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Design of Molecular Magnets

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Summary: The conventional magnetic materials used in present-day technology, such as Fe, Fe_2O_3, Cr_2O_3, $SmCo_5$, $Nd_2Fe_{14}B$, etc. are all atom-based, whose synthesis requires high-temperature routes. Employing ambient-temperature synthetic organic chemistry, it has become possible to engineer a bulk molecular material with long-range magnetic order, primarily due to the weak nature of intermolecular interactions in it. Typical synthetic approach to design molecule-based magnets consists of choosing molecular precursors, each bearing an unpaired spin, and assembling them in such a way that there is no compensation of spins at the scale of the crystal lattice. Magnetism being a co-operative effect, the spin-spin interaction must extend to all the three dimensions, either through space or through bonds. Specific occurrence of 'spin delocalisation' and 'spin polarisation' in molecular lattices is helpful in bringing about ferromagnetic interaction by facilitating necessary intermolecular exchange interactions. Since the first successful synthesis of molecular magnets in 1986, a large variety of them have been synthesized, which can be classified on the basis of the chemical nature of the magnetic units involved: organic systems, metal-based systems, hetero-bimetallic assemblies, or mixed organic-inorganic systems. The design of molecular magnets has also opened the doors for the unique possibility of designing polyfunctional molecular materials, such as magnets exhibiting second-order optical nonlinearity, liquid crystalline magnets, or chiral magnets. Solubility of molecular magnets, their low density and biocompatibility are attractive features. Being weakly colored, unlike the opaque classic magnets, possibilities of photomagnetic switching can be envisaged. Persistent efforts continue to design the ever-elusive polymer magnets for applications in industry. While providing a brief overview of the field of molecular magnetism, we highlight some recent developments, with emphasis on a few studies from the author's own lab.

Keywords: conjugated polymers; magnetic polymers

1. Introduction

Most molecular materials are organic in nature. Molecular crystals are made up of well-defined molecules, which do not change their geometries appreciably upon entering the crystal lattice. This is because intermolecular interactions are non-covalent in nature, viz. hydrogen bonding, van der Waals interactions, donor-acceptor charge transfer, etc., that are much weaker than the energies of typical chemical bonds, ionic or covalent. This provides an interesting possibility to modify the properties of a molecular solid in a predetermined way by attaching a *function* to the

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molecular building-block (i.e., functionalizing the molecule) to engineer a bulk molecular material with designer characteristics. Synthetic organic chemistry employs ambient temperatures, and is known for imparting immense flexibility in the synthesis of molecule-based compounds. This has given rise to the synthesis of new molecular materials designed to perform several functions originally attributed to the metallic lattices, such as high electric conductivity or photoactivity in polymers, and superconductivity in charge-transfer organic complexes/fullerenes. Quite obviously, there has been a strong urge to develop ferro(ferri)magnetic molecular materials, too, by designing new combinations of interactions between magnetic centres in organic (or polymeric) materials, preferably with p-orbital based spins. Theoretical models did predict the possibility of attaining long-range magnetic order in molecular materials. However, organic compounds are mostly diamagnetic, with closed-shell structures, and even if one (or more) unpaired electrons are maintained stable in an organic molecule, stabilization of a triplet state (parallel alignment of spins) requires that the orthogonality conditions be satisfied (Hund's rules), which is difficult. So, obtaining antiferromagnetic coupling with no spontaneous magnetic moment is preferred. No wonder, the conventional magnetic materials used in present-day technology, such as, Fe, Fe_2O_3, Cr_2O_3, $SmCo_5$, $Nd_2Fe_{14}B$, etc. are all atom-based materials, in which magnetic order arises from co-operative spin-spin interactions between unpaired electrons located in *d*-orbitals or *f*-orbitals. Their synthesis typically depends on solid-state chemistry or high-temperature metallurgical routes.

2. Purely Organic Magnets

The first two ferro(ferri)magnetic molecular compounds exhibiting a spontaneous magnetization below a certain temperature, T_c, were reported in 1986 [1,2], and subsequently molecular magnets of many different categories have been synthesized and interest in the field of molecule-based magnets has been growing steadily. The discovery of ferromagnetism involving *p*-electrons in iron-containing organic-based material [1] was an important step forward because magnetism in metal-free compounds must involve electrons from *p*-atomic orbitals, which was considered impossible not long ago. Although significant progress has been made in the preparation of π-conjugated oligomers and polymers with large values of spin quantum number *S*, persistent efforts to design polymer magnets which, when made, would have a huge impact on applications in industry have not borne fruit [3,4]. Most recently however, Rajca et al [5] have reported the observation of magnetic properties comparable to that of insulating spin glasses and blocked superparamagnets (S = 5000, and slow orientation of the magnetization by a small magnetic field of 1 Oe below 10 K) in a highly cross-linked organic π-conjugated polymer, obtained from polyethers. Inspired by recent observations of gate-induced superconductivity in oligomers like anthracene [6] and polymers like polythiophene [7], Arita et al [8] have proposed the possibility of band ferromagnetism in a purely organic polymer structures like PAT [poly(4-amino-1,2,4-triazole], which consists of a chain of five-membered rings. They have proposed that when the flatband of such materials is made half-filled, with appropriate dopings to be realized using a field-effect transistor structure, the ground state is ferromagnetic, as indicated by spin density functional calculations. This is interesting because organics exhibiting (single-)band ferromagnetism have yet to be synthesized, though multiorbital ferromagnets such as TDAE-C_{60} [9] are known, as discussed later.

