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Study of oxidation states of the transition metals in a series of Prussian blue analogs using x-ray absorption near edge structure (XANES) spectroscopy

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ABSTRACT

There have been renewed interests in metal-organic framework classes of materials such as Prussian blue analogues (PBAs) due to their potential usage in energy storage applications. In particular, due to their high surface areas, controllable structures and excellent electrochemical properties, PBAs such as hexacyanometalates $M^{II}{}_3[A^{III}(CN)_6]_{2*}nH_2O$ *(M = Mn, Fe, Co, Ni, Cu, Zn; A = Co, Fe, Cr; n = no. of water molecules present)*, $M^{II}{}_2[Fe^{II}(CN)_6]_{2*}nH_2O$ *(M = Mn, Co, Ni, Cu, Zn)* and mixed hexacyanometalates(III) $(Fe_{1-x}Co_x)_3[B^{III}(CN)_6]_2\cdot nH_2O$ (x = *0.25, 0.5, 0.75; B = Co, Fe) could have possible usage as* a new class of cathode and even anode materials for rechargeable batteries. Detailed knowledge of the oxidation states of the transition metals in PBAs is required to improve efficiency and durability of such devices. Furthermore, a link between the thermal expansion observed in these materials and the oxidation state of the transition metal is of interest to synthesize materials with a desired thermal expansion behavior, Here we demonstrate the use of Synchrotron based X-ray absorption near-edge structure (XANES) spectra to identify transition metal oxidation states. Our analysis reveals the presence of divalent, trivalent and/or mixed valence transition metals in the materials as well as high-spin and low-spin complexes.

1. Introduction

Prussian blue (PB) analogs have gained renewed interest recently because of their interesting characteristics as molecular magnets and their technologically important response to external stimuli, e.g., photo-excitation, hydrostatic pressure and reduced pressure etc. Moreover, some of the PB analogs have been found to exhibit counterintuitive negative thermal expansion (NTE) behavior and near-zero thermal expansion (ZTE) behavior both of which are of fundamental as well as of great technological importance. For example, Matsuda et al. [1] reported the occurrence of NTE in a few PB analogs while Chapman et al. [2] demonstrated the compositional dependence of the NTE behavior in some other PB analogs. Since it is possible to vary systematically the charge and ion size in these materials, PB analogs offer an interesting platform to explore possible correlation between NTE and electronic structure.

In a previous study, [3] our group reported the thermal expansion behavior of PB analog compounds. Our study indicates some of the compounds – hexacyanocobaltates(III) of Mn, Fe, Co, Ni, Cu, and Zn, hexacyanoferrates (III) of Co, Cu, Zn, and hexacynochromate (III) of Fe – show NTE behavior in the temperature range 300–123 K while the other compounds show either positive thermal expansion (PTE) behavior or complex NTE/PTE behavior. Simple parameters such as formal charge, ionic radius, electronegativity, or magnetic moments fail to correlate in any obvious way with the thermal expansion behavior of PBs. The presence of rigid unit modes (RUMs) remains a plausible explanation of the variety of thermal expansion behaviors in PBs providing the forces between octahedra mediated by the cyanide ligands varied from sample to sample. These forces are a consequence of chemical bonding, and, therefore, of the distribution of electronic density on the metal ion (oxidation state) and among the octahedra. Another contributing factor may be cyanide ligand disorder. A quick way to investigate these possibilities (electron distribution and ligand disorder) is to perform XANES measurements to determine formal charges on the metal cations and, possibly, some local structure information (lig-

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and orientation). Although EXAFS and XANES studies of other PB analogs have been reported, [4,5] results are missing for most of our compounds, particularly those displaying complex thermal expansion behavior. Previous synchrotron x-ray studies focused largely on electronic band structure, photoemission, and optical properties. We were unable to find any study devoted to oxidation states in our series of PB compounds. Hence, characterizing the formal oxidations states of the transition metals present in the studied series of Prussian blue analogs remains important.

In the present study, we used XANES to characterize the oxidation states of the transition metals in the PB analogs, at the Cr, Mn, Fe, Co, Ni and Cu *K*-edge in a systematic way.

2. Materials and experimental methods

2.1. Materials

2.1.1. Synthesis

Table 1 summarizes the list of materials investigated in this study. The compounds are synthesized *via* standard chemical precipitation using ACS quality reagents.

Hexacyanocobaltates(III) of the divalent metals Mn, Fe, Co, Ni, Cu and Zn were prepared by mixing the aqueous solutions of stoichiometric amounts of metal chloride or nitrate with the aqueous solution of $K_3[Co(CN)_6]$. The precipitated sample was filtered, washed multiple times with water, and air dried. Polycrystalline samples of hexacyanoferrates(III), hexacyanoferrates(II) and hexacyanohromates(III) were synthesized following the same synthesis route using $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ and $K_3[Cr(CN)_6]$, respectively.

Bimetallic hexacyanoferrates(III) and hexacyanocobaltates(III) were synthesized by mixing a combined solution of aqueous solutions of $FeCl_2$ and $CoCl_2$, prepared using the calculated stoichiometric amounts needed for a particular x-value, with aqueous solution of $K_3[Fe(CN)_6]$ and $K_3[Co(CN)_6]$ respectively. Powder samples were obtained following the same procedure as mentioned earlier.

