V-E Synthesis of New High-spin Molecule

Design and synthesis of organic molecules with high-spin ground states are current subjects of great importance. When three unpaired electrons are placed in proximity and allowed to interact magnetically. 1,3,5-Benzenetriyl unit can be deemed superior to *m*-phenylene unit in assembling organic free radical centers in higher concentrations within a molecule and aligning those spins in parallel for the purpose of designing and constructing very high-spin organic molecules. While some 1,3,5-trisubstituted benzene derivatives having nitronyl nitroxides, diarylmethyl radicals, diphenylamine cation radicals, phenylcarbene, and nitrenes as substituents are reported to be with high-spin ground states, they are either not persistent under ambient conditions or the intraradical couplings are not strong enough in magnitude.

V-E-1 Structure and Magnetic Property of the Organic Triradical with Triazine Skeleton;1,3,5-Tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)-phenyl}triazine

HAYAMI, Shinya; INOUE, Katsuya

[*Chem. Lett.* 545 (1999)]

1,3,5-tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}benzene has been known as persistent triradical with quartet ground state. New triradical with triazine skeleton was synthesized and characterized. Nitroxide triradical with triazine derivative 1,3,5-tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}triazine (**1**) exhibits stronger intramolecular ferromagnetic interaction than that with benzene derivative 1,3,5-tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}-benzene (**2**), the magnitude of the interactions depends on the planarity of the structures and/or on the spin density of center skeletons. Temperature dependence of the effective magnetic moments values observed for crystalline **1** in 1.8–350 K. The simulation of an isosceles-triangular exchange coupling model gave J_1/k_B = 14.7 K, γ = 0.87, and θ = –5.43 K.

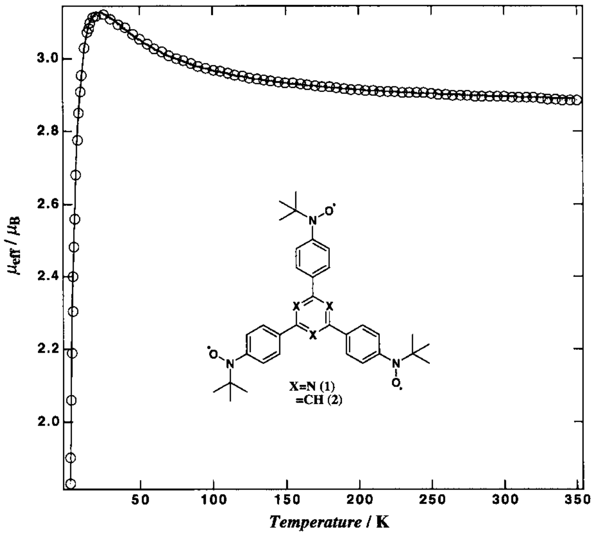


Figure 1. Temperature dependence of effective magnetic moment μ_{eff} values of **1** in neat crystals. Solid curve is a theoretical one.

V-F Construction of New Molecule-Based Magnets

Construction of molecular based magnetic materials which have well-defined one- or two-dimensional magnetic structure is a scientific subject of increasing interest. Heterospin systems consisting of paramagnetic transition metal ions and organic free radicals as ligands constitute one of the mainstreams of such studies. Several of these materials have been established to have finite critical temperature of a ferro- or ferrimagnetic transition.

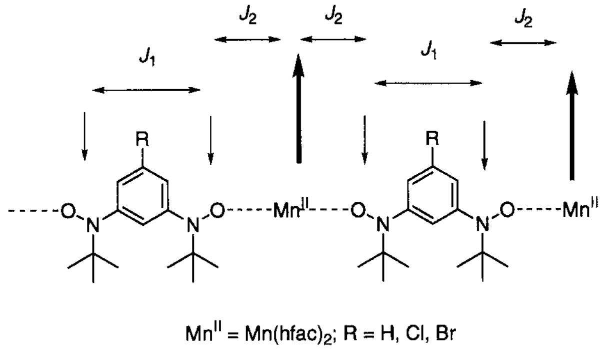
We have introduced a new strategy of employing π-conjugated polyaminoxyls as ligands in which the 2*p*-spins of the NO groups interact ferromagnetically ($J_1 > 0$). The dimensionality of the complex and the sign and magnitude of the exchange coupling between the neighboring spins may be readily tuned 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 2*p* and metallic 3*d* 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.

V-F-1 One-Dimensional Ferro- and Ferrimagnetic Chains Made up of an Alternating Array of 1,3-Bis(*N*-*tert*-Butyl-*N*-oxy-amino)-benzene Derivatives and Mn(II)(hfac)$_2$

INOUE, Katsuya; IWAHORI, Fumiyasu[1]; MARKOSYAN, Ashot S.[2,3]; IWAMURA, Hiizu[4]
([1]GUAS.; [2]M. V. Lomonosov Moscow State Univ.; [3]IMS; [4]Kyushu Univ.)

