

Design of molecular ferromagnets

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Abstract. A large variety of molecular ferromagnets have been synthesized since the discovery of the first organic ferromagnets, including pure organic compounds, organometallic charge-transfer complexes, metal complex–organic radical compounds, and transition metal complexes coupled to organic radicals. Besides, there are many reports on the observation of ferromagnetism in polymers and organic matrix composites. Molecular ferromagnets have great potential in different areas of technology such as low frequency magnetic shielding, magnetic imaging, magneto-optics and information storage. We provide a brief review on the current strategies for the design of molecular (organic) ferromagnets. This includes exploiting the inherent advantages of molecular systems, such as the ability to fine-tune the properties at the molecular level, and to control dimensionality, supramolecular structuring and hierarchy of spin interactions etc. for carrying out structural modifications and chemical functionalisations of stable open-shell molecules in order to generate supramolecular structures in which the natural prediction for antiparallel spin alignment (antiferromagnetism) is avoided.

Keywords. Organic ferromagnets; polymers; ferrimagnetic subunits; charge transfer complexes; dimensionality; hydrogen bonding.

1 Introduction

Ferromagnetic behaviour arises when unpaired spins in a material align collectively in the same direction resulting in a net magnetic moment and spontaneous magnetization below a characteristic temperature, T_c , called the Curie temperature. Ideally, in such structures, the spin carriers (viz. (i) organic radicals, where the unpaired spins reside in the p orbitals only; (ii) transition metal ions having their unpaired spins in the d orbitals; and (iii) their hybrids in which the unpaired spins are in both p and d orbitals) need to be incorporated into molecules which are functionalised so that when these molecules assemble in a 2D- or preferably a 3D- network, a ferromagnetic interaction may arise between the constituent molecules. However, synthesis of such materials is not easy because unlike most conventional magnetic materials used in modern technology such as, Fe, CrO_2 , Fe_2O_3 , SmCO_5 , Sm_2O_{17} or $\text{Nd}_2\text{Fe}_{14}\text{B}$, which are all atom-based materials, the molecular magnets under discussion are made up of discrete molecules and are mostly organic compounds, being essentially closed-shell structures and therefore diamagnetic. Even if one or more unpaired electrons are maintained stably in a given organic molecule, they prefer to get antiferromagnetically coupled with those on the adjacent radicals, owing to the orthogonality condition. Hund's rule allows a ferromagnetic alignment of the two spins only if the orbitals containing the

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unpaired electrons on the two spin-centres are orthogonal to each other, any non-zero overlap between orbitals leads to an antiparallel alignment of spins.

A theoretical proposal to design organic ferromagnets was made by McConnell (1963), according to which if two radicals A and B are packed such that the negative spin density sites of one radical locate directly above the positive spin density of the other, then the Heisenberg Hamiltonian for the interacting spins can be written as

$$H_{AB} = -2 \sum_{ij} J_{ij}^{AB} S_i^A S_j^B = -2 S^A S^B \sum_{ij} J_{ij} \rho_i^A \rho_j^B,$$

and the effective exchange interaction between the two radicals will be ferromagnetic when the product of spin densities ρ_i and ρ_j at sites i and j on A and B is negative. A second mechanism for the kinetic stabilization of a triplet state proposed by McConnell (1967) is based on the configuration interaction of the wavefunction of a virtual excited state with the wavefunction of the triplet ground state. However, it is only during the last decade that a variety of molecule-based ferromagnetic materials have been synthesized successfully by controlling the interactions between different magnetic centres during synthesis (Miller *et al* 1986, 1988a,b; Caneschi *et al* 1989a; Kahn *et al* 1992; Yakhmi 1992; Kahn 1993; Gatteschi *et al* 1994; Miller and Epstein 1994; Chavan *et al* 1995a). Using synthetic organic chemistry, however, one can exercise immense flexibility in controlling the relative positions of the molecular units within a molecular lattice. Intermolecular interactions being weaker than the energies of typical covalent bonds, the molecules prefer to retain their individual characteristics in a molecular solid. The properties of a molecular lattice are, therefore, derivable from those of the individual molecules and one should, in principle, be able to fine-tune its magnetic properties. The ultimate goal is to synthesize chemically stable molecular ferromagnets with T_c well above room temperature and magnetic characteristics optimized for applications. Being mostly organic in nature, they are lightweight, and easy to process and fabricate, and being soluble in organic solvents, can be exploited as liquid magnets, colloidal dispersions or Langmuir–Blodgett films. The possibility of perpendicular magnetic recording by their use makes them candidates for high density data storage. Their transparency in many spectral regions makes them suitable for photomagnetic switches and optical data storage. Besides, their “soft” magnetic nature and magnetostrictive response makes them attractive for applications in shielding, AC-motors, generators and transformers. In what follows, we provide a brief review on different categories of organic ferromagnets while highlighting current strategies adopted for their synthesis

