IIa = 0.09 mm/sec, IIIa = 0.16 mm/sec and IVa = 0.16 mm/sec. The isomer shift values varied slightly from those for the room-temperature samples; this may be due to the loss of water molecules. The samples heated

Table 3

Mössbauer parameters of heat-treated hexacyanoferrate(II) complexes

Complex	δ and Δ (mm/sec)	Temperature of heat treatment				
		100°	200°	300°	500°	700°
I $Al_4[Fe(CN)_6]_3 \cdot$	δ	0.15±0.03	0.11±0.03	0.59±0.03	0.57±0.03	0.47
12 H_2O	Δ	—	—	1.11±0.03	0.99±0.03	$\Delta_1 = 16.45$
						$\Delta_2 = 9.40$
						$\Delta_3 = 2.54$
II $As_4[Fe(CN)_6]_3 \cdot$	δ	0.09±0.03	0.09±0.03	0.61±0.03	0.63±0.03	0.32
12 H_2O	Δ	—	—	0.85≤0.03	0.67±0.03	$\Delta_1 = 16.45$
						$\Delta_2 = 9.40$
						$\Delta_3 = 2.62$
III $Sb_4[Fe(CN)_6]_3 \cdot$	δ	0.16±0.03	0.13±0.03	0.56±0.03	0.74±0.03	0.14
12 H_2O	Δ	—	—	0.88±0.03	0.59±0.03	$\Delta_1 = 15.51$
						$\Delta_2 = 9.50$
						$\Delta_3 = 0.75$
IV $Bi_4[Fe(CN)_6]_3 \cdot$	δ	0.15±0.03	0.11±0.03	0.68±0.03	—	0.20
6 H_2O	Δ	—	—	0.67±0.03	—	$\Delta_1 = 17.01$
						$\Delta_2 = 9.78$
						$\Delta_3 = 2.73$

at 200° have similar isomer shifts to those of the samples heated at 100°. The weight loss shows complete removal of the water molecules; this is supported by the infrared spectra, which indicate a decrease in the intensity of the absorption band due to the water molecules as compared to that for the cyanide. The removal of coordinated water changes the *s*-electron density at the iron nucleus. Dehydration of the hexacyanoferrates affects the crystal structure of the complexes without changing the cubic symmetry of the iron nucleus. The isomer shift of potassium hexacyanoferrate(II) trihydrate increases on dehydration [21]. A similar trend is observed in the present case.

The Mössbauer spectra of the samples heated at 300° (Ic, IIc, IIIc, IVc) are shown in Figs. 1b–4b. All these complexes yield a doublet in the Mössbauer spectra. This indicates the decomposition of the hexacyanoferrates. The infrared spectra show a very weak band due to the cyanide group. The isomer shift values reveal that the iron is in a high-spin state, with oxidation state +3. The quadrupole splitting values show that ferrites are formed. In the case of sample (Ic), $AlFeO_3$ and aluminium oxide are formed. In $AlFeO_3$ the iron is in the oxidation state +3 and five electrons are distributed in the *d*-orbitals (t_{2g} and e_g orbitals). It has been reported [22] that $FeAl_2O_4$ has a large quadrupole splitting, due to iron in the oxidation state +2. Our isomer shift and quadrupole splitting values are 0.59 mm/sec and 1.11 mm/sec, respectively, which are different from those for Fe^{2+} in the literature [22]. In the case of sample (IIc), our isomer shift and quadrupole splitting values are 0.61 mm/sec and 0.85 mm/sec, respectively, which show that the iron is in a high-spin state, with oxidation state +3. These values are in agreement with the reported values for $FeAsO_4 \cdot 2\,H_2O$, which indicates the formation of this compound. It is further supported by the infrared spectrum. In the case of sample (IIIc), $FeSbO_4$ is formed. The isomer shift (0.56 mm/sec) and quadrupole splitting (0.88 mm/sec) values for $FeSbO_4$ are in agreement with the literature values [23] and show that iron is in the high-spin state, with oxidation state +3; it possibly forms oxides similar to the arsenic-iron oxides ($FeAsO_4$). In the case of sample (IVc), $BiFeO_3$ is formed. Our isomer shift (0.68 mm/sec) and quadrupole splitting (0.67 mm/sec) values are similar to those reported in the literature [24]. $BiFeO_3$ contains iron in the oxidation state (+3), which displays quadrupole splitting, and has a perovskite crystal structure. The magnetic measurements on all these samples show that they are highly paramagnetic.

