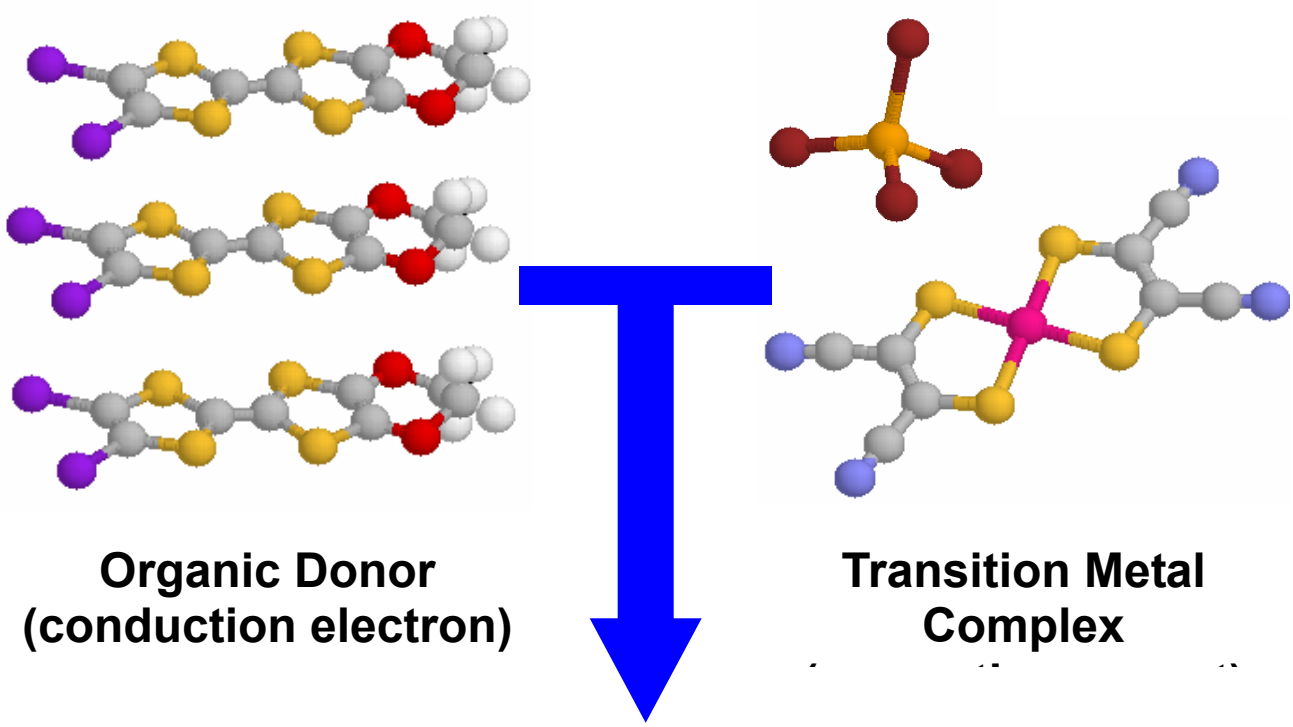
1.Introduction



Organic Donor
(conduction electron)

Transition Metal
Complex

π-d system

coexistence of conductivity and magnetic moment

π-d system is interesting because...

- **Foundation of molecular devices**

  For example
  conductivity controlled by magnetic field
  magnetization controlled by current

- **New strong correlated system**

  Organic strong correlated systems have made progress of material science. Creating new such system is effective way to develop the material science.

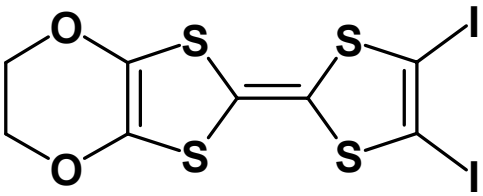
Typical π-d systems

- Antiferromagnetic Metal
- Antiferromagnetic Semiconductor

Ferromagnetic π-d systems are rare.

It is exciting challenge to create Ferromagnetic Metal!

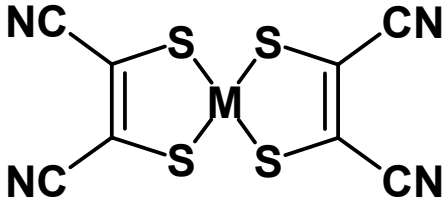
For the purpose, we use following molecules.



DIEDO

Iodine-bonded donors form coordination-bond-like strong interaction between the iodo group of the donor and cyano group or halogen of acceptors[†]. Therefor, strong π-d interaction through short contacts between donor and anion is expected.

[†] Imakubo, T., Sawa, H. and Kato, R. (1995).



