RESEARCH ACTIVITIES V
Department of Applied Molecular Science

V-A Magnetic Structure of Oligo-Nitroxide-Transition Metal Complexes

Since one or two decades, considerable attention has been devoted to stable nitroxide radicals and their metal complexes which are now widely used as building blocks for the design of molecular-based magnetic materials. In this field, we have introduced a new strategy of employing π-conjugated polyaminoxyls as ligands in which the 2p-spins of the NO groups interact ferromagnetically ($J_1 > 0$). The dimensionality of the complex and the sign and magnitude of the exchange coupling between the neighboring spins may be readily tuned by this strategy. Depending on the nature of the additional interchain or interlayer interaction, the polymers are expected to become an antiferromagnet or ferri/ferromagnet. By modifying and extending this design strategy to bis- and tris(aminoxyl) radicals having triplet and quartet ground states, respectively, we have been able to construct with the aid of magnetic metal ions one-dimensional (1D) chain, two-dimensional (2D) network and three-dimensional (3D) parallel-crosses structures in which both the organic 2p and metallic 3d spins have been ordered in macroscopic scales. Since such a rational approach by self-assembly to the tailored extended systems having relevant physical properties is of great importance in materials synthesis. For these materials, the magnetic structures of the crystals are also interesting.

V-A-1 Magnetic Properties of Layered Complexes $[M(hfac)_2]_3{\cdot}(R)_2$, M = Mn(II) and Cu(II), with Trisnitroxide Radicals Having Various Metal-Radical Exchange Interactions

TANAKA, Motoko; HOSOKOSHI, Yuko; MARKOSYAN, Ashot S.[1]; IWAMURA, Hiizu[2]; INOUE, Katsuya
([1]IMS and M.V. Lomonosov Moscow State Univ.; [2]Kyushu Univ.)

[*J. Phys.: Condens. Matter* **13**, 7429 (2001)]

A series of new layered 2D-network complexes $[M(hfac)_2]_3(R_\Delta)_2$ of M = Mn(II) and Cu(II) with trisnitroxide radicals R_Δ has been prepared and the magnetic properties were studied. Each triradical R_Δ has a quartet ground state and contributes not only to the formation of extended structures but essentially to the overall magnetism. Several exchange interactions, between M and nitroxide, intraradical nitroxide–nitroxide interactions, are responsible for the development of the characteristic magnetic properties in these heterospin systems. Depending on the nature of the interlayer interactions, they show either ferro/ferrimagnetic or antiferromagnetic long range order. The hierarchy of the different exchange interactions is established and the Mn–nitroxide and Cu–nitroxide exchange integrals are evaluated from the analysis of the temperature dependence of the paramagnetic susceptibility. With increasing intraradical exchange interaction, the complexes exhibit more pronounced 2D behavior.

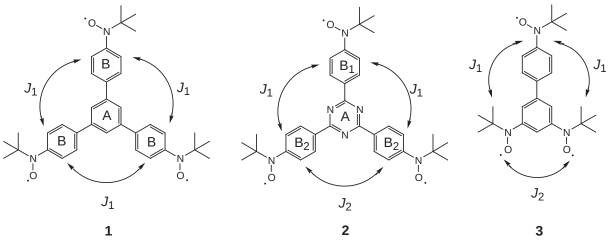

Figure 1. Triangular triradicals **1** (J_1/k_B = 6.8 K), **2** (J_1/k_B = 15.3 K, J_2/k_B = 11.8 K) and **3** ($J_1/k_B \approx 67$ K, $J_2/k_B > 200$ K) with three ligating sites, where A and B indicate the aromatic rings in different positions. J_1/k_B and J_2/k_B were found for the crystals of **1** and **2** or for isolated molecules of **3**. Only the radical **1** has threefold symmetry.

