RESEARCH ACTIVITIES V
Department of Applied Molecular Science

V-A Synthesis of Chiral Molecule-Based Magnets

Construction of molecule-based magnetic materials, which have additional properties such as conductivity or photo reactivity, is now becoming a challenging target. Specific goals aimed for these molecule-based magnets include: i) the ability to design the molecular building blocks and to organize them in the solid for desired dimensionality, ii) the optical transparency. The physical characteristic of current interest involves optical properties, particularly with respect to natural optical activity. When a magnet has optical transparency and chiral structure, the magnetic structure of crystal expects to be a chiral spin structure. These magnets will show an asymmetric magnetic anisotropy and magneto-chiral dichroism4. This category materials don't only have scientific interest but also have the possibility for use in new devices. When we construct chiral molecule-based magnets, chirality must be controlled not only in the molecular structure, but in the entire crystal structure. As a consequence of this difficulty, only few examples of this type of magnet exist. Up to the present reported chiral magnets have low dimensional magnetic structures, the magnetic ordering temperatures are below 10 K. To afford a high-T_C magnet, dimensionality of magnetic structure must be extended in two or three dimension. When we introduce magnetic bricks, which have more than three connections for the construction of magnets, we can expect to make two or three-dimensional magnets. To make high dimensionality molecule-based magnets, we recently discovered using cyano bridged complex with chiral organic ligands.

V-A-1 Structure and Magnetic Properties of a Chiral Two-dimensional Ferrimagnet with T_C of 38 K

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([1]IMS and Tokyo Metropolitan Univ.)

Synthesis, magnetic properties and structure of new chiral, transparent, high T_C = 38 K molecule-based two-dimensional ferrimagnet, $[Cr(CN)_6][Mn(S)\text{-}pnH(H_2O)](H_2O)$; ((*S*)-pn = (*S*)-1,2-diaminopropane) are described. The complex was obtained as green needle crystal by the reaction of $K_3[Cr(CN)_6]$, $Mn(ClO_4)_2$, and (*S*)-1,2-diaminopropane dihydrochloride ((*S*)-pn·2HCl) in 1:1:1 molar ratio in methanol/ H_2O (1:1) solution under argon atmosphere (adjusted pH 6–7 by KOH). X-ray structural analysis revealed a crystallized chiral space group of Orthorhombic, $P2_12_12_1$; moreover, the complex demonstrated a two-dimensional magnetic network. The magnetic measurements of the complex show Mn^{II} and Cr^{III} ions interact ferrimagnetically and magnetic transition occurs at 38 K.

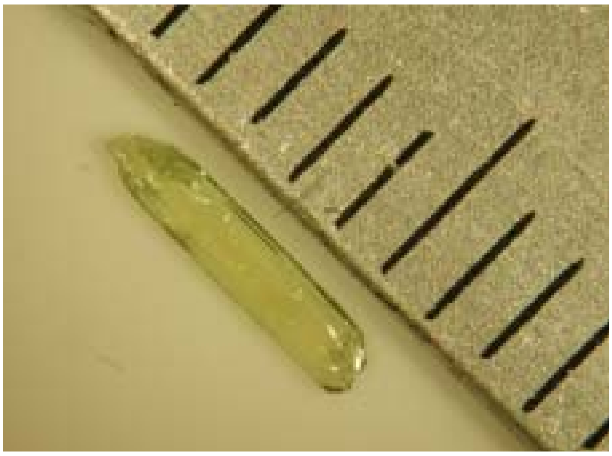

Figure 1. A single crystal of a chiral molecular ferrimagnet, $[Cr(CN)_6][Mn(S)\text{-}pnH(H_2O)](H_2O)]$.