[*Coord. Chem. Rev.* in press]

Bis(hexafluoroacetylacetonato) manganese (II), Mn(hfac)$_2$, reacts with the bisnitroxide radicals, 5-R-1,3-Bis(*N*-*tert*-butyl-*N*-oxyamino)benzene $\mathbf{1_R}$ (R = H, Cl and Br), yielding 1-dimensional polymeric complexes of formula [Mn(hfac)$_2$**1**$_R$]$_n$. X-ray analysis of the complexes has shown that they crystallize in the monoclinic, space group *P*2$_1$/*n*. In this structure, the manganese(II) ions and **1**$_R$ molecules make up 1-D chains with the bisnitroxide radical serving as a bidentate ligand to Mn(II)(hfac)$_2$. The **1**$_H$ complex orders antiferromagnetically at 5.5 K, while the **1**$_{Cl}$ and **1**$_{Br}$ complexes show ferrimagnetic order at 4.8 and 5.3 K, respectively. The intrachain exchange interaction parameters for a model of S = 3/2 ferromagnetic chains were found to be, $2J_{eff}/k$ = 23 ± 2 K in all the compounds. J_{eff} means effective magnetic exchange interaction between units of NO–Mn–NO. A change in the sign of the interchain exchange interaction is referred to the change of the shortest exchange path, from the Mn–F–N(*tert*-Bu)O·(**1**$_{Cl}$ and **1**$_{Br}$) to N(*tert*-Bu)O·–F–N(*tert*-Bu)O·(**1**$_H$).



Scheme 1.

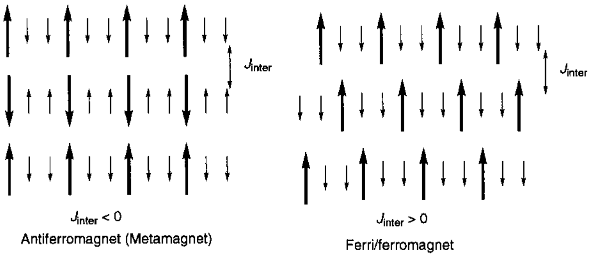


Figure 1. Schematic drawing of magnetic structure for the complex a) Mn(hfac)$_2$·**1**$_H$, b) Mn(hfac)$_2$·**1**$_{Cl}$ and Mn(hfac)$_2$·**1**$_{Br}$.

V-F-2 Influence of the Thermal Excitations of the Ferrimagnetic ($\bar{1}/2,5/2,\bar{1}/2$) Linear Trimer on the Paramagnetic Behavior of the Layered Metal-Radical Complex {Mn(hfac)$_2$}$_3$(R$_N$)$_2$·*n*-C$_7$H$_{16}$

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

[*Phys. Lett. A* in press]

The complex {Mn(hfac)$_2$}$_3$(**3R**$_\Delta$)$_2$·*n*-C$_7$H$_{16}$ forms a two-dimensional honeycomb-like spin network. It is shown that the spins of Mn(II) form with the two 1/2-spins of different adjacent triradicals **3R**$_\Delta$ linear ($\bar{1}/2,5/2,\bar{1}/2$) ferrimagnetic trimers, which determine the paramagnetic properties of the complex. The intratrimer excitations result in the decay of the trimers above 140 K.

The experimental data can well be described within this model both at high and low temperatures thus proving the importance of the thermal excitations within the trimers. The best agreement was obtained at J_{TR}/k_B = –176.4 K and = +0.333 emu/mol. The power series expansion for the 2D honeycomb network gives J_{TR}/k_B = –175.4 K and J_1/k_B = +0.226 K.

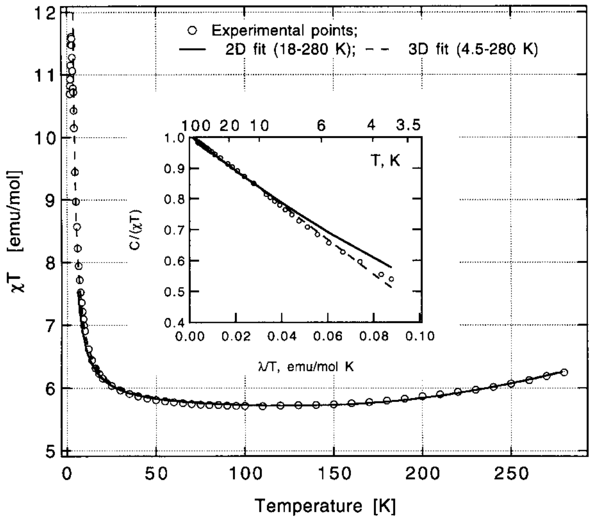


Figure 1. The temperature dependence of $\chi_m T$ for the 2D complex {Mn(hfac)$_2$}$_3$(**3R**$_\Delta$)$_2$·*n*-C$_7$H$_{16}$. Open circles are the experimental data, the solid and the dashed lines are the least squares fits for a 2D and 3D lattice, respectively. The inset shows the details of the low temperature behavior in the $C/\chi T$ versus λ'/T form.