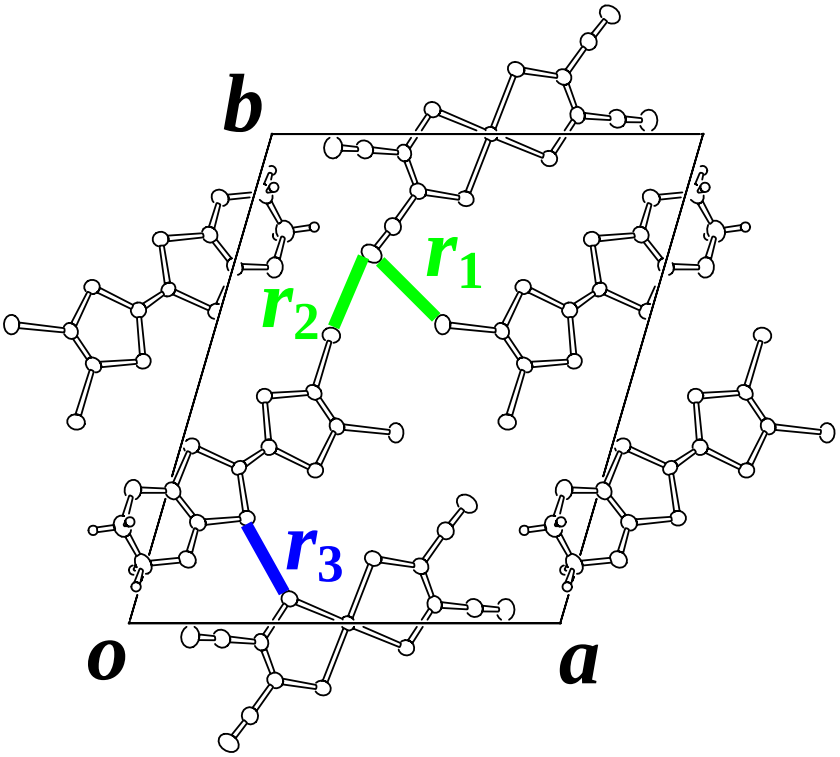
$M(mnt)_2$
(M=Ni,Pt)

These anions have localized magnetic moment *S*=1/2 and some salts of these anions show ferromagnetic interaction. In addition, these anion have cyano group. Consequently, strong π-d interaction is expected with DIEDO.

2.Experimental

X-ray analysis
Resistivity (ambient and high pressure)
Magnetic susceptibility
EPR spectrum