2. Polymers

Mataga (1968) and subsequently Ovchinnikov (1978) proposed a model for the possibility of ferromagnetic order in π -conjugated organic polymers having two sublattices. If, in a unit cell, the number of atoms belonging to the two sublattices are not equal, then there is a net spin for the unit cell giving rise to a high-spin ground state, examples of which are polycarbenes with $S = 9$ which have indeed been synthesized (Nakamura *et al* 1993) but the synthesis of a bulk ferromagnetic polymer remains a distant goal. According to Ovchinnikov’s model, free radicals (say phenoxy) if attached to the polyacetylene chain as pendants should interact ferromagnetically, yielding high spin polymers (figure 1a). However, pendant groups located thus have

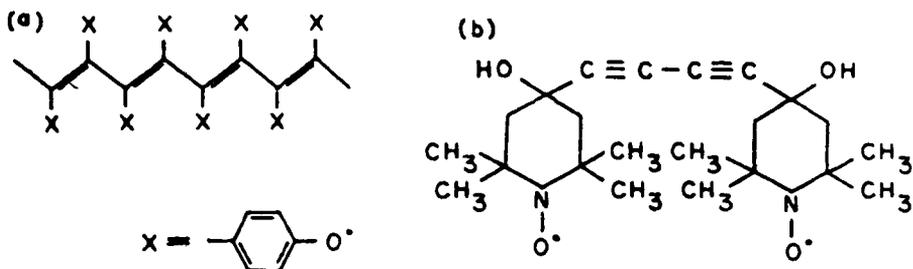


Figure 1. (a) Poly[4-oxophenyl]acetylene] molecule where X is a phenoxy free radical attached as pendant to the polyacetylene chain. Such molecules were suggested to become high-spin polymers by Ovchinnikov (1978), (b) Schematic of poly-BIPO structure.

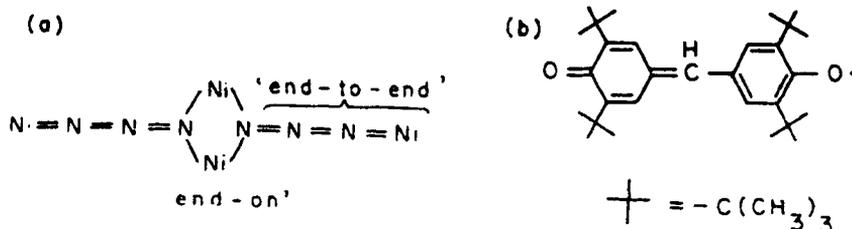


Figure 2. (a) End-to-end or end-on coordinations of azido group to $Ni(II)$ ions. (b) Molecular structure of galvinoxyl.

“direct” through-space interaction, due to close proximity, giving rise to antiferromagnetism. Phenoxy radicals if placed as pendants on alternate sites should, in principle, lead to “indirect” through-bond exchange interaction and a ID ferromagnet (Yoshizawa *et al* 1993). A polymer ferromagnet poly-BIPO based on a polyacetylene chain (figure 1b) with a T_c value as high as 420–460 K was indeed synthesized by Ovchinnikov and co-workers (Korshak *et al* 1986, 1987), although only a very tiny volume fraction (0.1%) of the sample was ferromagnetic. A rigorous theoretical treatment which takes into account the itinerancy of the chain π -electrons and also the strong electron-photon and electron-electron correlations (Fang *et al* 1994) has confirmed that the ground state is indeed a stable ferromagnetic state but a Peierls distortion overtakes and these π -electrons ultimately prefer to form an antiferromagnetic (SDW) state.