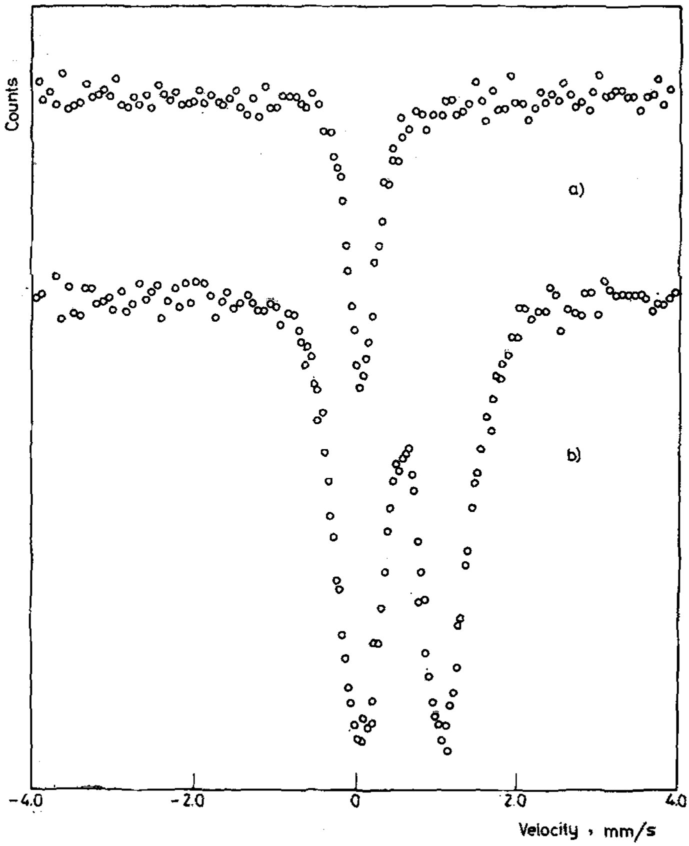

Fig. 1. Mössbauer spectrum of (a) aluminium hexacyanoferrate(II) at room temperature (25°) (I), (b) sample heat-treated at 300° (Ic)

bands due to water or the cyanide group. Magnetic measurements show that these are paramagnetic complexes.

The Mössbauer spectra of the samples heated at 500° do not show any change from those of the samples heated at 300°. The infrared spectra do not exhibit any

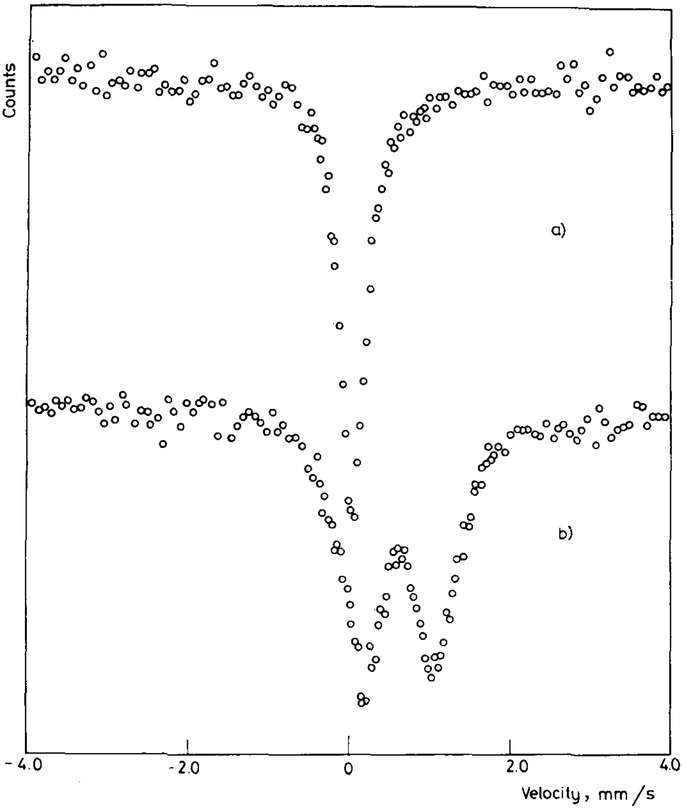

Fig. 2. Mössbauer spectrum of (a) arsenic hexacyanoferrate(II) at room temperature (25°) (II), (b) sample heat-treated at 300° (IIc)

All the samples heated at 700° for three hours have significantly changed Mössbauer spectra, as shown in Figs 5 and 6. The Mössbauer spectrum of complex(IIIe) contains a six-line pattern, due to Fe_3O_4. The doublet obtained at 500° is missing, which indicates that the sample undergoes a change at the higher temperature (Fig. 5b).

