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Structures and Physical Properties of Ferromagnetic Crystals with Supramolecular Cations

Kazuya Kubo

Research Institute for Electronic Science, Hokkaido University

3rd International Conference and Exhibition on Materials Science & Engineering
San Antonio, USA
6 October 2014

RIES Hokkaido University Research Institute for Electronic Science

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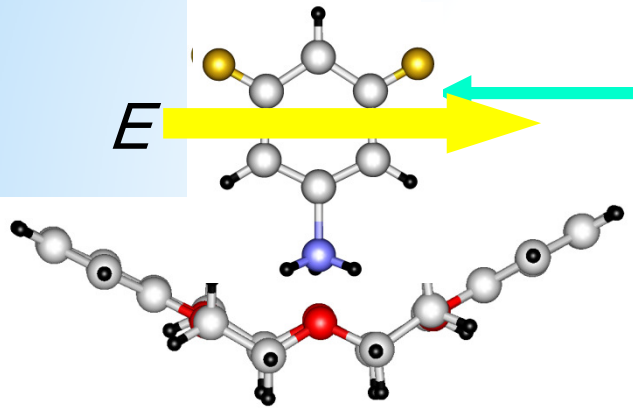
Chapter 1

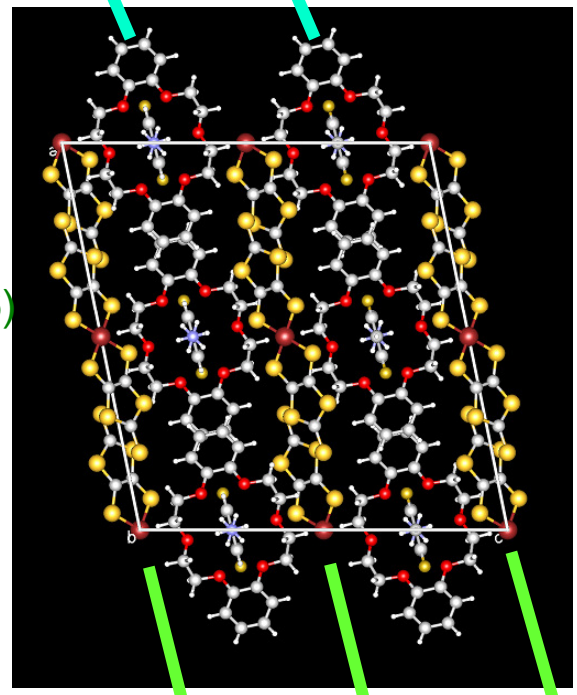
Motivation of development of multifunctional materials based on $[Mn^{II}Cr^{III}(oxalate)_3]^-$ complexes including supramolecular cations

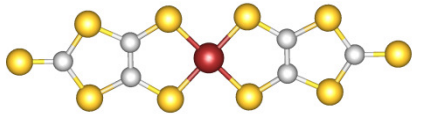
Introduction: Ferroelectricity based on the supramolecular cation

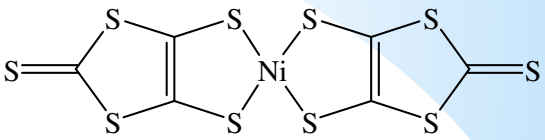
(*m*-fluoroanilinium)(dibenzo[18]crown-6)[Ni(dmit)$_2$]



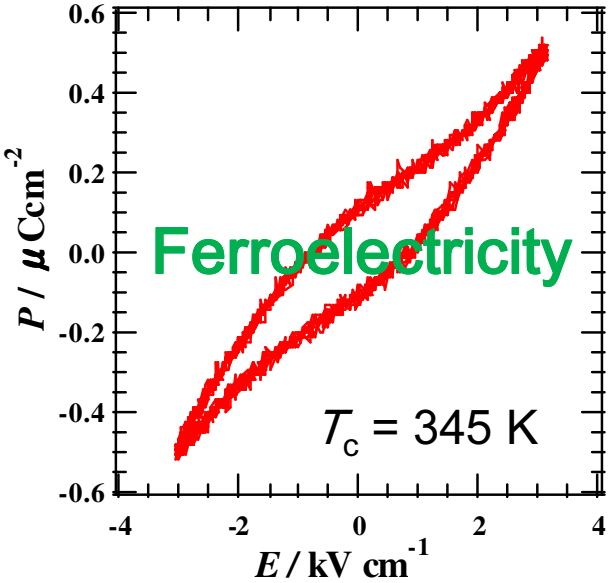
(*m*-fluoroanilinium$^+$)(dibenzo[18]crown-6)