V-G Mn(II)-Induced Formation of a [3+3] Benzene Dimer Derivatives

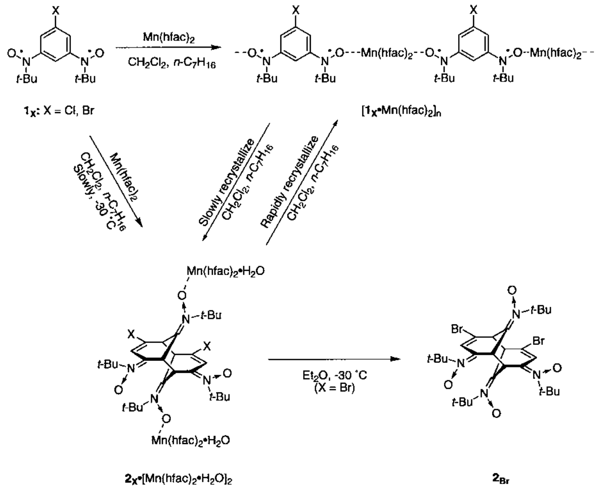
A number of studies have been conducted on the dimerization of aromatic compounds. Most of these compounds are formed by a Diels-Alder-type cycloaddition reaction, *i.e.* [2+2] or [2+4]. We found a unique aromatic [3+3] cycroaddition in the presence of Mn(II) ion. In the course of our study of self-assemblage of magnetic metal ions and bis- and tris(aminoxyl) radicals described in V-F, we found the formation of a unique [3+3] benzene dimer structure as a side reaction. Some reports have described the [3+3] cycroaddition of organic molecules but not of aromatic compound. Our crystallographic characterization would help shed light on the mechanistic detail of Lewis acid-catalysed cycroaddition and free-radical reactions.

V-G-1 Mn(II)-Induced Formation and Structural Elucidation of a [3+3] Benzene Dimer Derivative from *m*-Phenylenebis(*N*-*tert*-butylaminoxyl)

IWAHORI, Fumiyasu[1]**; INOUE, Katsuya; IWAMURA, Hiizu**[2]
([1]GUAS; [2]Kyushu Univ.)

[*J. Am. Chem. Soc.* **121**, 7264 (1999)]

One-dimensional ferrimagnetic complexes, [Mn-(hfac)$_2$·$\mathbf{1}_\mathrm{X}$]$_n$ (X = Cl or Br), are typically obtained by the reaction of Mn(hfac)$_2$ with $\mathbf{1}_\mathrm{X}$. When it takes a few days for crystallization, however, black solutions often turn yellow in about one day and yellow crystalline precipitates are obtained. A solution of $\mathbf{1}_\mathbf{Br}$ in CH_2Cl_2 was added to a suspension of Mn(hfac)$_2$ in *n*-C_7H_{16} at 0 °C and the mixture was stored at –30 °C. After a few days, yellow needles of $\mathbf{2}_\mathbf{Br}$·[Mn(hfac)$_2$·H_2O]$_2$$CH_2Cl_2$ were obtained (85.2%). An X-ray structure analysis revealed that $\mathbf{2}_\mathrm{X}$·[Mn(hfac)$_2$·H_2O]$_2$$CH_2Cl_2$ has a [3+3] benzene-dimer structure {X = Cl or Br; $\mathbf{2}_\mathrm{X}$ = 3,10-dihalo-5,8,11,12-tetrakis(*N*-*tert*-butylimino)-tricyclo[5,3,1,1^{2,6}]dodeca-3,9-diene *N,N',N",N'"*-tetraoxide}. When $\mathbf{2}_\mathbf{Br}$·[Mn(hfac)$_2$·H_2O]$_2$$CH_2Cl_2$ was dissolved in Et_2O and the solution was stored at –30 °C, white powder of $\mathbf{2}_\mathbf{Br}$·2H_2O free of Mn(hfac)$_2$ precipitated out in 30 minutes (68.8%). Spectroscopic data on $\mathbf{2}_\mathbf{Br}$ are in good agreement with its structure. The spectra of $\mathbf{2}_\mathbf{Br}$ in CH_2Cl_2 is time-dependent and converted eventually to that of monomeric biradical $\mathbf{1}_\mathbf{Br}$ by showing four isosbestic points. The result indicates that the dissociation process of $\mathbf{2}_\mathbf{Br}$ into two molecules of $\mathbf{1}_\mathbf{Br}$ is very clean.



Scheme 1. Transverse scheme between [3+3] benzene derivatives and ID ferrimagnetic complexes.

V-H Synthesis of Chiral Molecule-Based Magnets

There is a phenomenological resemblance between natural and magnetic optical activity. The former is due to the handedness of molecular structure, whereas the latter is due to the magnetic field-induced circular dichroism. In 1984 Barron and Vrbancich call "magneto-chiral dichroism" (MChD) for a link between two phenomena. In 1997, Rikken and Raupach observed the MChD effect of tris(3-trifluoroacetyl-±-camphorato)europium (III) in the paramagnetic state. However, the MChD effect in the paramagnetic state is small. It's important to make the fully chiral molecule-based magnets, which expected to be strong MChD effect. There are still no examples of molecule-based chiral magnet. Novel properties are expected for such compounds.

The design of molecular materials with interesting electrical and/or magnetic properties is one of the major challenges of science in the last few years. It's possible to modify the molecular structure in the molecule-based magnetic materials. Recently, we introduced a strategy of using π-conjugated polyaminoxyl radicals with high-spin ground states as bridging ligands for magnetic metal ions in order to assemble and align the electron spins on a macroscopic scale. The crystal structures of these complexes are known, and some cases, the magnetic structures are analyzed. 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. When we use a bidendate bisaminoxyl radicals as ligand and manganese(II) hexafluoroacetylacetonate, Mn(II)(hfac)$_2$, we can make one-dimensional complexes. If we use chiral triplet bisaminoxyl radicals for the construction of one-dimensional magnet, we can expect to make chiral molecule-based magnets.

