Mössbauer Studies of the Thermal Decomposition of Tris(2,2′-bipyridine)iron(II) Chloride and the Structures of the Isomers of 2,2′-Bipyridineiron(II) Chloride

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The thermal decomposition of $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$ in nitrogen was investigated by means of Mössbauer spectroscopy. Two isomers of $Fe(bipy)Cl_2$ were found to occur in the decomposition sequence; one of them appears to be identical with the rose-red form of $Fe(bipy)Cl_2$ prepared by the wet process. The structures of the two isomers were determined on the basis of the Mössbauer spectra, the infrared and Raman spectra, the powder X-ray patterns, and the magnetic moments of these compounds. It has been concluded that tris(2,2′-bipyridine)-iron(II) chloride presumably decomposes in the following sequence:

$$[Fe(bipy)_3]Cl_2 \cdot 5H_2O \longrightarrow Fe(bipy)_2Cl_2 \longrightarrow \text{orange } Fe(bipy)Cl_2 \text{ (monomeric, tetrahedral)} \longrightarrow \text{rose-red } Fe(bipy)Cl_2 \text{ (polymeric, octahedral)} \longrightarrow FeCl_2$$

Earlier papers of this series[1–3] have demonstrated that the structural changes during the step-by-step pyrolysis of iron(II) pyridine complexes and the ^{57}Co-labeled cobalt(II) pyridine complex can be monitored by Mössbauer spectroscopy. As a part of the Mössbauer studies of iron complexes with multidentate ligands, we have recently investigated the thermal decomposition of tris(2,2′-bipyridine)iron(II) chloride in nitrogen and found that two isomers of 2,2′-bipyridineiron(II) chloride arise in the pyrolysis sequence.[4] Since the structures of these isomers have not been known, however, we have now attempted to determine their structures by means of Mössbauer spectroscopy, together with other physicochemical methods.

The object of the present article is to give a more complete report on our work concerning the thermal decomposition process of tris(2,2′-bipyridine)iron(II) chloride and the structures of the two isomers of 2,2′-bipyridineiron(II) chloride obtainable as decomposition products.

Experimental

Materials. *Tris(2,2′-bipyridine)iron(II) Chloride*: A concentrated aqueous NaCl solution was added to an aqueous solution containing a 1:3 mixture (mole ratio) of iron (II) sulfate and 2,2′-bipyridine, and the separated crystals were washed and stored over P_2O_5 in a desiccator. The compound thus prepared was pentahydrate.[5] Found: C, 52.5; H, 4.7; N, 12.4%. Calcd for $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$: C, 52.6; H, 5.0; N, 12.3%.

2,2′-Bipyridineiron(II) Chloride (Rose-red Form): This compound was prepared from iron(II) chloride and 2,2′-bipyridine in an aqueous HCl solution in the manner described by Broomhead and Dwyer.[6] Found: C, 42.5; H, 2.9; N, 10.1%. Calcd for $Fe(bipy)Cl_2$: C, 42.5; H, 2.9; N, 9.9%.

Measurements. The thermogravimetric analysis and differential thermal analysis were performed in a nitrogen stream at a heating rate of 1, 2 or 5 °C/min. The powder X-ray patterns of the isomers of $Fe(bipy)Cl_2$ and $Co(bipy)Cl_2$ were made using a Rigaku Denki Geigerflex and Fe-$K\alpha$ radiation. The infrared spectra of $Fe(bipy)Cl_2$ isomers were recorded on a Hitachi EPI-L Spectrophotometer (for the 200—700 cm^{-1} region) or on a Hitachi EPI-G2 Spectrophotometer (for the 400—4000 cm^{-1} region). The Raman spectra were measured by means of a Spectra Physics 166-01 Spectrophotometer using the 6471 Å exciting line of a Kr-ion laser. The magnetic susceptibilities were determined at room temperature by the Faraday method.

The Mössbauer spectra of the parent complex, the decomposition products (including those obtained at intermediate stages), and the 2,2′-bipyridineiron(II) chloride prepared by the wet method (rose-red form) were taken at 78, 195, and 293 K by using a Shimadzu MEG-2 Mössbauer Spectrometer with a ^{57}Co source diffused into copper foil.