3.Structure

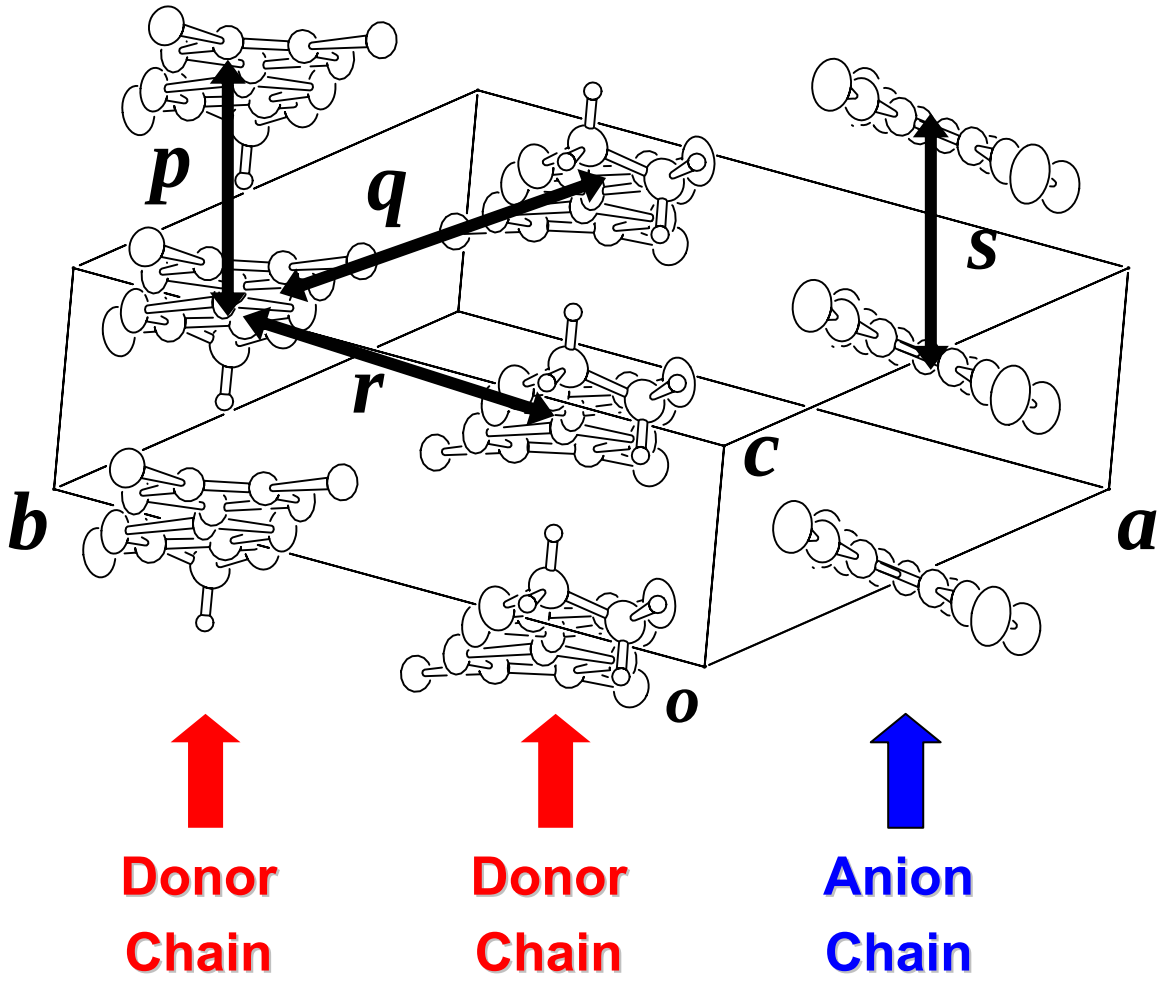


	M=Ni	M=Pt
Space Group	$P\bar{1}$	
a (Å)	13.99(3)	14.077(3)
b (Å)	16.67(4)	16.698(5)
c (Å)	4.18(1)	4.1580(9)
α (°)	98.4(1)	96.51(2)
β (°)	91.3(1)	91.43(2)
γ (°)	74.34(3)	73.77(2)
V (Å^3)	929(2)	932.3(4)
R	0.108	0.0288

	r_1 (N-I), Å	r_2 (N-I), Å	r_3 (S-S), Å
van der Waals	3.65	3.65	3.70
M=Ni	3.04	3.50	3.54
M=Pt	3.05	3.54	3.49

- 1D-chain structure of donor and anion
- Strong CN-I interaction causes short S-S contact between donor and anion (r_3).

4.Overlap Integral



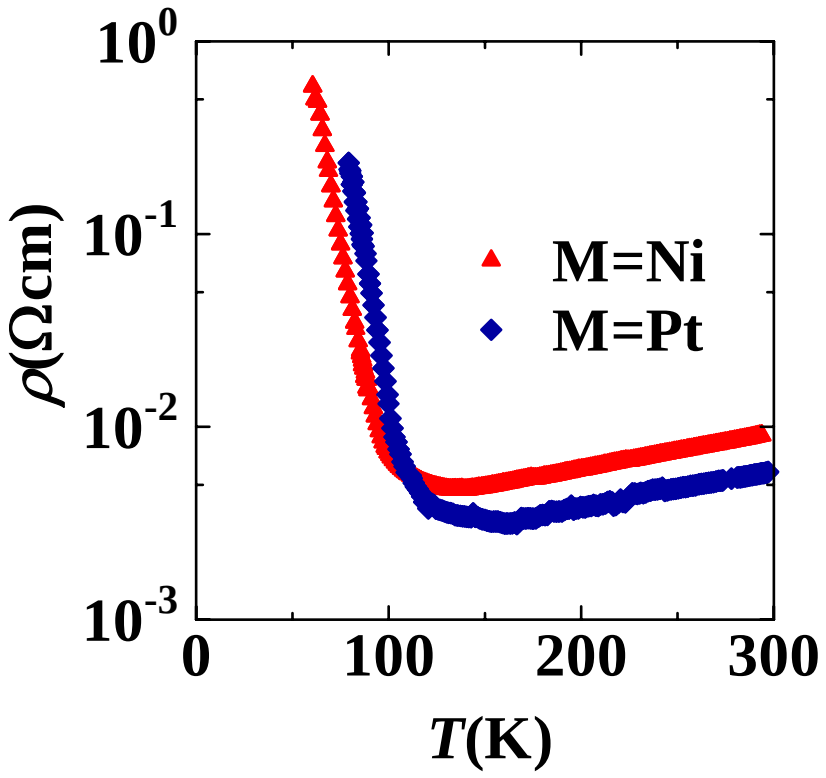
	p (10^{-3})	q (10^{-3})	r (10^{-3})	s (10^{-3})
M=Ni	16.3	3.26	6.54	0.43
M=Pt	16.7	3.00	6.44	0.78

Donor : 1D-3/4 filled band ⇨ 1D-metal

Anion : 1D-*S*=1/2 magnetic chain.

Quite small overlap between SOMOs of adjacent anions.