V-H-1 A Chiral Molecule-based Metamagnet Made by a Chiral Triplet Organic Radical and Manganese Ion

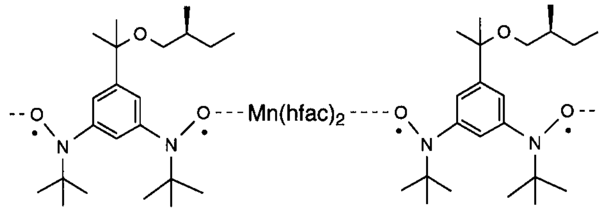
KUMAGAI, Hitoshi; INOUE, Katsuya

[*Angew. Chem., Int. Ed. Engl.* **38**, 1601 (1999).]

The chiral biradical, 1,3-bis(*N*-*tert*-butylamino-*N*-oxyl)-5-[1'-methyl-1'-{(*S*)-2"-methylbutoxy}]-ethylbenzene (**1**) was prepared and was mixed with an equimolar amount of dehydrated Mn(hfac)$_2$ in diethyl ether/*n*-heptane and the mixture was evaporated. Deep brown block crystals were obtained in 1 day at –30 °C.

X-ray crystal structure analysis of the complex revealed the formation of a one-dimensional structure. (Scheme 1) The oxygen atoms of the terminal aminoxyl radicals of biradical **1** are ligated to two different manganese ions in *trans* position to form a one-dimensional helical chain along the *c* crystal axis. The bisaminoxylbenzene unit is in a chiral conformation and forms a (*R*)-helical structure.

The magnetization at 1.8 K revealed metamagnetic behavior (Figure 1); while the response of the magnetization was not sensitive to the weak applied magnetic field below *ca.* 500 Oe, a behavior characteristic of an antiferromagnet. A sharp rise and approach to saturation of magnetization characteristic of a ferromagnet was observed at higher applied magnetic field. A saturation magnetization value of *ca.* 2.7 μ_B was reached at 1.8 K at 3 Tesla, which suggests the antiferromagnetic coupling between the manganese(II) ion and **1**.



Scheme 1. Polymeric chain structure of [**1**·Mn(hfac)$_2$]$_n$.

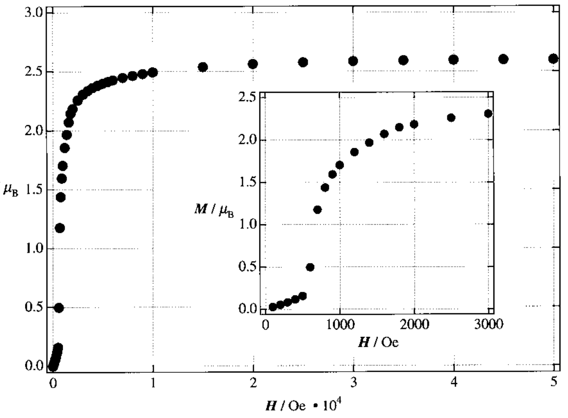


Figure 1. Field dependencies of the magnetic moment of a polycrystalline sample of [**1**·Mn^{II}(hfac)$_2$]$_n$ at 1.8 K. Inset shows magnetic field range of 0 to 3000 Oe.

V-H-2 Synthesis and Characterization of a Novel Chiral Molecular-based Ferrimagnet Prepared from a Chiral Nitronyl Nitroxide Radical and Manganese(II) Ion

KUMAGAI, Hitoshi; INOUE, Katsuya

The chiral radical **2** was synthesized and was mixed with an equimolar amount of dehydrated Mn(hfac)$_2$ in diethyl ether/*n*-heptane and the mixture was evaporated to *ca.* 10 ml. Green block crystals were obtained at –30 °C in 1 week.

The X-ray crystal structure analysis revealed that both crystals of **2** and complex [**2**·Mn^{II}(hfac)$_2$]$_n$ belongs to the same chiral space group $P2_12_12_1$ (No. 19). The molecular structure of [**2**·Mn^{II}(hfac)$_2$]$_n$ is depicted in Figure 1. One-dimensional chain elongates along the crystal *a*-axis. The radicals are bound to the Mn(II) ion in cis-coordination to each other. In this complex, the metal center exhibits the all Δ configuration. Because of the use of the chiral ligand, the complex crystallized in chiral space group and no Λ chirality of the Mn(II) are existed in this crystal. Since no inversion centers are present in this space group, chains are isotactic as all units and the crystal lattice as a whole is chiral.

Magnetization measurements have been performed at 2 K. The magnetization increases very rapidly, and reaches a plateau about 3.6 B.M. at 1.5 T. This value suggests the antiferromagnetic coupling between the manganese(II) ion and **2** (Theoretical value is 4 B.M. (5/2 – 1/2 = 4/2).) AC susceptibility measurements revealed that [**2**·Mn^{II}(hfac)$_2$]$_n$ behaves as ferrimagnet below 4.5 K. The existence of weak ferromagnetic interchain interaction is suggested.