Typical synthetic approach to design molecule-based magnets consists of choosing molecular precursors, each bearing an unpaired spin (the *function*, as shown in Fig. 1), and assembling them in such a way that there is no compensation of spins at the scale of the crystal lattice [4,10,11].

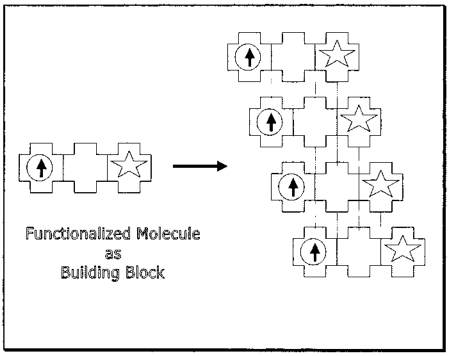


Fig. 1: Generation of a molecular lattice, through self-assembly, employing a functionalized molecule as a building block. The latter could have just one function attached – say, an unpaired electron denoted by an arrow, in which case the three-dimensional lattice is aimed to have a long-range magnetic order. A building block could also have an additional second function to facilitate the design of bifunctional molecular magnets possessing another property, such as chirality, liquid crystallinity, or ferroelectricity, etc. in addition to magnetism.

More recently, the design of molecular magnets has also employed the tools of supramolecular chemistry [12]. The interactions between spin carriers may occur through space, in which case we have a genuine molecular lattice, or, through bond when we are faced with a polymeric or extended structure. In the latter case, the interactions are usually much stronger, particularly so when the bridging ligands are conjugated.

The design of a molecular magnet requires that: (a) all the molecules in the lattice have unpaired electrons, and, (b) the unpaired electrons should have their spins aligned parallel along a given direction. Magnetism being a co-operative effect, the spin-spin interaction must extend to all the three dimensions. Specific occurrence of *spin delocalisation* and *spin polarisation* in molecular lattices, unlike in the case of ionic/metallic compounds, is helpful in bringing about ferromagnetic interaction by facilitating necessary intermolecular exchange interactions.

The delocalization of spin density in certain molecules makes it possible for magnetic interactions to take place across extended bridges between magnetic centres far apart from each other, propagating through conjugated bond linkages, which act as molecular wires. Spin polarization, i.e. the simultaneous existence of positive and negative spin densities at different location within a given radical is crucial for intermolecular exchange interactions to bring about ferromagnetic interaction between organic radicals, as per McConnell's model [13]. Spin density across different regions of the nitronyl nitroxide radical NITR (R=alkyl), a versatile building block with spin S = 1/2 ground state (Fig. 2), for instance, shows positive values, equally delocalized between N and O within each N-O group, and a small negative value on the bridging sp^2 carbon, due to spin polarization.

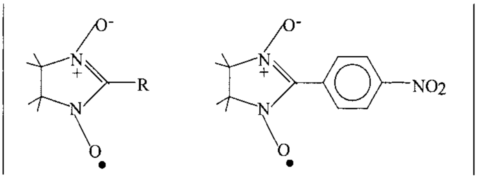


Fig. 2: Chemical structure of NITR; and *p*-NPNN (• indicates an unpaired electron).

By substituting different alkyl groups (like R = benzyl, isopropyl, methyl, ethyl, phenyl, etc.) in NITR, one can tune the single-radical ground state to establish new exchange pathways through varied coordination sites. For instance, ferromagnetism at 0.6 K arises solely from *p* orbital spins in the β-phase of R = phenyl compound, 4-nitrophenylnitronyl nitroxide) (*p*-NPNN, with formula $C_{13}H_{16}N_3O_4$, shown in Fig. 2), a metal-free organic magnet which contains only C, H, N, and O elements [14].

Ferromagnetism has also been obtained for the purely organic fullerene-based charge-transfer material, [tetrakis(dimethylamino)ethene][C_{60}] with T_c of 16.1 K [9]. Fullerene has no intrinsic magnetic moment. For a magnetic moment to exist, an electron must be transferred to C_{60} from a donor molecule. Another example of a fullerene-based ferromagnet was the cobaltocene-doped derivative, which has a T_c of 19 K [15]. The highest ordering temperature reported to date for an organic magnet has been for the β-phase of the (4-cyanotetrafluorophenyl)dithiadiazolyl, a sulfur-based free radical, which was found to be a weak ferromagnet below 35.5 K [16,17]. Under a pressure of 1.6 GPa, this temperature can be raised to 65 K [18]. Most interestingly, but raising some controversy nonetheless, Makarova et al [19] have reported recently strong magnetic signals (including saturation magnetization, hysteresis, and attachment to a magnet at room temperature), in a two-dimensional rhombohedric phase of C_{60}, that resembles graphite. The temperature dependence of saturation magnetization and remanence indicate a T_c of about 500 K, but the magnetic behavior is very sensitive to the preparation conditions. The material is obtained by converting a crystalline state of isolated molecules, held together only by van der Waals forces, into polymeric phases in which the molecules are covalently bonded, using a high-pressure, high-temperature polymerization route.

3. Ferrimagnetic Building Blocks

A powerful strategy to build a molecule-based magnet is based on the use of ferrimagnetic chains containing alternating spins of unequal magnitude $S_A \neq S_B$, and assembling them in such a way that there is a net spin, leading to a long-range magnetic order in the lattice [10,20]. Here, S_A stands for the large spin and S_B for the small spin on two different spin carriers, A and B, such as Mn(II) ions ($S = 5/2$) and Cu(II) ions ($S = 1/2$), respectively, within the same molecular precursor (Fig. 3). A large number of molecular (ferro)ferrimagnets have been assembled using this technique, the spin carriers in them being either two different metal ions [21,22] or a metal ion and an organic radical [23-26], with intervening ligands which serve as effective exchange pathways.