5.Resistivity at ambient pressure



M=Ni

ρ_{RT} = 110Scm^{-1}
T_{MI} = 88K
E_a ~ 700K

M=Pt

ρ_{RT} = 170Scm^{-1}
T_{MI} = 96K
E_a ~ 800K

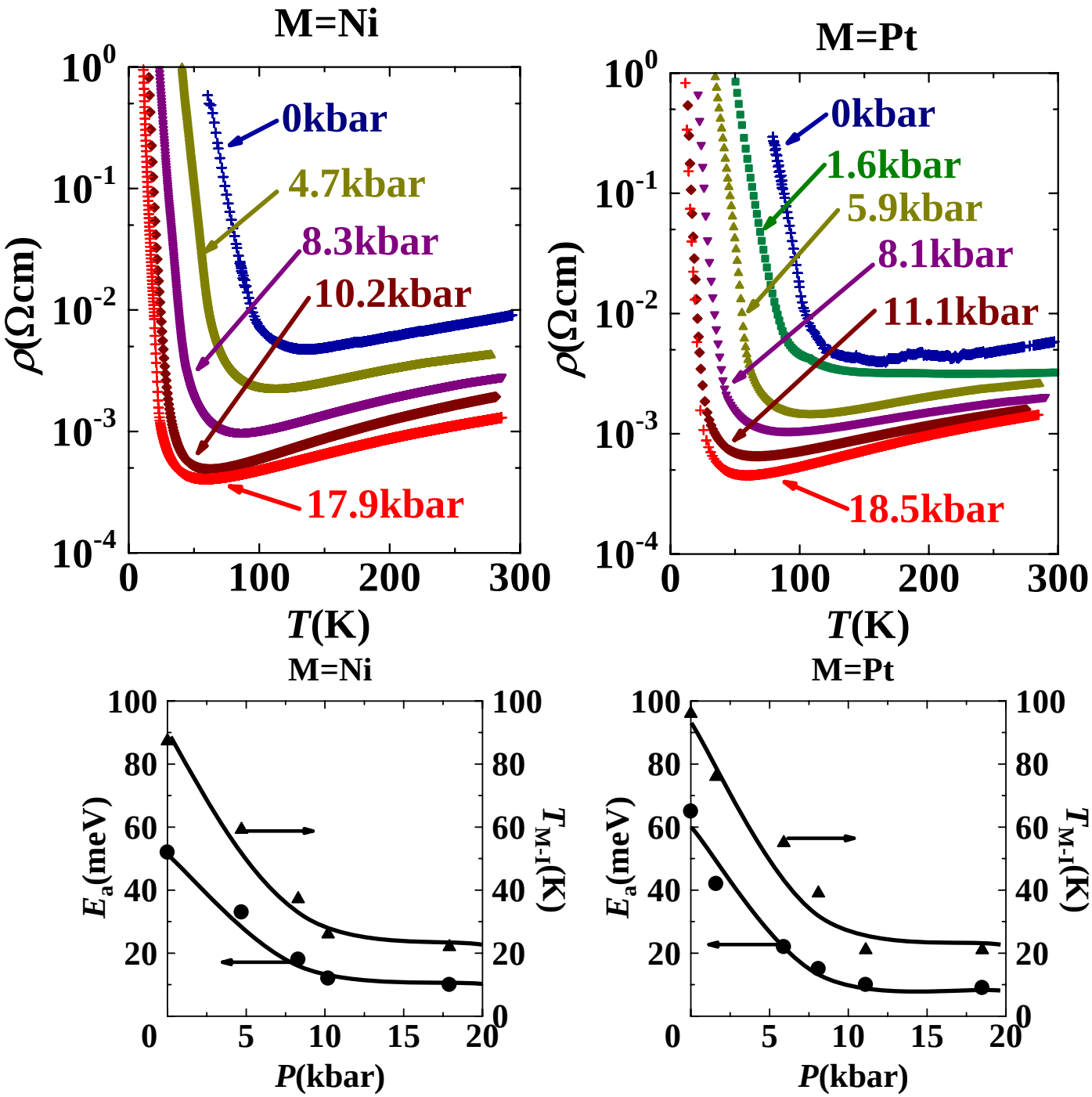
What's the origin of M-I

X-ray oscillation photographs (16K-300K)

Neither significant superlattice reflection nor discontinuous change in the lattice constant is observed.