[Ni(dmit)$_2$]$^-$



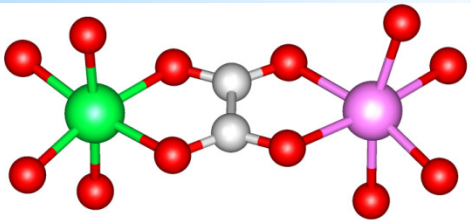
Weak antiferromagnetic interaction between S = ½ spins on the anion

Advantage of the supramolecular cations

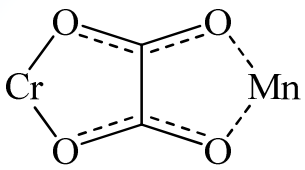
Various salts of the cation including functional anions can be obtained.

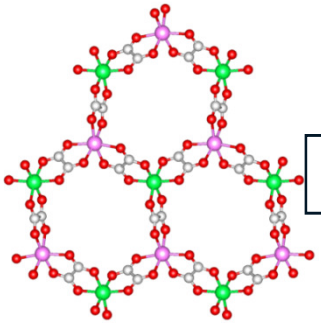
T. Akutagawa *et al*. *Nature Materials*., 2009 **8**, 342

Strategy: Combinations of the Supramolecular cations and ferromagnets

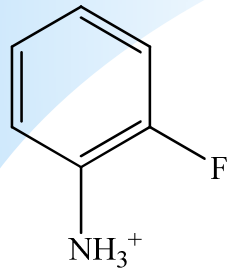


$[Mn^{II}Cr^{III}(ox)_3]$

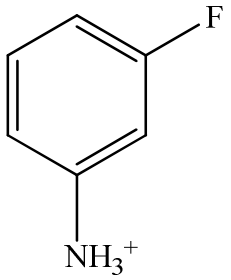




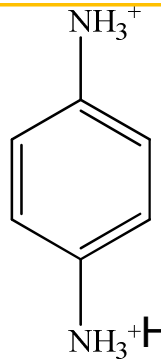
ferromagnet

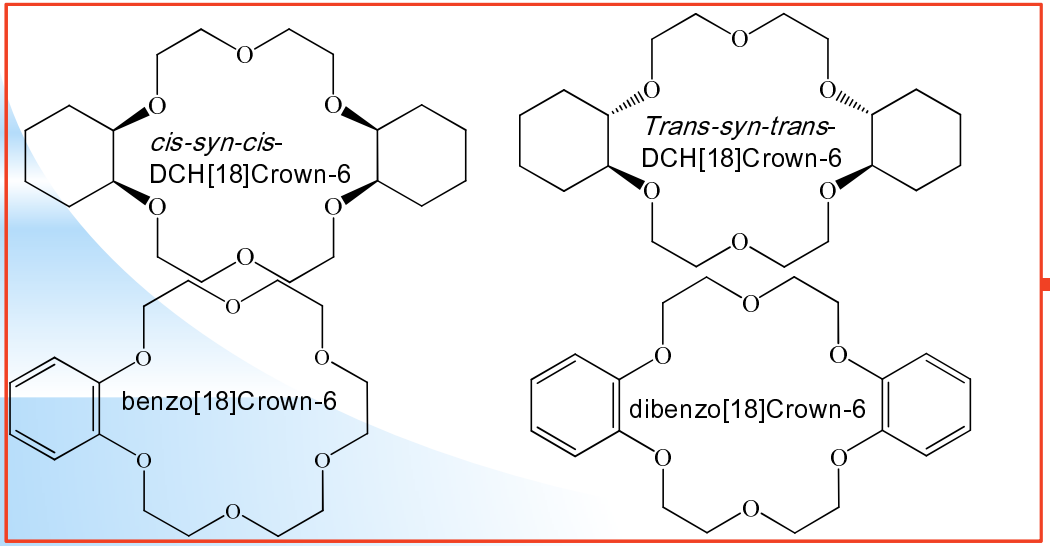


o-fluoroanilinium



m-fluoroanilinium





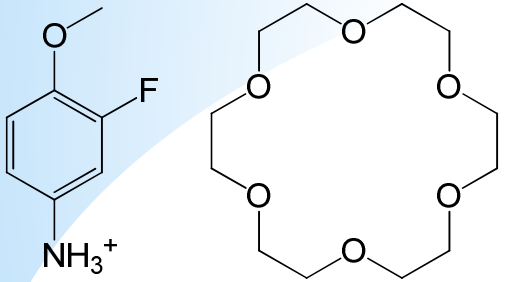
Supramolecular cation ferroelectricity

