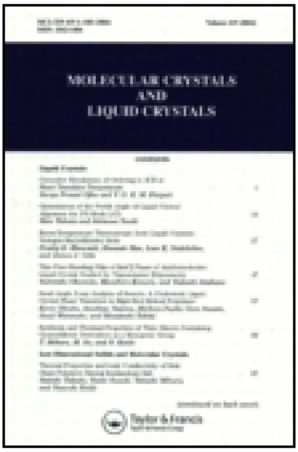

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# LOW-DIMENSIONAL MAGNETIC SYSTEMS WITH S=1, 3/2 AND 2

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## Abstract

New Haldane gap compounds with S=1 have been characterized by single-crystal X-ray analyses and magnetic measurements. From these results, it has been found that the magnitude of the Haldane gaps can be controlled by substituting the bridging groups and in-plane ligands. The magnetic measurements of quasi-one-dimensional halogen-bridged binuclear Ru complexes with S=3/2, $Ru_2(CH_3COO)_4X$ (X=Cl, Br and I) have revealed that the Br- and I-bridged compounds show one-dimensional antiferromagnetic interactions but no spin-Peierls transition over the temperature range measured, while the Cl-bridged compound shows no magnetic interaction among binuclear $Ru_2$ units through the bridging $Cl^-$ ions along the chain but spin-crossover behavior between S=3/2 and 1/2 in the binuclear $Ru_2$ unit. The oxalato-bridged $Fe^{2+}$ compound with S=2, Fe(ox).$2H_2O$ has no Haldane gap but shows metamagnetism under the high magnetic field.

## INTRODUCTION

Low-dimensional magnetic systems are of current interest because they show peculiar quantum effects. A striking phenomenon is the strong spin-dependent behavior at T=0, of the one-dimensional Heisenberg antiferromagnet (1D-HAF). Haldane predicted that for the integer spin values S the 1D-HAF exhibits a singlet ground states separated from the first triplet excited state by an energy gap Eg (Haldane gap), while for the half-integer spin values S the 1D-HAF has a gapless spectrum of the excitations.[1] More recently, Guo, Kennedy and Mazumdar have theoretically studied the low-dimensional magnetic system with the integer and half-integer spin values, and found qualitative differences between integer and half-integer spins.[2] That is, their results indicate the absence of spin-Peierls transitions in systems with integer spins and suggest transitions in systems with half-integer spins. Although there have been many theoretical works on low-dimensional magnetic systems,[3] only a few systematic works on syntheses and magnetic measurements have been carried out so far.[4] In this paper, we will describe the magnetic properties of quasi-one-dimensional metal coordination compounds with spin values of 1, 3/2 and 2.

## S=1 SYSTEMS

Since Haldane's prediction, only four compounds are regarded as Haldane gap compounds, that is, $[Ni(en)_2(NO_2)]ClO_4$ (abbreviated as NENP), $[Ni(tn)_2(NO_2)]ClO_4$ (NINO), $(CH_3)_4N[Ni(NO_2)_3]$ (TMNIN), and $[Ni(tn)_2N_3]ClO_4$ (NINAZ), where the former three compounds consist of the $NO_2^-$-bridged one-dimensional structures and the last one consists of $N_3^-$-bridged one-dimensional structures.[5] Therefore, we have synthesized new compounds with S=1, determined whether or not they are Haldane gap compounds, and investigated the effect of the in-plane ligands and bridging groups on Haldane gaps.