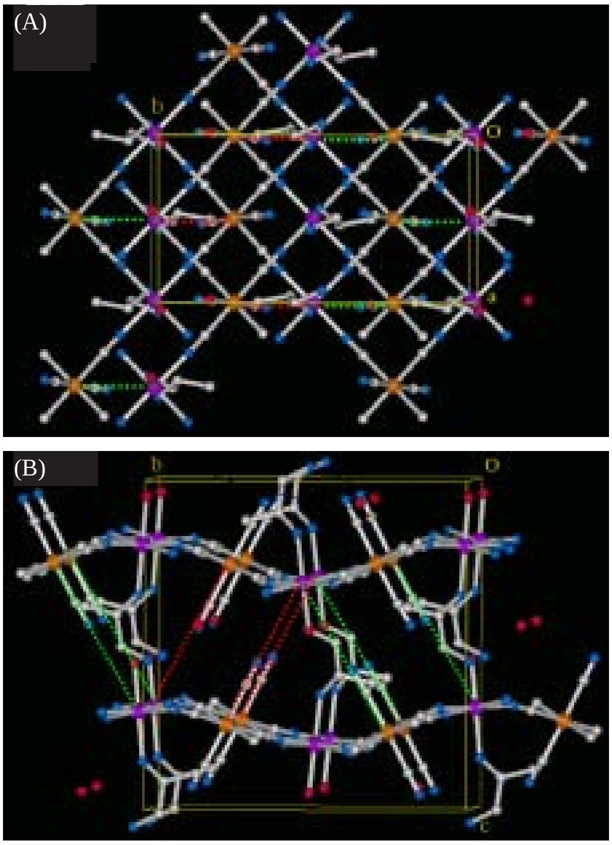

Figure 2. Crystal structure of $[Cr(CN)_6][Mn(S)\text{-}pnH(H_2O)](H_2O)]$. (A) Projection onto the *ab* plane. (B) Projection onto the *bc* plane.

V-B Hydrothermal Synthesis of Molecule-Based Magnets

Coordination polymers are attracting much interest due to the strength and rigidity of the extended lattices for gas absorption and intercalation and for the connectivity between magnetic ions in designing molecule-based magnets. They belong to a subset of organic-inorganic hybrid materials, and usually employ a central metal ion and a multitopic organic ligands or a coordination complex having ambidentate ligands, such as cyanide and oxalate. In some cases, other organic ligands are used to control the dimensionality or structure. The choice of the metals and of the ligands depends on the desired properties. On the one hand, there is strong interest by scientists studying catalysis and the absorption of gases originating from the possibility of creating structures with cavities, channels or pores and, consequently, large surface areas. On the other hand, there is increasing interest from magneto-chemists due principally to the realization of organizing the magnetic orbitals of the moment carriers to favor a particular magnetic ground state. The field of coordination polymers based on organic radicals is a very active area, indeed. Several ground states have been established and a clear molecular-orbital picture to explain the observations is emerging. For the realizing strong magnetic interaction, it is better to use simple and small organic ligands, such as cyanide or carboxylate ions. The metal complexes with such ligands are usually less solvability. The thermal synthesis is powerful method to make large single crystals for such complexes.

V-B-1 Self-Organized Metallo-Helicates and –Ladder with 2,2’-Biphenyldicarboxylate $(C_{14}H_8O_4)^{2-}$: Synthesis, Crystal Structures, and Magnetic Properties

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We report on the hydrothermal synthesis, single-crystal structures and magnetic properties of three one-dimensional coordination polymers employing the 2,2’-biphenylcarboxylate dianion, $(C_{14}H_8O_4)^{2-}$, as the bridging component. $[M^{II}(H_2O)_4(C_{14}H_8O_4)]$, where M = Co and Ni, consist of helical chains of square-planer $M^{II}(H_2O)_4$ bridged by $C_{14}H_8O_4$ with each carboxylate group acting as a mono-dendate ligand. The magnetic properties are those of paramagnets with an antiferromagnetic exchange for Co complex and a ferromagnetic exchange for Ni complex. $Cu(C_{14}H_8O_4)(H_2O)_2$ is composed of tetracarboxylato-dimeric units bridged into ladders by biphenyl units. The ladders are packed parallel to each other, and narrow channels are present due to insufficient space filling of the biphenyl rings. Its magnetic behavior follows that of a Bleany-Bowers singlet-triplet model with a gap of 470 K.

V-C Synthesis and Characterization of Quantum-Spin Systems

There has been considerable current interest in the study of a low-dimensional quantum-spin system with an energy gap. For such study, organic radicals will provide good examples of ideal Heisenberg spin systems, since they consist only of light elements. By the appropriate design of molecules, we can obtain a variety of spin systems. In these years, we focus on the spin-ladder system, which is interesting in terms of Haldane state and the high T_C superconductivity. For the $S = 1/2$ Heisenberg spin ladder with antiferromagnetic legs and rungs, the ground state of the resonating valence bond (RVB) state or the dimerized state is theoretically expected. Experimentally, the singlet ground state was observed in some ladder systems formed by Cu-based compounds. The study of spin ladder systems has been mainly devoted to that of $S = 1/2$, but that of $S = 1$ is also interesting. We have succeeded in synthesis of the first example of a spin ladder system of $S = 1$ by BIP-TENO. Peculiar properties are observed and theoretical study is also activated.