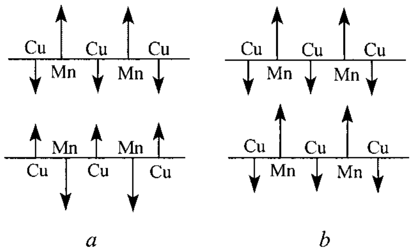


Fig. 3: Assembly of ferrimagnetic chains leading to a net (a) zero or (b) non-zero magnetic moment in bulk.

Heterobimetallic species, in which two different metal ions are bridged by extended bisbidentate ligands such as oxamato [27,28], oxamido [21,29], or oxalato [22], in particular, allow a variety of spin topologies. Using this priniciple, Kahn's group have synthesized several Mn(II)Cu(II) molecular magnets in which the ferrimagnetic interactions is propagated through bisbidentate ligands, viz. MnCu(opba).0.7DMSO which is synthesized by reacting the Cu(II) precursor Cu(opba)$^{2-}$ (Fig. 4), where opba stands for phenylenebis(oxamato), with a divalent ion, Mn(II) in a 1:1 stoichiometry, behaves as an amorphous magnet with a spontaneous magnetization below $T_c = 6.5$ K.

[Cu(opbz)]$^{2-}$ [Cu(obbz)]$^{2-}$

Fig. 4: A schematic of the copper dianion precursors [Cu(opba)]$^{2-}$and [Cu(obbz)]$^{2-}$, where ‘opba’ and ‘obbz’ stands for phenylenebis(oxamato) and oxamidobis(benzoato) ligands, respectively.

Aiming at increasing the Curie temperatures of this class of compounds led to the synthesis of 2:3 Mn(II)Cu(II) compounds $A_2M_2[Cu(opba)]_3.n$solv with two-dimensional character, by employing [Cu(opba)]$^{2-}$ to crosslink the chains in a two-dimensional network, in the presence of two equivalents of non-coordinating cation A^+. Among them is $(NBu_4)_2Mn_2[Cu(opba)]_3.6DMSO.1H_2O$, exhibiting a transition at T_c = 15 K towards a ferromagnetically ordered state [27], the T_c value of which rises to 22.5 K when all the solvent molecules are removed [27,30]. Elucidation of structure of 1:2 Mn(II)Cu(II) compound $(NBu_4)_2Mn[Cu(opba)]_2$ by us, recently, revealed a new crystallographic arrangement among the class of 'opba' molecular magnets [31]. It crystallizes in orthorhombic structure (with space group $Pna2_1$) consisting of a zig-zag chain with terminal ‘opba’ groups. It is a filled structure with most of the space filled by cations; the clefts in the space in-between are filled with two NBu_4 cations (Fig. 5). So far they have been known to exist as one-dimensional chains for the 1:1 proportion, and as planar graphite-like sheet structures for the 2:3 ratio.

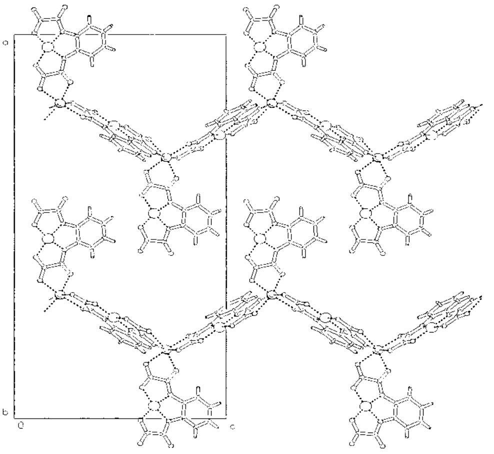


Fig. 5: Structure of 1:2 Mn(II)Cu(II) compound $(NBu_4)_2Mn[Cu(opba)]_2$ consisting of a zig-zag chain with terminal ‘opba’ groups.

An effective process for assembling spin-bearing precursors is when polymerization is associated with dehydration. When the precursors are linked to each other after polymerization, the interaction involving a spin carrier A from a given unit and a spin carrier B from the adjacent unit becomes large, and the resulting ground state spin of the polymer $[AB]_n$, where n is the number of units, becomes $n(S_A - S_B)$. If n is infinite and the system is three-dimensional, a long-range ferrimagnetic ordering should occur, which can also be considered as a ferromagnetic coupling of the ground state spin ($S_A - S_B$) of the AB units, which in the case of Mn(II)Cu(II)-

based compounds is $S = 2$. The compound MnCu(obbz).$5H_2O$ [21], which was obtained by the polymerization of ferrimagnetic molecular precursor units obtained by reacting the copper dianion $[Cu(obbz)]^{2-}$ (Fig. 4), where obbz is the oxamidobis(benzoato) ligand, with Mn(II) ions, exhibits a minimum at 44 K in its $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility and T the temperature, a signature of a one-dimensional ferrimagnet, and a sharp maximum at 2.3 K due to a three-dimensional antiferromagnetic ordering. Upon dehydration it yields the monohydrate, MnCu(obbz).$1H_2O$, which orders ferromagnetically below the critical temperature (T_c) of 14 K, due to the non-compensation of the magnetic moments on Mn(II) and Cu(II) [21,32]. Subsequently, Ni(II)-, Fe(II)- and Co(II)-based bimetallic chain compounds have also been synthesized using the $[Cu(obbz)]^{2-}$ precursor [21,32-35]. Using the mixed metal ion spin-organic radical spin approach, a 46 K magnet was synthesized by the reaction of a trinitroxide radical, with three parallel spins ($S = 3/2$), with bis(hexafluoroacetylacetonato)manganese(II), $[Mn(II)(hfac)_2]$ [26].