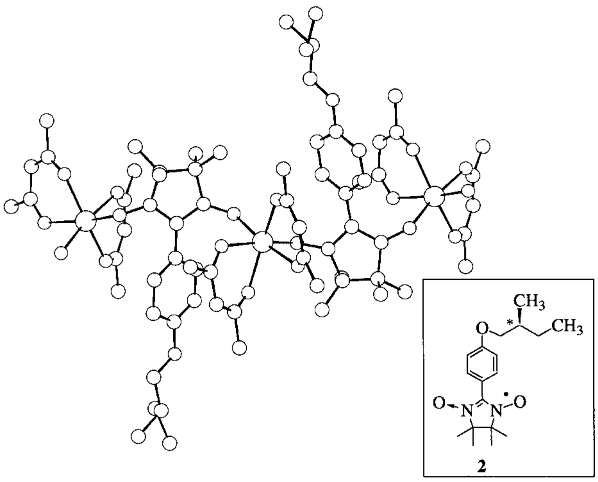


Figure 1. View of a helical chain formed by chiral nitronyl nitroxide **2** and Mn(II)(hfac)$_2$. Hydrogen atoms and florine atoms are omitted for clarity

V-I Synthesis and Characterization of Quantum-Spin Systems

Quantum spin systems have been much attracted for several decades. Haldane's conjecture in 1983 on the difference between a Heisenberg antiferromagnetic chain of integer-spin magnitude and that of half-integer-spin magnitude called renewed interest. The properties of S = 1 spin chain with a finite energy gap between the ground state and excited states have been extensively studied both theoretically and experimentally. Then, interested is the crossover between the dimer state and Haldane state, for example, in the S = 1/2 alternating chain with ferromagnetic and antiferromagnetic interactions. We have desigined and synthesized two types of S = 1/2 chains with ferromagnetic and antiferromagnetic interactions. Moreover, we made a two-dimensional antiferromagnetic lattice of the ferromagnetic spin pairs. Another topic is the double chain systems, which is interesting from the aspect of the Haldane state and high T_C superconductivity. We designed and synthesized a railroad trestle compound and observed the existence of an energy gap above the singlet ground state.

V-I-1 Magnetic Properties of Low Dimensional Quantum Spin Systems Made of Stable Organic Biradicals PNNNO, F_2PNNNO and PIMNO

HOSOKOSHI, Yuko; NAKAZAWA, Yasuhiro; INOUE, Katsuya; TAKIZAWA, Kohichi[1]; NAKANO, Hiroki[1]; TAKAHASHI, Minoru[1]; GOTO, Tsuneaki[1]
([1]ISSP, Univ. Tokyo)

[*Phys. Rev. B* in press]

Stable organic biradical crystals PNNNO, F_2PNNNO and PIMNO of the PNNNO family were synthesized. (PNNNO = 2-[4'-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide, F_2PNNNO = 2-[2',6',-difluoro-4'-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide, PIMNO = 2-[4'-(*N*-*tert*-butyl-*N*-oxyamino)-phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl) PNNNO and PIMNO crystallize to form quasi-one-dimensional lattices, but F_2PNNNO to form a quasi-two-dimensional lattice. The temperature dependences of the susceptibility and the high-field magnetization process up to 34 T were measured down to 0.5 K. The results are analysed by comparing with the theoretical calculations based on the crystal structures. PNNNO and PIMNO are considered to be antiferromagnetic Heisenberg spin chains consisting of $S = 1/2$ spin pairs (dimers) in which the two spins are coupled ferromagnetically. Both compounds undergo antiferromagnetic phase transitions at 1.1 and 2.5 K, respectively due to weak interchain interactions. The three-dimensional nature of the transition is examined by the thermodynamic discussion through specific heat measurements. On the other hand, F_2PNNNO is thought to be a two-dimensional Heisenberg system, in which the spin pairs are connected by two types of antiferromagnetic interactions. The magnetism of F_2PNNNO is characterized by the singlet ground state and a plateau in the magnetization isotherm.

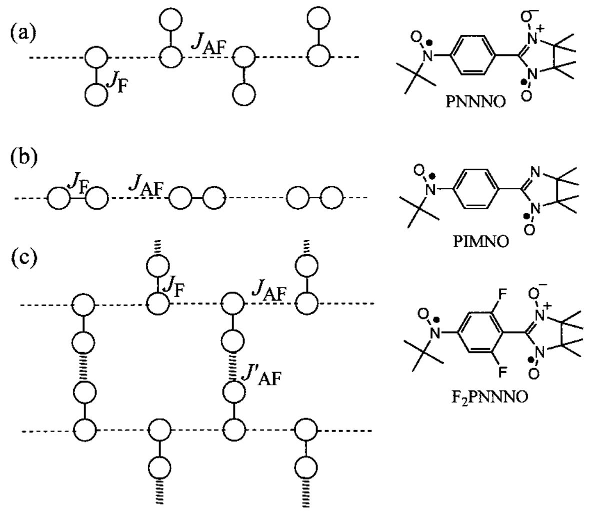


Figure 1. Scheme of the magnetic interactions in (a) PNNNO, (b) PIMNO and (c) F_2PNNNO with their molecular structures.

