Thermal Decomposition of Prussian Blue Analogues of the Type $Fe[Fe(CN)_5NO]$

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The structure and properties of the thermal decomposition products of $Fe[Fe(CN)_5NO] \cdot x\,H_2O$ ($x = 5 \sim 6$) have been studied by Mössbauer and FT-IR spectroscopy, X-ray diffraction, and conductivity measurements. The valence state and coordination environment of the iron ions change dramatically when the nitrosyl ligand is eliminated by heat-treatment under vacuum at 200 °C. The dark blue product obtained by heat-treatment under vacuum at 250 °C is characteristic of the mixed-valence state in Prussian blue analogues. The electrical conductivity of the dark blue product is higher by a factor of 10^3 than that of the starting material because of the mixed-valence state between $Fe(III)[Fe(II)(CN)_5]$ and $Fe(II)[Fe(III)(CN)_5]$. Heat-treatment under vacuum at 350°C yields a new product $Fe(II)[Fe(II)(CN)_4]$ the crystal structure of which is different from that of the starting material. The electrical conductivity of the decomposition product obtained at 350 °C is about 10^5 times higher than that of the starting material.