Designer Prussian Blue Analogues Molecular Magnets with Possible Applications

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We have investigated structural and magnetic properties of a large variety of Prussian blue based molecular magnetic compounds. These materials show promising multifunctional properties that are important for various technological applications. The present article gives an overview of some of these results.

Magnetic materials are the key components of many electronics devices for storage and retrieval of information, such as computer hard drives and video tapes. Magnetic materials are also in high demand in power generation, non-polluting electric vehicles, medical science, telecommunication, etc. Due to wide technological applications of magnetic materials, there have always been quests for new magnetic materials. Presently, an intense level of research is dedicated to fabricate new magnetic material based electronic devices. Historically, magnetic materials used so far for devices are inorganic in nature. However, organic or molecule-based materials offer possibility of using light-weight flexible materials that include magnetic functionalities. Magnets fabricated using organic/molecular compounds having unpaired electrons, located either in s-or p-orbitals (in pure organic radicals), or in d- or f-orbitals (in transition or lanthanide metal ions) are termed as molecular magnets. The first molecular ferromagnet was discovered in 1986 which was magnetically ordered at very low temperature of 4.8 K, demonstrated that a magnet could be made using organic chemistry and without usual high temperature energy intensive processing [1, 2]. This discovery opened a new branch of magnetism called molecular magnetism, with endless possibilities of tailoring new magnetic materials for organic electronics and spintronic applications by using organic, organo-metallic and coordination metal chemistry [3, 4].

The pioneering concept of “designer magnets” refers to the possibility of creating the desired magnetic materials using flexible chemical synthesis methods. Molecular magnets offer the possibility to create the magnetic system of one’s choice by changing the molecular building blocks and their arrangement in these compounds. For example, one can vary the transition metal ions to obtain various spin values. By proper choice of the organic ligands, one can tune the magnetic interaction, its symmetry, and range. Depending upon the starting organic/molecular species used for synthesis, molecule-based magnets can be purely organic or hybrid organic-inorganic. The hybrid organic-inorganic magnets are 3D compounds where the organic building blocks/ligands act as either active spin centre i.e. net spin localized both on metallic ions as well as on the organic species {e.g., tetracyanoethylene (TCNE)}, or passive spin centre i.e. net spin located mainly on the metallic site, such as hexacyanometallate or Prussian blue analogues (PBAs) based magnets. We have investigated various molecular magnetic compounds [5-36] mainly belonging to the PBA [8-36] type compounds.

Crystal structure:

The compounds of PBAs are represented by a common formula, $X_A\{B(CN)_{6}\}_{m}H_2O$ in which $A$ and $B$ are $3d$ transition metal ions which are periodically arranged in a cubic structure, and $X$ is an alkali metal ion, such as $K^+$ or $Rb^+$. The PBA compounds crystallize in a face centered cubic (fcc)
structure, space group Fm3m, as shown in Fig. 1. The transition metal \( A \) and \( B \) ions are located at the \( 4a \ (0, 0, 0) \) and \( 4b \ (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) crystallographic positions, respectively. The alkali metal ions and water molecules occupy the interstitial sites. Two types of water molecules i.e., coordinated and non-coordinated are generally present in PBA compounds depending on their stoichiometry (ratio \( k/l \)). When \( k/l = 1 \), no \([\text{B(CN)}_6]^{-}\) vacancies are present in the structure, and only non-coordinated water molecules occupy the interstitial positions of \( 8c \) and \( 32f \). However, when \( k/l > 1 \), \([\text{B(CN)}_6]^{-}\) vacancies are present, and the crystal structure allows both types of water molecules. Besides the non-coordinated water molecules at \( 8c \) and \( 32f \) sites, the coordinated water molecules occupy the empty nitrogen sites of \([\text{B(CN)}_6]^{-}\).

**Effect of crystal field on magnetic ordering**

\( A \) and \( B \) ions are surrounded octahedrally by N and C, respectively, in fcc lattice (Fig. 2). Since, the N octahedra are bigger than the C octahedra, the metal ion \( B \), surrounded by carbon octahedron, experiences a strong ligand field, resulting in a large splitting of the \( t_{2g} \) and \( e_{g} \) electronic levels of \( 3d \) orbitals. In case of \( B \) ions, the splitting energy is greater than the pairing energy, giving a low-spin state for \( B \) ions. For \( A \) ions, because of a relatively weaker ligand field of the N octahedron, usually a high spin state is observed.

