Structure and Intra-Dimer Ferromagnetic Interaction of $[MnX_2Saloph(NCS)]$ (X = Cl, Br, I)

Junichi Nishijo and Tomohiro Yoshida (Meisei University)

1. Introduction

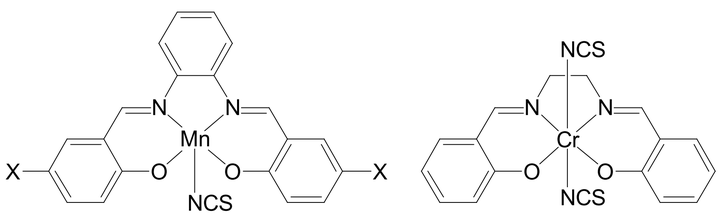
Inter-molecular ferromagnetic exchange interaction is useful for many purposes:

- Magnetic data storage
- Single molecule and single chain magnets
- Magneto-optical devices etc.

However, ferromagnetic interaction is somewhat rare in molecule-based magnetic materials because SOMO overlaps of adjacent magnetic molecules promptly bring antiferromagnetic interactions, which is generally much stronger than ferromagnetic one. Therefore, it is significant to find a new ferromagnetically coupled systems.

Here, we report three new ferromagnetically-coupled molecule-based materials $[MnCl_2Saloph(NCS)](PhCN)$, $[MnBr_2Saloph(NCS)]$ and $[MnI_2Saloph(NCS)]$.

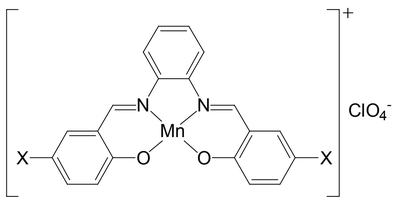
The complexes are obtained by the in-situ ligand transfer from $[CrSalen(NCS)_2]^-$ to $[MnX_2Saloph]^+$.

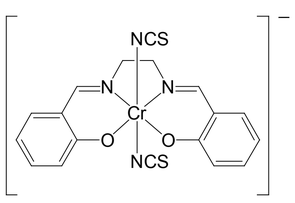


$[MnX_2Saloph(NCS)]$ X = Cl, Br, I

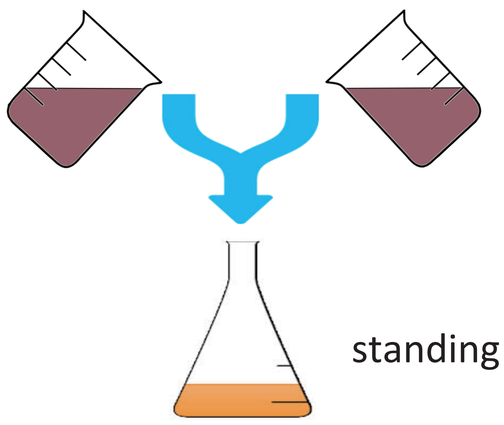
$[CrSalen(NCS)_2]^-$

2. Experimental





ca. 20 mg in solution (25 ml)



ca. 20 mg in solution (25 ml)

standing for a week...

X = Cl — Solvent: $PhCN + CH_2Cl_2$ (1:1)

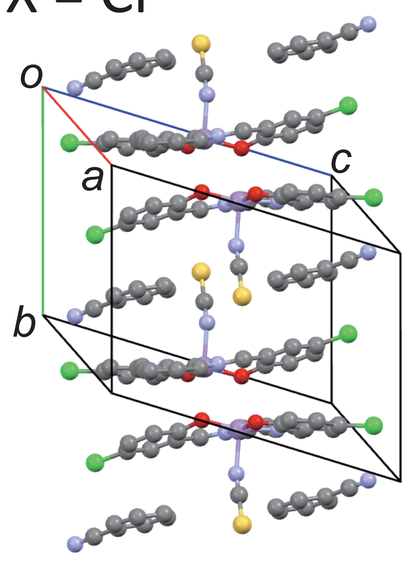
※No single crystal was obtained from $CH_3CN + CH_2Cl_2$

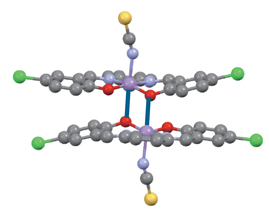
X = Br, X = I — Solvent: $CH_3CN + CH_2Cl_2$ (1:1)

Structural analysis: Rigaku R-AXIS RAPID (Imaging Plate, Mo *K*α)
Initial structure: SIR2004, Refine: Shelxl97
Magnetic measurements: Quantum Design MPMS-XL