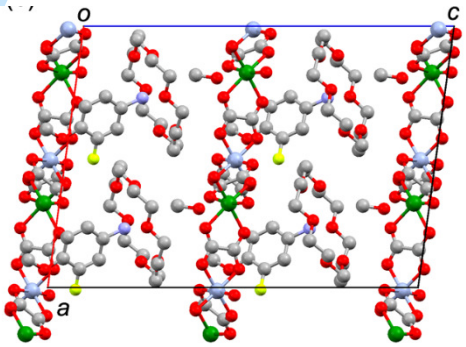
Coexistence?

This work: Three crystals were synthesized.

- (3-fluoro-4-methoxyanilinium$^+$)([18]crown-6)[$Mn^{II}Cr^{III}$(oxalate)$_3$]$^-$ (acetone) (**1**)
- (anilinium$^+$)(benzo[18]crown)[$Mn^{II}Cr^{III}$(oxalate)$_3$]$^-$ (**2**)
- (*m*-fluoroanilinium$^+$)(dicyclohexano[18]crown-6)[$Mn^{II}Cr^{III}$(oxalate)$_3$]$^-$ (**3**)

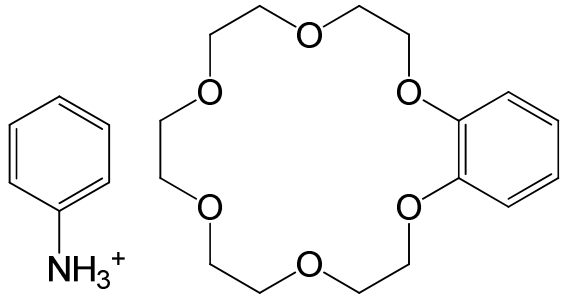
Crystal 1

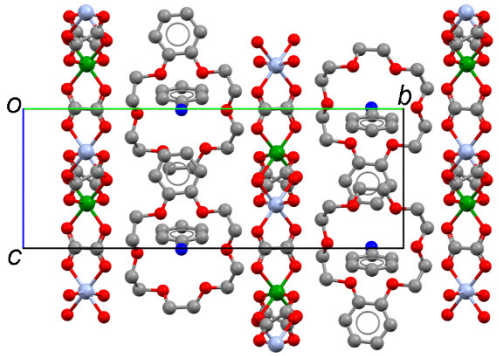




Space group: *Cc*
Magnetic behavior:
Ferromagnetic
Dielectric response:
Not observed
(*Chem. Lett.* **2013**, *42*, 137)

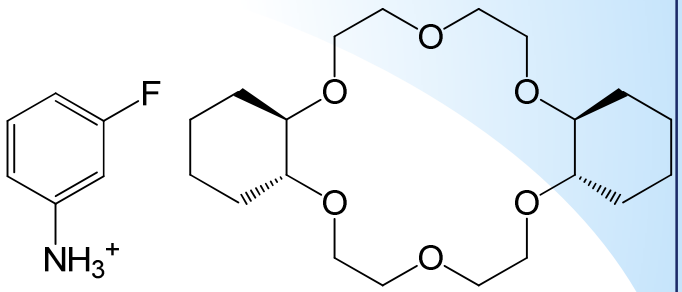
Crystal 2

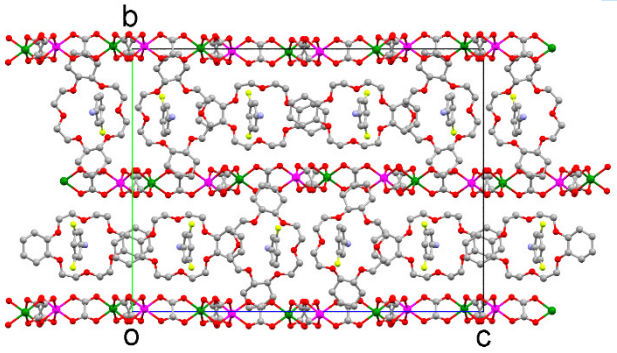




Space group: $P2_1$
Magnetic behavior:
Ferromagnetic
Dielectric response:
Observed