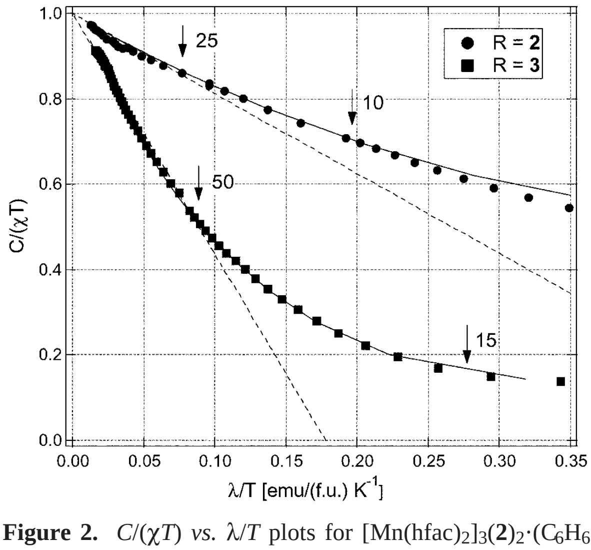

Figure 2. $C/(\chi T)$ *vs.* λ/T plots for $[Mn(hfac)_2]_3(\mathbf{2})_2{\cdot}(C_6H_6)_3$ and $[Mn(hfac)_2]_3(\mathbf{3})_2$. The solid and dot lines show the behavior for the 2D and 3D models, respectively. Some temperatures are indicated by arrows for clarity.

V-B Synthesis of Chiral Molecule-Based Magnets

The design of molecular materials with interesting magnetic and optical or electrical properties is one of the major challenges in the last few years. The synthesis and study of chiral molecular-based magnetic materials which are transparent for light are of great interest. Novel magneto-optical phenomena have been theoretically predicted and observed in chiral paramagnetic materials in 1997. Although novel properties are expected for such compounds, few examples of chiral molecular-based magnetic materials are still known. To get more insight in their properties it is therefore important to construct such chiral molecule-based magnets in a systematic way. We designed and synthesized a chiral organic radical which can be employed to construct chiral molecular-based magnets.

V-B-1 Synthesis and Structure of Chiral Molecule-Based Three-Dimensional Ferrimagnet

INOUE, Katsuya; IMAI, Hiroyuki; GHALSASI, Prasanna S.[1]; KIKUCHI, Koichi[2]; OHBA, Masaaki[3]; OKAWA, Hisashi[3]; YAKHMI, J. V.[4]
([1]IMS and Univ. Mumbai; [2]Tokyo Metropolitan Univ.; [3]Kyusyu Univ.; [4]Bhabha Atomic Res. Cent.)

New chiral, transparent, high T_C = 53 K molecule-based three-dimensional ferrimagnet, $K_{0.4}[Cr(CN)_6][Mn(S)\text{-pn}](S)\text{-pnH}_{0.6}$; ((*S*)-pn = (*S*)-1,2-diaminopropane) are synthesized. The complex was obtained as pale yellow needle crystal by the reaction of $K_3[Cr(CN)_6]$, $Mn(ClO_4)_2$, and (*S*)-1,2-diaminopropane dihydrochloride ((*S*)-pn·2HCl). X-ray structural analysis revealed a crystallized chiral space group of hexagonal $P6_1$; moreover, the complex demonstrated a three-dimensional magnetic network. (Figure 1) The magnetic measurements of the complex show Mn^{II} and Cr^{III} ions interact ferrimagnetically and magnetic transition occurs at 53 K.

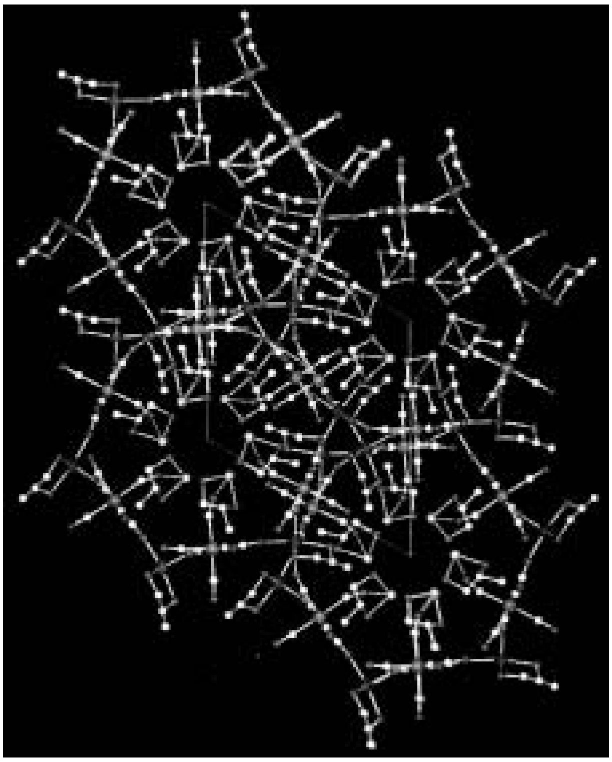

Figure 1. Crystal structure of $K_{0.4}[Cr(CN)_6][Mn(S)\text{-pn}](S)\text{-pnH}_{0.6}$. View along the *c* axis and showing the connection of helical dimetallic loops.

