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Temperature and Light Induced Bistability in a $Co_3[Os(CN)_6]_2$ $6H_2O$ Prussian Blue Analog

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Abstract: To expand the field of new cyanide materials of the 5d elements, we incorporated the $[Os(CN)_6]^{3-}$ anion into PB architectures in combination with the Co^{II} cation. Herein, we report the first example of a photomagnetic PB analog containing Os^{III} ions. In a similar vein as the prototypical CoFe PB analogs, this compound exhibits a wide variety of properties including Charge Transfer Induced Spin Transition (CTIST), Temperature Induced Excited Spin State Trapping (TIESST), and magnetic ordering.

Among the fascinating discoveries in the area of cyanide chemistry in recent years is the ability of cyanide bridged assemblies to exhibit magnetic bistability.[1−4] Of particular interest are materials whose magnetic properties can be manipulated by irradiation. Light induced magnetic bistability, referred to as photomagnetism, was pioneered in 1984 by Gütlich and co-workers who discovered the light induced excited spin state trapping (LIESST) phenomenon for the SCO compound $[Fe(ptz)_2]$ $(BF_4)_2$.[5]

More recently a new paradigm for photomagnetic behavior of cyanide materials has emerged which relies on a charge transfer induced spin transition to trigger changes in the magnetic properties.[6] The first such cyanide compounds reported to exhibit a photoinduced charge transfer induced spin transition (CTIST) magnetic behavior are CoFe Prussian blue (PB) analogs which have been extensively studied by a number of groups since the first report by the Hashimoto group.[1,7−12] The $K_{0.2}Co_{1.4}[Fe(CN)_6]_1\cdot 6.9H_2O$ phase is the first compound for which a metal-to-metal photoinduced charge transfer was observed, a process that converts the redox state of the $[Co^{III}_{L.S.}{-}NC{-}Fe^{II}_{L.S.}]$ pairs to $[Co^{II}_{H.S.}{-}NC{-}Fe^{III}_{L.S.}]^*$ at low temperatures.

Our group is actively engaged in the study of 3*d* transition metal containing cyanide molecules that exhibit bistability including CTIST behavior.[13−15] Recently, we embarked on the synthesis of molecules with 4*d* and 5*d* cyanometallate anions in order to probe the effect on the magnetism of the increased single ion anisotropy of the heavier elements as well as differences in magnetic exchange coupling related to the degree of overlap and covalency.[16−19] The group 6 hexa- and heptacyanomolybdate(III) anions are convenient precursors for this research[3,20,21] as are the group 8 hexacyanoruthenate(III) and hexacyanoosmate(III) building blocks.[22] A particularly intriguing recent finding from our laboratories is that a bipyramidal (TBP) molecule with $[Os(CN)_6]^{3-}$ and Fe^{II} ions undergoes an unprecedented type of CTIST.[22−25]

To further expand the field of new cyanide materials of the 5*d* elements, we are incorporating $[Os(CN)_6]^{3-}$ into PB architectures in combination with the Co^{II} ion. As in the case of the prototypical CoFe PB analogs, the Os analog exhibits a wide variety of properties including CTIST, temperature induced excited spin state trapping (TIESST), magnetic ordering, and photomagnetic behavior. The latter property has been observed only for CoFe and MnFe PB phases to date; the present example is the first photomagnetic compound based on the $[Os^{III}(CN)_6]^{3-}$ ion.[7,26]

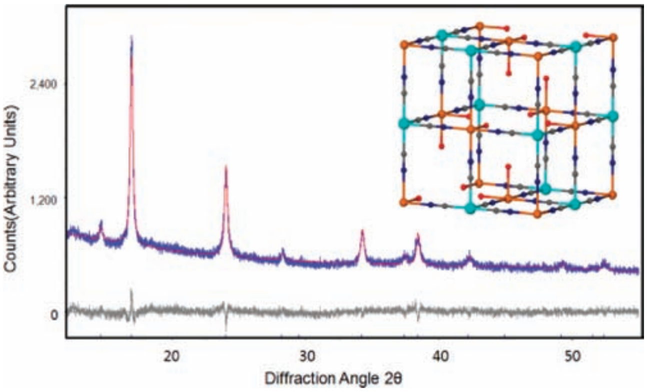

Figure 1. Powder diffraction pattern, fit for $Fm\bar{3}m$ face centered cubic space group with $a = 10.48$ Å. Schematic cell representation of the $Co_3[Os(CN)_6]_2$ Prussian Blue analog. Light blue spheres represent Os ions; orange spheres represent Co ions.