Crystal 3





Space group: $P2_12_12_1$
Magnetic behavior:
Ferromagnetic
Dielectric response:
Not observed

Chapter 2

2-1. Synthesis of (anilinium)(benzo[18]crown-6)[$Mn^{II}Cr^{III}$(oxalate)$_3$]$^-$ (**2**)

2-2. Crystal structure of **2**

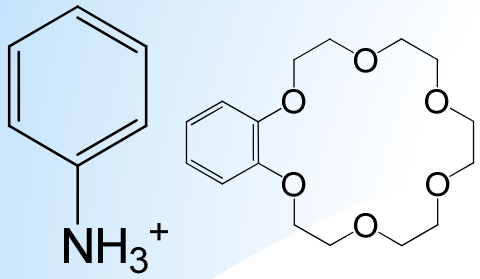
2-3. Magnetic susceptibility of **2**

2-4. Solid state ^{2}H-NMR of **2**

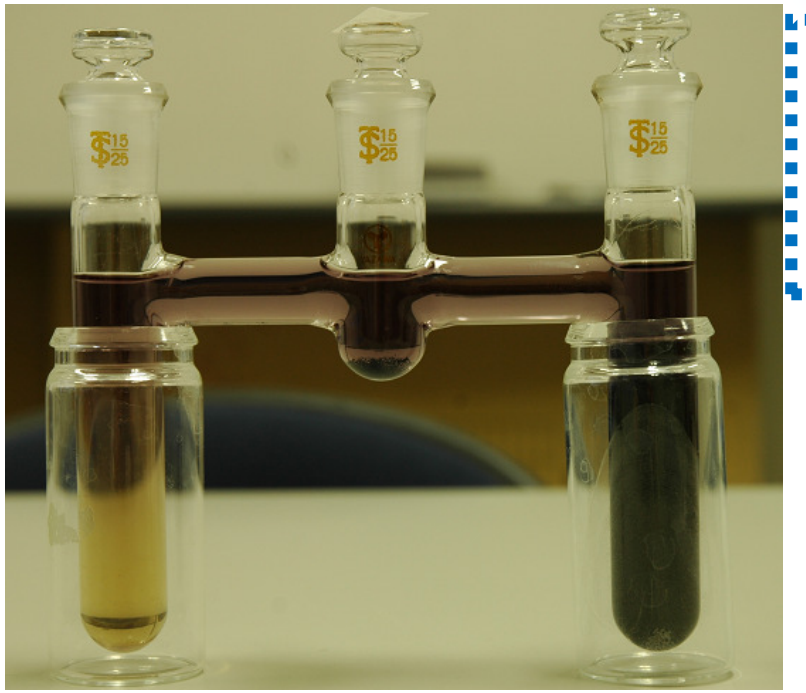
2-5. Potential energy calculation for molecular motions in **2**

2-6. Dielectric property of **2**

2-1. Preparation of (anilinium)(benzo[18]crown-6) $[Mn^{II}Cr^{III}(oxalate)_3]^-$ (1)