As in-plane ligands, we used 2,2-dimethylpropylenediamine (dmpn), 1,4,8,12-tetraazacyclopentadecane ([15]ane$N_4$) and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($Me_6$[14]ane$N_4$). The compounds were obtained by mixing of $[NiL](ClO_4)_2$ (L= in-plane ligands) and $NaN_3$ in aqueous solutions. Single-crystals were obtained by slow evapolation. Diffraction data were collected at room temperature on a four-circle diffractometer (Rigaku AFC-5R) with a rotating anode generator and Mo K$\alpha$ radiation ( $\lambda$ =0.71069 A) monochromated by a graphite plate. Crystal data of $[Ni(Me_6[14]aneN_4)N_3]ClO_4$ are: formula

$NiClO_4N_7C_{16}H_{36}$, Molecular weight=484.7, orthorhombic, space group $Pna2_1$, a=12.098(8), b=16.124(3), C=11.519(3) A, V=2245(2) $A^3$, Z=2, R=0.039 and Rw=0.048.

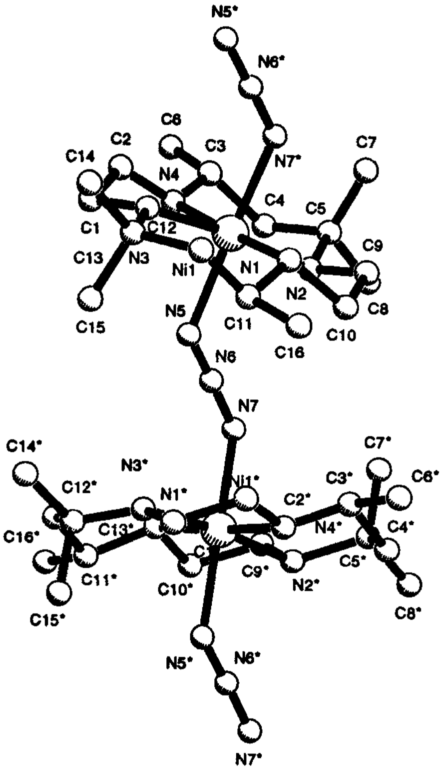

FIGURE 1 Crystal structure of $[Ni(Me_6[14]aneN_4)N_3]ClO_4$.
Ni-N1=2.068(10) A
Ni-N2=2.11(1)
Ni-N3=2.09(1)
Ni-N4=2.075(9)
Ni-N5=2.22(2)
Ni-N7=2.13(2)

The structure of $[Ni(Me_6[14]aneN_4)N_3]ClO_4$ consists of linear chains where nickel ions and azido groups alternate following the sequence $-Ni-N_3-Ni-N_3-$ as shown in Fig. 1. Each chain is separated by $ClO_4^-$ ions. The Ni ions are surrounded pseudo-octahedrally by four nitrogens of $Me_6[14]aneN_4$ ligands and two nitrogen atoms of two azido groups in the trans form. The structure of $[Ni(Me_6[14]aneN_4)N_3]ClO_4$ is almost similar to that of $Ni(dmpn)_2N_3(ClO_4)$ previously reported,[6] except for the difference in repeating fashions such as -Ni-Na-Nb-Nc-Ni-Na-Nb-Nc-Ni- for $[Ni(Me_6[14]aneN_4)N_3]ClO_4$ and -Ni-Na-Nb-Na-Ni-Na-Nb-Na-Ni- for $[Ni(dmpn)_2N_3]ClO_4$.

The magnetic susceptibilities of polycrystalline samples of these compounds show a rounded maximum at about 90K for $[Ni(dmpn)_2N_3]ClO_4$,[5] about 70K for $[Ni(Me_6[14]aneN_4)N_3]ClO_4$ and about 60K for $[Ni([15]aneN_4)N_3]ClO_4$, and then decrease rapidly as shown in Fig. 2, indicating the existence of energy gaps.[5] The solid lines are the