Results and Discussion

Thermal Decomposition of $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$. In Fig. 1 are represented the TGA and DTA curves for tris(2,2′-bipyridine)iron(II) chloride, $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$. Three phases, II, III, and IV, can be observed distinctly during the thermal decomposition of this compound (Phase I). Based on the TGA curve, the II, III, and IV phases were assumed to indicate the products which were obtainable by the loss of all the water and one molecule of 2,2′-bipyridine from the parent complex in the first step, and then by the successive loss of an additional molecule each of 2,2′-bipyridine: the II, III, and IV phases correspond to $Fe(bipy)_2Cl_2$, $Fe(bipy)Cl_2$, and $FeCl_2$ respectively. The results of elementary analysis were also in good agreement with the values expected for the assumed compounds. Found for the product at Phase II: C, 54.7; H, 3.7; N, 12.7%. Calcd for $Fe(bipy)_2Cl_2$: C, 54.7; H,

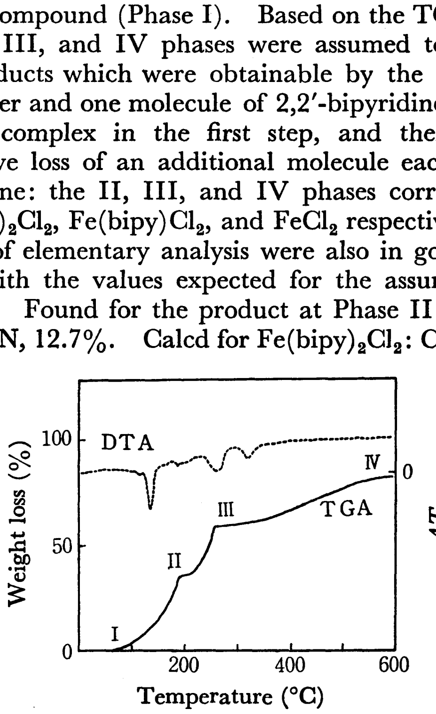

Fig. 1. TGA and DTA curves of $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$ (heating rate: 2 °C/min).

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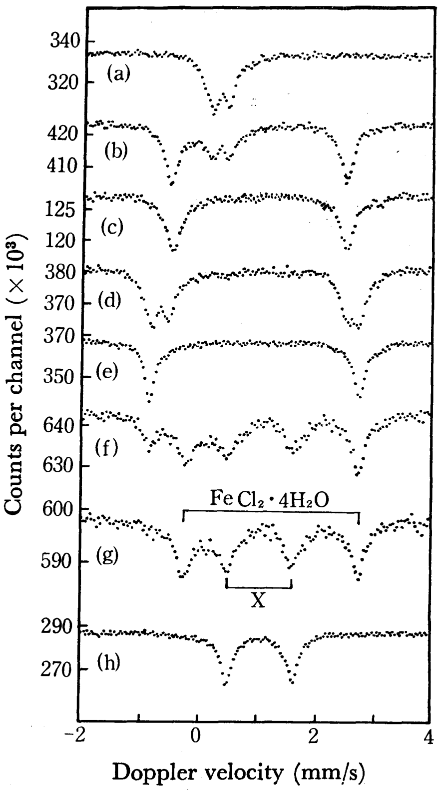

Fig. 2. Mössbauer spectra at 293 K of $[Fe(bipy)_3]Cl_2\cdot5H_2O$ and thermal decomposition products: (a) phase I ($[Fe(bipy)_3]Cl_2\cdot5H_2O$); (b) intermediate stage, phase I→phase II; (c) phase II ($Fe(bipy)_2Cl_2$); (d) intermediate stage, phase II→phase III; (e) phase III (orange $Fe(bipy)Cl_2$); (f) intermediate stage obtained at about 400 °C, phase III→phase IV; (g) intermediate stage obtained at 460 °C, phase III→phase IV; (h) rose-red $Fe(bipy)Cl_2$ prepared by the wet process.

3.7; N, 12.8%. Found for the product at Phase III: C, 42.5; H, 2.8; N, 9.9%. Calcd for $Fe(bipy)Cl_2$: C, 42.5; H, 2.9; N, 9.9%.

Figure 2 reveals some typical Mössbauer spectra at 293 K of $[Fe(bipy)_3]Cl_2\cdot5H_2O$, the products at the II and III phases, and the products (mixtures) obtained at intermediate stages between the distinct phases. The Mössbauer parameters of tris-, bis-, and mono-(2,2′-bipyridine)iron(II) chloride are summarized in Table 1. The detailed process of thermal decomposition can be elucidated by comparing the Mössbauer spectra taken at various stages of the reactions, as will be done below.

