Ferromagnetic Interaction Between $[Ni(bdt)_2]^-$ Anions in $[Mn_2(Saloph)_2(\mu\text{-OH})][Ni(bdt)_2](CH_3CN)_2$

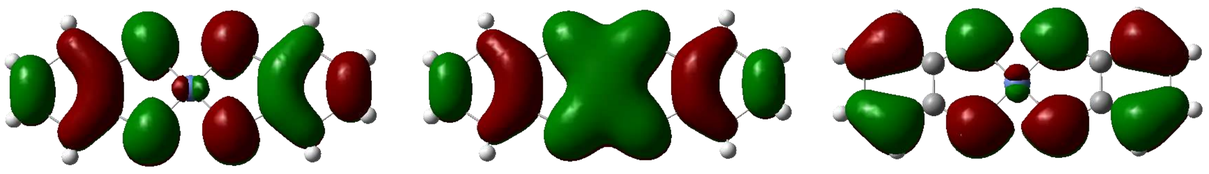
Junichi Nishijo and Nobuyuki Nishi

Institute for Molecular Science, Japan

Introduction

$[Ni(bdt)_2]^-$: SOMO and NHOMO spread over the benzene ring of the anion.

Suitable for constructing strong intermolecular exchange interaction

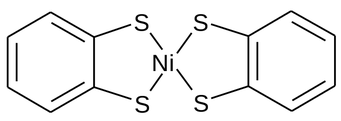


SOMO **NHOMO** **NHOMO–1 (close to NHOMO)**

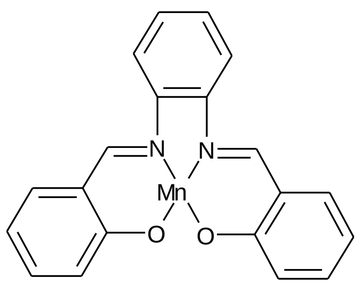
In this presentation, we will show the structure and the magnetic property of the new molecule-based magnetic material,

$[Mn_2(Saloph)_2(\mu\text{-OH})][Ni(bdt)_2](CH_3CN)_2$

where a ferromagnetic interaction between $[Ni(bdt)_2]^-$ anions is observed.



$[Ni(bdt)_2]^-$



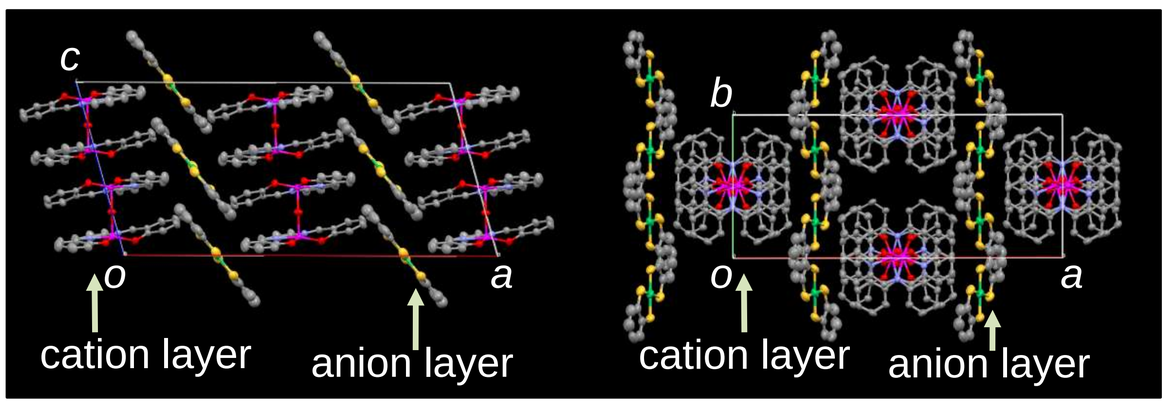
$[Mn(Saloph)]^+$

Crystal structure

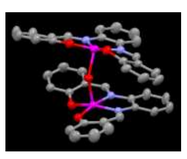
Sample preparation:

Acetonitrile solution of TBA$[Ni(bdt)_2]$ and $[Mn(Saloph)]ClO_4$ are mixed and standing for 1 week.