The \( \text{Fe}^{3+} \) based PBA compound, \( \text{Fe}[\text{Fe(CN)}_6]_4\cdot4\text{H}_2\text{O} \) [8,9], studied by us, shows an excellent example of high-spin and low-spin states (Fig. 3). This compound orders ferromagnetically below 17.4 K. Our low temperature neutron diffraction study revealed a ferromagnetic ordering between high spin (\( S = 5/2 \)) and low spin (\( S = 1/2 \)) \( \text{Fe}^{3+} \) ionic moments in this compound.
Because of their multifunctional magnetic properties, such as photo/pressure/humidity induced magnetization, magnetic pole inversion, zero/negative thermal expansion, as well as ion sensing, and gas storage properties, these materials can be used in hydrogen gas storage, memory storage, photo switching based electronic devices, etc. [37-40] (Fig. 4).

Enhancement of magnetic ordering temperature:
Magnetic transition temperature for most of this class of compounds is well below the room temperature. Therefore, appropriate choices of the transition metal ions (A and B) and their valence modulation can enhance magnetic properties, such as magnetic exchange interaction, ordering temperature ($T_c$), saturation magnetization, coercive field, and remanence. We have shown that the magnetic transition temperature of thin films of PBAs $K_xFe_iCr(CN)_6nH_2O$ can be enhanced by varying electrode reduction voltage and deposition time in the electro-deposition method [19]. Fig. 5 shows $M$ vs $T$ curves at different values of thickness (a), and reduction voltage (b) for the films. As the film thickness increases from 0.5 µm to 5 µm, the $T_c$ increases from 11 to 21 K. However, with varying reduction voltage from -0.5 to -0.9 V, the $T_c$ increases up to -65 K. The enhancement in $T_c$ is mainly attributed to the change in the Fe(II)/Cr(III) ratio because of incorporation of $K^+$ ions with increasing electrode voltage. The films also show a change in color with varying reduction voltage, useful for photochromic applications.

In another example, the $T_c$ has been enhanced by using 4d ion (Ru$^{3+}$) substitution in the cyanide-bridged molecular magnets, $Ru_{x}Ni_{3-3x/2}[Cr(CN)_6]_3zH_2O$ ($0 \leq x \leq 0.5$) [17] as shown in Fig. 6. The $T_c$ increases with increasing Ru substitution. The maximum $T_c$ of -62K has been observed for the compound with $x = 0.2$. The observed variation in the $T_c$ with composition has been understood by considering the change in effective number of the magnetic nearest neighbors and their average spin values [17].

Quantification of structural disorder by reverse Monte Carlo simulation:
PBAs contain lots of vacancies as described earlier. The stoichiometry decides the $B(CN)_6$ vacancies and...
the water content. We have used reverse Monte Carlo (RMC) simulation method on the neutron diffraction data to correlate magnetic properties of PBAs with their structural disorder [11,12,15,17,20,33]. The observed and the RMC fitted neutron diffraction patterns for Fe$_{1.5}$[Cr(CN)$_6$]$_z$H$_2$O [33] are plotted in terms of the F(Q), the sum of the scattering amplitudes from all the atoms in the reciprocal space at a given Q value in Fig. 7 (left). It is interesting to note that the first Bragg peak (100) is forbidden under Fm$ar{3}$m space group. Also, modulations in the background of the diffraction data show a large amount of diffuse scattering present in the compound. Here, we note that the forbidden Bragg peak (100) in the neutron diffraction pattern has been fitted well by RMC analysis; suggesting that this peak is related to an inherent structural disorder present in the compound.

The distribution of oxygen atoms in the two dimensional plots has been shown in the right panel of Fig. 7. The clustering (size = 3–4 Å) of the non-coordinated oxygen atoms around the coordinated oxygen atoms in the compound has been observed. Our RMC analysis shows that the oxygen clustering is mainly responsible for the structural disorder and reduction of T$_C$.

Particle size dependent magnetic properties:
The variation of magnetic properties with crystallite size is an important issue in the design of molecular nanomagnets for practical applications in nanodevices. We have studied the particle size dependence of magnetic properties of nanoparticles of the Fe[Fe(CN)$_z$]$_2$H$_2$O and Cu$_{1.5}$[Cr(CN)$_6$]$_z$H$_2$O PBA compounds using x-ray and neutron diffraction, transmission electron microscopy, and dc magnetization techniques [13,18]. The transmission electron microscopy images of nanoparticles of the Cu$_{1.5}$[Cr(CN)$_6$]$_z$H$_2$O compound are shown in Fig. 8 (a), and the variation of saturation magnetization is shown in Fig. 8 (b). Magnetic study of the nanoparticles of above compounds has revealed weaker magnetic properties (e.g., T$_C$, M$_{sat}$) with reduced particle size due to increased surface spin disorder.