The Mn(II) ion is not able to prevent the domains from rotating freely under an applied field because it is a magnetically isotropic ion. Most of the Mn(II)Cu(II)-based magnets, though exhibit a high value of T_c (12 to 30 K), are soft ferromagnets, therefore, exhibiting rather narrow magnetic hysteresis loops below T_c with rather weak coercive field values ($H_c < 50$ Oe at 4.2 K) [27,36-38]. The same is generally true for Fe(II)Cu(II)-based magnets (Fig. 6). It is the coercivity of a magnet which confers a memory effect on it. Rather strong coercive fields are expected for Co^{2+}-based molecular magnets where Co^{2+} ion in distorted octahedral environment, being magnetically anisotropic, can assume preferred orientations. Replacing Mn(II), with an orbital singlet state ($^6A_1$), by Co(II) with an orbital triplet ground state ($^4T_1$) in $(cat)_2Mn_2[Cu(opba)]_3$ [27,36,37], where 'cat' denotes a cation, results in a dramatic rise in coercivity. For instance, $H_c = 3000$ Oe for $(NBu_4)_2Co_2[Cu(opba)]_3.3DMSO.3H_2O$ and 3100 Oe for $(rad)_2Co_2[Cu(opba)]_3.0.5DMSO.3H_2O$ [38], where "rad" stands for the radical cation 4,4,5,5-tetramethyl-2-(1-methylpyridin-1-ium-4-yl)-4,5-dihydroimidazol-1-oxyl 3-oxide and "opba" denotes phenylenebis(oxamato). The compound $[(Etrad)_2Co_2\{Cu(opba)\}_3(DMSO)_{1.5}].0.25H_2O$, having formula $C_{61}H_{63.5}N_{12}O_{23.75}S_{1.5}Co_2Cu_3$, exhibits quite high coercivity, up to 24 kOe at 6 K for a sample of small crystals [39]. Here, $Etrad^+$ deonotes an ethyl radical cation, 2-(1-ethylpyridinium-4-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-1-oxyl 3-oxide. These values are much higher than those for the commercial atom-based materials Fe_2O_3 or CrO_2. The synthetic procedures employed to obtain molecular materials are different from those employed in solid-state chemistry and the molecular crystal lattice is characteristically *soft*, as compared to the ionic or metallic lattices. We have exploited these attributes to demonstrate that for certain molecular magnets, assembled from Co(II)Cu(II)-based ferrimagnetic chains, it is possible to modify the magnetic properties dramatically and reversibly through a mild dehydration-rehydration process, and have named this class of compounds as *molecular magnetic sponges* [33,34,40,41]. This is because they show 'sponge'–like characteristics, viz. a reversible cross-over under dehydration to a polymerized long-range magnetically ordered state with spontaneous magnetization, and transforming back into the isolated units underlying the initial non-magnetic phase by reabsorbing water, i.e. rehydration of both noncoordinated and coordinated water molecules (Fig. 7).

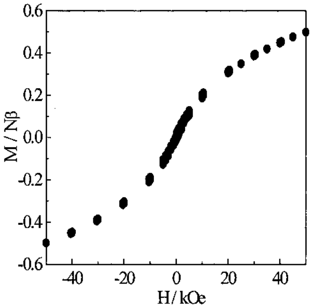


Fig. 6: Magnetization data at 5 K for $Fe^{II}Cu^{II}(obbz).1H_2O$ as a function of applied field.

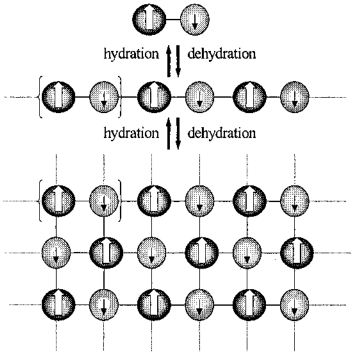


Fig. 7: The dehydration-polymerization process, typically applicable to the reversible sponge-like behaviour of $CoCu(obbz).nH_2O$.

Coercivity values for these sponges are high and for some of these a colour change, too, occurs reversibly and simultaneously with the change in magnetic properties at the transition temperature corresponding to the dehydration-rehydration process. In the case of $[CoCu(obbz)].nH_2O$, we confirmed that the Co-O bonds could be broken and created without destroying the essence of the molecular architecture. The main features of the four Co(II)Cu(II)-based *molecular magnetic sponges* synthesized by our group, viz. $CoCu(pbaOH)(H_2O)_3.2H_2O$, $CoCu(pba)(H_2O)_3.2H_2O$, $CoCu(obbz)(H_2O)_4.2H_2O$ and $CoCu(obze)(H_2O)_4.2H_2O$ are high values of T_c (38, 33, 25 and 25 K, respectively) and H_c (5.66, 3, 1.3 and 1 kOe, respectively). The symbols pbaOH, pba and obze denote 2-hydroxypropane-1,3-diylbis(oxamato), propane-1,3-diylbis(oxamato) and oxamido-*N*-benzoato-*N'*-ethanoato, respectively.