SDW or $4K_F$ CDW is suggested

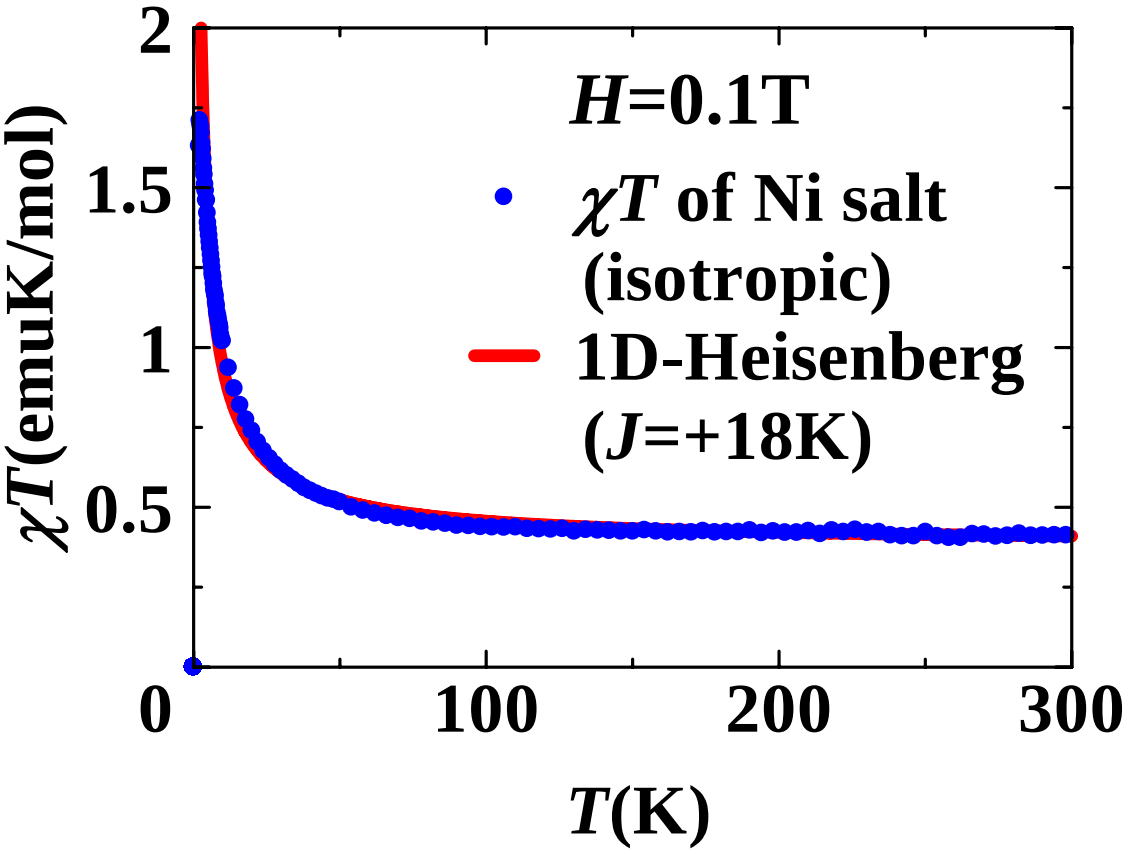
6.Resistivity at high pressure



One dimensionality is kept at high pressure because donor chains are sandwiched between anion chains.

M-I transition is not suppressed by

7.Magnetic susceptibility of Ni salt



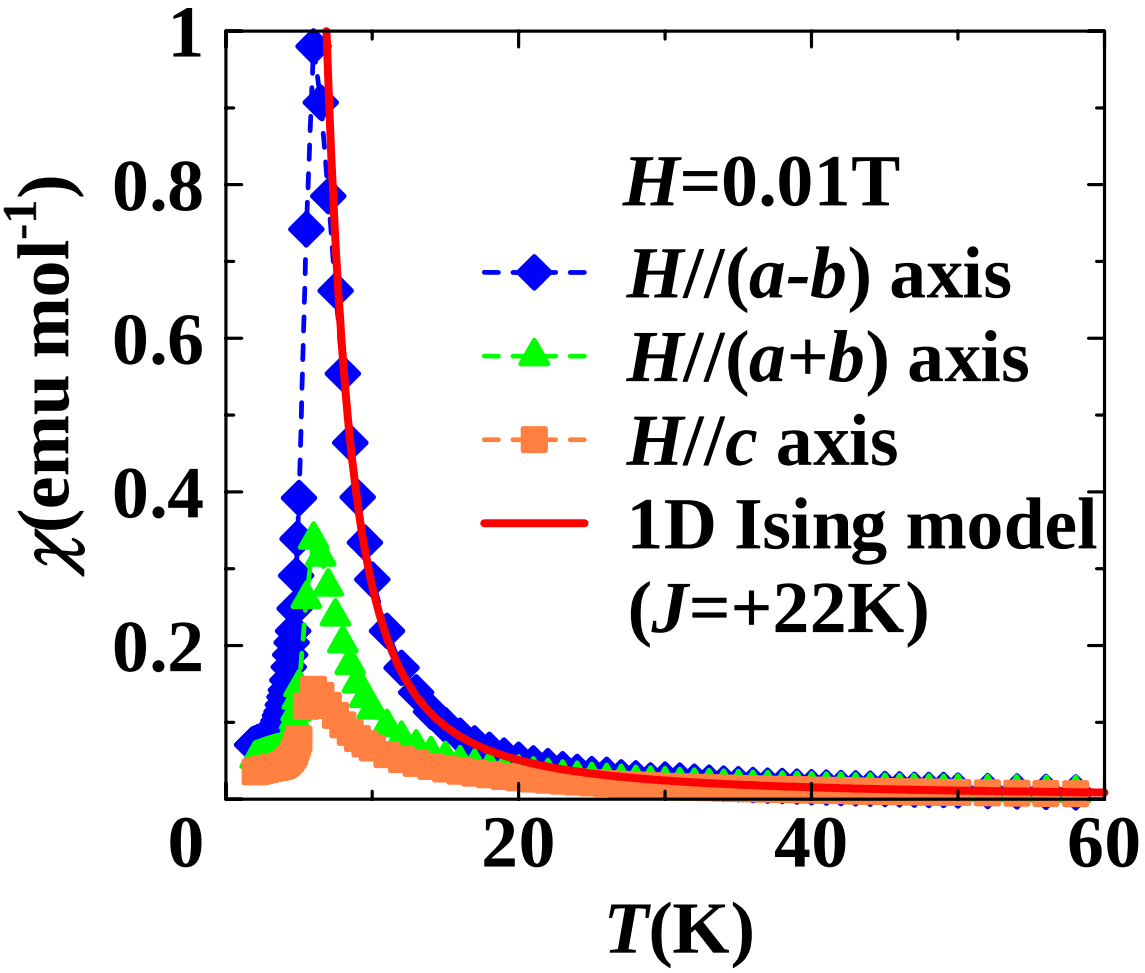
χT value increasing at low

Ferromagnetic interaction between anion spins!