During the last few years, there have been a number of reports of observation of ferromagnetism in polymers at room temperature, namely pyrolysed polyacrylonitrile (PAN) (Katulevskii *et al* 1991), indigo polymer (Tanaka *et al* 1990) and triarylmethane resins (Ota *et al* 1989). However, the volume fraction of the ferromagnetic component in all the cases is low ($< 3\%$), and the $M(H)$ hysteresis loop, if observed, shows little width with poor values of saturation magnetization and coercive field. Majority of these reported polymer ferromagnets suffer from non-reproducibility and poor chemical characterization, although in certain cases the samples do get attracted towards a horseshoe magnet at room temperature. A welcome trend is that radically new approaches are currently being tried to tune bulk ferromagnetism in polymers. For instance, the azido group if coordinated to two $Ni(II)$ ions in an end-on fashion can give rise to a ferromagnetic coupling (figure 2a) whereas end-to-end coordination leads to

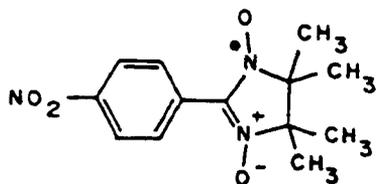


Figure 3. The chemical structure of *p*-NPNN. The black dot indicates an unpaired electron.

antiferromagnetic coupling. Using this idea, Ribas *et al* (1994) have been able to tune long-range ferromagnetism (though weak) below 60 K in an infinite bidimensional polymer $\text{Ni}(\text{N}_3)_2(2,2\text{-dimethylpropane-1,3-diamine})_n$. Dougherty's group at Caltech (Murray *et al* 1994) has been able to establish ferromagnetic spin alignment along polymer chains when polaronic spin-containing units are coupled through suitable coupling units, although synthesis of a 3D bulk ferromagnet from such 1D prototypes is yet to be achieved.

3. Purely organic radical clusters/compounds

The galvinoxyl radical ($\text{C}_{29}\text{H}_{41}\text{O}_2$) (figure 2b) is known to exhibit ferromagnetic intermolecular interactions with positive paramagnetic Curie temperature ($\theta_p = 18$ K), but the paramagnetic susceptibility disappears below 85 K (Awaga *et al* 1986). Galvinoxyl as well as tanol suberate ($\text{C}_{26}\text{H}_{46}\text{N}_2\text{O}_6$) radicals are truly speaking metamagnetic, exhibiting only 2D ferromagnetic behaviour in the *ac*-plane, but antiferromagnetic alignment along the *b*-direction.

Bulk ferromagnetism has been reported in purely organic (containing only C, H, N, and O) material β -phase of *p*-NPNN (*p*-nitrophenyl nitronyl nitroxide) (figure 3), the structural and magnetic characterization of which has been established but the Curie temperature is only 0.6 K (Tamura *et al* 1991; Nakazawa *et al* 1992). Ferromagnetism has also been reported for the α -phase of HQNN, another nitronyl nitroxide derivative (Sugawara *et al* 1994). The highest Curie temperature for a purely organic non-ionic material has been reported as 1.48 K for the nitroxide biradical $\text{N,N}'$ -dioxyl-1,3,5,7-tetramethyl-2,6-diazaadamantane arising from a 3D ferromagnetic order, though it exhibits no magnetic hysteresis (Chiarelli *et al* 1993). Ferromagnetism arising from 2D ordering of radical spins has also been reported recently for 4-benzylideneamino-TEMPO ($T_c = 0.18$ K) (Nogami *et al* 1994) and 4-(*p*-phenylbenzylideneamino)-TEMPO ($T_c = 0.4$ K) (Ishida *et al* 1994), where TEMPO stands for 2,2,6,6-tetramethylpiperidin-1-oxyl.

In fullerene based molecular material *tetrakis*(dimethylamino) ethylene- C_{60} , too, ferromagnetism was reported at 16.1 K (Allemand *et al* 1991; Stephens *et al* 1992), but it is a soft ferromagnet with no practical value since it displays S-shaped $M(H)$ curves with absence of hysteresis, coercivity and remanence. Films of polymer (PVDF)- C_{60} composite have recently been reported to exhibit ferromagnetism with measurable hysteresis at room temperature ($T_c = 350$ K) (Ata *et al* 1994).

4. Charge transfer salts

The first organic ferromagnet to be synthesized was the charge-transfer salt, decamethylferrocenium tetracyanoethenide, $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^+ [\text{TCNE}]^-$ (Chittipedi