4. Polycyanometallates

A unique feature of the molecular magnets is that they are usually weakly coloured unlike the opaque classic magnets. Design of molecular ferromagnets of low density that are transparent and have a tunable, high T_c is a cherished goal. Photomagnetic switching has been reported in molecular magnets, especially where hexacyanometallates $[M(CN)_6]^{n-}$ are used as molecular building blocks.

Most metal hexacyanometallates have a cubic structure as shown in Fig. 8. Metal ions are situated at the corners of the cube and they are octahedrally coordinated by the nitrogen or carbon atom of the cyanide group. The cyanide groups are bridging the metal ions along the cube edges. Depending on the number of charges of the N- and C-coodinated metal ions, a certain number of cations can occupy interstitial positions for charge compensation. These interstitial metal ions may be the same as the N- and C-coordinated metal ions, or they may be alkali metal ions. In this context, much interest has been focused recently on the molecule-based cyanides related to the well-known Prussian Blue, $Fe^{III}_4[Fe^{II}(CN)_6]_3.15H_2O$, whose structure was described by Ludi and Gudel [42] as highly disordered cubic cell consisting of alternating ferrocyanide and ferric ions, with linear Fe^{III}-N-C-Fe^{II} bridges.

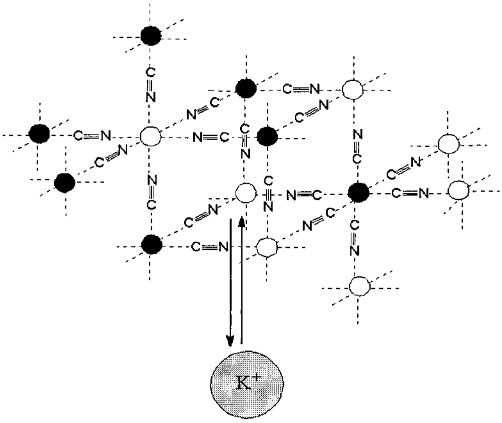


Fig. 8 : Scheme of the structure of metal hexacyanometallates (dark circles denote Fe^{3+}, Co^{3+}, etc. and empty circles denote Cu^{2+}, Ni^{2+}, Fe^{3+}, etc.)

The cyano bridge is known to mediate strong antiferromagnetic or ferromagnetic interactions, as in the case of Prussian Blue analogues, $A_k[B(CN)_6].xH_2O$, where A and B are transition metal ions [43]. T_c values above room temperatures, viz. 376 K [44], have been reported for hexacyanometallates but their high fcc symmetry is often accompanied by inherent disorder among different cationic sites, making it difficult to grow single crystals or to study any magnetic anisotropy. Recently, we have demonstrated the use of a Langmuir monolayer of octadecylamine as a templating agent at the air-water interface for growing oriented crystals of the Prussian-Blue-related metal(II) hexacyanoferrate(III) in a Langmuir-Blodgett trough, where metal ion can be Ni, Co or Cu [45]. X-ray diffraction pattern for one of them is compared with the polycrystalline material in Fig. 9.

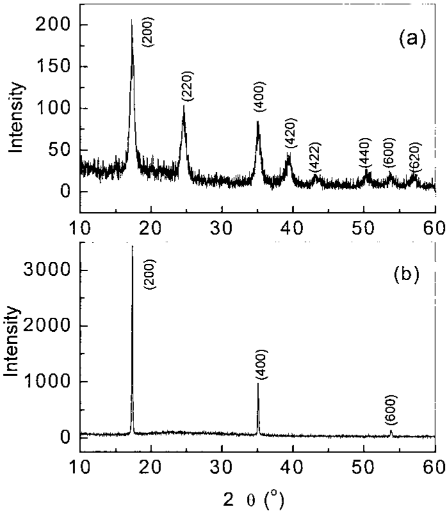


Fig. 9 : CuK_α XRD pattern of (a) bulk randomly oriented $Ni_3[Fe(CN)_6]_2.nH_2O$ powder, and (b) Ni hexacyanoferrate film transferred on glass from the air-water interface. Electron diffraction pattern confirmed that the crystallites have their {100} planes parallel to the monolayer.

An alternative strategy adopted by us to grow single crystals was to employ the heptacyano anion $[Mo^{III}(CN)_7]^{4-}$ as a precursor because its pentagonal bipyramidal coordination sphere is incompatible with a cubic lattice. Moreover, the Mo^{3+} ion in the $[Mo^{III}(CN)_7]^{4-}$ chromophore is low-spin, with a local spin of $S_{Mo} = 1/2$, and the g-tensor associated with the ground Kramers doublet is very anisotropic. Reaction of Mn(II) ions with the heptacyano $[Mo^{III}(CN)_7]^{4-}$ precursor led to lowering of symmetry and high values of Curie temperatures (T_c = 51 K) arising from a ferromagnetic interaction between the low-spin Mo^{3+} and the high-spin Mn^{2+} through the Mo^{III}-C-N-Mn^{II} bridges. The use of a macrocycle reduced the symmetry further by imposing heptacoordination on Mn(II) ion, too. A low T_c (3 K) for the compound $[Mn^{II}L]_6[Mo^{III}(CN)_7][Mo^{IV}(CN)_8]_2.19.5H_2O$, where L is a macrocycle, was attributed to the existence of diamagnetic Mo^{4+} along certain CN bridges, in addition to the paramagnetic Mo^{3+} [46].