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. For the ground state of the $S = 1$ ladder with antiferromagnetic legs ($J_{\|}$) and rungs ($J_{\perp}$), the Haldane state is expected in the extreme limit of $J_{\perp} \rightarrow 0$, and the dimer state in $J_{\|} \rightarrow 0$. In its ground state phase diagram on the $J_{\|}/J_{\perp}$ versus the energy gap (Δ), the phase transition from the dimer state to the Haldane state through a gapless point can be expected. A similar behavior of an existence of a gapless point between two different phases with their own finite excitation gaps is known for the $S = 1$ Heisenberg alternating antiferromagnetic chain system.

V-C-1 Magnetic Properties of Organic Spin Ladder Systems

HOSOKOSHI, Yuko; KATOH, Keiichi[1]; MARKOSYAN, Ashot S.[2]; INOUE, Katsuya
([1]GUAS; [2]IMS and M.V. Lomonosov Moscow State Univ.)

[*Synth. Met.* **121**, 1939 (2001)]

Novel organic polyradicals, BIP-BNO and BIP-TENO, are synthesized and crystallized to form ladder systems, where BIP-BNO and BIP-TENO denote 3,5'-bis(*N*-*tert*-butylaminoxyl)-3',5-dibromobiphenyl and 3,3',5,5'-tetrakis(*N*-*tert*-butylaminoxyl)biphenyl, respectively. The BIP-BNO crystals form a two-leg ladder of S = 1/2 with antiferromagnetic legs and rungs. The BIP-TENO crystals can be regarded as a two-leg ladder of S = 1 species. The magnetic measurements revealed that both compound have singlet ground states.

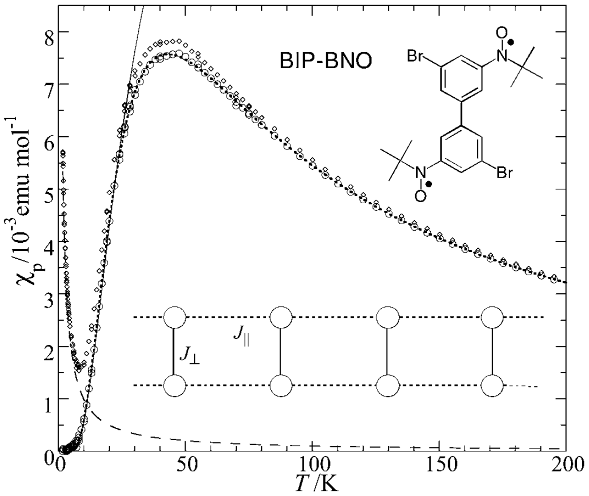

Figure 1. Temperature dependence of the paramagnetic susceptibility (χ_p) of BIP-BNO. Observed data are represented by diamonds (◇).Open circles represent data after the subtraction of the Curie impurity (broken curve). The dotted curve is the calculation for the ladder system (12 spins) with $2J_\perp/k_B$ = –66.4 K and $2J_\parallel/k_B$ = –26 K. The solid curve is the fit of $\chi \propto \exp(\Delta/T)/\cdot T$ with Δ = 47 K.

V-C-2 Observation of Magnetization Plateau of 1/4 in a Novel Double Spin Chain of Ferromagnetic Dimmers formed by an Organic Tetraradical

GOTO, Tsuneaki[1]; BARTASHEVICH, M. I.[1]; HOSOKOSHI, Yuko; KATOH, Keiichi[2]; INOUE, Katsuya
([1]ISSP, Univ. of Tokyo; [2]GUAS)

[*Physica B* **294**, 43 (2001)]

We have measured the susceptibility and low temperature magnetization curve of the novel organic tetraradical crystal BIP-TENO. The susceptibility data indicate that double spin chains of ferromagnetic dimmers are formed in the crystal and the spin system is regarded as an S = 1 antiferromagnetic two-leg ladder. The magnetization is nearly zero up to 10 T and the spin gap is closed at 11.6 T. Above 12 T, the magnetization increases and a plateau corresponding to a quarter of the saturation magnetization appears at 44.8 T.