V-I-2 Construction of a Quantum-Spin System of *S* = 1/2 Antiferromagnetic Chain with the Next-Nearest-Neighbor Interactions

HOSOKOSHI, Yuko; KATOH, Keiichi[1]; INOUE, Katsuya; GOTO, Tsuneaki[1]
([1]ISSP, Univ. Tokyo)

[*J. Phys. Soc. Jpn.* **68**, 2910 (1999)]

We have succeeded in synthesizing a new compound with a railroad trestle structure, *i.e.*, a zigzag chain with next-nearest-neighbor interactions. We have newly synthesized organic radicals F_2PIMNH and Cl_2PIMNH, where F_2PIMNH = 2-[4'-*N*-*tert*-butylamino-2',6'-difluorophenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl and Cl_2PIMNH = 2-[4'-*N*-*tert*-butylamino-2',6'-dichlorophenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl. Both crystals include zigzag uniform chains made of hydrogen bondings. The magnetism of Cl_2PIMNH is explained by the Heisenberg antiferromagnetic uniform chain model with $2J/k_B = -3.6$ K and gapless ground state is suggested. On the other hand, static magnetic measurements of F_2PIMNH suggest the nonmagnetic ground state and the existence of a finite gap in its excitation spectrum. In this crystal, the next-nearest-neighbor contacts are seen, which are believed to be the origin of the energy gap.

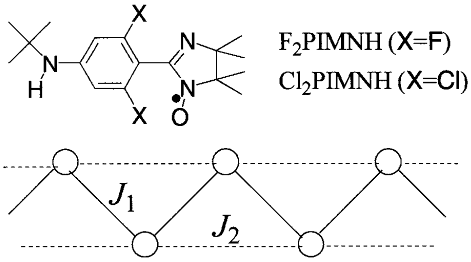


Figure 1. Scheme of the magnetic interactions in F_2PIMNH. Uniform chain with the next nearest neighbor interactions.

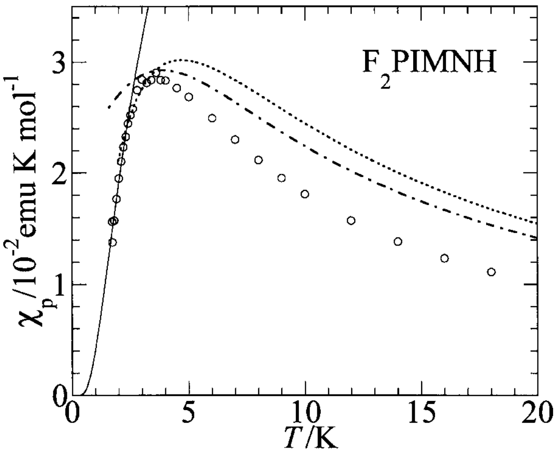


Figure 2. (a) Temperature dependence of χ_p of F_2PIMNH. The solid curve is the fit of $\chi \propto \exp\{(-\Delta/T)\}$ with $\Delta = 3.1$ K. The dotted broken curve is the calculation for the uniform chain with $2J/k_B = -6$ K, the interchain interactions by the mean-field treatment of $2zJ'/k_B = -5.2$ K are adopted. The dotted curve represents the calculation for the alternating chain with $2J_1/k_B = -7.9$ K and $2J'_1/k_B = -6.3$ K.

V-J Pressure Effects on Magnetic Materials

“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 exhibit large pressure effects. For the magnetic measurements with high-accuracy, we have developed a small high-pressure clamp cell made of 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. The maximum pressure maintained is *ca.* 7 kbar, the reproducibility is good, and the temperature variation of pressure in the cell is within *ca.* 0.3 kbar.

We study the pressure effects on the molecule-based chain compounds. We have observed the pressure-induced phenomena of (1) crossover from an alternating chain to a uniform chain, (2) dimensional-crossover from 2D to 1D, and (3) change of the sign of the interchain interactions. We also apply the pressure to some intermetallic compounds which show large volume effects.

V-J-1 Pressure-Induced Crossover from Alternating to Uniform Interaction in an S = 1/2 One-Dimensional Heisenberg Antiferromagnet

MITO, Masaki[1]; KAWAE, Tatsuya[1]; HOSOKOSHI, Yuko; INOUE, Katsuya; KINOSHITA, Minoru[2]; TAKEDA, Kazuyoshi[1]
([1]Kyushu Univ.; [2]Sci. Univ. Tokyo in Yamaguchi)

[*Solid State Commun.* **111**, 607 (1999)]

We have confirmed the pressure-induced crossover from the alternating to the uniform one-dimensional (1D) spin system in an organic compound as a function of applied pressure (p) by the measurements of heat capacity. The pentafluorophenyl nitronyl nitroxide radical (F_5PNN), which is the 1D alternating Heisenberg antiferromagnet of spin S = 1/2 with $\alpha = J_2/J_1$ ~0.4 at ambient pressure, has transformed into the uniform one (α = 1) at p = 6.5 kbar. This pressure induced crossover was made clear by observing the change of initial gradient of heat capacity, which transformed from exponential to linear at low temperature. The crystal structure of F_5PNN at the room temperature and ambient pressure is of the uniform spin chain, and the pressure must play the role of suppressing the structural transition into the alternating system.