The new material was prepared by reacting a 2:3 ratio of $PPN_3[Os^{III}(CN)_6]$ and Co^{II} ions in a H_2O/methanol mixture. The reaction leads to the formation of the $Co_3[Os(CN)_6]_2\cdot 6H_2O$ Prussian Blue analog as an insoluble purple microcrystalline solid. Indexing of the powder X-ray diffraction data indicates a face centered cubic structure (space group $Fm\bar{3}m$) with $a = 10.48$ Å (Figure 1). The diffuse reflectance spectrum (Figure S1) exhibits a broad feature at ~600 nm which is assigned to a metal-to-metal charge-transfer transition from Co^{II} to Os^{III}. The IR spectrum exhibits a sharp band at 2134 cm^{-1} attributed to the $\nu(C{\equiv}N)$ stretching mode for the $Os^{III}{-}C{\equiv}N{-}Co^{II}$ pair and a weak feature at 2085 cm^{-1} which is attributed to the terminal stretching mode of $[Os^{III}(CN)_6]^{3-}$.[22−24]

The room temperature χT value of 4.12 emu·K/mol is higher than the spin-only value (3.19 emu·K/mol) for the empirical formula of $Co_{1.5}[Os(CN)_6]\cdot 3H_2O$ which is due to significant orbital contributions expected for both the HS Co^{II} ($S = 3/2$) and LS Os^{III} ($S = 1/2$) ions. Given the fact that the room temperature χT values for $PPN_3[Os(CN)_6]$ and HS Co^{II} ions are 0.35 and 2.0−3.2 emu·K/mol,[8] respectively, the room temperature value is in the expected range for the sum of 1.5 HS Co^{II} ions and one LS Os^{III} ion. As the temperature decreases, the compound undergoes a reversible CTIST centered at 235 K (Figure 2a, blue line). The origin of the CTIST is a change in the redox state of the PB material from $[Co^{II}_{H.S.}{-}Os^{III}_{L.S.}]$ to $[Co^{III}_{L.S.}{-}Os^{II}_{L.S.}]$. After the transition, the χT value decreases slowly to reach 1.7 emu·K/mol, a value that indicates that the spin transition does not lead to a completely diamagnetic state $[Co^{III}_{L.S.}{-}Os^{II}_{L.S.}]$ due to residual paramagnetism from the presence of remaining cobalt(II) centers,[27] as found for the CoFe PB analogs. At 37 K, the increase in χT is in accord with

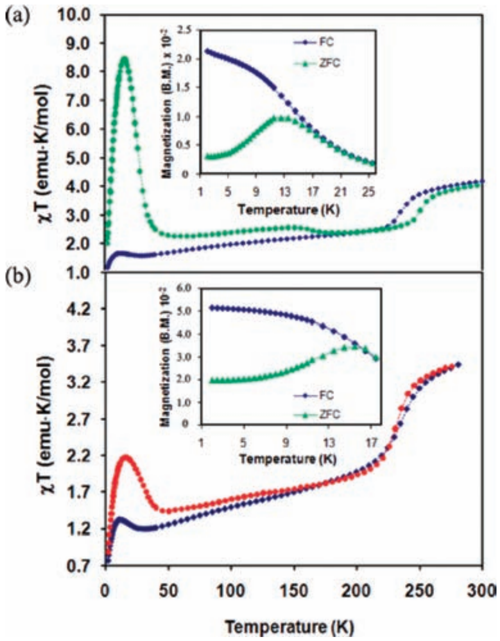

Figure 2. Temperature dependence of χT from 2 to 300 K for (a) CoOs PB (blue) and the room temperature trapped state (TIESST: green). Inset: TIESST ZFC/FC data with an ordering temperature of 17.5 K and the (b) nonirradiated (blue) and irradiated (red) sample of Co_3Os_2 PB. Inset: ZFC/FC plot of the photomagnetic state for which $T_C = 16.5$ K.