Precursors of Supramolecles



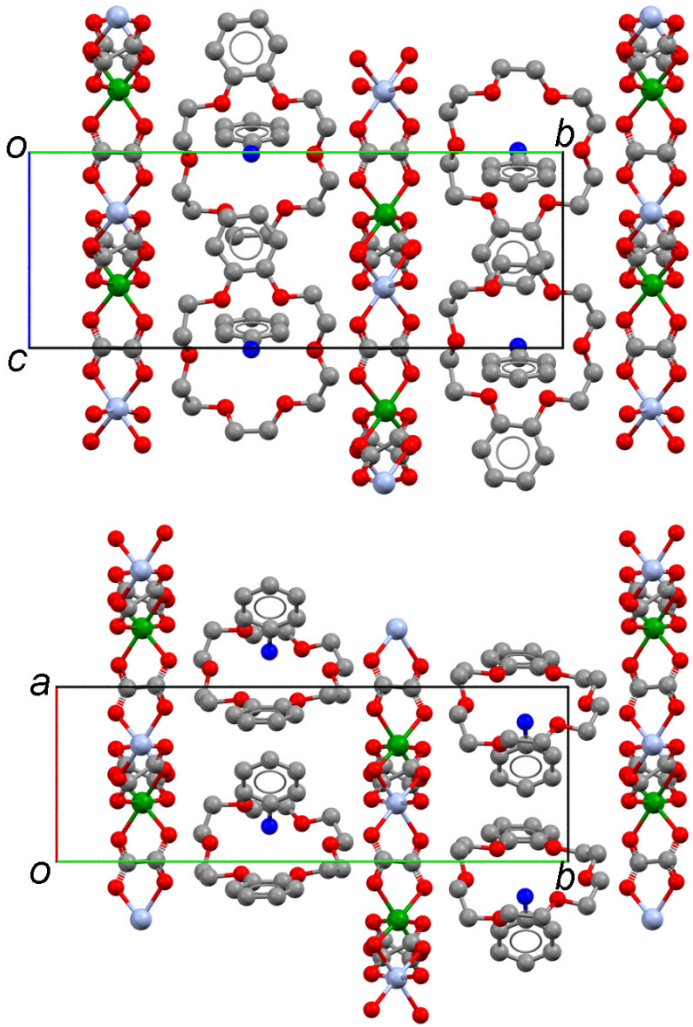
Precursors of $[Mn^{II}Cr^{III}(oxalate)]^-$

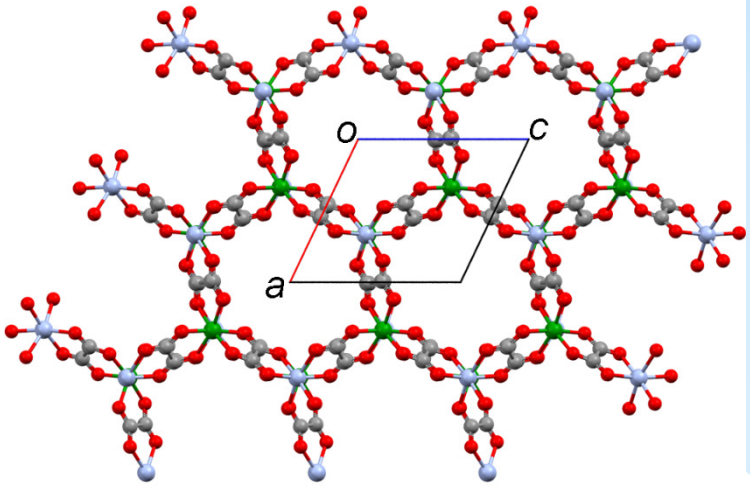
Conditions

Diffusion method; Temperature: 25 ºC; Period: 1 week; solvents: CH_3OH and CH_3CN mixtures

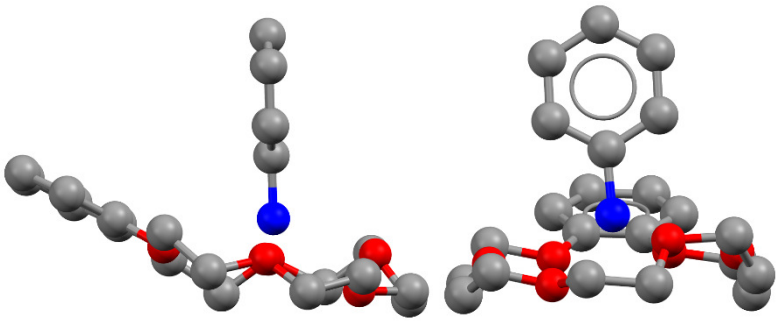
Confirmation of the formula: X-ray crystallographic, elemental, and Thirmogramometric analyses

2-2. Crystal structure of (anilinium)(benzo[18]crown-6)[$Mn^{II}Cr^{III}(oxalate)_3$]$^-$





