学位論文要旨

Study of Magnetic Materials Combining Nitroxide Radicals and Coordination Complexes

ニトロキシドラジカルと遷移金属錯体からなる磁性体に関する研究

固体物性化学研究グループ　　GAO YANLI

The field of “Molecule-based Magnetism” has been evolving in various directions but the essential process remains the building of networks using organic ligands and transition (*d*-electrons) and lanthanide (*f*-electrons) metals. Since the organic ligands is increasing in size and the moments of adjacent metal centers are getting further apart that the critical temperature for long-range ordering is progressively being lowered. To overcome this difficulty open-shell organic ligands have been employed in the construction of molecular magnets. A wide range of magnetic materials has been produced and in some cases with exceptional properties that include transition temperature above 50 K, and magnetic hardness with coercive field exceeding 50 kOe. Organic radicals have therefore attracted a great deal of attention in the designs and have delivered controlled synthesis of the different enantiomers of chiral magnets as well as their racemic form. In addition, an unusual bi-stable phase transition has been observed, which is described as “spin-crossover-like” when Cu(II) is the metal spin carrier. Based on these recent results, my thesis was originally aimed at the synthesis of related chain compounds with copper as well as other metals. Our aim was to understand the physics of these transitions from structural and magnetic point of views, so as to have a control on it and its possible applications.

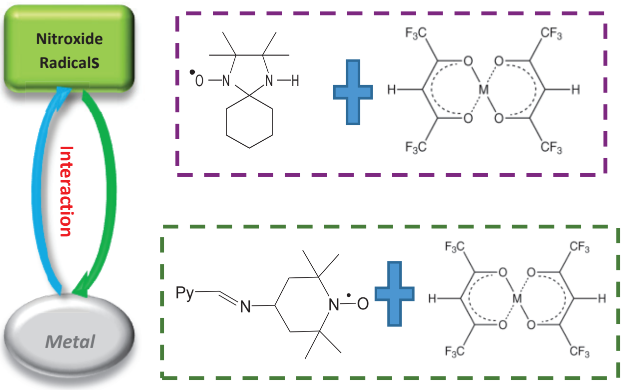

Figure 1. Chemistry approach for this study.

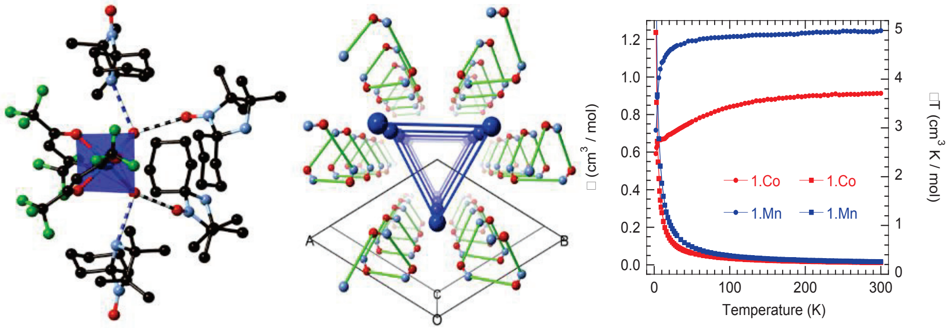

Figure 2. Structure and magnetic properties of Co-Crystals **1·Co** and **1·Mn**.

The main approaches (Figure 1) were to explore the possibility of using C(sp^3)-spaced organic radicals in the creation of new magnetic molecular compounds. The first approach was not successful due to the presence of steric effect preventing coordination to the metal centers. However, intra- and inter-molecular interactions led to the realization of chiral co-crystals; that is crystals composed of components of different crystalline materials. While these have been a method of choice in the pharmaceutical industries for favorable properties, solubility for example, in the administration of drugs, they were unknown in the realm of molecular magnetism. As expected the interactions between the radical moments and those of the metals were minimal even though we choose strong electron drawing groups hfac anion (hfac = hexafluoroacetyl-acetonate) to increase the acidity of the metal centers. Interestingly, it is a rare case of crystallization of chiral structures from achiral components and achiral solvents.

