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ON THE INTERACTIONS OF OZONE WITH MANGANOUS HEXACYANOFERRATES

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Abstract—The ozonization of manganous ferro- and ferricyanides has been studied in the solid state using IR, Mössbauer and XRD techniques. Ferrocyanides are oxidized to ferricyanides without disruption of the complex anions, while Mn^{2+} is oxidized to the Mn^{3+} and Mn^{4+} states. On aging the Mn^{3+} and Mn^{4+} species are reduced to Mn^{2+}. The ferricyanide is not reduced to ferrocyanide, except in the case of the mixed K, Mn salt. The unstable product $Mn_3^{4+}[Fe^{III}(CN)_6]_4 \cdot xH_2O$ has been determined as a cubic species with $a_0 = 10.36(1)$ Å.

Ozone is a strong oxidizing agent, capable of transforming Mn^{2+} in solution to Mn^{3+}, Mn^{4+}, Mn^{6+} and Mn^{7+} species.[1] It also oxidizes ferrocyanides to ferricyanides in solution and in the solid state.[2–5] In the present communication we present a study of ozonization of the solid manganous hexacyanometallates $Mn_2[Fe^{II}(CN)_6] \cdot 8H_2O$, $Mn_3[Fe^{III}(CN)_6]_2 \cdot 14H_2O$ and $K_2Mn[Fe^{II}(CN)_6] \cdot 4H_2O$, which we will label $Fe^{II}Mn^{2+}$, $Fe^{III}Mn^{2+}$ and $Fe^{II}K_2Mn^{2+}$, respectively. The reactions have been followed by IR, Mössbauer and XRD techniques.

EXPERIMENTAL

Potassium ferro- and ferricyanides (BDH) and $MnCl_2$ (Merck) were all commercial samples. The mixed $K_2Mn[Fe^{II}(CN)_6] \cdot 4H_2O$ salt was obtained by mixing aqueous solutions of $K_4[Fe^{II}(CN)_6] \cdot 3H_2O$ and $MnCl_2$. The precipitate was filtered, washed with distilled water, dried in air up to 60°C and kept in a desiccator. In order to avoid contamination with K, the manganous ferro- and ferricyanides were prepared from the corresponding acids, as reported in the literature.[6]

Ozone was produced from dried oxygen as an O_3/O_2 mixture in a glass ozonizer with a metal high-voltage electrode. The O_3 concentration in this mixture was *ca* 20 mg $dn^{-3}L$, measured by UV spectrophotometry at 254 nm.

IR spectra were recorded on an M80 Carl Zeiss spectrometer in Nujol mulls between CaF_2 windows, with a maximum error of ± 2 cm^{-1}. The XRD powder patterns were obtained using an HZG-4 diffractometer (Carl Zeiss) with monochromated Cu-K_α radiation. The degree of hydration was determined by thermogravimetric analysis (TGA) using MOM Q-1500 equipment.

Mössbauer spectra were recorded at room temperature with a ^{57}Co in rhodium source and in the transmission mode using a constant acceleration spectrometer. A special cell was used to obtain the Mössbauer spectra *in situ* under a controlled flow of the O_3/O_2 mixture. Before recording the Mössbauer spectra *in situ*, the samples were kept for some hours in an ozone atmosphere. All Mössbauer spectra were fitted with an iterative least-squares minimization algorithm using Lorentzian line shapes to obtain the values of the isomer shift (δ), quadrupole splitting (Δ), line-width (Γ) and relative area (A).

RESULTS AND DISCUSSION

Ozonization of $Mn_3[Fe^{III}(CN)_6]_2 \cdot 14H_2O$

The complex $Fe^{III}Mn^{2+}$ has a cubic structure with $a_0 = 10.503(4)$ Å, similar to other Prussian Blue analogues.[7] TGA shows the presence of up to 14 water molecules per formula weight. The Fe^{III} is octahedrally coordinated to six carbon atoms, $[Fe^{III}C_6]$, while the Mn^{2+} is octahedrally coordinated to four nitrogen and two oxygen atoms of

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