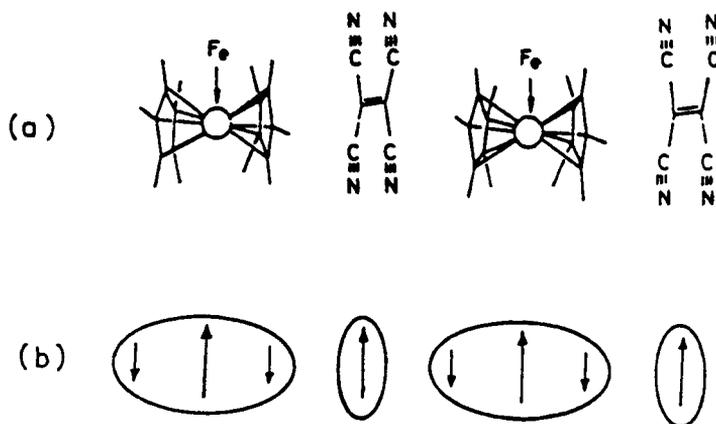


Figure 4. Stacking of $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^+$ and $[\text{TCNE}]^-$ ions each having a spin $S = 1/2$ (a), and schematic of spin polarisation in the donor units (b).

et al 1987; Miller *et al* 1988c) wherein both the donor (D^+) and acceptor (A^-) ions, each having a spin $S = 1/2$ (where unpaired spins reside on d - and p -orbitals, respectively) are alternately stacked (figure 4a). It has a Curie temperature of 4.8 K, and exhibits a field-dependent magnetic hysteresis with a coercive field of ~ 1 kG at 2 K. The saturation magnetization value for single crystals in a direction parallel to $\text{D}^+\text{A}^-\text{D}^+\text{A}^-$ stacking axis was 36% greater than that for pure iron on a gram-atom basis (Miller *et al* 1988a). ^{57}Fe Mossbauer spectra for this complex, recorded under zero applied field, confirmed large internal fields of 400–450 kG at 4.3 K (Miller *et al* 1988a,b). It is believed that spin polarisation in $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$ units leads to a large positive spin density around the iron atom and some negative spin density at the periphery around the C_5Me_5 rings. Coupling with a radical line $[\text{TCNE}]^-$ in a donor-acceptor stack may then become ferromagnetic (figure 4b). Use of higher spin molecular components led to increased intramolecular spin-spin interactions and a higher value of $T_c = 6.2$ K for the bulk 3D ferromagnet $[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+ [\text{TCNQ}]^-$, where $S_{\text{D}} = 1$ and $S_{\text{A}} = 1/2$ (Broderick *et al* 1990). Substitution of a smaller acceptor anion $[\text{TCNE}]^-$ should lead to a greater spin interaction, which was indeed the case, since a higher T_c of 8.8 K is observed for $[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+ [\text{TCNE}]^-$, where, too, $S_{\text{D}} = 1$ and $S_{\text{A}} = 1/2$ (Yee *et al* 1991). Subsequently, Miller's group extended the reaction to the $[\text{V}(\text{C}_6\text{H}_6)_2]^+$ donor which is isoelectronic to $[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+$, and isolated a highly disordered covalently bound polymeric $\text{V}(\text{TCNE})_{x,y}$ (solvent) magnet with a T_c exceeding room temperature (400 K) (Manriquez *et al* 1991). However, it is reported to be metastable. Bulk ferromagnetism ($T_c = 18$ K) has been reported, subsequently, for a stable covalently bonded extended linear chain (1D) metallomacrocyclic complex $[\text{Mn}^{\text{III}}\text{TPP}]^+ [\text{TCNE}]^-$ where TPP is mesotetraphenylporphinato (Miller *et al* 1992).

5. Materials assembled from ferrimagnetic subunits

Synthesis of molecular ferrimagnets provides a convenient route to overcome the difficulties related with imposing parallel alignment of moments on the scale of the lattice while designing ferromagnets. A clever strategy, therefore, is to design quasi-one

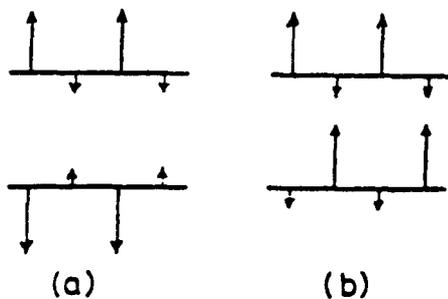


Figure 5. Two different ways of assembling bimetallic ferrimagnetic chains in a lattice giving rise to (a) antiferromagnetic, or (b) ferromagnetic order. The size of the arrows indicates the magnitude of spin.