Phase I: The Mössbauer spectrum of $[Fe(bipy)_3]Cl_2\cdot5H_2O$ (Phase I) consists of a doublet with δ and ΔE_Q values indicating low-spin iron(II) (Fig. 2a). The anhydrous salt, $[Fe(bipy)_3]Cl_2$, prepared by dehydration in an Abderhalden's dryer, reveals a spectrum identical with the pentahydrate's.

Intermediate Stages between Phases I and II: The intermediate products obtained at 140 °C between Phases I and II indicate a composite spectrum composed of the Mössbauer peaks of $[Fe(bipy)_3]Cl_2\cdot5H_2O$ (Phase I) and $Fe(bipy)_2Cl_2$ (Phase II), as is shown in Fig. 2b. However, the spectrum of the products obtained at 130 °C was identical with that of Phase I, while the spectrum of the products obtained at 150 °C was identical with that of Phase II. While Phase II is attained at about 200 °C on the TGA curve, the large endothermic peak due to the *Phase I→Phase II* transition appears at 140 °C on the DTA curve. No plateau for the anhydrous $[Fe(bipy)_3]Cl_2$ phase was detectable on the TGA curve. These observations imply that the dissociation of one 2,2′-bipyridine molecule occurs quickly at about 140 °C before dehydration is completed, but that the volatilization of the dissociated 2,2′-bipyridine molecules from crystals proceeds rather slowly below 200 °C.

Phase II: The Mössbauer spectrum of $Fe(bipy)_2Cl_2$ (Phase II) consists of a doublet with large δ and ΔE_Q values corresponding to high-spin iron(II) (Fig. 2c). The Mössbauer parameters of this compound at room temperature were reported by König *et al.*;[7] they are in agreement with the values obtained in the present work.

Intermediate Stages between Phases II and III: In the stages between Phases II and III, mixtures of the absorption peaks of $Fe(bipy)_2Cl_2$ (Phase II) and $Fe(bipy)Cl_2$ in the orange form (Phase III) were observed (Fig. 2d); the intensity of the $Fe(bipy)Cl_2$ peaks relative to that of the $Fe(bipy)_2Cl_2$ peaks increased with the increase in the reaction temperature.

Phase III: The spectrum of $Fe(bipy)Cl_2$ in the orange form (Phase III) is composed of a doublet with an even larger quadrupole splitting than that of $Fe(bipy)_2Cl_2$, characteristic of high-spin iron(II) (Fig. 2e).

Intermediate Stages between Phases III and IV: The Mössbauer spectrum of the intermediate products obtained between Phases III and VI indicates a new doublet of high-spin iron(II) in addition to the peaks ascribable to known products expected at Phases III and IV (Figs. 2f and 2g). In the meantime, the color of the mixture of products changes from orange to dark red upon the formation of the new compound. Since the new rose-red compound (hereafter designated as X)

Table 1. Mössbauer parameters of tris(2,2′-bipyridine)iron(II) chloride, thermal decomposition products and rose-red form of 2,2′-bipyridineiron(II) chloride prepared by the wet process

Compound	Isomer shift[a)] δ(Fe) (mm/s)			Quadrupole splitting[a)] ΔE_Q (mm/s)		
	78K	195K	293K	78K	195K	293K
$[Fe(bipy)_3]Cl_2$ $\cdot5H_2O$	0.39	0.36	0.33	0.34	0.31	0.28
$Fe(bipy)_2Cl_2$	1.11	1.04	1.01	3.40	3.29	2.98
$Fe(bipy)Cl_2$ (orange form)	1.08	1.00	0.93	3.71	3.65	3.58
Compound X[b)]	1.1_8	1.0_7	1.0_4	1.7_8	1.4_4	1.0_9
$Fe(bipy)Cl_2$ (rose-red form)	1.18	1.09	1.07	1.76	1.38	1.14

a) Errors: ±0.02 mm/s. b) Because of the uncertainty due to the complexity of overlapping peaks and to the counting statistics, parameters of compound X involve relatively large errors of ± 0.06 mm/s.