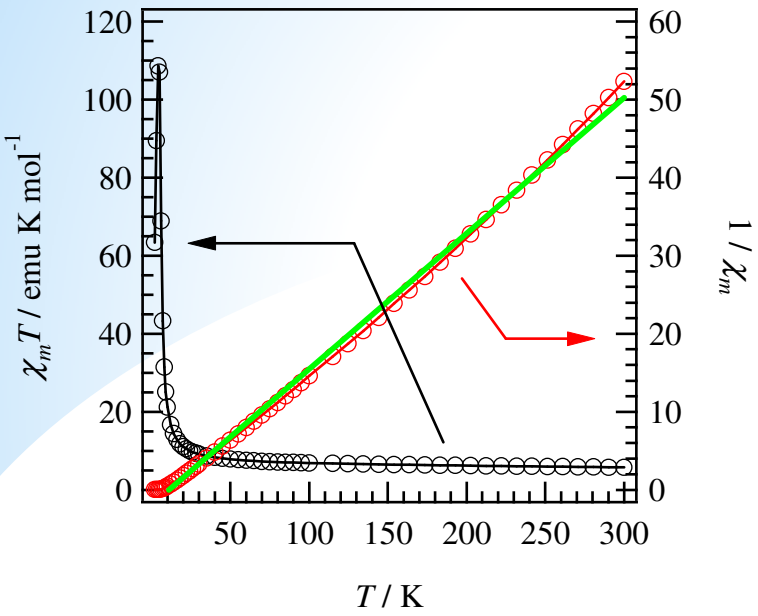
The two dimensional honeycomb structure
Diameter of the ring ca. 10 Å
Distance between the layers ca. 11 Å

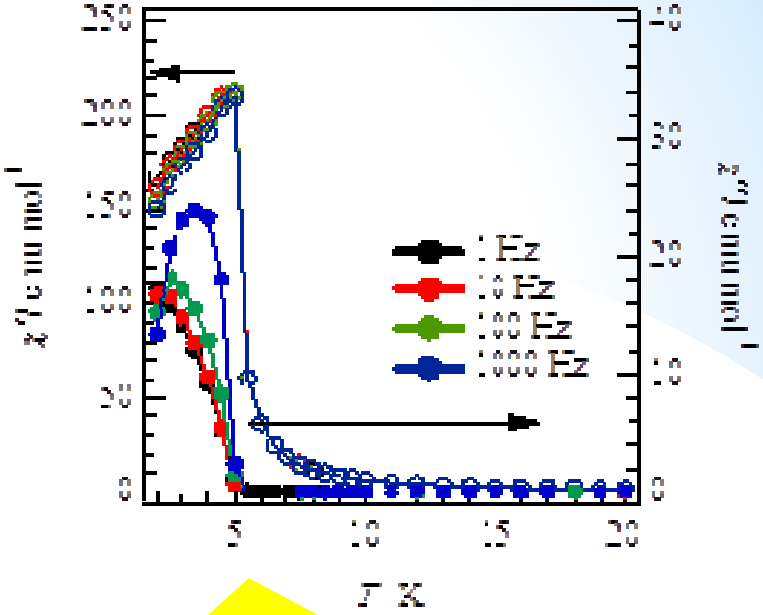


Hydrogen bonds between N and O atoms: 2.782-2.957 Å
Formation of the supramolecular cation

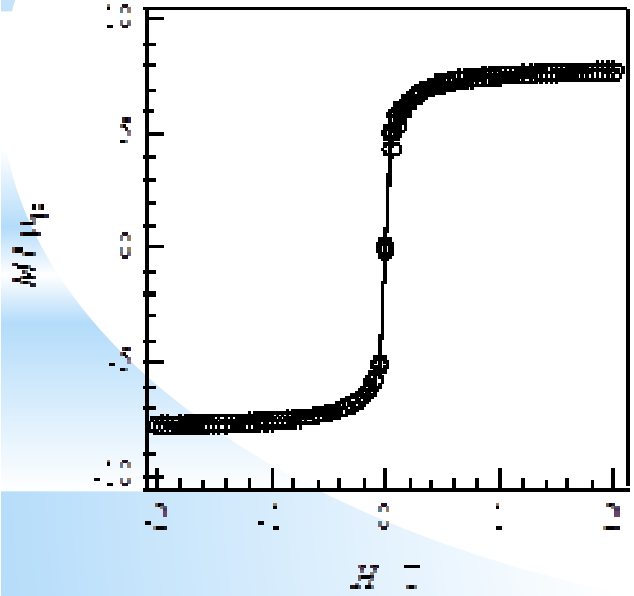
Crystal data of **2**
Monoclinic; $P2_1$ (#4); a = 8.7986(8) Å; b = 23.315(3) Å; c = 9.4749(13) Å; β = 115.483(3)°; V = 1754.6(3) Å^3; T = -100 °C; R_1 = 0.0725; R_w = 0.1706