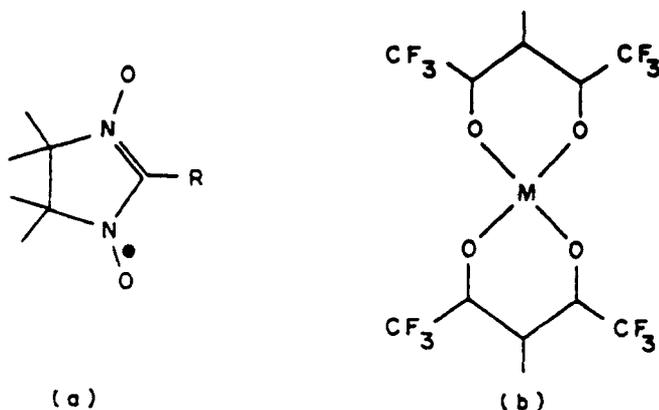


Figure 6. The radicals (a) NITR, and (b) metal hexafluoroacetylacetonate. The black dot indicates an unpaired electron.

dimensional ferrimagnetic chains, comprising antiparallel alignment of uncompensated ($S_A \neq S_B$) spins, and then position them in a bulk lattice in such a way as to provide a net ferromagnetic alignment of spins, as shown in figure 5b where the interchain separation is shortest for the unequal spins S_A and S_B . It is easy to see that if equal spin sites are located facing each other in adjacent chains, antiferromagnetism results (figure 5a).

Two parallel approaches have been followed to construct the basic ferrimagnetic subunits for the synthesis of this class of organic ferromagnets, viz (i) the metal-radical approach, where one alternates a metal ion spin (d orbital based) with an organic radical with unpaired spin (p orbital based) and (ii) the bimetallic approach, where two dissimilar metal-ion spins are alternated with intervening organic bridging groups used to transmit the spin-spin interactions.

5.1 Metal radical approach

Gatteschi's group has pioneered the use of the metal-radical approach to assemble extended lattices (Caneschi *et al* 1989a; Gatteschi and Sessoli 1992). The organic

radicals used are the nitronyl nitroxides NITR (for 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide and R denotes methyl, ethyl, phenyl or propyl groups) (figure 6a) which are stable radicals having N-O groups with one unpaired electron in a π^* orbital and can be used as ligands towards many different metal ions. When the nitroxide binds through its oxygen atom to a paramagnetic metal ion, in say a metal hexafluoroacetylacetonate (figure 6b), the spins can orient, and the exchange interaction can be transmitted without attenuation, since the unpaired electron is delocalised on the two equivalent N-O groups. Ferromagnetic compound $\text{Mn}(\text{hfac})_2\text{NITet}$ with $T_c = 8.1$ K has been thus designed from quasi 1D ferrimagnetic chains built up of Mn^{II} ($S = 5/2$) and NITet ($S = 1/2$) spins (Caneschi *et al* 1989c). Other examples are the bulk 3D ferromagnet $\text{Mn}(\text{hfac})_2\text{NIT-}i\text{-Pr}$ with $T_c = 7.6$ K (Caneschi *et al* 1989b), the $S = 1/2$ Heisenberg antiferromagnet $\text{Y}(\text{hfac})_3\text{NITet}$ with $T_N = 6$ K (Benelli *et al* 1989), the ferromagnet $[\text{Mn}(\text{F}_5\text{Benz})_2]_2\text{NITet}$ with $T_c = 21$ K (Caneschi *et al* 1989d) and the 1D Heisenberg ferromagnet $\text{Cu}(\text{hfac})_2\text{NIT-}i\text{-Pr}$ (Cabello *et al* 1990).

Iwamura's group (Inoue and Iwamura 1994; Inoue *et al* 1996) has recently utilised high-spin π -conjugated polynitroxides as bridging ligands to construct transition metal polymer complexes with ferromagnetic characteristics. The diradical (figure 7a) has a triplet ground state ($S = 1, J > 0$), with spin density being localised at N-O moieties. It forms a 1D chain if ligated antiferromagnetically with an Mn-ion when complexed with $\text{Mn}^{\text{II}}(\text{hfac})_2$. But one obtains only a metamagnetic state below 5.5 K in this case because the interchain interaction between such 1D array of spins is quite weak, in the form of superexchange through F atoms (Inoue and Iwamura 1994a). However, increasing the dimensionality of the subunits has led to very encouraging results. A hexagonal 2D graphite-like layered structure is obtained when a 3:2 complex is formed from the trinitroxide radical ($S = 3/2$) (figure 7b) and $\text{Mn}^{\text{II}}(\text{hfac})_2$, and the McConnell mechanism gives rise to ferromagnetic layer stacking ($T_c = 3.4$ K) (Inoue and Iwamura 1994b). More interestingly, the use of a quartet triradical (figure 7c) in

