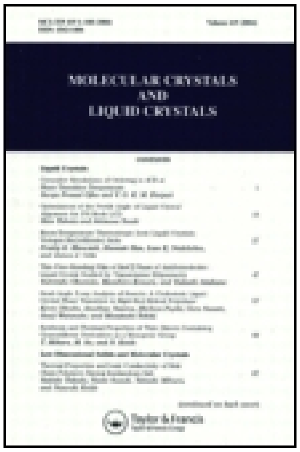

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Magnetic Properties of Metal Complexes with Chelating Nitronylnitroxide and Iminonitroxide

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Version of record first published: 04 Oct 2006

To cite this article: Naoki Yoshioka, Munetoshi Irisawa, Masahiro Abe, Takashi Aokl, Naoyuki Aizawa, Hidenari Inoue & Shigeru Ohba (1997): Synthesis and Magnetic Properties of Metal Complexes with Chelating Nitronylnitroxide and Iminonitroxide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 397-402

To link to this article: http://dx.doi.org/10.1080/10587259708044593

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 397–402
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SYNTHESIS AND MAGNETIC PROPERTIES OF METAL COMPLEXES WITH CHELATING NITRONYLNITROXIDE AND IMINONITROXIDE

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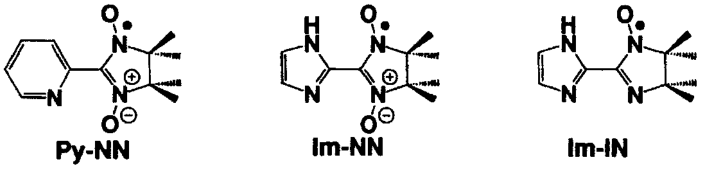
Abstract Several metal complexes of chelating pyridyl nitronylnitroxide, imidazolyl nitronylnitorxide, and imidazolyl iminonitroxide were synthesized and their magnetic properties were characterized.

INTRODUCTION

Metal complexes possessing strong dπ-pπ interaction are drawing much research attention, because these compounds have potentiality to exhibit cooperative magnetism,[1] electrical conductivity,[2] and nonlinear optical phenomenon.[3] As earlier papers, magnetic interaction between metal ions in poly Schiff base iron complex[4] and oxidized poly dithiolate nickel complexes[5] has been described by Lions and Cassoux, respectively.

Our research interests is to design of a molecular assembly exhibiting magnetic cooperatibity based on strong dπ-pπ interaction. To obtain such kind of materials we started our research on the control of structure and magnetic properties of chelating radical complexes by the modification of counter anions or by the introduction of hydrogen-bonding interaction. As a metal complex with hydrogen bonding site, 2,2-biimidazole complexes have been widely used[6] because the ligand has multi-proton donor property and three types of bidentate mode i.e. neutral, mono-deprotonated, and di-deprotonated state. Interesting coordination structures accompanying magnetic interaction have been reported in biimidazole iron complexes.[6d]

We have been interested in the electronic structure of imidazole derivatives which have both proton donor site (NH) and proton acceptor site (=N) and in the migration of active hydrogen, and designed the radical ligands bearing imidazole ring such as Im-NN and Im-IN (SCHEME 1). These ligands form hexagonal and pentagonal chelate ring with metal ions, respectively, and also have two mode of chlelation: neutral and mono-deprotonated state. In the neutral state, intraligand hydrogen bond between NH site and and negatively charged nitroxide oxygen or association with the counter anion is also expected.



SCHEME 1

Copper Complexes of Py-NN Ligand

Complexation of these chelating radical ligands were carried out by conventional method using alcohol and dichloromethane as a solvent. Two mole of chelating radicals and one mole of metal salts were mixed and kept in the refrigerator to give the expected complexes as a black crystal.