V-C-1 Magnetic Properties of Organic Two-Leg Spin Ladder Systems with $S = 1/2$ and $S = 1$

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[*J. Phys. Chem. Solids* **63**, 1277 (2002)]

Magnetic properties of spin systems on the two-leg ladder made of organic radicals are studied. The magnetization measurements below 4.2 K in pulsed magnet fields up to about 50 T were done for BIP-BNO as an $S = 1/2$ ladder and for BIP-TENO as an $S = 1$ ladder. An energy gap above the singlet ground state is observed in each compound. Experimental results of magnetizations and susceptibilities are understood from the analysis using the results of the numerical diagonalizations.

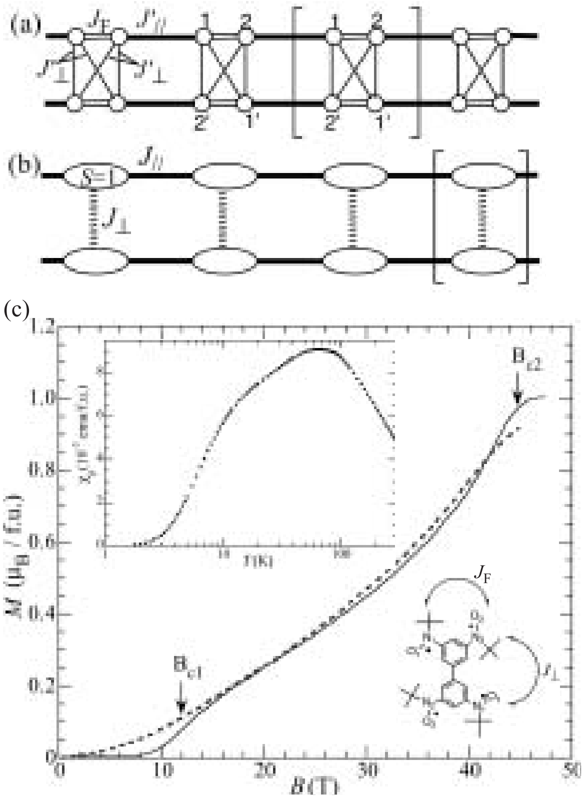

Figure 1. Magnetic exchange coupling scheme in BIP-TENO crystals. A circle and a bond represent an S = 1/2 and the exchange coupling, respectively: J_F and $J_\perp$ correspond to intramolecular exchange couplings and $J_{//}$ is intermolecular one. (b) Extreme limit of the model (a) when $J_F \to \infty$. (c) Magnetization curves of BIP-TENO in pulsed high magnetic fields. Solid and dotted curves are the results for 1.7 and 4.2 K, respectively. Inset: Temperature dependence of the paramagnetic susceptibility of BIP-TENO.

V-C-2 Low Dimensionality Observed by ESR Measurements in *S* = 1 Spin Ladder Substance BIP-TENO

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[*J. Phys. Soc. Jpn.* **71**, 2640 (2002)]

X-band ESR measurements of BIP-TENO single crystal, which is an S = 1 spin ladder model substance, have been performed in the temperature region from 3.5 to 300 K. At room temperature, the angular dependences of g-value and line width were observed. The line shape and the angular dependence of the line width showed the typical behavior of the low dimensional antiferromagnet. The temperature dependence measurements showed the minimum of the line width and the dynamical g-shift, which were also the typical behavior of the low dimensional antiferromagnet. However, the direction of the dynamical g-shift does not coincide with the well known Nagata's theory, and the comparison with the recent direct ESR calculation by Miyashita *et al.* is discussed.

V-D Organic Ferrimagnetism

In the last decades, the magnetism of molecule-based material has drawn much interest. After the discovery of the organic ferromagnet in1991, search for an organic ferrimagnet attracts great interest and is considered as one of today's challenging targets in material science. Although a number of ferrimagnets are realized in inorganic-organic hybrid systems, a genuine organic ferrimagnet has not yet been realized. In 1980's, ferrimagnetism is proposed as an effective strategy to give organic materials spontaneous magnetizations by the alternant arrangement of two kinds of organic radicals having different spin-multiplicities. All the reported ferrimagnets include at least two magnetic components: bimetallic compounds or metal complexes with organic radicals. In order to achieve this challenging subject of an organic ferrimagnet from a different viewpoint, we propose here a single-component strategy: utilizing a triradical including an S = 1 and an S = 1/2 units within a molecule and connecting the S = 1 and S = 1/2 units by intra- and intermolecular antiferromagnetic interactions. Our new strategy to use a single component has the advantages of the easiness of controlling the crystal structure and the good crystallinity for quality and size.