The Mössbauer spectrum of sample(Ie) contains a doublet, along with the six-line spectrum of α-Fe_2O_3. This shows that sample (Ie) is a mixture of ferrite and α-Fe_2O_3, together with aluminium oxide. Aluminium oxide has a higher surface area and interacts more strongly with iron oxide. Due to this, the complete formation of α-Fe_2O_3, is hindered (Fig. 6b).

The Mössbauer spectrum of sample (IIe) is that of magnetite (Fe_3O_4), which is a spinel ferrite $Fe^{3+}(Fe^{2+}, Fe^{3+})O_4$. It has been reported that a fast electron transfer process takes place between the Fe^{2+} and Fe^{3+} ions at the octahedral sites at higher temperature. However, at lower temperature the iron has discrete valence states and the material has an orthorhombic crystal structure. The temperature-dependences of site *A* (Fe^{3+}) and site *B* (Fe^{2+}, Fe^{3+}) have been reported within the range 300–800 K [25] (Fig. 5a).

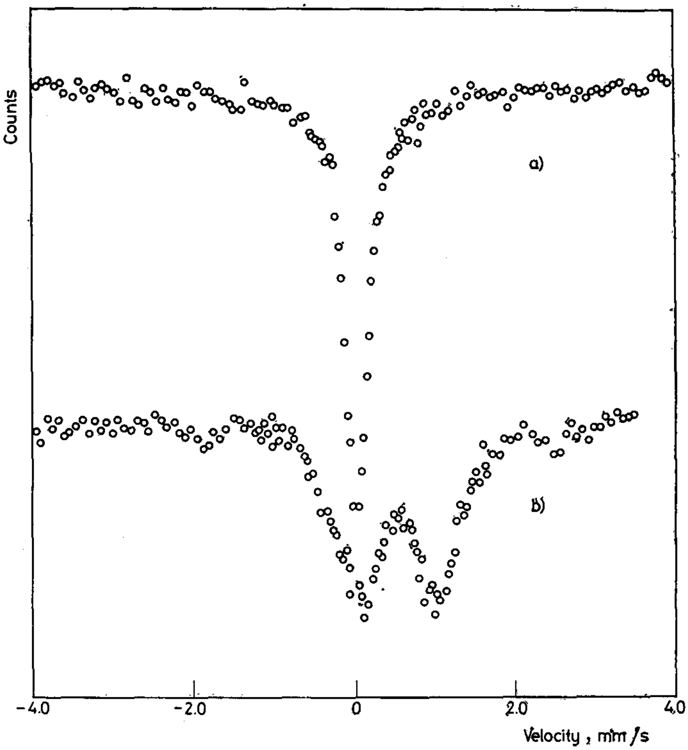

Fig. 3. Mössbauer spectrum of (a) antimony hexacyanoferrate(II) at room temperature (25°) (III), (b) sample heat-treated at 300° (IIIc)

In the case of sample (IVe), the Mössbauer spectrum contains the six-line pattern due to α-Fe_2O_3. The doublet obtained at 500° is missing, which shows that the ferrite undergoes a change due to aerial oxidation at higher temperature (Fig. 6a).

Brar and coworkers reported the thermal decomposition of tin(IV) [7], zirconium(IV) [8] and thorium(IV) hexacyanoferrates [9]. In the case of tin(IV) hexacyanoferrate, it has been observed that the tin becomes partially oxidised to tin

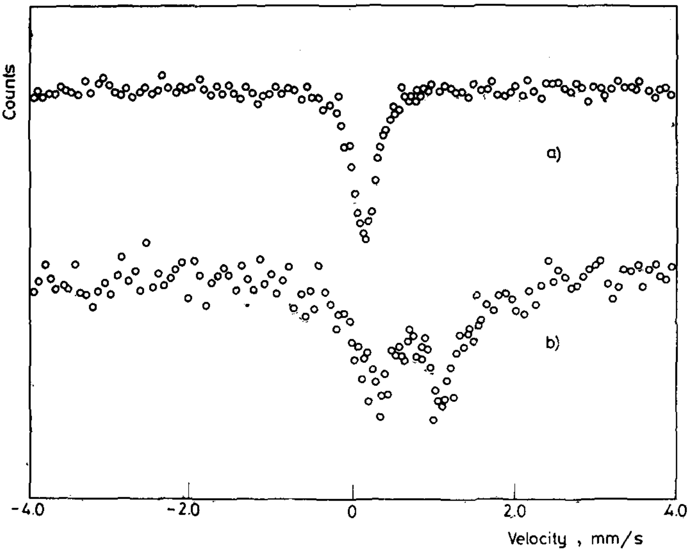

Fig. 4. Mössbauer spectrum of (a) bismuth hexacyanoferrate(II) at room temperature (25°) (IV), (b) sample heat-treated at 300° (IVc)