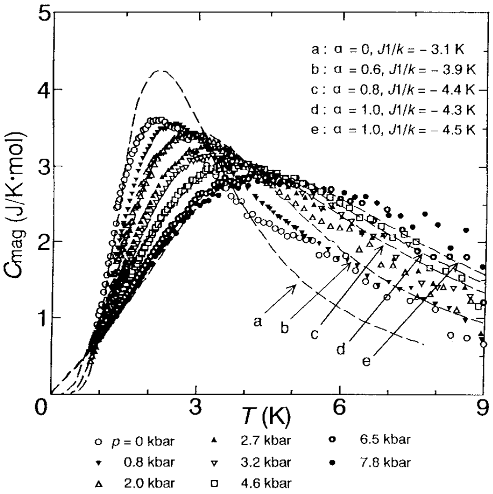


Figure 1. Temperature dependence of C_{mag} of F_5PNN under the pressure up to 7.8 kbar. The broken lines (a-e) express Duffy *et al.*’s theoretical curves of C_{mag} up to 7.8 kbar with such two parameters as α and J_1/k_B.

V-J-2 Pressure Effects on Organic Radicals with Ferromagnetic and Antiferromagnetic Interactions

HOSOKOSHI, Yuko; INOUE, Katsuya

[*Synth. Met.* **103**, 2323 (1999)]

Magnetic properties of stable organic biradicals under pressure are presented. The dimensional crossover from two-dimension to one-dimension is induced by pressure in F_2PNNNO, whereas the properties of the corresponding one-dimensional material, PNNNO is almost independent of the pressure. The phase transition temperature of the quasi-one-dimensional antiferromagnet, PIMNO become higher with applied pressure. The increase of the interchain interactions by pressurization has been observed, whereas the intrachain interactions are almost independent of the pressure.

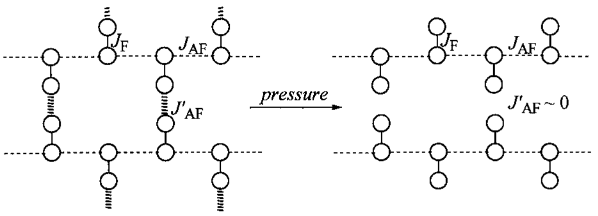


Figure 1. Scheme of the magnetic interactions in F_2PNNNO. Pressure-induced dimensional crossover from 2D to 1D.

V-J-3 Pressure Effect on Mn Complexes of Bisaminoxyl Radicals

HOSOKOSHI, Yuko; SUZUKI, Kentaro[1]; INOUE, Katsuya; IWAMURA, Hiizu[2]
([1]GUAS; [2]Kyushu Univ.)

[*Mol. Cryst. Liq. Cryst.* in press]

The pressure effects on magnetic properties of one-dimensional Mn complexes with 1,3-bis(*N-tert*-butylaminoxyl)benzene and 5-chloro-1,3-bis(*N-tert*-butylaminoxyl)benzene have been studied. These complexes have weak interchain interactions with different signs and the former is a metamagnet and the latter is a ferrimagnet at ambient pressure. The interchain interactions of the former is enhanced by pressurization. The transition temperature becomes higher and the critical field becomes larger with applying pressure. The closer spacing of each chains caused by pressurization, yields larger antiferromagnetic interchain interactions in this compound.

On the other hand, the response to the pressure of the latter ferrimagnet, is rather complicated. The transition temperature becomes higher and the antiferromagnetic interchain interactions are induced by pressurization. The interchain exchange coupling in this compound should be sensitive to the relative orientation of the chain structure. The decrease of the ferromagnetic contribution and/or the increase of the antiferromagnetic one in the interchain interactions is brought about by pressurization.

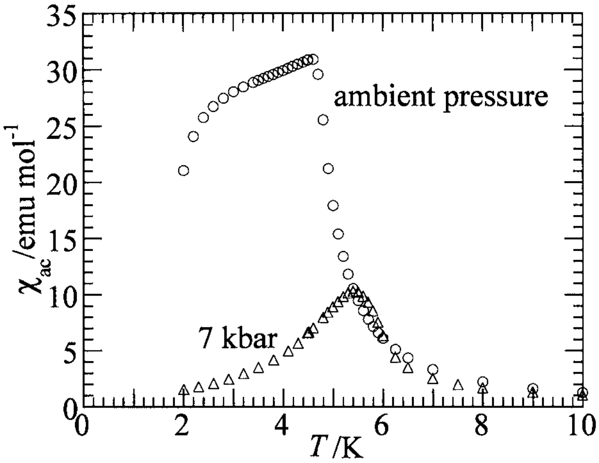


Figure 1. Temperature depemdemce of the ac susceptibilities of [Mn(hfac)$_2$]·{5-chloro-1,3-bis(*N*-*tert*-butylaminoxyl)benzene} at ambient pressure and under 7 kbar.

V-J-4 The Magnetic Phase Diagram and Pressure Effect on the Magnetic Properties of the $Y_{1-x}Gd_xMn_2$ Intermetallic Compounds

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[*J. Phys.: Condens. Matter* **11**, 2937 (1999)]

Magnetization up to 50 kOe, magnetic susceptibility under external pressure up to 5 kbar and thermal expansion of the cubic Laves phase compounds $Y_{1-x}Gd_xMn_2$ were studied in a wide temperature range. Two well defined concentration regions were isolated in the x-T phase diagram: $0 \le x < 0.2$, in which the antiferromagnetic structure is primarily determined by the d-d interaction (YMn_2-type), and $0.2 < x \le 1$, in which the f-d interaction plays a dominant role ($GdMn_2$-type). It is concluded that both the Gd and Mn sublattices are ordered in $GdMn_2$ below T_N = 108 K, the change in the magnetic characteristics at 40 K interpreted as an antiferromagnetism – non-collinear ferrimagnetism transition. The intermediate $Y_{0.8}Gd_{0.2}Mn_2$ compound shows a freezing and time dependent effects at low temperatures characteristic for short range order. The effects can also be induced by external pressure at higher Gd concentrations.