2.1.2. Structure of materials

Most of the studied PBAs crystallize in the cubic space groups $Fm\bar{3}m$, $F\bar{4}3m$ or $Pm\bar{3}m$ (Fig. 1a–c). $Mn_2[Fe(CN)_6].9H_2O$ and $Zn_2[Fe(CN)_6]\cdot 5H_2O$, on the other hand, crystallize in the monoclinic $P2_1/n$ and trigonal $P\bar{3}$ space groups (not shown in Fig. 1), respectively, which are distortions of the cubic structures. All structures invariably consist of two types of octahedra, $M(N{\equiv}C)_6$ and $M'(C{\equiv}N)_6$, arranged in an essentially cubic lattice with cyanide ligands linking the metal centers. Each metal has a coordination number of 6. In the above notation for the octrahedra, we neglected the possibility of *O* atoms replacing "*C*" or "*N*" since the oxygen atom

Table 1
List of compounds, space groups and room temperature lattice parameters a and coefficient α of thermal expansion for all studied compounds. *Already published [3].

Sample	PB analogs	Space group	*a* [Å]	α [$10^{-6}K^{-1}$]
Metal(II) Hexacyanocobaltates (III)				
(a)*	$Mn_3[Co(CN)_6]_2.12H_2O$	$F\bar{4}3m$	10.3327(5)	−48.0(2.5)
(b)*	$Fe_3[Co(CN)_6]_2.28H_2O$	$F\bar{4}3m$	10.2241(12)	−39.3(6.0)
(c)*	$Co_3[Co(CN)_6]_2.12H_2O$	$F\bar{4}3m$	10.1277(18)	−35.5(5.1)
(d)*	$Ni_3[Co(CN)_6]_2.16H_2O$	$F\bar{4}3m$	10.0532(14)	−30.0(4.4)
(e)*	$Cu_3[Co(CN)_6]_2.17H_2O$	$Fm\bar{3}m$	09.9964(7)	−20.0(1.2)
(f)*	$Zn_3[Co(CN)_6]_2\cdot 9H_2O$	$F\bar{4}3m$	10.1437(10)	−33.7(2.6)
Metal(II) Hexacyanoferrates (III)				
(g)*	$Mn_3[Fe(CN)_6]_2.14H_2O$	$F\bar{4}3m$	10.3218(13)	+47.8(3.4)
(h)*	$Co_3[Fe(CN)_6]_2.18H_2O$	$F\bar{4}3m$	10.0616(14)	+7.9(5.1)
(i)*	$Ni_3[Fe(CN)_6]_2.14H_2O$	$F\bar{4}3m$	10.1834(12)	+5.9(1.9)
(j)*	$Cu_3[Fe(CN)_6]_2.18H_2O$	$Fm\bar{3}m$	10.0635(6)	−19.9(0.6)
(k)*	$Zn_3[Fe(CN)_6]_2.14H_2O$	$Fm\bar{3}m$	10.1615(15)	−39.6(6.2)
Metal(II) Hexacyanochromates (III)				
(l)	$Fe_3[Cr(CN)_6]_2.10H_2O$	$Fm\bar{3}m$	10.1623(8)	−4.92
(m)	$Co_3[Cr(CN)_6]_2.14H_2O$	$Fm\bar{3}m$	10.1412(15)	+59.16
(n)	$Ni_3[Cr(CN)_6]_2.14H_2O$	$Fm\bar{3}m$	9.9503(24)	+10.05
Metal(II) Hexacyanoferrates (II)				
(o)*	$Mn_2[Fe(CN)_6].9H_2O$	P 1 21/n 1	9.9254(21)	+20.2(5.0)
(p)*	$Co_2[Fe(CN)_6].18H_2O$	$Pm\bar{3}m$	10.2269(9)	+19.5(10.7)
(q)*	$Ni_2[Fe(CN)_6].18H_2O$	$Pm\bar{3}m$	10.0383(19)	+19.9(3.0)
(r)*	$Cu_2[Fe(CN)_6].16H_2O$	$Pm\bar{3}m$	9.9321(6)	+20.1(9.7)
(s)*	$Zn_2[Fe(CN)_6]\cdot 5H_2O$	$P\bar{3}$	6.9172(20)	+43.1(2.7)
Bimetallic Hexacyanocobaltates (III)				
(t)	$(Fe_{0.75}Co_{0.25})_3[Co(CN)_6]_2.xH_2O$	$F\bar{4}3m$	10.1829(11)	−19.53
(u)	$(Fe_{0.50}Co_{0.50})_3[Co(CN)_6]_2.xH_2O$	$F\bar{4}3m$	10.2279(14)	−0.29
(v)	$(Fe_{0.25}Co_{0.75})_3[Co(CN)_6]_2.xH_2O$	$F\bar{4}3m$	10.2469(20)	−19.42
Bimetallic Hexacyanoferrates (III)				
(w)	$(Fe_{0.75}Co_{0.25})_3[Fe(CN)_6]_2.xH_2O$	$Fm\bar{3}m$	10.0250(22)	+10.00
(x)	$(Fe_{0.50}Co_{0.50})_3[Fe(CN)_6]_2.xH_2O$	$Fm\bar{3}m$	10.0067(16)	−5.98
(y)	$(Fe_{0.25}Co_{0.75})_3[Fe(CN)_6]_2.xH_2O$	$Fm\bar{3}m$	10.0898(12)	1.98