No magnetic transition

Natural consequence of 1D Heisenberg spin system

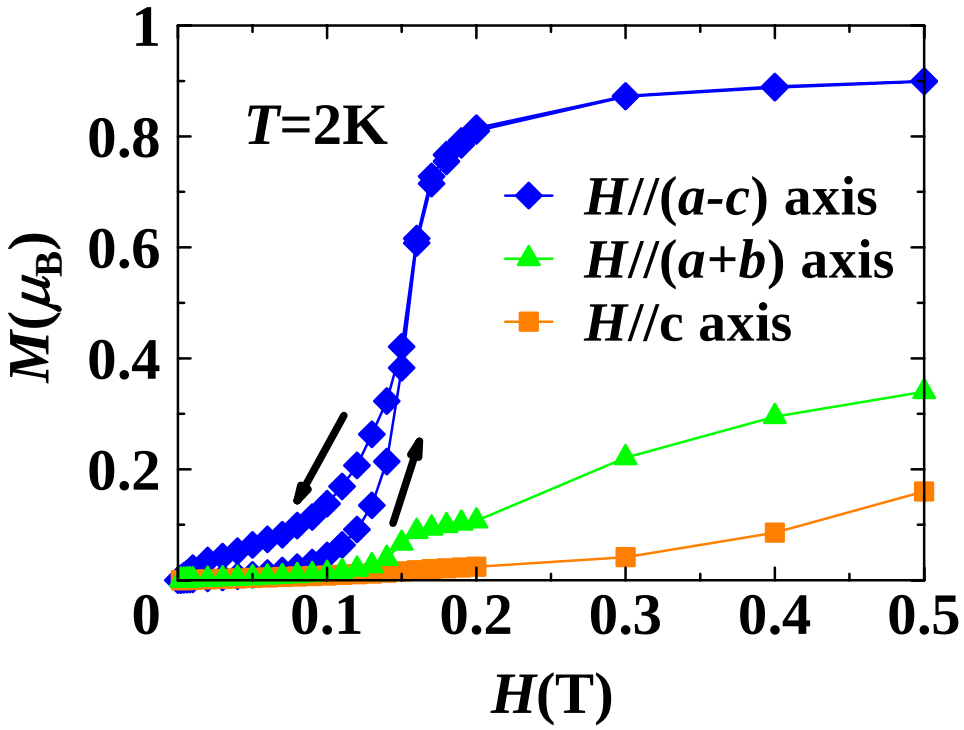
8.Magnetic susceptibility of Pt salt



1D ferromagnetic Ising spin system

- **Ising spin (large anisotropy)**
  Due to large spin-orbit interaction of Pt
- **Ferromagnetic behavior (T>7K)**
  Intrachain strong ferromagnetic interaction (J~22K)
- **Antiferromagnetic transition (T_N=5.5K)**
  Weak interchain antiferromagnetic interaction.
  Large magnetic anisotropy enhance the role of inter chain dipole-dipole interaction.

Magnetization curve of Pt salt



Metamagnetic transition field H_{MM}~0.15T

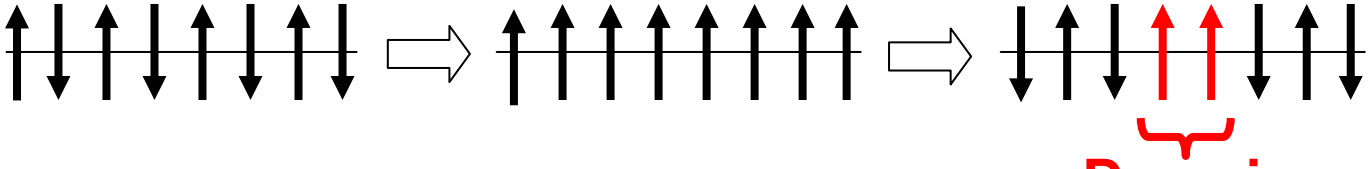
↳Inter chain interaction J_{inter}~-0.06K

J_{inter} is comparable to the contribution of the dipole-dipole interaction.