3. Crystal structures and magnetism

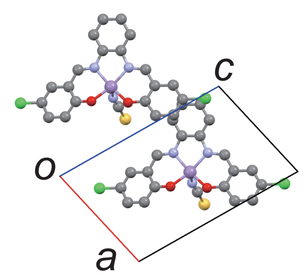
X = Cl





dimer structure

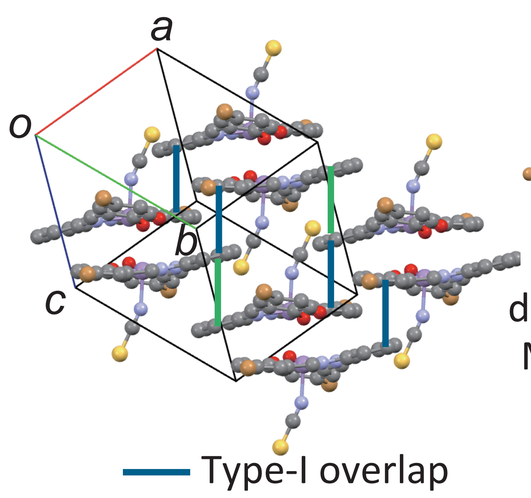
Mn-O: 2.534 Å



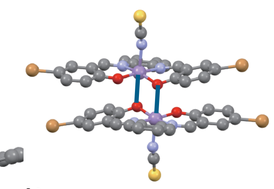
Inter-dime small overlap

C-C: 3.777 Å
C-Cl: 3.758 Å

X = Br, I (isostructural)

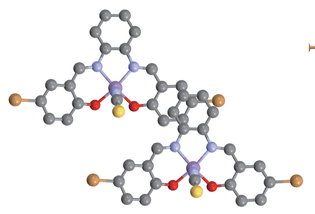


Type-I overlap
Type-II overlap

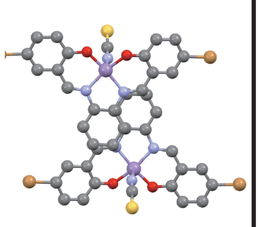


dimer structure
Mn-O
2.537 Å (Br)
2.532 Å (I)

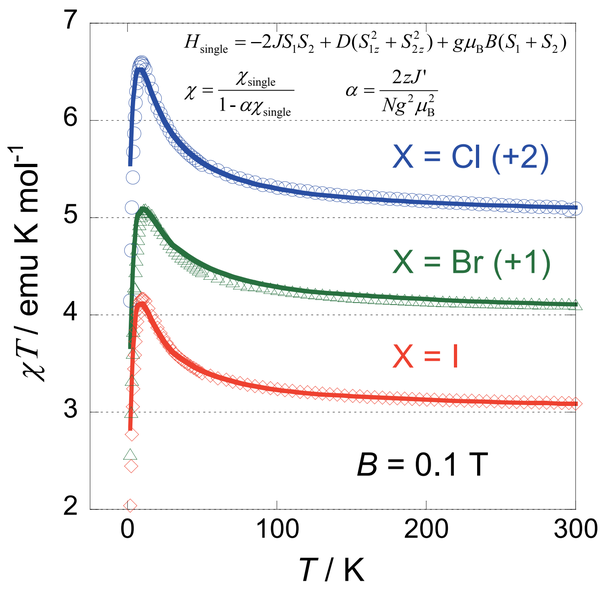
Inter-dime overlaps

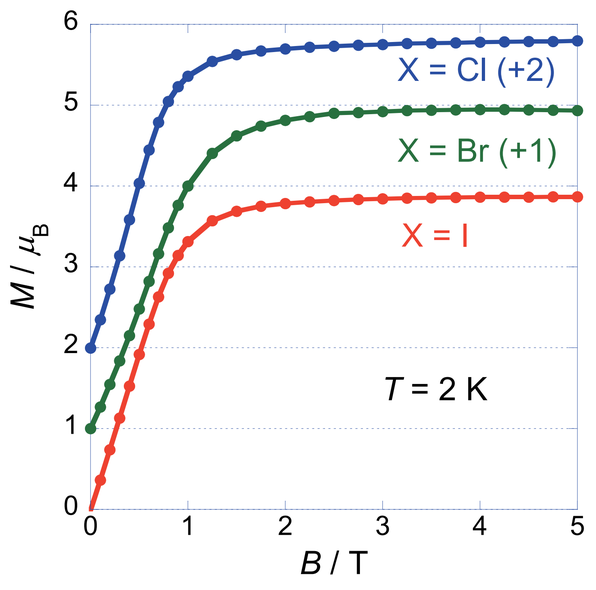


Type I
C-C
3.567 Å (Br)
3.595 Å (I)



Type II
C-C
3.460 Å (Br)
3.434 Å (I)





Intra-dimer intgeraction $2J / k_B$: +6.3 (Cl), +6.2 (Br) and +4.7 K(I)

Inter-dimer intgeraction $2zJ' / k_B$: -0.06 (Cl), -0.20 (Br) and -0.17 K(I)

D = -2.2 (Cl), -2.0 (Br) and -2.3 (I) cm^{-1} *uncertain values

No magnetic transition down to 2.0 K.

4. Conclusion

New dimeric complexes, $[MnX_2Saloph(NCS)]$ (X = Cl, Br, I) are prepared by the slow ligand transfer from $[CrSalen(NCS)_2]^-$ to $[MnX_2Saloph]^+$.

Magnetic measurements reveal that the intra-dimer interactions are ferromagnetic with $2J / k_B$: +6.3 (Cl), +6.2 (Br) and +4.7 K(I) for X = Cl, Br and I, respectively, while the inter-dimer interactions are antiferromagnetic.

The results suggest that the slow decomposition of $[CrSalen(NCS)_2]^-$ is a useful method to construct a ferromagnetically coupled dimer of [Mn(salen-type ligand)(NCS)].

5. Acknowledgement

We thank to Dr. Masaya Enomoto, Tokyo University of Science, for the magnetic measurements.