V-D-1 Magnetic Properties on an Organic Ferrimagnetic Compound and Related Materials

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[*Synth. Met.* in press]

Search for an organic ferrimagnet has been one of the challenging targets in the field of material science. Recently, we have reported the successful results for the crystals of a novel organic triradical of PNNBNO, 2-[3',5'-bis(*N-tert*-butylaminoxyl)phenyl]-4,4,5,5-

tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide. This is the first example of a genuine organic ferrimagnetic material having well-defined chemical and crystal structure with T_C = 0.28 K. The properties of PNNBNO are described and the magnetic interactions of this system are discussed in comparison with the related oligoaminoxyl.

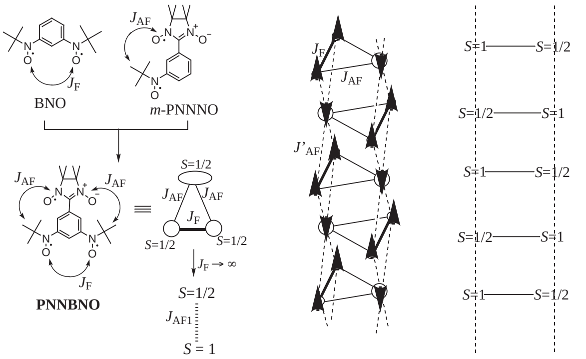

Figure 1. Scheme of the single component strategy for organic ferrimagnetism.

V-E Pressure Effects on Molecular Magnetism

‘Pressure’ is a powerful tool to control the molecular packings and physical properties. The molecule-based materials with small densities are ‘soft’ and can be expected to show large pressure effects. For the magnetic measurements with high-accuracy, we have developed a small high-pressure clamp cell made of non-magnetic Cu–Ti alloy which can be equipped to a Quantum Design SQUID magnetometer for the *dc* and *ac* magnetic measurements. The inner pressure of the clamp cell has been calibrated by the superconducting transition temperature of Pb. We have already discovered that some kind of structural change can be suppressed by pressurization. We are now studying the pressure effects on the molecule-based magnetic materials in wider range. In molecular materials, the spin density are delocalized and distributed in a molecule and the spin-density-distribution plays an important role in the exchange interactions. It is attractive to control the sign of the exchange coupling by pressurization. The pressure effects on the related compounds with similar crystal structures are studied.

V-E-1 Pressure Effects on Molecular Magnets of Mn Complexes with Bisaminoxylbenzene Derivatives

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[*Mol. Cryst. Liq. Cryst* **379**, 247 (2002)]

Pressure effects on the magnetic properties of a series of quasi-one-dimensional molecular magnets have been studied. The complexes of $Mn(hfac)_2$ (hfac = hexafluoroacethylacetonate) with 1,3-bis(*N-tert*-buthylaminoxyl)benzene and it’s 5-halo- derivatives, abbreviated as $\mathbf{1}_X$ (X = H, F, Cl and Br), have almost the same ferrimagnetic chain structure. The difference is seen in the interchain molecular arrangement. The complexes of $\mathbf{1}_H$ and $\mathbf{1}_F$ are metamagnets with weak interchain antiferromagnetic interactions, whereas $\mathbf{1}_{Cl}$ and $\mathbf{1}_{Br}$ are ferrimagnets with weak interchain ferromagnetic interactions. In two metamagnets ($\mathbf{1}_H$, $\mathbf{1}_F$), the pressurization simply results in the enhancement of the interchain antiferromagnetic interactions, which is reflected by the higher transition temperature and spin-flipping field. On the other hand, in the ferrimagnet ($\mathbf{1}_{Cl}$), the metamagnetic behavior is observed under pressure. It is suggested that the subtle change of the relative arrangement of chain structures affects the interchain ferromagnetic interactions.

V-E-2 Pressure-Induced Metamagnetic Behavior in a Quasi-One-Dimensional Molecule-Based Ferrimagnet

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[*Chem. Lett.* 316 (2002)]

Pressure effects on a molecule-based ferrimagnet of $[Mn(hfac)_2]\cdot$(Br-BNO) ($\mathbf{1}_{Br}$) were studied, where hfac = hexafluoroacetylacetonate and Br-BNO = 5-bromo-1,3-bis(*N-tert*-butylaminoxyl)benzene. At ambient pressure, $\mathbf{1}_{Br}$ is a ferrimagnet with T_C = 5.4 K. We observed the metamagnetic behavior of $\mathbf{1}_{Br}$ under pressure.