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Solid-State Voltammetric Probing of Spin Transition in Cobalt Hexacyanoferrate Molecular Magnet

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There has been growing interest in molecular units and molecular based assemblies, which exhibit bistability in their properties, e.g. in magnetic or redox characteristics. This work concerns electroanalytical characterization in solid-state (i.e. in the absence of contact with external supporting electrolyte) of a molecule-based magnetic material that is an analogue of classic Prussian blue. Solid-state voltammetric measurements in two-electrode sandwich configuration provide indirect evidence for the expected structural isomerization involving reorganization of cobalt(II) hexacyanoferrate(III) to cobalt(III) hexacyanoferrate(II) in the presence of certain (e.g. K+, Na+) countercations. It has been demonstrated for metal hexacyanoferrates that their redox potential shifts upon replacement of alkali metal cations in supporting electrolyte. It comes from solid-state voltammetric data that the exchange of potassium with sodium cations induces an electron transfer from Co (II) to Fe (III) in cobalt(II) hexacyanoferrate(III) and leads to the formation of mixed-valence hexacyanoferrate (III, II) redox centers. Direct evidence for spin transition in the oxidized cobalt hexacyanoferrate, details of stoichiometry and localization of redox processes are provided using high-resolution X-ray photoelectron spectroscopy (XPS). Chemical shifts reflect the oxidation state and the chemical environment of cobalt and iron ions depending on the nature of structural alkali metal countercations. In the case of transition metal ions unique patterns of multiplet splitting possess diagnostic value to elucidate the spin state of transition metals in coordination compounds. Such results should lead to better understanding of magnetic ordering and would permit electrochemical manipulation and control over the system?s reactivity, magnetic and electronic properties.