Magnetic susceptibility of (anilinium)(benzo[18]crown-6) $[Mn^{II}Cr^{III}(oxalate)_3]^-$ (2)



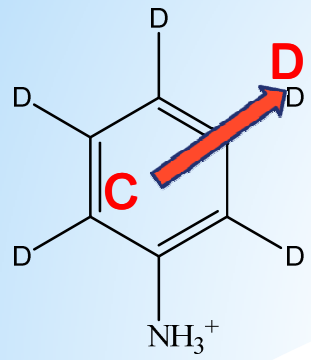


Ferromagnetic transition at 5.0 K



(1) Crystal **2** exhibits ferromagnetic behavior.
(2) Crystal **2** is a good candidate of a multifunctional material with coexistence of a ferromagnetism and a ferroelectricity.

Solid state ^{2}H-NMR of (anilinium-*d5*)(benzo[18]crown-6) $[Mn^{II}Cr^{III}(oxalate)_3]^-$ (2)

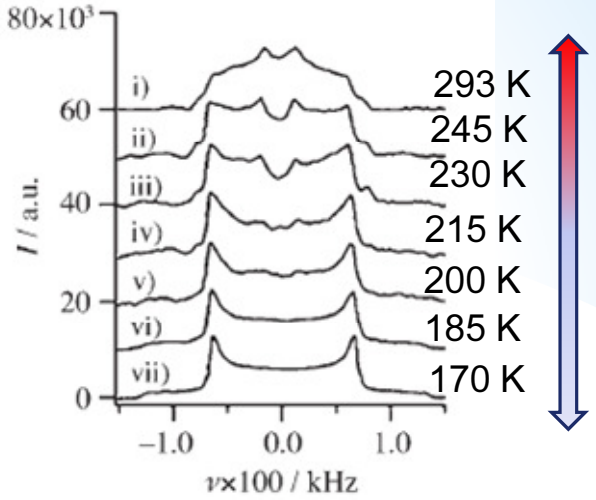


Anilinium-*d5*

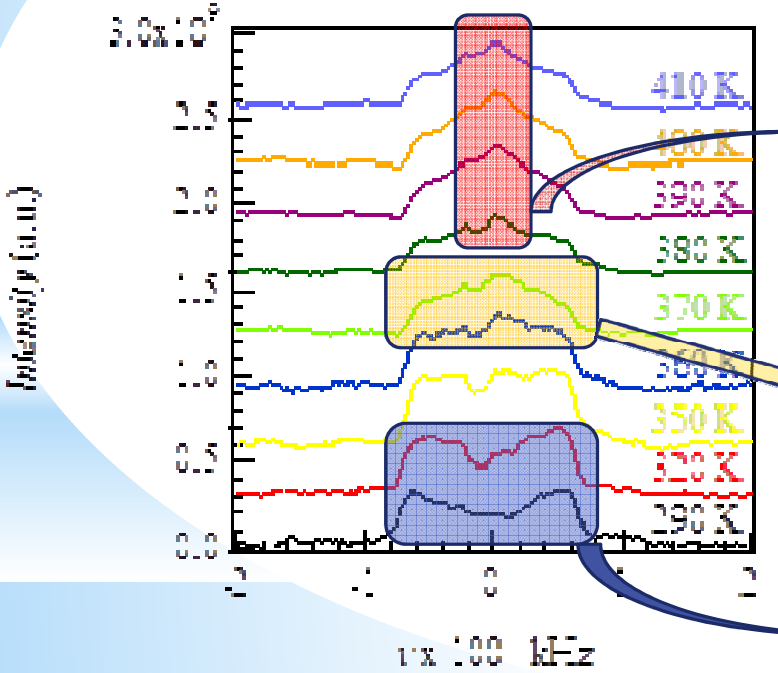
Nuclear spin of ^{2}H: $I = 1$

electrical field gradient of anilinium-*d5*: C-D direction

Previous work



^{2}H-NMR of (anilinium-*d5*)([18]crown-6) $[Ni(dmit)_2]^-$
S. Nishihara *et al.*, *Chem. Asian J.* **2007**, *2*, 1083



Another peak is observed.