More recently, octacyanometallates have also been used as versatile building blocks [47]. In order to examine the role of Mo^{IV} ion exclusively in the propagation of spin-spin interactions in 3*d*-based polycyanomolybdates, polycyanoferrates(II) were synthesized. $Fe^{II}_2[Mo^{III}(CN)_7].8H_2O$ orders ferromagnetically below 65 K (Fig. 10), but $Fe^{II}_2[Mo^{IV}(CN)_8].8H_2O$ is paramagnetic down to 2 K.

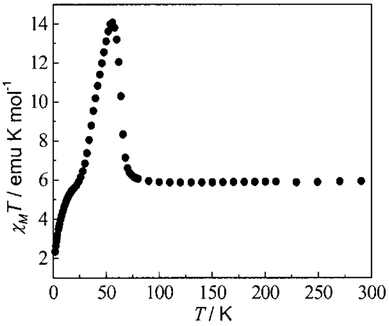
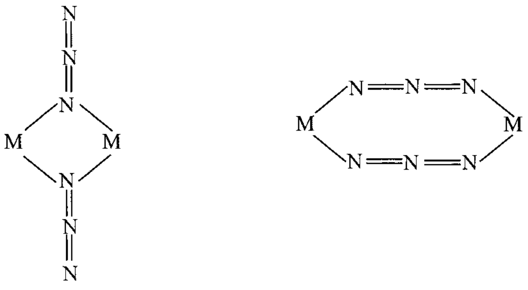


Fig. 10: $\chi_M T$ versus T curve for $Fe_2[Mo(CN)_7].8H_2O$.

5. Role of the Azido Bridge

An end-to-end (e-e) coordination of the azido group (N_3) results in moderate to strong antiferromagnetic coupling whereas an end-on (e-o) coordination gives rise to ferromagnetic coupling between paramagnetic centres (Fig. 11).



end-on

end-to end

Fig. 11: End-on and end-to-end bridging modes of the azido ligand (N_3^-) connecting two metal ions.

We have recently designed a unique *trans*-coordinated azido-Mn(II) 1-D chain compound of the formula $[Mn(L)(N_3)(PF_6)]_n$ by using a macrocyclic pentaaza ligand, a molecular building block which occupies the equatorial plane of the Mn(II) ion, thus forcing the two incoming N_3^- (azido) ligands to coordinate to the metal in the *trans* position. The crystal structure of $[Mn(L)(N_3)(PF_6)]_n$ is orthorhombic, with space group *Pbca*, and consists of 1-D arrays of Mn(II) units linked by single *trans* e-e azido bridges propagating along the *a* axis (Fig. 12). Magnetic susceptibility measurements indicate antiferromagnetic interactions between the Mn(II) centres ($S_{Mn} = 5/2$) below 30 K which are mediated through the azide group with a very small value of $J = -5.0(1)\ cm^{-1}$ [48]. Both the EPR and magnetic behaviour confirm that $[Mn(L)(N_3)(PF_6)]_n$ consists of 1-D Mn(II) arrays magnetically well isolated from the neighboring chains.

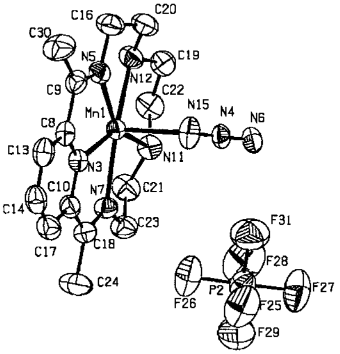


Fig. 12: ORTEP view of $[Mn(L)(N_3)(PF_6)]$ with numbering scheme.

6. The Current Scenario and Future Perspectives

Synthetic activity in molecular magnets has recently led to the development of what are known as *single molecule magnets* (SMMs), such as $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$, which are magnetic clusters with large spin ground state (e.g. $S = 10$). Crystals of SMMs function as collections of monodisperse nanomagnets, unlike other nanoscale magnetic materials which have size distribution. Having mesoscopic dimensions, these magnetic aggregates are on the border between the classic and quantum regimes, and serve as model systems to study quantum tunneling and quantum coherence etc. [49,50]. Single molecule magnets are exciting new sources of magnetic phenomena relevant to materials such as magnetocaloric effect, QuBits, etc. [51].

The field of molecular magnetism is throwing up other potentially useful materials, such as those exhibiting negative magnetizations [52], spin-crossover materials with large hysteresis effects above room temperature [53], those exhibiting photomagnetic switching [54], and materials whose properties can be modulated electrochemically. Photoinduced magnetization has been demonstrated recently in the organic-based magnet $Mn(TCNE)_x.y(CH_2Cl_2)$ [55]. Solubility of molecular magnets and their low density are attractive features. So is their biocompatibility which makes them useful in drug-targeting or as high-relaxivity magnetic resonance imaging (MRI) contrasting agents. New amphiphilic Gd(III) chelates, capable of self-organizing by forming micelles in aqueous solutions, have been designed with the aim of obtaining a high-relaxivity MRI contrasting agent [56]. Some groups are attempting to utilize the high degree of directionality of hydrogen bonding between open-shell molecules to obtain supramolecular self-organization aimed at achieving new molecular ferromagnets.