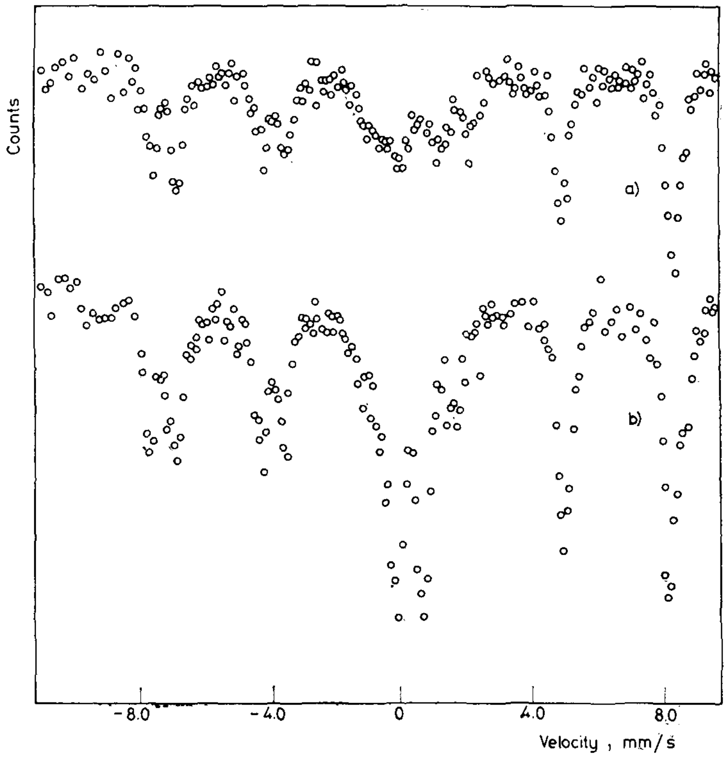

Fig. 5. Mössbauer spectrum of (a) arsenic hexacyanoferrate(II) heat-treated at 700° (IIe), (b) antimony hexacyanoferrate(II) heat-treated at 700° (IIIe)

oxides and iron(III) hexacyanoferrate is formed, followed by the decomposition of the hexacyanoferrate moiety. Thus, the oxides of the outer cation may catalyse the decomposition hexacyanoferrates [7]. A similar observation has been described in the case of the thermal decomposition of thorium(IV) and zirconium(IV) hexacyanoferrates(II). In the present case, the oxides of Al, As, Sb and Bi are not such effective catalysts for the decomposition of the $[Fe(CN)_6]^{4-}$ moiety. The temperatures of decomposition of these hexacyanoferrates are higher than those of tin, thorium and zirconium hexacyanoferrates(II).

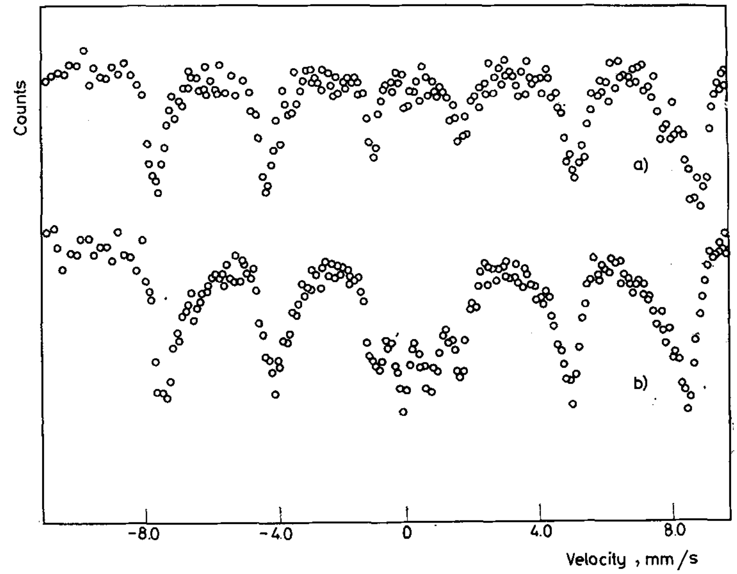

Fig. 6. Mössbauer spectrum of (a) bismuth hexacyanoferrate(II) heat-treated at 700° (IVe) (b) aluminium hexacyanoferrate(II) heat-treated at 700° (Ie)