Tuning magnetism by external field:

We have shown an external magnetic field driven transition from an antiferromagnetic (AFM) ground state to a ferrimagnetic (FIM) state in Rb$_{0.19}$Ba$_{0.3}$Mn$_{1.1}$[Fe(CN)$_6$]$_{0.48}$H$_2$O Prussian blue analogue [28]. In the presence of an external dc magnetic field, a decrease in AFM ordering temperature and an appearance of a FIM phase is evident in ac susceptibility measurements. With increasing H, the AFM phase shrinks and the FIM phase grows, and for $H > 4$T, the AFM phase disappears completely and the system transforms to the FIM phase. An H-T phase diagram for the system is shown in Fig. 9.

Magnetization reversal and mean field calculation
We have observed a peculiar phenomenon of magnetization reversal or negative magnetization (Top layer in Fig.10) for the Cu$_{0.73}$Mn$_{0.77}$...
[Fe(CN)₆]·₂H₂O PBA system. The observed magnetization reversal has been successfully explained experimentally [15] and theoretically [16]. The molecular field theory (MFT) has been used to calculate Cu, Mn and Fe sublattice magnetizations. Under MFT, the net magnetic fields acting at the Cu, Fe and Mn sites are given by

\[ H_{Cu} = H + \gamma_{CuFe} M_{Fe} \]
\[ H_{Mn} = H + \gamma_{MnFe} M_{Fe} + \gamma_{MnMn} M_{Mn} \]
\[ H_{Fe} = H + \gamma_{CuFe} M_{Cu} + \gamma_{MnFe} M_{Mn} \]

Here, \( M \) is sublattice magnetization, \( H \) is external field, and \( \gamma_{ij} \) is molecular field coefficient between \( i \)-th and \( j \)-th magnetic sublattices. The \( \gamma_{ij} \) are related to the magnetic exchange coefficients (\( J_{ij} \)) by the relation

\[ \gamma_{ij} = \frac{2Z_{j} \gamma_{i,j}}{Z_{N}(g \mu_{B})} \]

where \( Z_{j} \) are number of \( j \)-type magnetic neighbors surrounding an \( i \)-type ion, \( \gamma_{i} \) is the molar fraction of the \( i \)-th ionic site, and \( N \) is the total number of magnetic ions per unit volume. The \( g \) is Lande g-factor, and \( \mu_{B} \) is Bohr magneton.

The sub-lattice magnetizations for Cu, Mn and Fe ionic-sites have the Brillouin function \( B_{S}(x) \) dependence as given below

\[ M_{i} = \gamma_{i} N g \mu_{B} S_{i} B_{S}(g \mu_{B} S_{i} H_{0} / k_{B} T) \]

The above equations have been solved numerically to get the temperature and magnetic field dependencies of Cu, Mn and Fe sublattice magnetizations. The MFT calculated magnetization curves (bottom layer in Fig.10) have successfully reproduced the observed magnetization reversal in this PBA system.

Applications of PBA compounds

(a) Hydrogen storage

A possible application of PBAs is in the field of hydrogen storage [41, 42]. The presence of vacancies and interstitial sites in the crystal structure of PBAs offers an ideal platform for storage of hydrogen in such compounds. We have recently synthesized \( \text{Mn}_{1.5}[\text{Cr(CN)₆}]·m\text{H}_2\text{O}@\text{Ni}_{1.5}[\text{Cr(CN)₆}]·n\text{H}_2\text{O} \) core-shell structure of PBAs in order to improve the hydrogen storage capacity [42]. We have observed that the core–shell compound shows an

Fig. 9: Magnetic phase diagram for the \( \text{Rb}_{0.19}\text{Ba}_{0.3}\text{Mn}_{1.1}[\text{Fe(CN)₆}]·0.48\text{H}_2\text{O} \) PBA system in the temperature-magnetic field plane [28]

Fig. 10: Observed (upper) and the MFT-calculated (lower) magnetization reversal in \( \text{Cu}_{0.723}\text{Mn}_{0.77}[\text{Fe(CN)₆}]·z\text{H}_2\text{O} \) PBA system [16]

Fig. 11: The hydrogen adsorption isotherms of the \( \text{Mn}_{1.5}[\text{Cr(CN)₆}]·m\text{H}_2\text{O}@\text{Ni}_{1.5}[\text{Cr(CN)₆}]·n\text{H}_2\text{O} \) core–shell PBA compound at various temperatures [42]
enhancement in the hydrogen capacity (of −2.0 wt% at 123 K, shown in Fig. 11) as compared to other previously reported PBAs molecular magnets [42].