In first work, we report magnetic co-crystals from the C(sp^3)-spaced mono-radical, 2,2-pentamethylene-4,4,5,5 -tetramethylimidazolidine-l-oxyl, and coordination complexes, $M^{II}(hfac)_2(H_2O)_2$, where M = Co or Mn. The extensive intramolecular H-bond is the cause for the segregation of the two entities but the supramolecular interactions between these two neutral building blocks resulted in a rare chiral co-crystal system. The directional properties of the supramolecular interactions, N-O···OH_2, N-H···OH_2, N-O···CH_3, N-O···CH_2, F···CH_3, F···CH_2, work in tandem to generate the chiral structure from achiral components in achiral solvents. From X-ray structural analyses, infrared spectroscopy and magnetization data it is evident that these supramolecular interactions have very little electronic influence to induce charge or proton transfer and magnetic coupling allowing one to describe these solids as genuine co-crystals. It is important to highlight that chiral co-crystals are rather rare and the realization of chiral crystalline form achiral components can be very beneficial for the pharmaceutical industries.

The second project concerns about the six coordination compounds (named **3-8**) constructed with pyridine iminomethyl-TEMPO radicals and [M(hfac)$_2$] (M = Cu^{II} or Mn^{II}) which were selectively obtained from CH_2Cl_2 mixed with heptane. Complexes **3** {[**1**Cu(hfac)$_2$]$_n$} and **4** {[**1**Mn(hfac)$_2$]$_n$}, exhibit a one-dimensional chain structure in which Cu or Mn ions are linked by the oxygen atoms of NO• groups and the N atoms of the pyridine rings, whereas complexes **7** {[**2**Cu(hfac)$_2$]} and **8** {[**2**Mn(hfac)$_2$]},are coordinated to the nitrogen atoms of the pyridine rings of the radicals and the imino nitrogen atom. When the ratio of nitroxide ligand/$M^{II}(hfac)_2(H_2O)_2$ was changed, new complexes **5** {[**1**$_2$Cu(hfac)$_2$]} and **6** {[**1**$_2$Mn(hfac)$_2$]} were obtained and the metal moieties connected by two radicals through the pyridine rings. Characterization and magnetic properties of six coordination compounds based on two TEMPO derivative radicals, 3-Py-CH=N-TEMPO (**1**) and 2-Py-CH=N-TEMPO (**2**) are described. The crystal structures of the compounds of Cu^{II} or Mn^{II} showed that this rather simple bidentate ligand is a valuable scaffold for the construction of different molecular architectures consisting of discrete molecules and chains. This structural diversity proceeds from the presence of two different oxygen-nitrogen coordination sites in one molecule, a nitroxide radical and a pyridine. The magnetic studies revealed ferromagnetic (compounds **3** and **7**) and antiferromagnetic (compounds **4**, **5**, **6** and **8**) interactions within the compounds, since the magnetic interactions between the spin carriers are weak, as expected by considering the sp^3 carbon skeleton of the TEMPO derivative radical as an interaction path.

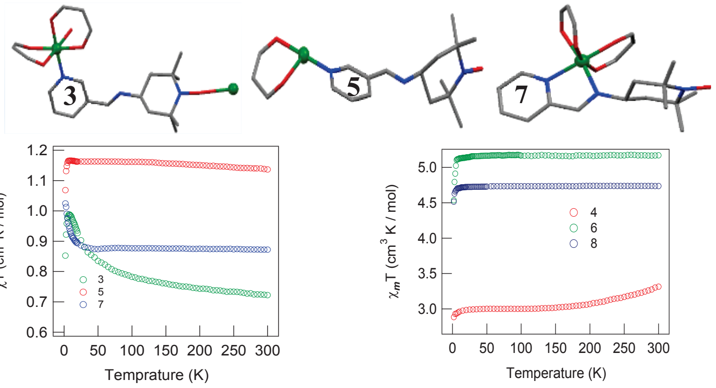

Figure 3. Crystal structure and magnetic properties of complexes **3-8**.

The results of these unique metal-nitroxide radical systems bring two extra dimensions, (a) co-crystallization of organic radical and paramagnetic metal complexes inducing chirality by supramolecular interactions and (b) a series of nitroxide radical bridged 3d compounds with different structures through self-assembly with different ratios of reactants, which were unknown to this interesting field of research.