could not be isolated as a pure product, but was usually found as mixtures with the other decomposition products corresponding to Phases III and IV (*i.e.*, Fe(bipy)Cl_2 in the orange form, $FeCl_2$, and its hydrates),[8] it was not readily identified by ordinary physicochemical methods of analysis. Although Compound X was observed distinctly in the Mössbauer spectra of the reaction products obtained above the temperature range of Phase III, the weight loss was negligible and its formation was not detectable on the TGA curve. Therefore, it is unlikely that Compound X is a product formed by the further decomposition of Fe(bipy)Cl_2 (orange form).[9] The Mössbauer parameters at 78, 195, and 293 K of the rose-red Compound X are entirely different from those of the orange-form Fe(bipy)Cl_2 obtained by thermal decomposition, whereas they are in agreement with those of the rose-red form of Fe(bipy)Cl_2 prepared by the wet process in hydrochloric acid (Table 1 and Fig. 2h). Thus, we may presume that the rose-red Compound X formed in the intermediate stages between Phases III and IV is identical with the rose-red form of Fe(bipy)Cl_2 prepared by the wet process, which appears to be isomeric with the orange form of Fe(bipy)Cl_2 obtained by the thermal decomposition (Phase III).

Phase IV: In the Mössbauer spectra of the products at Phase IV we often observed the hydrates of iron(II) chloride, $FeCl_2 \cdot 2H_2O$, and $FeCl_2 \cdot 4H_2O$, since anhydrous iron(II) chloride is so hygroscopic that it is partially hydrated before the Mössbauer measurements.

Structures of Fe(bipy)Cl_2 Isomers. Both [Fe(bipy)$_3$]$Cl_2 \cdot 5H_2O$ (Phase I) and Fe(bipy)$_2Cl_2$ (Phase II) are octahedral monomers. Although a marked discrepancy has been reported between the magnetic moments of Fe(bipy)Cl_2 samples prepared by different methods,[6,10] the structures of the two isomers of Fe(bipy)Cl_2 have never been studied before. According to the following data of the Mössbauer spectra, powder X-ray patterns, infrared and Raman spectra, and magnetic moments of the orange Fe(bipy)Cl_2 obtained by the thermal decomposition and the rose-red Fe(bipy)Cl_2 prepared by the wet process, we may conclude that the orange-form Fe(bipy)Cl_2 is monomeric and tetrahedral, while the rose-red form Fe(bipy)Cl_2 (or the compound, X, obtained between Phases III and IV) is polymeric and octahedral, with chloride bridges.

Mössbauer Spectra: It has been found for high-spin iron(II) complexes that a tetrahedral complex generally gives a smaller isomer shift as compared with the octahedral complex containing similar ligands.[11–13] Since the isomer shift of the rose-red Fe(bipy)Cl_2 is larger than that of Fe(bipy)$_2Cl_2$, which is octahedral, the former may not be tetrahedral, but octahedral (Table 1). Accordingly, the orange form of Fe(bipy)Cl_2, with a smaller isomer shift, is probably tetrahedral.

Powder X-Ray Patterns: The structures of the α and β isomers of Co(bipy)Cl_2 have been reported as an octahedral polymer and a tetrahedral monomer respectively on the basis of their electronic and infrared spectra.[14,15] As is shown in Fig. 3, the two isomers of Fe(bipy)Cl_2 (or Co(bipy)Cl_2) give different powder X-ray patterns, while the pattern of each isomer of Fe(bipy)Cl_2 is quite similar to that of the corresponding analogue of Co(bipy)Cl_2. Hence, a comparison of their powder X-ray patterns reveals that the orange Fe(bipy)Cl_2 and β-Co(bipy)Cl_2 are isomorphous and tetrahedral, while the rose-red Fe(bipy)Cl_2 and α-Co(bipy)Cl_2, octahedral: these results confirm the conclusion derived from the Mössbauer data.

Infrared and Raman Spectra: In a number of transition-metal complexes, the metal-halogen stretching vibrations are affected by whether or not the halogen is bridging.[16–18] Hence, the region of iron-chlorine stretching vibrations of FeL_2Cl_2 (L=py, 1/2bipy, *etc.*) can be expected to shift to lower frequencies in the polymeric octahedral isomer (in the vicinity of 200 cm^{-1}),[18,19] as compared with the region for the monomeric tetrahedral isomer (in the vicinity of 300 cm^{-1}).[20] In the infrared and Raman spectra of the orange form of Fe(bipy)Cl_2 we observed a band at 360 cm^{-1} (Fig. 4) which can be ascribed to the Fe–Cl stretching vibrations, in accordance with the assignment by Strukl *et al.* of the 361/369 cm^{-1} region of this compound as such.[21] In the case of the rose-red Fe(bipy)Cl_2, no strong band was observed in the 270—340 cm^{-1} region, while the