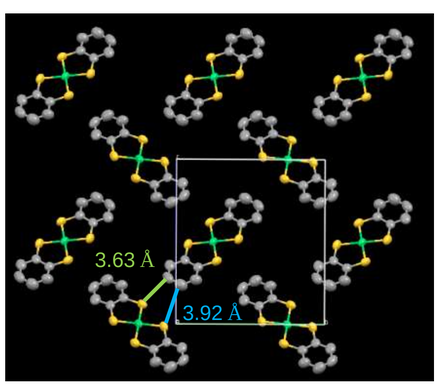
Crystal Structure



Alternately stacked layered structure
- 1D chain of $[Mn_2(Saloph)_2(\mu\text{-OH})]^+$
- 2D sheet of $[Ni(bdt)_2]^-$

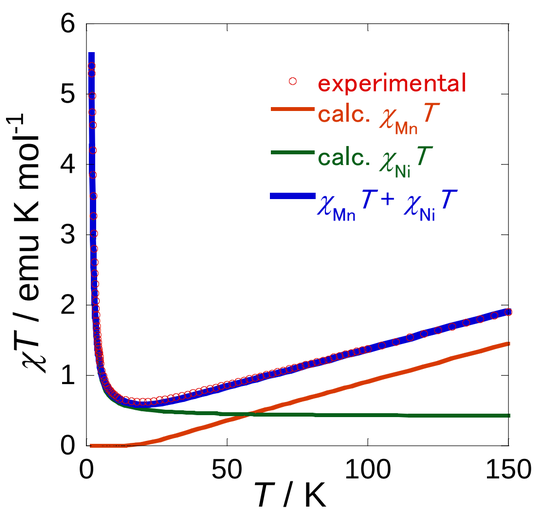


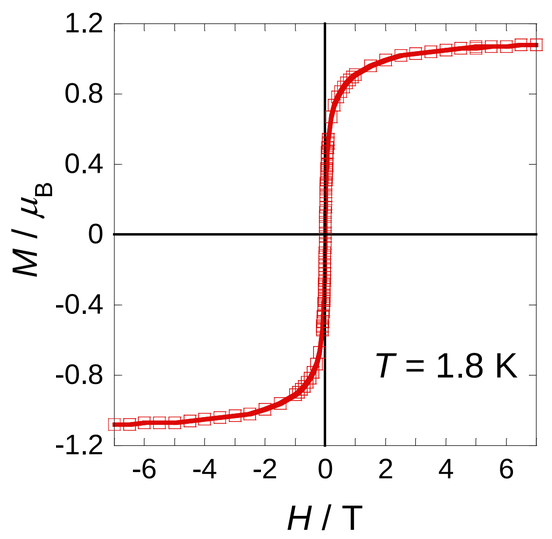
$[Mn_2(Saloph)_2(\mu\text{-OH})]^+$ binuclear complex
Strong antiferromagnetic Mn-Mn interaction



Anion layer:
- Square lattice
- T-shaped stacking pattern
- Short CH-S contacts (3.63 and 3.92 Å)

Magnetic property





The susceptibility is well described by the sum of
- **S = 2 Van Vleck dimer model (antiferromagnetic binuclear complex, $2J_{Mn}$ = -93 K)**

and
- **S = 1/2 Heisenberg ferromagnetic square lattice (constant coupling approximation, $2J_{Ni}$ = +4.5 K)**

$$\chi_{Mn} = \frac{N g_{Mn}^2 \mu_B^2}{k_B T}\left[\frac{30 + 14x^8 + 5x^{14} + x^{18}}{9 + 7x^8 + 5x^{14} + 3x^{18} + x^{20}}\right], \quad \chi_{Ni} = \frac{N g_{Ni}^2 \mu_B^2}{4 k_B T}\exp\left(\frac{2J_{Ni}}{k_B T}\right)$$

$$x = \exp\left(-\frac{J_{Mn}}{k_B T}\right)$$

Ferromagnetic interaction between anions!