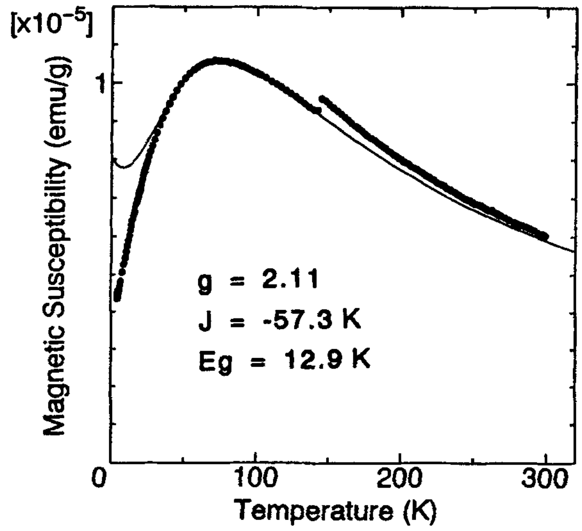

FIGURE 2 Magnetic susceptibilities of $[Ni(Me_6[14]aneN_4)N_3]ClO_4$.

theoretically calculated susceptibilities of S=1 linear-chain Heisenberg antiferromagnet using the equation of $\chi = N\beta^2 g^2/kT\{(2+0.0194X+0.777X^2)/(3+4.346X+3.232X^2+5.834X^3)\}$ $(X=|J|/kT)$. In order to estimate the energy gap Eg (Haldane gap), the low temperature data below 10K are fitted by the following equation: $\chi(T) = \chi_0 + \chi_1 \exp(-Eg/kT)$. Their values of g, J and Eg are listed in Table I.

TABLE I

| Compound | g | J/K | Eg/K |
|---|---|---|---|
| $[Ni(dmpn)_2N_3]ClO_4$ (1) | 2.21 | -70.6 | 21.6 |
| $[Ni(Me_6[14]aneN_4)N_3]ClO_4$ (2) | 2.11 | -57.3 | 12.9 |
| $[Ni([15]aneN_4)N_3]ClO_4$ (3) | 2.07 | -51.8 | 13.0 |

The existence of the Haldane gap has been also proved by the high field magnetization measurements.[5,6] The relation between Haldane gaps and intra-chain exchange energies of these compounds are shown in Fig. 3, along with those of other Haldane gap compounds. All data obey roughly the theoretical relation, $Eg=0.41|J|$. The absolute values of J and Eg of the $N_3^-$-bridged compounds are larger than those of the

$NO_2^-$-bridged compounds. This is due to the stronger coordination ability of $N_3^-$ to Ni ions compared with that of $NO_2^-$. In the same $N_3^-$-bridged compounds, the absolute values of the J and Eg are in the order; NINAZ > $[Ni(dmpn)_2N_3]ClO_4$ > $[Ni(Me_6[14]aneN_4)N_3]ClO_4$ ~ $[Ni([15]aneN_4)N_3]ClO_4$. This is due to the differences of $Ni\text{-}N_3^-$ distances, which might be caused by the bulkiness of the in-plane ligands. From these results, it has been found that the magnitude of the Haldane gaps can be controlled by substituting the bridging groups and in-plane ligands.