magnetic ordering at low temperatures. It is important to point out that magnetization measurements are not useful in this case for ascertaining the nature of the magnetic coupling and the ground state because of the population of low lying excited states. Nevertheless, the slow decrease of χT as the temperature is lowered suggests that the Co^{II} and Os^{III} ions are antiferromagnetically coupled as in the case of the CoFe PB analogs.[7,9] Incomplete cancellation of spins from the antiferromagnetic coupling of the Co^{II} and Os^{III} ions results in ferrimagnetic ordering. AC susceptibility measurements revealed that the compound has an ordering temperature of less than 2 K (Figure S2).

Temperature induced excited spin state trapping (TIESST) measurements (Figure 2a green line) were performed to test the possibility of photomagnetic behavior. This experiment is based on the premise that when the sample is rapidly thermally quenched, thermal relaxation from the high temperature (HT) phase to the low temperature (LT) phase will be suppressed, hence leading to a majority of the sample being “trapped” in the $[Co^{II}_{H.S.}-Os^{III}_{L.S.}]$ state. As the temperature is increased from 2 to 300 K there is a rapid increase in χT and a maximum is observed at 18 K. At higher temperatures, a rapid decrease occurs and a plateau appears at 50 K. The sample reverts to the LT state at 170 K. As the sample is further heated, a CTIST is observed at ~250 K. The difference in the CTIST temperature between the original DC and the TIESST measurements results in a hysteresis loop centered at 245 K. ZFC/FC susceptibility measurements performed on the TIESST state (Figure 2a inset) revealed an increase in the ordering temperature to 17.5 K. This observation is consistent with the majority of the sample being “trapped” in the $[Co^{II}_{H.S.}-Os^{III}_{L.S.}]$ state which leads to an enhancement of the Curie temperature (T_C) owing to an increase in the number of paramagnetic pairs present in the TIESST sample.

Photomagnetic measurements were performed using white light as the irradiation source (Figure 2b, red line). The measurement was performed by slowly cooling the sample followed by irradiation at low temperatures until the χT value reached a saturation value. At this stage, irradiation was ceased and the temperature was slowly increased. The photoexcited state exhibits magnetic behavior similar to that of the TIESST state. As the temperature is increased from 2 to 300 K a maximum appears at 15 K, and at higher temperatures, a rapid decrease occurs as the sample reverts to the LT phase at 165 K. A CTIST is observed at ~245 K. ZFC/FC measurements (Figure 2b inset) revealed an ordering temperature of 16.5 K for the photomagnetic state (Figure 2b inset). As in the TIESST experiment, an enhancement of the T_C is consistent with a majority of the sample being present in the $[Co^{II}_{H.S.}-Os^{III}_{L.S.}]$ state.

The new findings allow, for the first time, a comparison of the nature of photomagnetic 5*d* transition metal analogs to the well-studied 3*d* congener.[7,9,10] Given that the structural parameters are essentially the same, differences in magnetic phenomena are ascribed to the nature of the exchange interactions and charge-transfer properties of the 5*d* Os versus the 3*d* Fe ions.

The data obtained thus far are promising and provide a benchmark for in-depth investigations analogous to those carried out for the CoFe PB analogs. Future studies include alkali metal dilution studies, detailed spectroscopic measurements such as EXAFS and XANES which lend insight into the electronic states and bond distances, and magnetic X-ray circular dichroism (MXCD) studies which can aid in the evaluation of the magnetic coupling. The new CoOs material represents a valuable addition to the magnetism literature for chemists and physicists alike as they strive to understand the parameters that influence the properties of Prussian Blue analogs and bistable magnetic materials.

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Supporting Information Available: Experimental procedures and fitting details of the powder pattern are available, as well as diffuse reflectance measurements and AC susceptibility and hysteresis data for typical DC, TIESST, and photomagnetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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