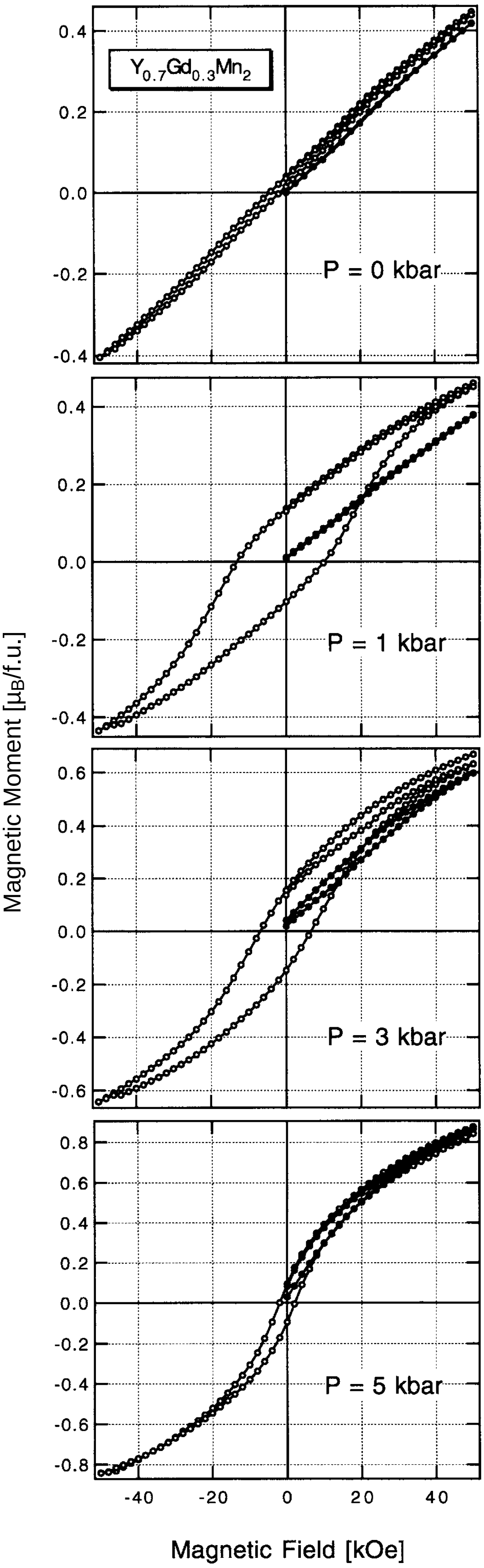

Figure 1. The hysteresis loops of $Y_{0.7}Gd_{0.3}Mn_2$ at 4 K under pressures 0, 1, 3 and 5 kbar. Full and open symbols correspond to the z.f.c. and f.c. (50 kOe) sample, respectively.

V-J-5 Concentration and Pressure Dependence of the Magnetic Ordering in the $Y(Mn_{1-x}Me_x)_2$ Compounds with Me = Al, Fe and Ni

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[*J. Magn. Magn. Mater.* **195**, 687 (1999)]

Magnetic susceptibility of the $Y(Mn_{1-x}Me_x)_2$ (Me = Al, Fe and Ni) compounds was measured in the temperature range 2 ÷ 400 K under external pressure up to 5 kbar. The role of the interatomic Mn-Mn spacing in stabilising the antiferromagnetic transformed phase has been revealed. The value of $\partial T_N/\partial P \approx -50$ K/kbar was found essentially higher than in the mother compound YMn_2. A freezing effect was observed in the non-transformed phase which was related to the break-down of the quantum spin liquid state.

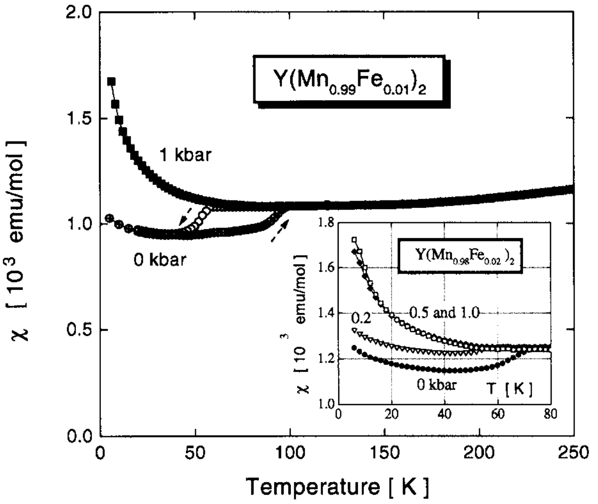

Figure 1. The temperature dependence of χ_{DC} for $Y(Mn_{0.99}Fe_{0.01})_2$ at 1 kbar and ambient pressure. The inset shows the variation of χ_{DC} *vs.* *T* on cooling for $Y(Mn_{0.98}Fe_{0.02})_2$ at different pressures.