The (Py-NN)$_2$CuCl$_2$ has a centrosymmetric tetragonally distorted octahedral structure, whose apical sites are occupied by the chloride ions. The molecular structure is almost identical to those of nickel and manganese complexes.[7] For the chloride

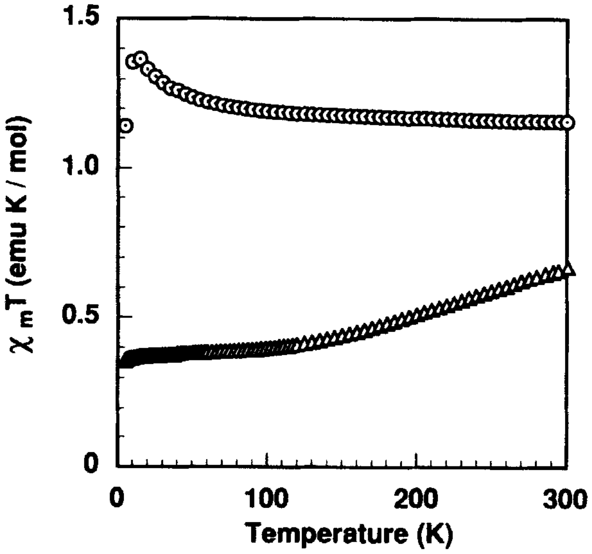


FIGURE 1 Temperature dependence of χ_mT for (Py-NN)$_2$CuCl$_2$ (○), (Py-NN)$_2$Cu(ClO$_4$)$_2$ (△).

complex $\chi_m T$ value at 300 K is 1.16 emu K /mol, which is almost equivalent to the non-interacting three spin system. The value slightly increases with a lowering temperature. In contrast to the chloride complex, the perchlorate complex, $(Py\text{-}NN)_2Cu(ClO_4)_2$ showed a reduced $\chi_m T$ value. By the theoretical analysis based on a three spin system, $J = +8$ cm^{-1} for the chloride complex and -141 cm^{-1} for the perchlorate complex were obtained, respectively. Magnetic properties of these two complexes are rationally explained by the difference in the arrangement of magnetic orbitals. In the chloride complex an NO group axially coordinates to copper ion, leading to weak ferromagnetic coupling, while in the perchlorate complex an equatorial coordination leading to antiferromagnetic interaction occurs.[1a,b] Thus, the magnetic properties of Py-NN copper complexes can be controlled by modifying a counter anion.

Metal Complexes of Im-NN Ligand

Molecular structure of $(Im\text{-}NN)_2Cu(ClO_4)_2$ is centrosymmetric tetragonally distorted octahedral, and apical sites are occupied by the two weakly coordinated perchlorate ions. For the complex the chelate ring is relatively planar compared to that in a pyridyl derivative, and intraligand hydrogen bond is present between NH site and non-coordinating NO group. The short contact between the NH group and the neighboring perchlorate oxygen atom makes up the close packing of the complex in the crystal.

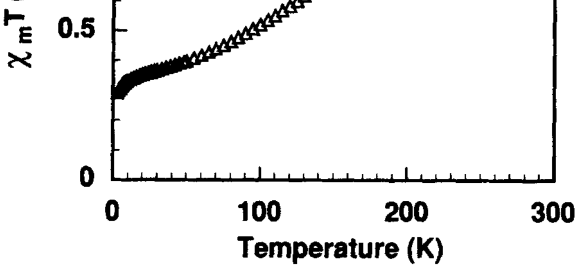


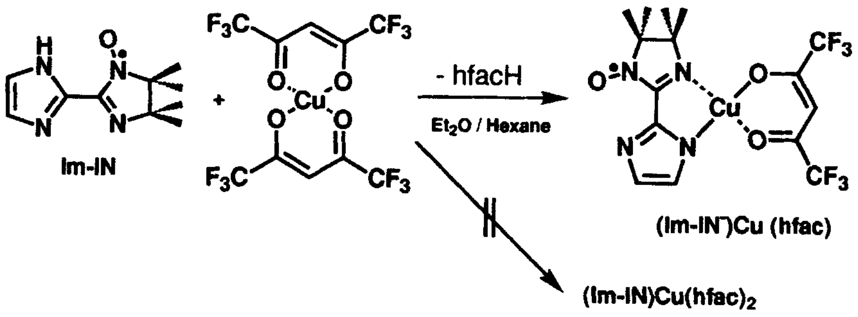
FIGURE 2 Temperature dependence of $\chi_m T$ for $(Im\text{-}NN)_2Cu(PF_6)_2$.