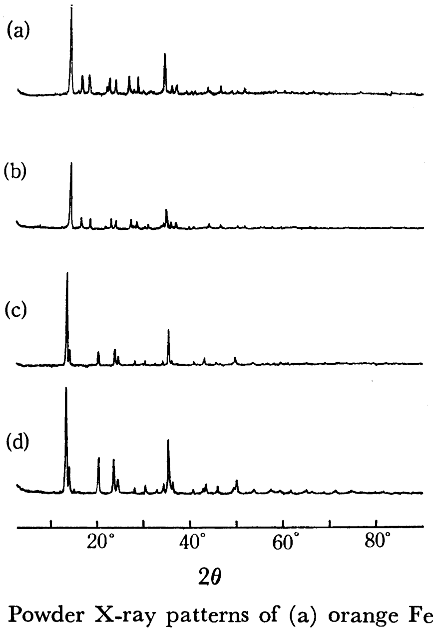

Fig. 3. Powder X-ray patterns of (a) orange Fe(bipy)Cl_2, (b) β-Co(bipy)Cl_2, (c) rose-red Fe(bipy)Cl_2, and (d) α-Co(bipy)Cl_2.

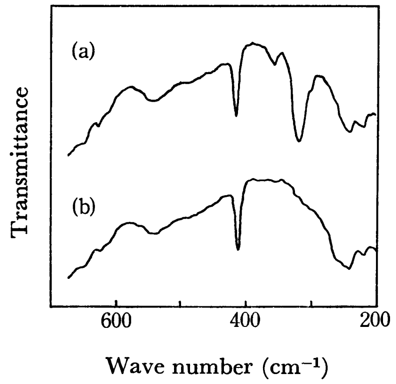

Fig. 4. Infrared spectra of (a) orange Fe(bipy)Cl_2, and (b) rose-red Fe(bipy)Cl_2.

band occurring at 152 or 187 cm^{-1} in the Raman spectrum may possibly correspond to the Fe–Cl streching vibrations. Therefore, the infrared and Raman spectra of these isomers also support the structures presumed on the basis of the Mössbauer and powder X-ray data.

Magnetic Moments: There has been a considerable disagreement among the reported values of the magnetic moments of Fe(bipy)Cl_2: 1.8 B.M.[10] and 4.8 B.M.[6] for the Fe(bipy)Cl_2 samples prepared by decomposition in a vacuum, and 5.72 B.M.[6] for the Fe(bipy)Cl_2 prepared by the wet process. The magnetic moments obtained in the present work are 4.9±0.1 B.M. for the orange Fe(bipy)Cl_2 and 5.3±0.1 B.M. for the rose-red Fe(bipy)Cl_2. Hence, it may be concluded that the low value of 1.8 B.M. reported by Basolo *et al.*[10] is in error, as has been suggested.[6] This is further confirmed by the fact that no low-spin iron(II) was observed in the Mössbauer spectra of the products from the pyrolysis of $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$ in nitrogen or a vacuum. The observation that the magnetic moment of the rose-red Fe(bipy)Cl_2 is larger than that of the orange Fe(bipy)Cl_2 is compatible with the assignment of the rose-red isomer as octahedral and the orange isomer as tetrahedral.[22]

In conclusion, we can say that the thermal decomposition of tris(2,2′-bipyridine)iron(II) chloride in nitrogen presumably proceeds as follows:

$$\begin{aligned}&[Fe(bipy)_3]Cl_2 \cdot 5H_2O \longrightarrow Fe(bipy)_2Cl_2 \longrightarrow \\ &\quad \text{orange } Fe(bipy)Cl_2 \text{ (monomeric, tetrahedral)} \longrightarrow \\ &\quad \text{rose-red } Fe(bipy)Cl_2 \text{ (polymeric, octahedral)} \longrightarrow \\ &\quad FeCl_2\end{aligned}$$

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8) The Mössbauer peaks of Compound X, orange Fe(bipy)Cl_2, and hydrates of $FeCl_2$ were observed in the spectrum of the reaction products obtained at about 400 °C (Fig. 2f), while the peaks of the orange Fe(bipy)Cl_2 disappeared in the products obtained at 460 °C (Fig. 2g).

9) The small endothermic peak at 330 °C on the DTA curve may not be related to the conversion of the orange Fe(bipy)Cl_2 into the rose-red isomer, since a similar endothermic peak is also observable on the thermal decomposition of the rose-red form and an exothermic peak appears at about the same temperature on the cooling of the orange form. The Mössbauer spectra indicate the presence of mixtures of both forms over a fairly wide temperature range between Phases III and IV.

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