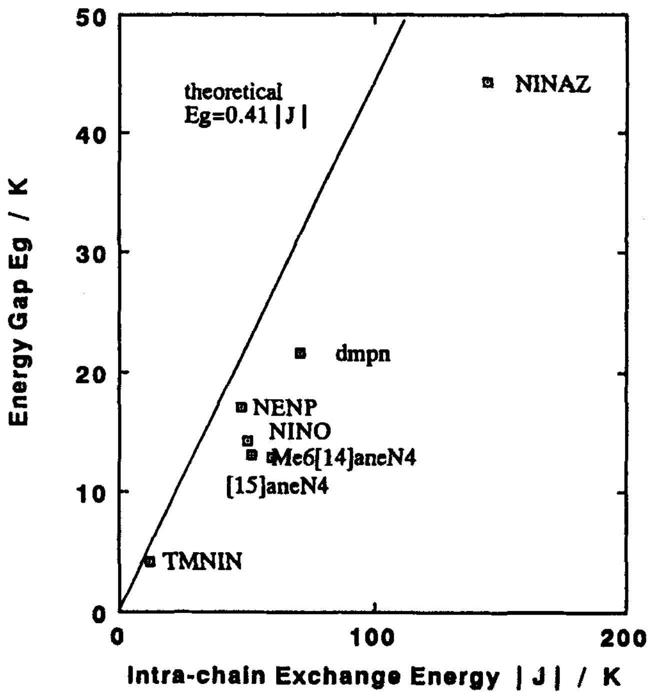

FIGURE 3 Relation between Haldane gaps and exchange energies

S=3/2 SYSTEMS

The $Ru_2(CH_3COO)_4X$ (X=Cl, Br and I) consist of quasi-one-dimensional halogen-bridged binuclears, where each Ru atom is bridged by four $CH_3COO^-$ to form a lantern structure. Since each bridging halogen is located at midpoint between neighboring two binuclear $Ru_2$ units, the oxidation state of each Ru atom is +2.5 and each binuclear unit has

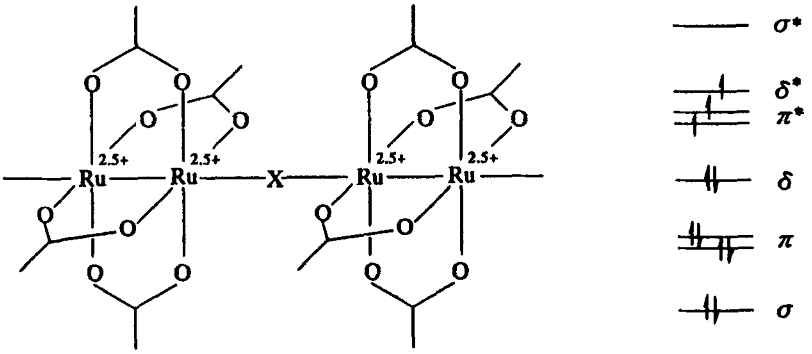

FIGURE 4 Proposed crystal structure and electronic structure.

three unpaired electrons, that is, S=3/2 shown in Fig. 4.[7]

The magnetic susceptibilities of $Ru_2(CH_3COO)_4X$ (X=Br and I) show rounded maxima at about 20 K and decrease to finite values as the

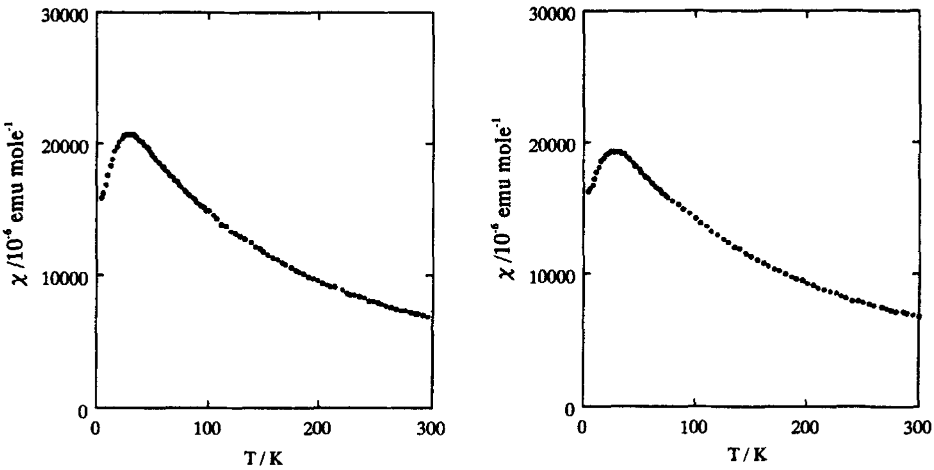

FIGURE 5 Magnetic susceptibilities of $Ru_2(CH_3COO)_4X$ (X=Br, left; I, right).

temperature decreases as shown in Fig. 5, indicating the antiferromagnetic interactions between unpaired electrons on each binuclear units, through the bridging halogens. In spite of their half-integer spin values, no spin-Peierls transitions have been observed over the temperature range measured.