Hysteresis loop at low field

↳Contribution of domain wall

H=0T *H*>0.2T *H*=0.1T

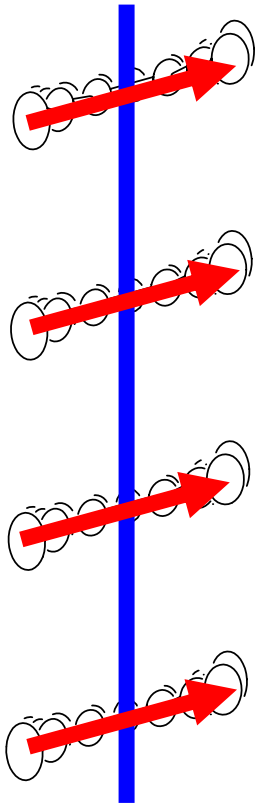


Domain Wall

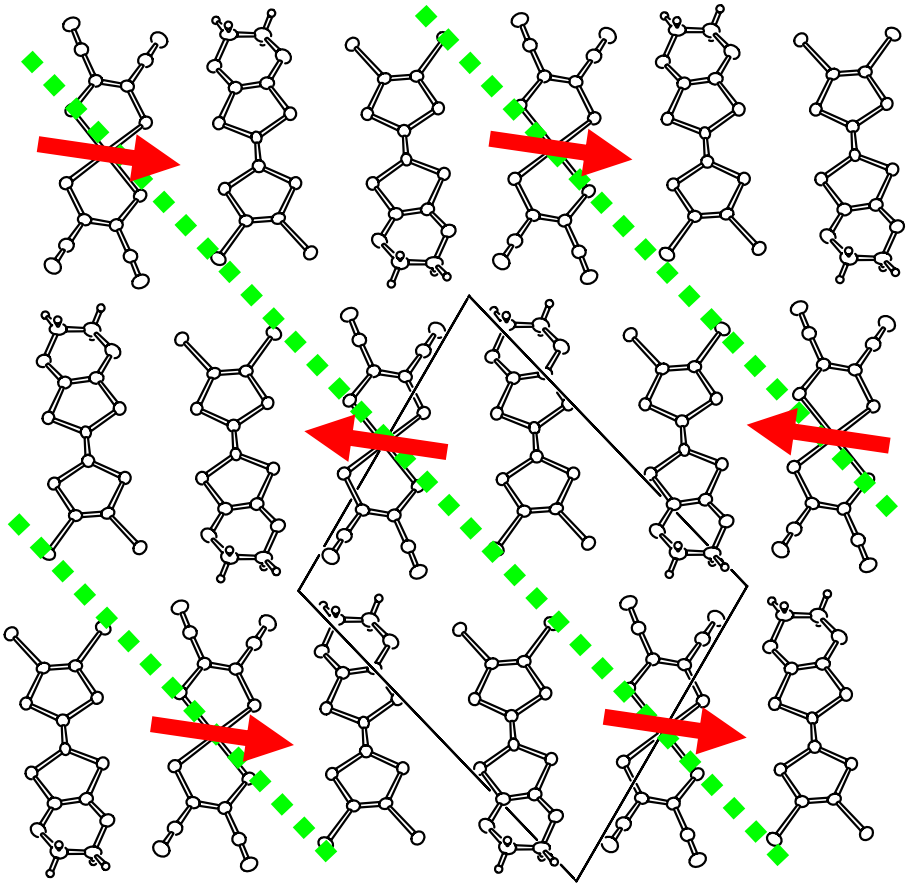
↑ = represents the ferromagnetic ordered anion chain viewed from stacking axis

9.Spin structure of Pt salt

Intra chain



Inter chain



Ferromagnetic
(*J* ~+22K)

Antierromagnetic
(dipole-dipole, *J* ~-0.06K)

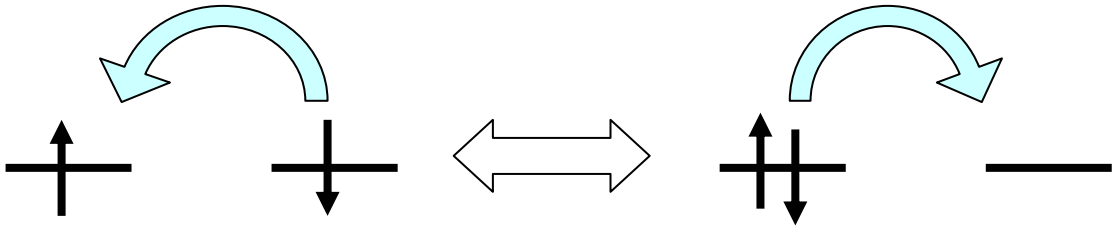
10.Origin of ferromagnetic interaction

There are two important factors to explain the origin of ferromagnetic interaction.

- Small overlap between SOMOs
- McConell's first model

1. Quite small overlap between SOMOs

Generally, overlap between SOMOs causes antiferromagnetic interaction.

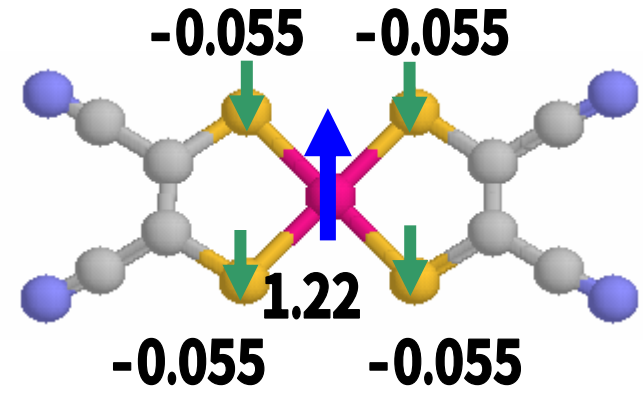


Therefore, quite small overlap between SOMOs of anions causes quite weak antiferromagnetic interaction.

2. McConell's first model

Spin polarization of

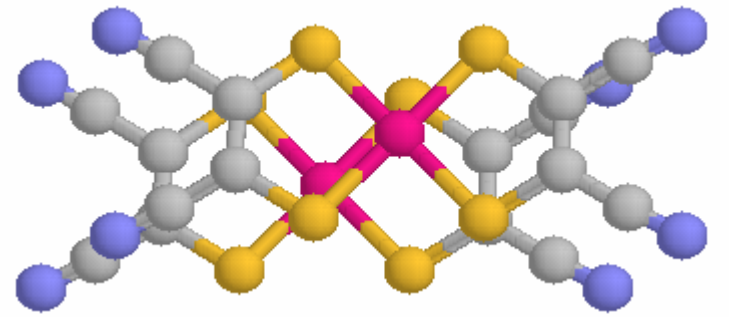
- Sulfur atoms have negative spin density.



