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Novel mechanism of reversible photoinduced magnetism in Prussian blue analogs MUKUL KABIR, KRISTYN J. VAN VLIET, Dept of Materials Science and Engineering, Massachusetts Institute of Technology — Prussian blue (PB) crystals are metallorganic materials that exhibit several modes of inducible changes in oxidation state, and thus changes in physical and functional properties. Reversible switching of magnetic state by external stimuli has been demonstrated experimentally for PB and PB analogs, with many potential applications including information storage and processing. For example, at low temperature, illumination of visible light (500-700 nm) induces bulk magnetization in $\text{KCo}[\text{Fe}(\text{CN})_6]\cdot 5\text{H}_2\text{O}$, which can be eliminated by near-IR wavelengths of ~ 1319 nm). However, the molecular-scale mechanisms by which such magnetic state switching occurs have not yet been elucidated, and are required to facilitate design of this and other such magnetic switch-inducible materials. Here we report our simulations and proposed switching mechanism for this PB analog crystal. We apply density functional theory, corrected for on-site Coulomb interaction (DFT+U), to describe the structure and energetic ground state of anhydrate $\text{KCo}[\text{Fe}(\text{CN})_6]$. This ground state has large octahedral ligand-field splitting, and consequently exhibits a low-spin structure. We find that the low-spin to high-spin transition is a two step process involving charge transfer between the metal atoms via the carbon-nitrogen ligand, followed by electron transfer within the cobalt atom. This spin-crossover results in 10% increase in C-N bondlength, and proceeds via a strong Jahn-Teller active metastable intermediate state.

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