On the other hand, $Ru_2(CH_3COO)_4Cl$ does not show a one-dimensional antiferromagnetic behavior. This is due to the weaker inter-binuclear interaction through the chloro-bridging compared with the bromo- and

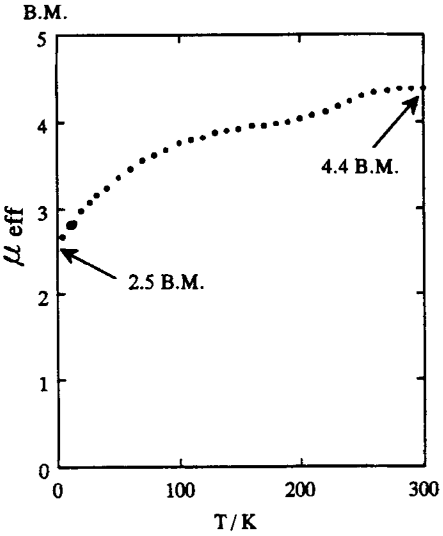

FIGURE 6 Magnetic moments of $Ru_2(CH_3COO)_4Cl$

iodo-bridging. The temperature dependent magnetic moments of this compound are shown in Fig. 6, indicating the spin-crossover behavior between S=3/2 at room temperature and 1/2 at low temperature in the binuclear unit.[8]

## S=2 SYSTEMS

So far no Haldane gap compounds with S=2 have been reported. Therefore, we prepared Fe(ox).$2H_2O$ (ox=$C_2O_4^{2-}$),[9] which is assumed to have an oxalato-bridged linear-chain structure and a pseudo-octahedral structure around iron ions with four oxygen atoms of two oxalato ligands and two oxygen atoms of two water molecules in trans form. The temperature dependence of the magnetic susceptibility shows a rounded maximum at about 40K, and then decrease as the temperature decreases (Fig. 7). However, below 10 K, the magnetic susceptibility is almost constant. This is considered to be due to the three-dimensional interaction. Therefore, this is not considered to be a Haldane gap compound. Then, we measured the magnetization of this compound. It shows the metamagnetism with two steps, which means the phase transition between antiferromagnet and ferromagnet (Fig. 8).[10] The magnetic moment is about 4 BM at 20 T, which corresponds to four spins. It indicates that above 20 T, four spins on each Fe atom are arranged ferromagnetically.

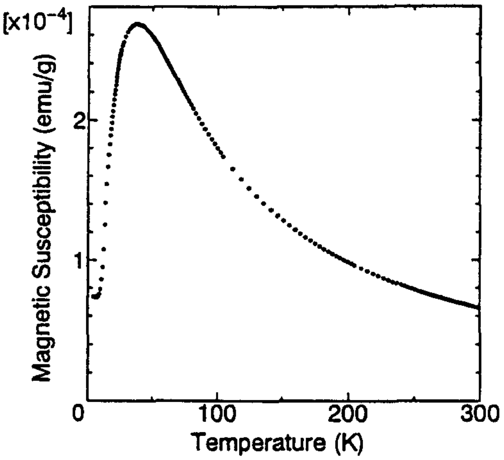

FIGURE 7 Magnetic susceptibility of Fe(ox).$2H_2O$.

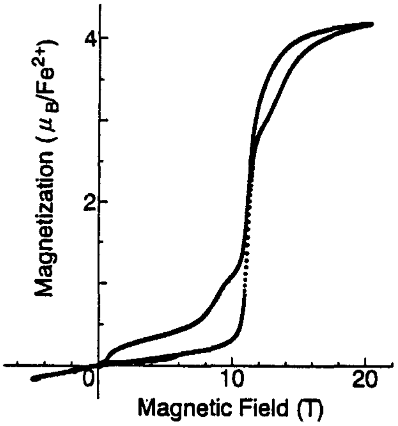

FIGURE 8 Magnetization

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