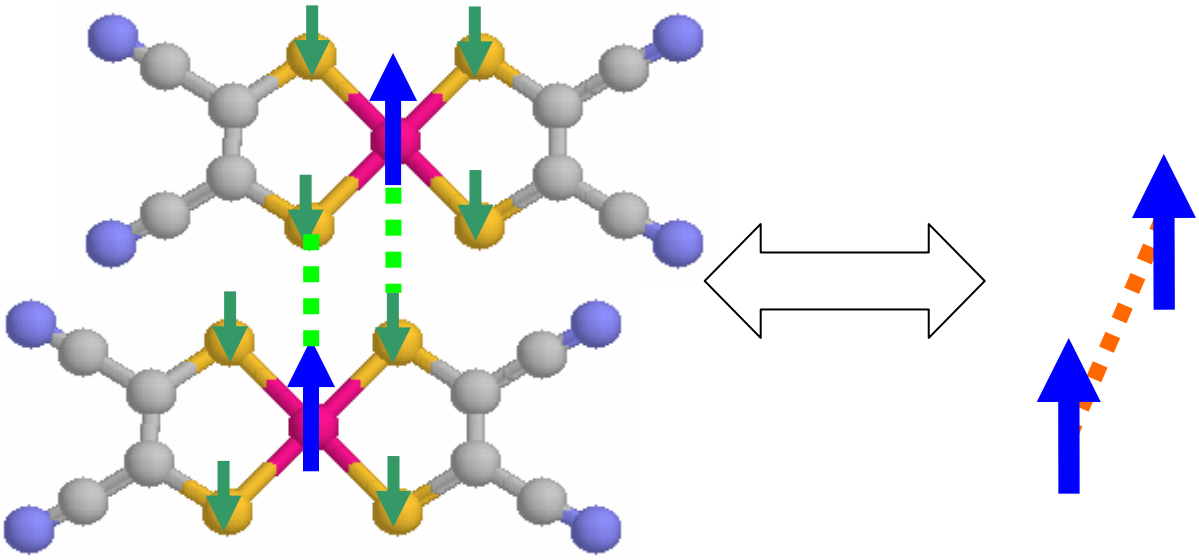
Calculation of $Ni(mnt)_2^-$

A. T. Coomber *et al.* (1996)

- Arrangement of adjacent anions



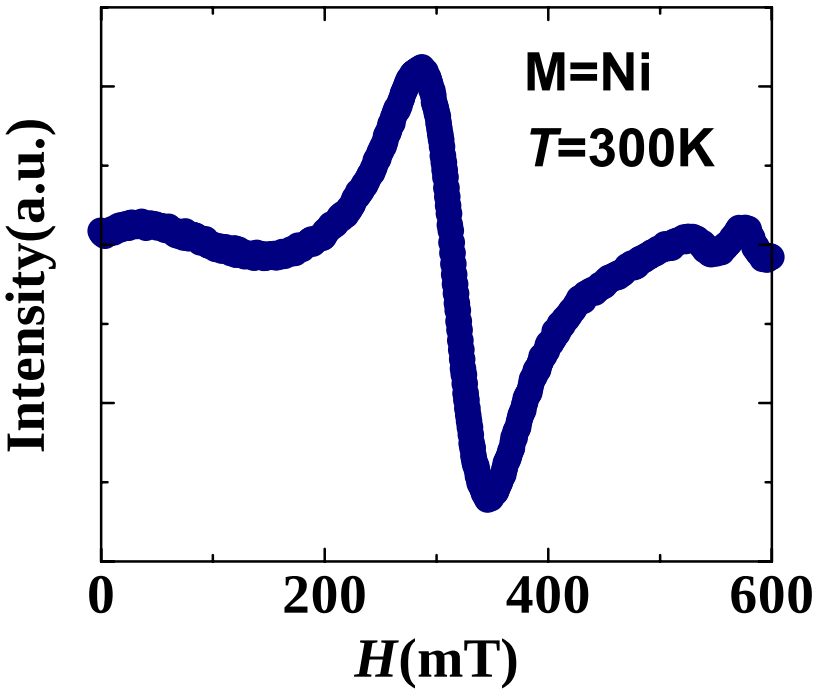
- Intermolecular interaction



Local antiferromagnetic interactions = **Total ferromagnetic interactions**

11.EPR spectrum

Only one broad peak was observed.



H//easy axis
Peak to Peak
92mT
g-value
2.10

Conductive π-electron (Sharp peak) + Localized d-electron (Broad peak)

↓

π-d interaction

↓

One broad peak

EPR spectrum suggests strong π-d interaction

12.Summary

$(DIEDO)_2M(mnt)_2$ Organic Metal with Ferromagnetic Interaction

	M=Ni	M=Pt
Conductivity	1D-Metal M-I transition (SDW or $4K_F$ CDW) $T_{M\text{-}I}$~90K	
Magnetic Properties	1D-Ferromagnetic	1D-Ferromagnetic (high temperature) Antiferromagnetic (T_N=5.5K)
Spin Character	Heisenberg	Ising