Origin of the ferromagnetic interaction

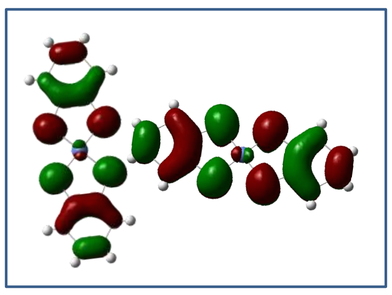
T-shaped stacking:

→ Small overlap between SOMOs (orthogonal)

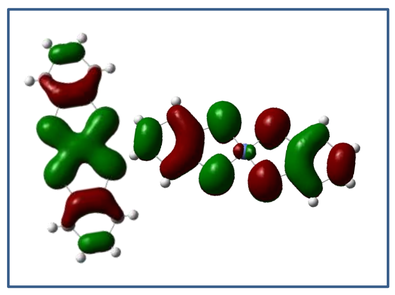
→ Suppress antiferromagnetic interaction

→ Large overlap between SOMO and NHOMO

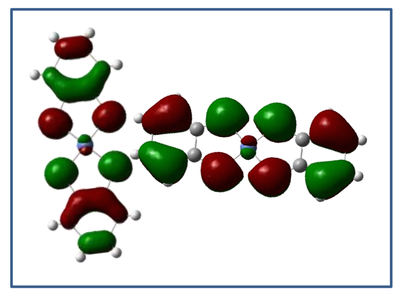
→ Induce ferromagnetic interaction



SOMO-SOMO (orthogonal)

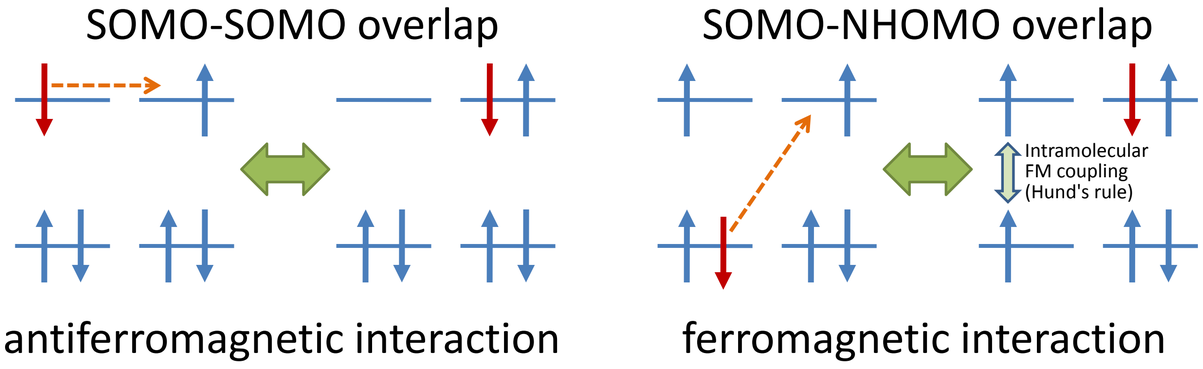


NHOMO-SOMO (overlap)



SOMO-NHOMO-1 (overlap)

Orbital overlap and exchange interaction



antiferromagnetic interaction

ferromagnetic interaction

Summary

New magnetic material $[Mn_2(Saloph)_2(\mu\text{-OH})][Ni(bdt)_2](CH_3CN)_2$
- Antiferromagnetic binuclear complex $[Mn_2(Saloph)_2(\mu\text{-OH})]^+$
- Ferromagnetic square lattice of $[Ni(bdt)_2]^-$

Origin of the ferromagnetic interaction
- SOMO-SOMO orthogonality (suppress AF interaction)
- SOMO-NHOMO overlap (induce FM interaction)