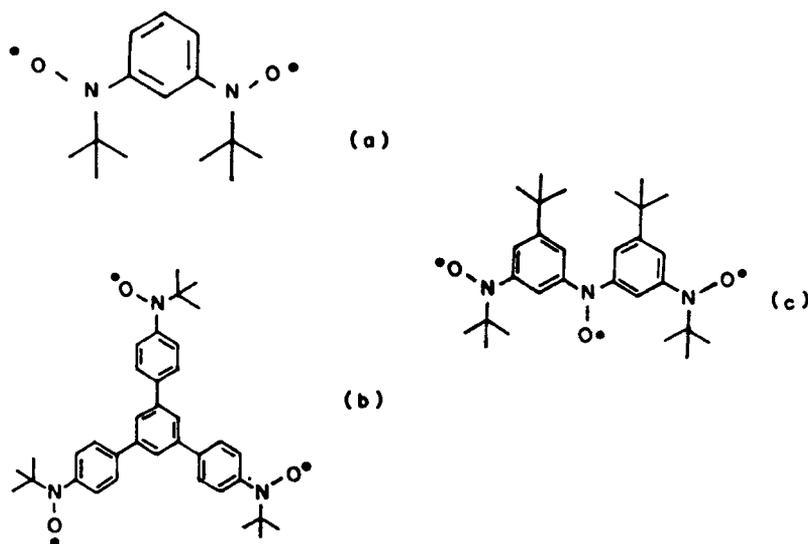


Figure 7. High-spin polynitroxides used to construct TM polymer complexes.

a similar 3:2 complex gives rise to a 3D network using the middle nitroxide group to interlink the chains, which results in ferromagnetic behaviour at 46 K (Inoue *et al* 1996).

5.2 Bimetallic approach

Olivier Kahn and co-workers have employed ordered bimetallic ferrimagnetic chains containing, for instance, alternating Mn^{II} ($S = 5/2$) and Cu^{II} ($S = 1/2$) spin sites and have synthesized a large number of binuclear molecular magnets such as $MnCu(obbz) \cdot 1H_2O$ ($T_c = 14$ K) (Nakatani *et al* 1989), $MnCu(pbaOH)(pyrazine)(H_2O)$ ($T_N = 2.7$ K) (Nakatani *et al* 1990) and $MnCu(obze)(H_2O)_2$ ($T_c = 4.6$ K) (Pei *et al* 1991), and have obtained interesting information on the magnetic interactions involved. In the case of the ferromagnet $MnCu(pbaOH)(H_2O)_3$ ($T_c = 4.6$ K) warming the compound at $100^\circ C$ for 48 h causes removal of one water molecule, thus increasing the interchain exchange interaction (J_{inter}) sharply and bringing about a sharp rise in T_c for $MnCu(pbaOH)(H_2O)_2$ ($T_c = 30$ K) (Nakatani *et al* 1991). More recently, Kahn's group has reported the synthesis of a number of ferromagnets containing Co(II) and Cu(II) with ($T_c > 30$ K, viz. $(NBu_4)_2 Co_2[Cu(opba)]_3 \cdot 3DMSO \cdot 3H_2O$ with $T_c = 32$ K and $(NBu_4)_2 Co_2[Cu(opba)]_3 \cdot 2H_2O$ ($T_c = 34$ K) (Stumpf *et al* 1994) and $CoCu(pbaOH)(H_2O)_2$ ($T_c = 38$ K) (Turner *et al* 1996). Okawa *et al* (1994) have used alternating arrays of Cr^{III} and M^{II} through oxalato bridges to obtain ferromagnetic behaviour below 14 K for $\{(NBu_4) \cdot [Ni^{II}(Cr^{III}(ox)_3)]\}$. Changing the bridging group from oxalato to dithiooxalate (dto) yields ferromagnetism in $\{(NPr_4)[M^{II}Cr^{III}(dto)_3]\}_x$ at $T_c = 8, 16$ and 23 K for $M = Fe, Co$ and Ni .