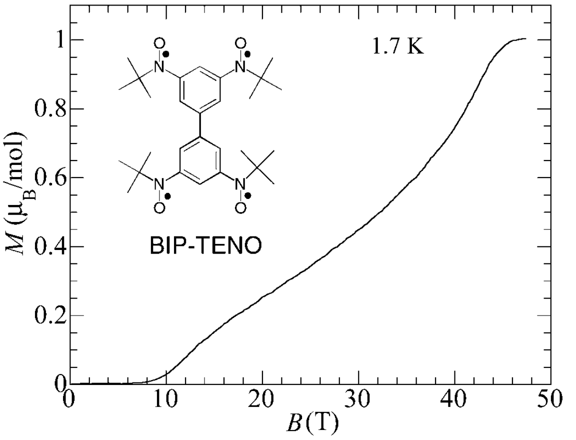

Figure 1. Magnetization curve of BIP-TENO at 1.7 K in pulsed high magnetic fields up to about 50 T.

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 in 1991, 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 Approach to a Single-Component Ferrimagnetism by Organic Radical Crystals

HOSOKOSHI, Yuko; KATOH, Keiichi[1]; NAKAZAWA, Yasuhiro[2]; NAKANO, Hiroki[3]; INOUE, Katsuya
([1]GUAS; [2]Osaka Univ.; [3]Univ. Tokyo)

[*J. Am. Chem. Soc.* **123**, 7921 (2001)]

A novel organic triradical of 2-[3',5'-bis(*N-tert*-butylaminoxyl)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide, abbreviated as PNNBNO, were synthesized. The PNNBNO molecule includes three $S = 1/2$ spins and is regarded as the antiferromagnetic pair of an $S = 1/2$ and $S = 1$. In the crystals, the planar PNNBNO molecules stack along the b axis forming the alternant array of the $S = 1/2$ and the $S = 1$. This can be regarded as a ferrimagnetic ladder, with rungs of intramolecular antiferromagnetic interactions and legs of intermolecular antiferromagnetic interactions between the $S = 1/2$ and $S = 1$. In the static magnetic susceptibility measurements, clear ferrimagnetic behavior is observed. Moreover, we must mention that the crystals include the 3D ferrimagnetic network. Each ladder is surrounded by four neighboring ladders with the alternant alignment of the $S = 1/2$ and $S = 1$. The heat capacity measurements revealed that the effective $S = 1/2$ species (ferrimagnetic spins) undergo a magnetic phase transition at 0.28 K. This is the first example of a genuine organic ferrimagnetic material having well-defined chemical and crystal structure.

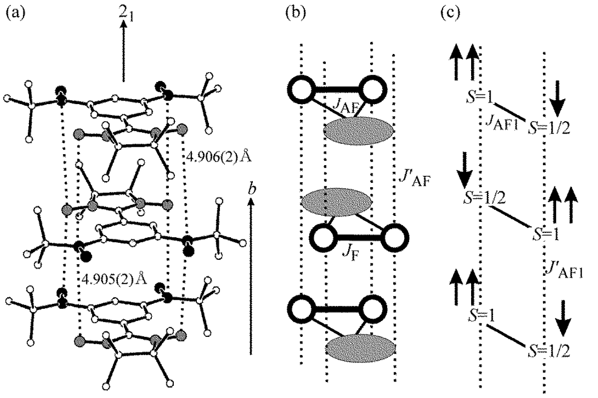

Figure 1. (a) Uniform chain structure in PNNBNO crystals. (b) Schematic illustration of the chain structure. (c) Ferrimagnetic ladder structure in the extreme limit when $J_F \to \infty$.

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 Effect on Mn Complexes of Bisaminoxyl Radicals

HOSOKOSHI, Yuko; SUZUKI, Kentaro[1]; INOUE, Katsuya
([1]GUAS)

