



Transformation of cadmium ferricyanide by heating, milling and sonication

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Abstract—On heating, milling and sonication, cadmium ferricyanide decomposes and reduces to cadmium ferrocyanide. Two compositions were studied, pure cadmium ferricyanide and mixed potassium–cadmium ferricyanide. The role of reducing agent is played by the CN[−] anions liberated during the decomposition process. The solid decomposition product is composed by several phases of cadmium ferrocyanide, an Fe³⁺ phase and also potassium ferrocyanide in the case of the mixed complex salt. The decomposition process was monitored using DTA, XRD, IR and Mössbauer techniques. No occurrence of linkage isomerization in cadmium ferricyanide was detected. © 1998 Elsevier Science Ltd. All rights reserved

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Transformation of hexacyanometallates through linkage isomerization was predicted and observed approximately 30 years ago [1–3]. The phenomena have been well established for ferrous chromicyanide and manganicyanide which transform spontaneously into the corresponding ferrocyanides [2–5]. The change in the structural chain M—NC—M' can be envisaged as a flipping of the CN ligands through an unstable intermediate ferric salt produced by an electron transfer which reduces the inner cation to Cr^{II} and Mn^{II} [5]. Other results such as the isomerization of cobaltous chromicyanide [2] and silver cobalticyanide [6] have been contested [5,7]. House *et al.* have reported the isomerization of K₃Cd[Fe(CN)₆]·5H₂O on heating at above 110°C [8] and on sonication [9]. In this report we present evidence that Cd₃[Fe(CN)₆]₂·12H₂O and K₃Cd[Fe(CN)₆]·5H₂O undergo reduction to ferrocyanides when heated, milled or sonicated, without linkage isomerization. The processes were followed by DTA, XRD, IR and Mössbauer techniques.

EXPERIMENTAL

Cadmium ferricyanide was prepared in two different compositions: Cd₃[Fe(CN)₆]₂·12H₂O and K₃Cd[Fe(CN)₆]·5H₂O; in the following, Cd₃Fe^{III} and K₃CdFe^{III}, respectively. The former composition was obtained mixing five-fold excess of cadmium chloride with potassium ferricyanide as aqueous solutions. The precipitate was filtered, washed several times with distilled water and dried in a desiccator over silica gel. K₃CdFe^{III} was prepared in the same manner but using a large excess of potassium ferricyanide. By the same procedure cadmium ferrocyanide (Cd₃[Fe(CN)₆]·xH₂O) and mixed potassium–cadmium ferrocyanide (CdK₂[Fe(CN)₆]·xH₂O), which we will label Cd₃Fe^{II} and CdK₂Fe^{II}, were also prepared. In the preparation of Cd₃Fe^{II} and CdK₂Fe^{II}, ferrocyanic acid and potassium ferrocyanide, respectively, were used. Mixed potassium–cadmium ferrocyanide was also obtained by mechanochemical reduction of Cd₃Fe^{III} and K₃CdFe^{III} by milling with KBr [10,11]. These last two complexes together with manganous ferrocyanide (Mn₂[Fe(CN)₆]·8H₂O), in the following Mn₂Fe^{II}, were used as reference compounds. The preparation of Mn₂Fe^{II} is reported elsewhere [12]. The compositions

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