We have carried out some studies recently on binuclear systems. DC magnetization data for the compound $MnCu(obbz) \cdot nH_2O$ after dehydration ($T_c = 15$ K) are shown in figure 8. Detailed magnetization and TG studies conducted on this MnCu-system

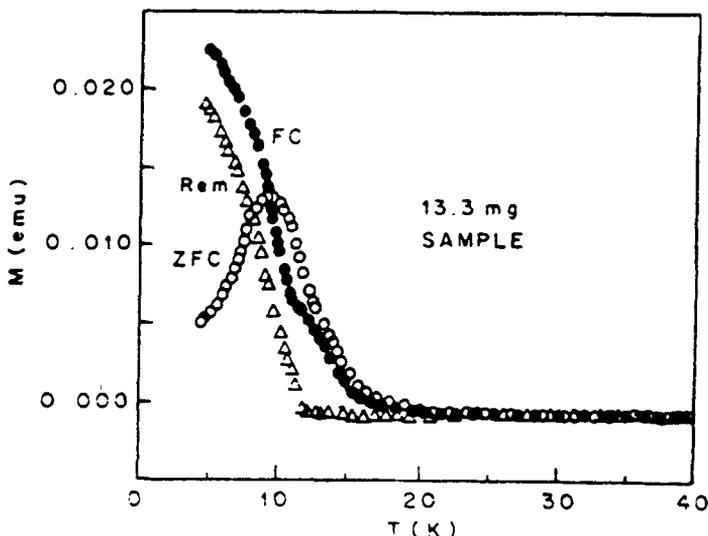


Figure 8. DC magnetization (VSM) data on $MnCu(obbz) \cdot nH_2O$ after dehydration. ZFC, FC and Rem denote the plots corresponding to zero-field cooling, field cooling and remanent magnetization (Chavan *et al* 1995b)

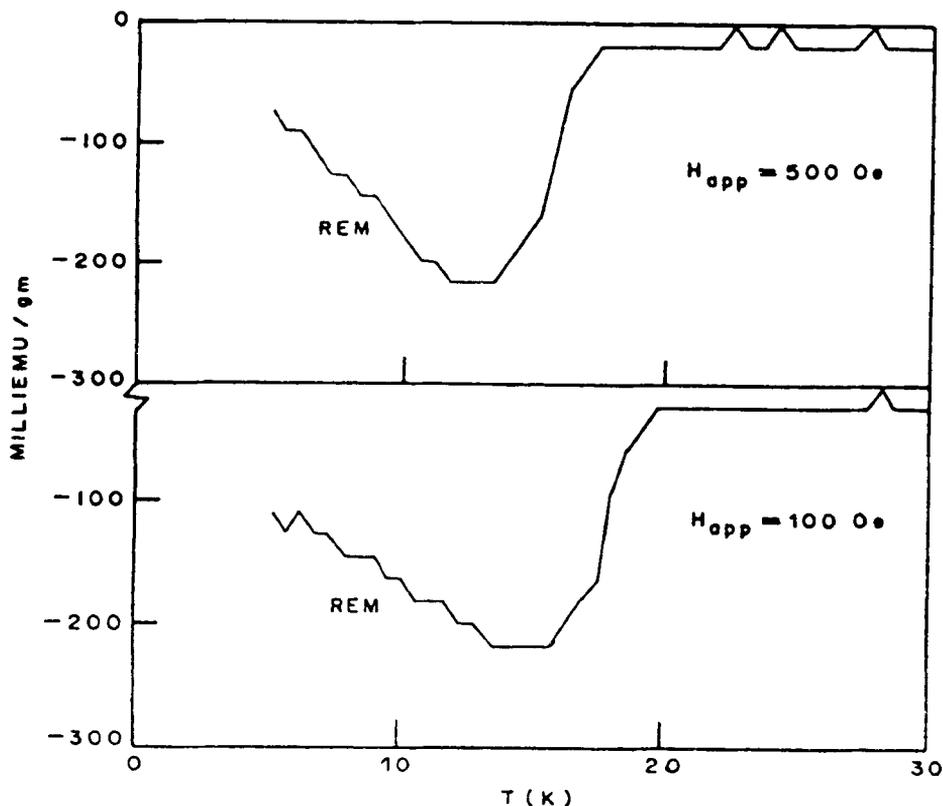


Figure 9. Negative remanence observed for $(\text{NBu}_4)_2\text{Mn}_2[\text{Cu}(\text{opba})]_3$ ($T_c = 22\text{ K}$) after it was cooled to 5 K in applied fields of 100 Oe and 500 Oe, respectively (Chavan *et al* 1996b).