(b) Magnetic random access memory
In another example, where Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_z$H$_2$O PBA compound shows the magnetization reversal phenomenon, the possible application of this phenomenon as a bipolar switching of magnetization (using low magnetic fields) has been demonstrated [16]. Fig. 12 shows the flipping of the field-cooled magnetization of the PBA in real time under two different values of external magnetic field [16]. The magnetic-field-controlled bistable switching of the magnetization has the potential for its usage in magnetic memory applications.

(c) Applications exploiting magnetic entropy
The sign reversal of magnetic entropy change (−Δ$S_m$) under varying temperature in systems showing a magnetization sign reversal can have practical applications. For example, the studied molecular PBA compound Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_z$H$_2$O (which depicts magnetization reversal) also shows both positive and negative magneto-caloric effects (MCEs) below its magnetic ordering temperature as depicted in Figure 13. The observed bipolar MCE in the Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_z$H$_2$O compound may be utilized in a constant temperature bath application [16] as explained below. The Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_z$H$_2$O compound as a refrigerant in a magnetic refrigerator would give an equilibrium temperature of 13 K. When any temperature fluctuation that tries to raise the temperature of the magnetic refrigerator above 13 K, the normal MCE (−Δ$S_m$ > 0) in Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_z$H$_2$O compound will bring down the temperature of the system to 13 K. On the other hand, when the temperature of magnetic refrigerator goes down below 13 K, the inverse MCE (−Δ$S_m$<0) will produce heating, and the temperature of the system will rise back to 13 K. In other words, any temperature fluctuation in the vicinity of 13 K would be compensated by the two opposite MCEs, and the system (Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_z$H$_2$O compound in a magnetic refrigerator) has the potential for its use as a constant temperature bath of 13 K.

(d) Application in radioactive waste management
PB and its analogues find their applications in waste management as well. The radio-isotopes of 134-Cs and 137-Cs, with 2.06 and 30 years half-life, respectively, are hazardous as they radiate beta-particles and strong gamma rays. In this regard, the
PBAs can be used to remove radioactive 134-Cs and 137-Cs elements [43]. Moreover, PBAs can be used as a medicine for removing radioactive as well as nonradioactive elements (cesium and thallium) from the body. PBA traps cesium and thallium compounds in the intestines, and keeps them away from being re-absorbed by the body. The radioactive materials then move through the intestines and are passed (excreted) in bowel movements. Moreover, Prussian blue reduces the biological half-life of cesium from about 110 days to about 30 days and for thallium from about 8 days to about 3 days. Recent literature describes that magnetic Prussian blue/graphene oxide nanocomposites have been used for the removal of radioactive cesium in water [43].

(e) PB graphene devices for spintronics

Very recently, one of us fabricated micro-devices [Figure 14] comprising of graphene-PB composites for their possible device applications [36]. Graphene is considered an attractive material for spintronics applications [44], the effect of a non-covalently attached PB molecular magnet on the electronic transport properties of graphene has, therefore, been studied. Remarkably, the electronic transport properties of graphene are largely preserved after the ~ 40 nm thick PB coating. The results clearly indicate that strategies involving covalent functionalization of graphene to achieve stronger magnetic exchange coupling should be devised.

Summary

The Prussian blue analogues molecular magnets have great potential for technological applications in information storage, displays, or as components in electronic or spintronic devices. However, commercially, it is still in the state of exploration of devices working at ambient conditions. It is uncertain to predict the timescale before any molecule-based room-temperature magnetic device may reach the market. However, with the unique properties of low weight (density: ~ 1g/cc), low-cost synthesis, biocompatibility, flexibility, multifunctional magnetic properties, etc., there is an immense scope of using such materials for possible technological applications in near future.

References

32. A. Kumar, BARC Newsletter, Special issue, 190 -193, October 2013.
44. A.K. Geim and K.S. Novoselov, Nat Mater 6, 183 (2007).