

STUDY OF THE LINKAGE ISOMERIZATION PROCESS IN
HEXACYANOMETALLATES

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Abstract—The linkage isomerism in several transition metal hexacyanometallates was studied by Mössbauer, IR and XRD techniques. Ferrous chromicyanide and manganicyanide transform into Cr^{3+} ferrocyanide and Mn^{2+} ferrocyanide, respectively, through an unstable intermediate ferric salt produced by the mean of an electron transfer which reduces the inner cation to Cr^{II} and Mn^{II} .

Linkage isomerism in transition metal hexacyanometallates was discovered approximately three decades ago.^{1–3} Ferrous chromicyanide ($\text{Cr}^{\text{III}}\text{Fe}^{2+}$), ferrous manganicyanide ($\text{Mn}^{\text{III}}\text{Fe}^{2+}$) and cobaltous chromicyanide ($\text{Cr}^{\text{III}}\text{Co}^{2+}$) were found to transform into the corresponding ferrocyanides and cobalticyanide at room temperature. The change in the structural chain, $\text{M}—\text{NC}—\text{M}'$ to $\text{M}—\text{CN}—\text{M}'$ can be envisaged as a flipping of the CN ligands or as a cation exchange between inner and outer positions.^{1–3} X-ray diffraction (XRD), IR and Mössbauer spectroscopy were used to monitor the reactions in the solid state. The data was interpreted on the basis of the Keggin and Miles model for Prussian Blue, with two different sites for the outer cations; one octahedrally coordinated to six nitrogen atoms of the cyano ligands (structural sites) and one coordinated to water molecules and located in the cubic voids of the network (interstitial sites).⁴ This model has been superseded by the model of Ludi *et al.*⁵ in which there are no interstitial positions. In order to balance the stoichiometry, an equivalent number of hexacyanometallate anions were left vacant, creating a rather open structure. The outer cations, all in structural sites, are of two types, one octahedrally coordinated to six nitrogen atoms and the other with a mixed coordination sphere of four cyano groups and two water molecules.

The Mössbauer spectra in those pioneering works^{2,3} were of poor quality, which led to an inaccurate deconvolution of the Mössbauer envelope into separate sub-spectra of the different species. No recent work has been published on the subject, the matter resting today as it was nearly 30 years ago.

We have studied the same hexacyanometallates as Shriver *et al.*^{2–3} with manganese, chromium, iron and cobalt as the inner and outer cations using XRD, IR and Mössbauer techniques. Our spectra allow a correct and physically significant deconvolution of the Mössbauer spectra, giving a reliable view of the initial, intermediate and final species, in terms of the Ludi model,⁵ for the linkage isomerization of $\text{Cr}^{\text{III}}\text{Fe}^{2+}$ and $\text{Mn}^{\text{III}}\text{Fe}^{2+}$. However, our experiments indicate, contrary to published results³ that $\text{Cr}^{\text{III}}\text{Co}^{2+}$ is stable and does not undergo changes even on heating to 200°C.

EXPERIMENTAL

All compounds were prepared by mixing aqueous solutions of the metal cation (Cr^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} and Co^{2+}) and of the hexacyanometallate anion $\{[\text{Cr}(\text{CN})_6]^{3-}$, $[\text{Mn}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}\}$, using analytical grade reagents (BDH), except in the case of $\text{K}_3[\text{Cr}(\text{CN})_6]$ and $\text{K}_3[\text{Mn}(\text{CN})_6]$ which were synthesized and purified according to literature procedures.⁶ The precipitates were filtered, washed several times with distilled water and dried in a

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