indicate that the number of non-coordinated water molecules which govern the through-space interaction in the system is uncertain (Chavan *et al* 1995b). The compound $\text{CoCu}(\text{obbz}) \cdot 2\text{H}_2\text{O}$ gives magnetic data consistent with a 1D ferrimagnet (Chavan *et al* 1996a). Our recent studies on the opba-based Mn_2Cu_3 compounds $(\text{NBu}_4)_2\text{Mn}_2[\text{Cu}(\text{opba})]_3 \cdot 6\text{DMSO} \cdot \text{H}_2\text{O}$ ($T_c = 15\text{ K}$), its desolvated analogue $(\text{NBu}_4)_2\text{Mn}_2[\text{Cu}(\text{opba})]_3$ ($T_c = 22\text{ K}$) and ferromagnets obtained after solvating the latter with acetonitrile and methanol have shown an interesting new magnetization feature, negative remanence, in the ordered state (figure 9), which we believe arises from the typical nature of the MnCu -ferrimagnetic units from which these opba ferromagnets are constructed (Chavan *et al* 1996b, c). Muon spin relaxation (Cywinski *et al* 1996) and EPR (Kadam *et al* 1996a, b) studies conducted by us recently on $\text{MnCu}(\text{obbz}) \cdot \text{H}_2\text{O}$ and $(\text{NBu}_4)_2\text{Mn}_2[\text{Cu}(\text{opba})]_3 \cdot \text{DMSO} \cdot \text{H}_2\text{O}$ have shown the co-existence of long-range ferromagnetic order and spin fluctuations both above and below Curie temperatures in these soft ferromagnets.

6. Inorganic molecular compounds

Ferromagnetic behaviour is known to arise in Prussian Blue salt, ferric ferrocyanide $\text{F}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot 15\text{H}_2\text{O}$. But its T_c is low (5–6 K) because the spin carriers Fe^{III} are

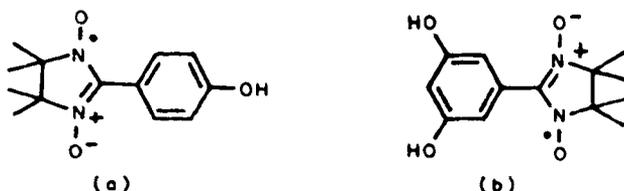


Figure 10. Examples of substituted phenyl α -nitronyl aminoxy radicals with one (a) or two (b) hydroxylic groups in the aromatic ring.

located 10.6 Å away. Recently, ferromagnetism has been reported in $\text{Cs}^{\text{I}}\text{Ni}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ below 90 K, and ferrimagnetic behaviour observed in a number of hexacyanometalates (Prussian Blue analogues) with the general formula $\text{A}_k[\text{B}(\text{CN})_6]_l \cdot n\text{H}_2\text{O}$ with alternating A and B metal ions having non-zero spins in octahedral surroundings in an *fcc* cell. Examples are $\text{Cs}_2\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]$ with $T_c = 125$ K (Entley and Girolami 1994) and $(\text{V}_{0.42}^{\text{II}} \text{V}_{0.58}^{\text{III}})[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ with $T_c = 315$ K (Ferlay *et al* 1995). Ohba *et al* (1994) have designed a new bimetallic ferromagnet ($T_c = 18.6$ K) with a rope-ladder chain structure having a formula $[\text{Ni}(\text{en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ where en = 1, 2, ethanediamine.

7. Use of hydrogen bonds

Borrowing the idea from nature, which uses non-covalent interactions such as hydrogen bonds, in a very economical and successful way for molecular self-assembly of superstructures at the cellular level, some research groups have attempted the use of hydrogen bonds between open-shell molecules to obtain supramolecular self-organisation aimed at achieving intermolecular ferromagnetic interactions along pre-established spatial directions utilising the high degree of directionality displayed by H-bonds (Cirujeda *et al* 1995a,b). The H-bonds provide intermolecular contacts among atoms with positive and negative spin densities giving rise to ferromagnetic interactions when 2D networks of hydroxylated phenyl α -nitronyl nitroxides (figure 10) are self-assembled. Akita *et al* (1995) have obtained ferromagnetic behaviour at 30 K ascribed to H-bonds in the 1:1 complex between phenyl nitronyl nitroxide and phenyl boronic acid, the latter being used as a spin coupler for enhanced spin interaction between neighbouring nitroxide radical centres.

8. Conclusions

A deeper understanding of the guiding principles of molecular magnetism is evolving as a result of extensive studies being conducted in many laboratories. Efforts are now being directed towards exploration of complex cooperative systems so that syntheses of nanoscale magnetic particles become possible. Given the present rate of growth in this multidisciplinary field, the next decade may witness the design of organic ferromagnets with improved magnetic properties to enable their use in devices.

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