The Langmuir-Blodgett technique is a powerful tool to organize molecules in a multilayer architecture. A weak ferromagnetic state has been established in LB films of manganese octadecylphosphonate $[n\text{-}C_{18}H_{37}PO(OH)O]_2Mn$ [57]. New hybrid ferromagnetic LB films based on ferri-ferrocyanide Prussian Blue have been deposited as multilayer lamellar structures in which the magnetic properties of the inorganic sheets are combined with other functions arising from the organic part, such as dimethyldioctadecylammonium bromide (DODA) [58]. LB films of the Mn_{12} acetate cluster (SMM) have also been reported, which exhibit hysteresis [59].

Multilayer LB architectures have been organized from Prussian Blue magnets as well as those of the Mn_{12} acetate SMM.

Magnetic spin ladder systems like bis(piperidinium) tetrabromocuprate(II), $(C_5H_{12}N)_2CuBr_4$ have been reported recently [60]. Apart from the fact that a molecule is the ultimate unit for data storage, the design of molecular magnets has also opened the doors for the unique possibility of designing polyfunctional materials at the molecular level such as those exhibiting ferromagnetic behaviour and second-order optical nonlinearity [61], or liquid crystallinity and magnetism [62]. Recently, we have been involved in the design of a three-dimensional chiral, transparent ferrimagnet $K_{0.4}[Cr(CN)_6][Mn((S)\text{-pn})](S)\text{-pnH}_{0.6}$ with $T_c = 53$ K, where (*S*)-pn stands for (*S*)-1,2-diaminopropane [63]. Most recently, Itkis et al [64] have succeeded in obtaining, for the first time, a trifunctional phenalene-based neutral radical, which exhibits magneto-opto-electronic bistability with hysteresis loops centred near room temperature at 335 K, which opens the possibility of a new type of electronic devices, where multiple physical channels can be used for writing, reading, and transferring information. Magnetic bistability, have been reported in the past in molecular systems, such as doped spin-crossover compounds [65] and in the 1,3,5-trithia-2,4.6-triazapentalenyl organic radical [66], for which the magnetic transition is accompanied by a change of color, too.

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[1] J.S. Miller, J.C. Calabrese, A.J. Epstein, R.B. Bigelow, J.H. Zang, and W.M. Reiff, J. Chem. Soc., Chem. Commun. (1986) 1026.

[2] Y. Pei, M. Verdaguer, O.Kahn, J. Sletten, and J.-P. Renard, J. Am. Chem. Soc. 108 (1986) 428.

[3] A.A. Ovchinnikov, Theor. Chim. Acta 47 (1978) 297.

[4] K. Itoh and M. Kinoshita, Eds. *Molecular Magnetism*, Gordon and Breach Science, Publishers, Amsterdam (2000).

[5] S. Rajca, J. Wongsriratanakul and S. Rajca, Science 294 (2001) 1503.

[6] J.H. Schoen, S. Berg, C. Kloc and B. Batlogg, Science 287 (2000) 1022.

[7] J.H. Schoen, A. Dodabalapur, Z. Bao, C. Kloc, O. Schenker and B. Batlogg, Nature 410 (2001) 189

[8] R. Arita, Y. Suwa, K. Kuroki and H. Aoki, Phys. Rev. Lett. 88 (2002) 127202.

[9] P. Allemand, K. Khemani, K. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner and J.D. Thompson, Science 253 (1991) 301.