The $\chi_m T$ value of $(\text{Im-NN})_2\text{Cu}(\text{ClO}_4)_2$ at 300 K was almost equivalent to the value calculated by a non-interacting three spin system. The value rapidly increased with a lowering temperature down to 75K and reached a maximum. Afterward the value gradually decreased and reached plateau at 37 K. Interestingly the change in $\chi_m T$ value show the thermal hysteresis effect between cooling process and heating one. While the several NN metal complexes have been reported to show abrupt spin transition,[8] thermal hysteresis phenomena have not been described yet.

In order to investigate the mechanism of spin transition, several complexes with different metal ions or counter anions were prepared. The Ni complex of Im-NN was obtained as a dark blue powder, had also intramolecular ferromagnetic interaction between nickel ion and two radical ligands. However the complex exhibited no thermal hysteresis effect. Copper complexes with other anions such as chloride, tetrafluoroborate, and hexafluorophosphate were also prepared, and exhibited antiferromagnetic interaction between copper ion and NO group (FIGURE 2).

Metal Complexes of Im-IN Ligand

Iminonitroxides have such a strong binding properties to metal ion at imino nitrogen as to coordinate to less acidic and less crowded metal ions. For these reasons, various metal complexes of pyridyl iminonitroxide have been reported.[9] However, investigation on the other chelate formation than pyridyl derivative has been undeveloped. Since we recently obtained the new iminonitroxide derivative, Im-IN, its binding property to metal ion was studied. In contrast to Im-NN, Im-IN readily react with Cu(hfac)_2 to give a



SCHEME 2

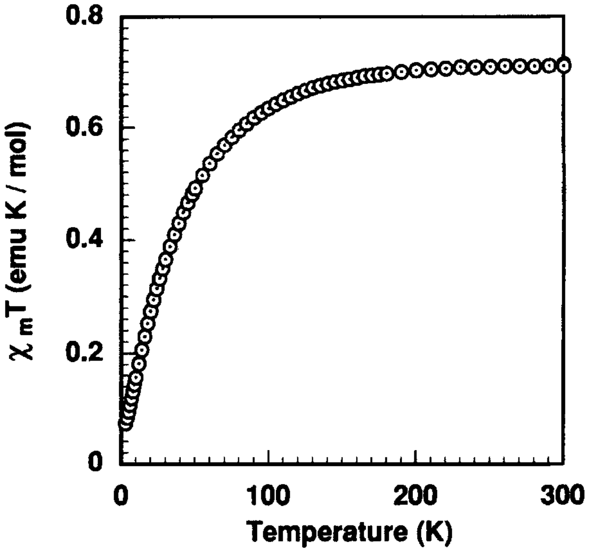


FIGURE 3 Temperature dependence of $\chi_m T$ for **(Im-IN$^-$)Cu(hfac)**.

dark blue material (mp. 256-257 °C), which was insoluble in various solvents, but showed a satisfactory analytical data (C; 38.3, H; 2.8, N; 11.7, F; 24.9; Cu; 12.9 (%)) corresponding to the ligand exchanged species, (Im-NN$^-$)Cu(hfac) (SCHEME 2). The ligand exchange reaction was not observed for Py-IN complexes.

The $\chi_m T$ of the complex at room temperature is 0.71 emu K/ mol, which is lower than that of a non-interacting two spin system. The $\chi_m T$ value rapidly decreases with a lowering temperature and reaches 0.07 emu K/mol at 3 K, indicating that inter- or intra-molecular interaction is antiferromagnetic(FIGURE 3). Structural analysis of (Im-NN$^-$)Cu(hfac) is in progress.

Overall, modification of counter anion or introduction of hydrogen bonding site to radical complexes is a useful way of designing molecular assembly with interesting magnetic property.

ACKNOWLEDGMENT

This work was supported by the Grant-in-Aid for Scientific Research (No. 07750980) form the Ministry of Education, Science and Culture, Japan.

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