The pressure effects on the magnetic properties of one-dimensional Mn(hfac)$_2$ complexes with 1,3-bis(*N-tert*-butylaminoxyl)benzene ($\mathbf{1}_\mathrm{H}$) and 5-halo-1,3-bis(*N-tert*-butylaminoxyl)benzene ($\mathbf{1}_\mathrm{F}$, $\mathbf{1}_\mathrm{Cl}$, $\mathbf{1}_\mathrm{Br}$) have been studied. These complexes have similar chain structures and undergo three-dimensional magnetic phase transitions at low temperature, due to weak interchain interactions. At ambient pressure, $\mathbf{1}_\mathrm{H}$ and $\mathbf{1}_\mathrm{F}$ are metamagnets with weak interchain antiferromagnetic interactrions, whereas $\mathbf{1}_\mathrm{Cl}$ and $\mathbf{1}_\mathrm{Br}$ are ferrimagnets with weak interchain ferromagnetic interactrions. The opposite sign of the interchain interactions in these materials is attributed to the different way of packing between the chains. The pressurization of the both metamagnets, results in the monotonous increase of the interchain antiferromagnetic interactions. The enhancement of T_N and H_C with applying pressure was observed. On the other hand, the both ferrimagnets show curious pressure dependences. The change of the interchain interaction is very sensitive to pressure. In some pressure region, temperature dependence of the ac susceptibility shows two peaks. One of the peaks is readily broadened in the existence of the small external DC field of 5–25 Oe. The mechanism of the interchain interaction is discussed.

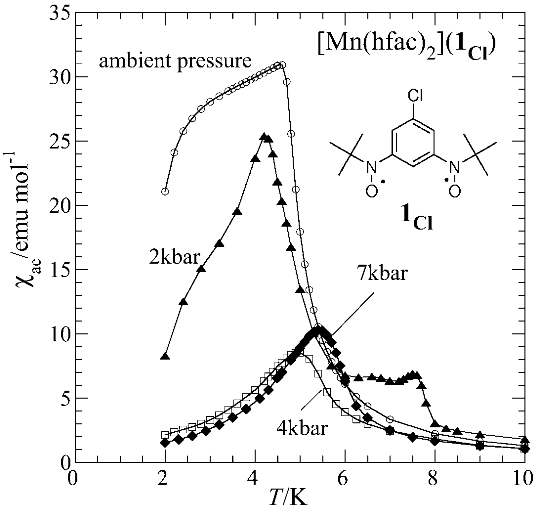

Figure 1. Temperature dependence of the ac susceptibility of [Mn(hfac)$_2$]·$\mathbf{1}_{Cl}$ under several pressures.

V-E-2 Suppression of the Structural Change under Pressure of Cu(hfac)$_2$ Complex with 5-Bromo-1,3-phenylenebis(*N-tert*-butyl-aminoxyl)

HOSOKOSHI, Yuko; SUZUKI, Kentaro[1]; IWAHORI, Fumiyasu[1]; INOUE, Katsuya
([1]GUAS)

The pressure effect on the magnetic properties of 3:2 complex of Cu(hfac)$_2$ with 5-Bromo-1,3-phenylenebis-(*N-tert*-butyl-aminoxyl) ($\mathbf{1}_{Br}$) has been studied. At ambient pressure, sudden decrease of magnetic susceptibility at 48 K was reported, which suggests the structural change at this temperature. Our magnetic measurements under pressure revealed that the structural change is sufficiently suppressed at 6 kbar. We also found that the weak stress when the sample is dipped in oil, affects the structural change. The behavior suggests that, at 6 kbar, the high-temperature phase is preserved down to low temperature as metastable state. The enhancement of the energy barrier of the structural transition under pressure is suggested.

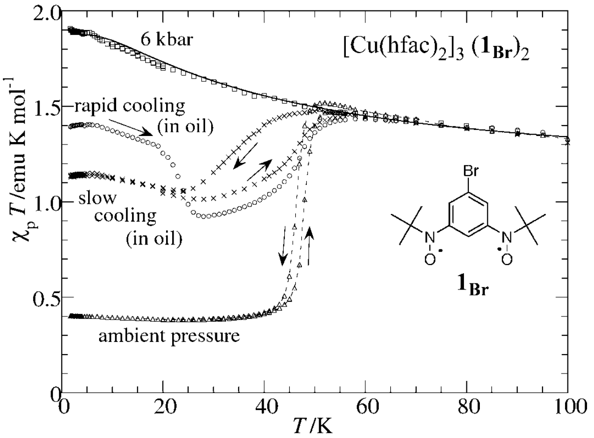

Figure 1. Temperature dependence of $\chi_p T$ of [Cu(hfac)$_2$]$_3$·($\mathbf{1}_{Br}$)$_2$ at ambient pressure (△), at 6 kbar (□), and in oil (○, ×).