On the basis of the Mössbauer data, the following decomposition paths are suggested:

$$\text{(I) } Al_4[Fe(CN)_6]_3 \cdot 12\,H_2O \xrightarrow{200^\circ} Al_4[Fe(CN)_6]_3 + 12\,H_2O$$

$$Al_4[Fe(CN)_6]_3 + 21/2\,O_2 \xrightarrow{300-500^\circ} 3\,AlFeO_3 + 1/2\,Al_2O_3 + 9\,(CN)_2$$

$$2\,AlFeO_3 \xrightarrow{700^\circ} \alpha\text{-}Fe_2O_3 + Al_2O_3$$

$$\text{(II) } As_4[Fe(CN)_6]_3 \cdot 12\,H_2O \xrightarrow{200^\circ} As_4[Fe(CN)_6]_3 + 12\,H_2O$$

$$As_4[Fe(CN)_6]_3 + 27/2\,O_2 \xrightarrow{300-500^\circ} 3\,FeAsO_4 + 1/2\,As_2O_3 + 9\,(CN)_2$$

$$6\,FeAsO_4 \xrightarrow{700^\circ} 2\,Fe_3O_4 + 3\,As_2O_5 + 1/2\,O_2$$

$$\text{(III)}\ Sb_4[Fe(CN)_6]_3 \cdot 12\ H_2O \xrightarrow{200^\circ} Sb_4[Fe(CN)_6]_3 + 12\ H_2O$$

$$Sb_4[Fe(CN)_6]_3 + 27/2\ O_2 \xrightarrow{300-500^\circ} 3\ FeSbO_4 + 1/2\ Sb_2O_3 + 9\ (CN)_2$$

$$6\ FeSbO_4 \xrightarrow{700^\circ} 2\ Fe_3O_4 + 3\ Sb_2O_5 + 1/2\ O_2$$

$$\text{(IV)}\ Bi_4[Fe(CN)_6]_3 \cdot 6\ H_2O \xrightarrow{200^\circ} Bi_4[Fe(CN)_6]_3 + 6\ H_2O$$

$$Bi_4[Fe(CN)_6]_3 + 21/2\ O_2 \xrightarrow{300-500^\circ} 4\ BiFeO_3 + 1/2\ Bi_2O_3 + 9\ (CN)_2$$

$$2\ BiFeO_3 \xrightarrow{700^\circ} \alpha\text{-}Fe_2O_3 + Bi_2O_3\,.$$

Although the mechanisms of the solid-state decompositions of these hexacyanoferrates may be complex, on the basis of the above observations the dehydration is complete at 200°, and ferrites are formed at 300°, which are stable up to 500°. At higher than 700°, α-Fe_2O_3 and Fe_3O_4 are formed, which shows that the decomposition products are influenced by the nature of the outer cations.

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Résumé — On a étudié dans l'air jusqu'à 700°, la décomposition thermique des ferrocyanures de métaux trivalents (Al, As, Sb, Bi), par spectroscopies Mössbauer et infrarouge, ainsi que par les techniques d'analyse thermique. Le déplacement des isomères de ces ferrocyanures augmente lors de la déshydratation à 200°, à l'exception du bismuth. La déshydratation est complète à 200°, la décomposition en ferrite à 300°, la formation d'α-Fe_2O_3 à partir des ferrocyanures d'aluminium et de bismuth ainsi que du Fe_3O_4 à partir des ferrocyanures de l'antimoine et de l'arsenic à 700°

Zusammenfassung — Die thermische Zersetzung von Metall(III)ferrocyaniden (Al, As, Sb, Bi) wurde bis zu 700° in Luft unter Anwendung der Mössbauer und Infrarotspektroskopie, sowie thermoanalytischer Techniken untersucht. Die Isomerverschiebung dieser Ferrocyanide nimmt mit der Dehydratisierung bei 200° zu, mit Ausnahme des Wismuts. Die Dehydratisierung ist bei 200° abgeschlossen, die Zersetzung zum Ferrit bei 300° und die Bildung von α-Fe_2O_3 aus Aluminium- und Wismutferrocyanid, von Fe_3O_4 aus Antimon- und Arsenferrocyanid bei 700°.

Резюме — Используя мессбауэровскую-, ИК спектроскопию и методы термического анализа, изучено термическое разложение ферроцианидов тнехвалентных металлов — Al, As, Sb, Bi — до температуры 700° в атмосфере воздуха. Изомерный сдвиг в ряду ферроцианидов, за исключением соли висмута, увеличивается при температуре дегидратации 200°. Дегидратация происходят полностью при температуре 200°, а при 300° ферроцианиды алюминия и висмута разлагаются до ферритов и α-Fe_2O_3. Ферроцианиды сурьмы и мышьяка разлагаются при 700° с образованием Fe_3O_4.