[10] O. Kahn, *Molecular Magnetism*, VCH, New York (1993).
[11] J.S. Miller, Inorg. Chem. 39, (2000) 4392.
[12] O. Kahn, Ed. *Magnetism: A Supramolecular Function*; NATO ASI Series C, Vol. 484, Kluwer, Dordrecht. (1996).
[13] H.M. McConnell, J. Chem. Phys. 39 (1963) 1910.
[14] M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, Chem. Phys. Lett. 186 (1991) 401.
[15] A. Merzel et al. Chem. Phys. Lett. 298 (1998) 329.
[16] A.J. Banister, N. Bricklebank, I. Lavender, J.M. Rawson, C.I. Gregory, B.K. Tanner, W. Clegg, M.R.J. Elsegood and F. Palacio, Angew. Chem. Int. Ed. Engl. 35 (1996) 2533.
[17] F. Palacio et al. Phys. Rev. Lett. 79 (1997) 2336.
[18] M. Mito et al., Polyhedron 20 (2001) 1509
[19] T.L. Makarova, B. Sundqvist, R. Hohne, P. Esquinazi, Y. Kopelevich, P. Scharff, V.A. Davydov, L.S. Kashevarova, and A.V. Rakhmanina, Nature 413 (2001) 716.
[20] O. Kahn, Adv. Inorg. Chem., 43 (1995) 179.
[21] K. Nakatani, J.Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J.P. Renard, Y. Pei, J. Sletten, and M. Verdaguer, J. Am. Chem. Soc. 111 (1989) 5739.
[22] H. Okawa, M. Mitsumi, M. Ohba, M. Kodera, and N. Matsumoto 1994, Bull. Chem. Soc. Jpn., 67 (1994) 2139.
[23] A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, Acc. Chem. Res. 22 (1989) 392.
[24] W.E. Broderick, J.A. Thompson, P. Day and B.M. Hoffman, Science 249 (1990) 410.
[25] K. Inoue and H. Iwamura, J. Am. Chem. Soc. 116 (1994) 3173.
[26] K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizume and Y. Ohashi, J. Am. Chem. Soc. 118 (1996) 1803.
[27] H.O. Stumpf, Y. Pei, O. Kahn, J. Sletten, and J.P. Renard, J. Am. Chem. Soc. 115 (1993) 6738.
[28] O. Kahn, Y. Pei, M. Verdaguer, J.P. Renard and J. Sletten, J. Am. Chem. Soc. 111(1988) 7823.
[29] Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Mathoniere and J. Sletten, J. Am.Chem. Soc. 113 (1991) 6558.
[30] S.A. Chavan, R. Ganguly, V.K. Jain and J.V. Yakhmi, J. Appl. Phys. 79 (1996) 5260.
[31] A. Neels, H. Stoeckli-Evans, S.A. Chavan and J.V. Yakhmi, Inorg. Chim. Acta 326 (2001) 106.
[32] S.A. Chavan, J.V. Yakhmi and I.K. Gopalakrishnan, Mol. Cryst. Liq. Cryst. 274 (1995) 11.
[33] J. Larionova, S.A. Chavan, J.V. Yakhmi, A.G. Froystein, J. Sletten, C. Sourisseau, and O. Kahn, Inorg. Chem. 36 (1997) 6374.
[34] O. Kahn, J. Larionova and J.V. Yakhmi, Chem. Eur. J. 5 (1999) 3443.
[35] A.K. Sra, M. Tokumoto and J.V. Yakhmi, Philos. Mag. B (April 2001) to appear
[36] H.O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, and O. Kahn, Science 261 (1993) 447.
[37] H.O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat, and O. Kahn, J. Am. Chem. Soc. 116 (1994) 3866.
[38] H.O. Stumpf, Y. Pei, C. Michaut, O. Kahn, J.P. Renard, and L. Ouahab, Chem. Mater. 6 (1994) 257.
[39] M.G.F. Vaz et al Chem. Eur. J. 5 (1999) 1486
[40] S. Turner, O. Kahn and L. Rabardel, 1996, J. Am. Chem. Soc. 118 (1996) 6428.
[41] S.A. Chavan, J. Larionova, O. Kahn and J.V. Yakhmi, Philos. Mag. B 6 (1998) 1657.
[42] A. Ludi and H.U. Gudel, Struct. Bonding (Berlin), 14 (1973) 1.
[43] W.R. Entley and G.S. Girolami, Science 268 (1995) 397.
[44] S.M. Holmes and G.S. Girolami, J. Am. Chem. Soc. 121 (1999) 5593.
[45] S. Choudhury, N. Bagkar, G.K. Dey, H. Subramanian and J.V. Yakhmi, Langmuir 18 (2002) 7409.
[46] A.K. Sra, M. Andruh, O. Kahn, S. Golhen, L. Ouahab and J.V. Yakhmi, Angew. Chem. Int. Ed., 38 (1999) 2606.
[47] A.K. Sra, G. Rombaut, F. Lahitete, S. Golhen, L. Ouahab, C. Mathoniere, J.V. Yakhmi and O. Kahn, New J. Chem. 24 (2000) 871.
[48] A.K. Sra, J.-P. Sutter, P. Guionneau, D. Chasseau, J.V. Yakhmi and O.Kahn, Inorg. Chim. Acta 300-302 (2000) 778.
[49] J.R. Friedman, M.P. Sarachik, J. Tejada and R. Ziolo, Phys. Rev. Lett. 76 (1996) 3830.
[50] B. Barbara and L. Gunther, Phys. World (March 1999) 35.
[51] M.N. Leuenberger and D. Loss, Nature 410 (2001) 789.
[52] C. Mathoniere, S.G. Carling, D. Yusheng, and P. Day, J. Chem. Soc., Chem. Commun., (1994) 1551.
[53] J. Krober, E. Codjovi, O. Kahn, F. Groliere, and C. Jay, J. Am. Chem. Soc. 115 (1993) 9810.
[54] K. Hashimoto and S. Ohkoshi, Philos. Trans. R. Soc. Lond. A 357 (1999) 2977.
[55] D.A. Pejakovic, C. Kitamura, J.S. Miller and A.E. Epstein, Phys. Rev. Lett. 88 (2002) 057202.

[56] J.P. Andre, E. Toth, H. Fischer, A. Seelig, H.R. Macke and A.E. Merbach, Chem. Eur. J. 5 (1999) 2977.

[57] C.T. Seip, G.E. Granroth, M.W. Meisel and D.R. Talham, J. Am. Chem. Soc. 119 (1997) 7084.

[58] C. Mingotaud, C. Lafuente, J. Amiell and P. Delhaes, Langmuir 15 (1999) 289.

[59] M.C. Leon, H. Soyer, C. Mingotaud, C.J.G. Garcia, E. Coronado and P. Delhaes, Mol. Cryst. Liq. Cryst. 334 (1999) 669.

[60] B.C. Watson et al., Phys. Rev. Lett. 86 (2001) 5168.

[61] S. Benard, P. Yu, J.P. Audiere, E. Riviere, R. Clement, J. Guilhem. L. Tchertanov and K. Nakatani, J. Am. Chem. Soc. 122 (2000) 9444.

[62] K. Binnemans et al, J. Am. Chem. Soc. 122 (2000) 4335.

[63] K. Inoue, H.Imai, P.S. Ghalsasi, M. Ohba, H. Okawa and J.V. Yakhmi, Angew. Chem. Int. Ed. Eng. 40 (2001) 4242.

[64] M.E. Itkis, X. Chi, A.W. Cordes and R.C. Haddon, Science 296 (2002) 1443.

[65] J. Krober, E. Codjovi, O. Kahn, F. Groliere and C. Jay, J. Am. Chem. Soc. 115 (1993) 9810.

[66] W. Fujita and K. Awaga, Science 286 (1999) 261.