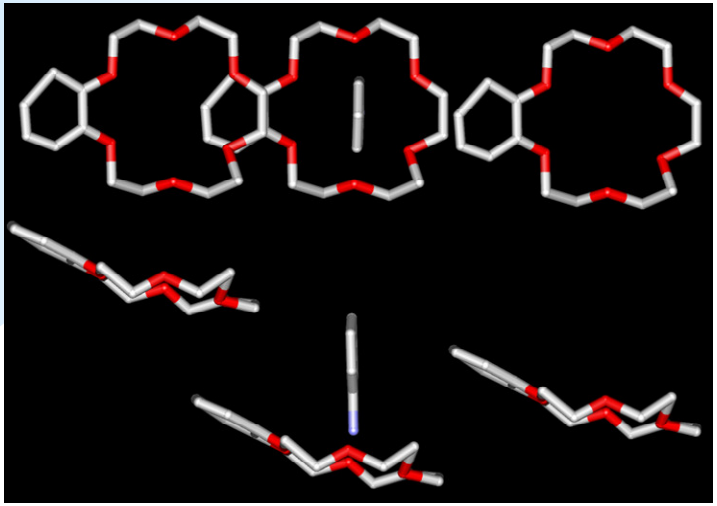
large flip-flop motion

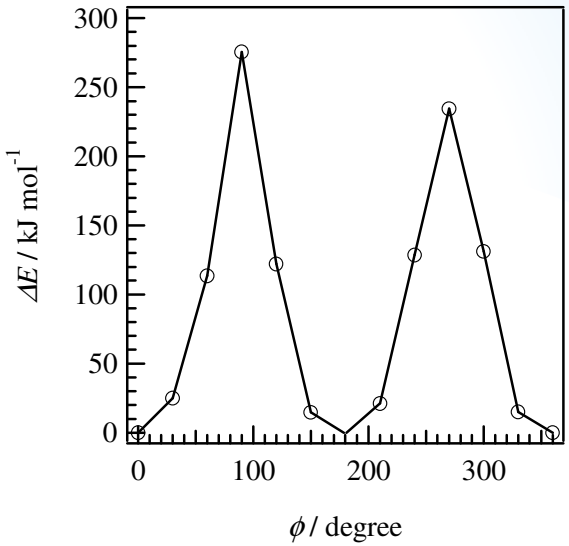
Weak flip-flop motion

Another molecular motion ?

Potential energy calculations of (anilinium)(benzo[18]crown-6) $[Mn^{II}Cr^{III}(oxalate)_3]^-$ (2)

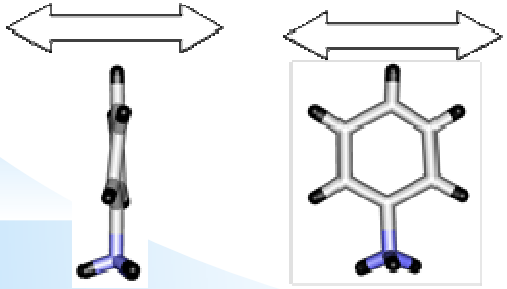
flip-flop motion



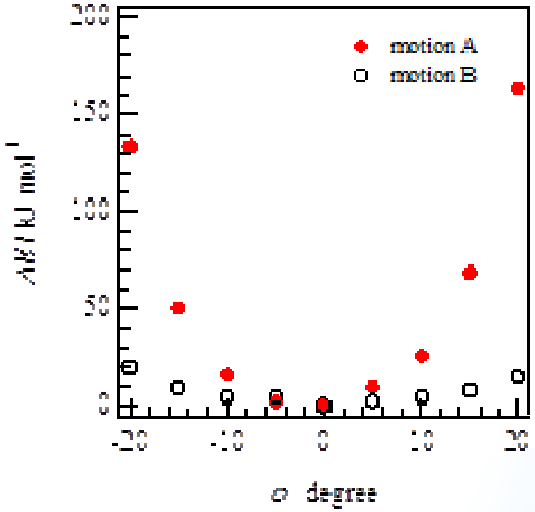


cf. Energy barrier for the flip-flop motion in the ferroelectric salt, (*m*-fluoroanilinium)(dibenzo[18]crown-6)(Ni(dmit)$_2$): ca. 250 kJ mol^{-1}

Pendulum motions

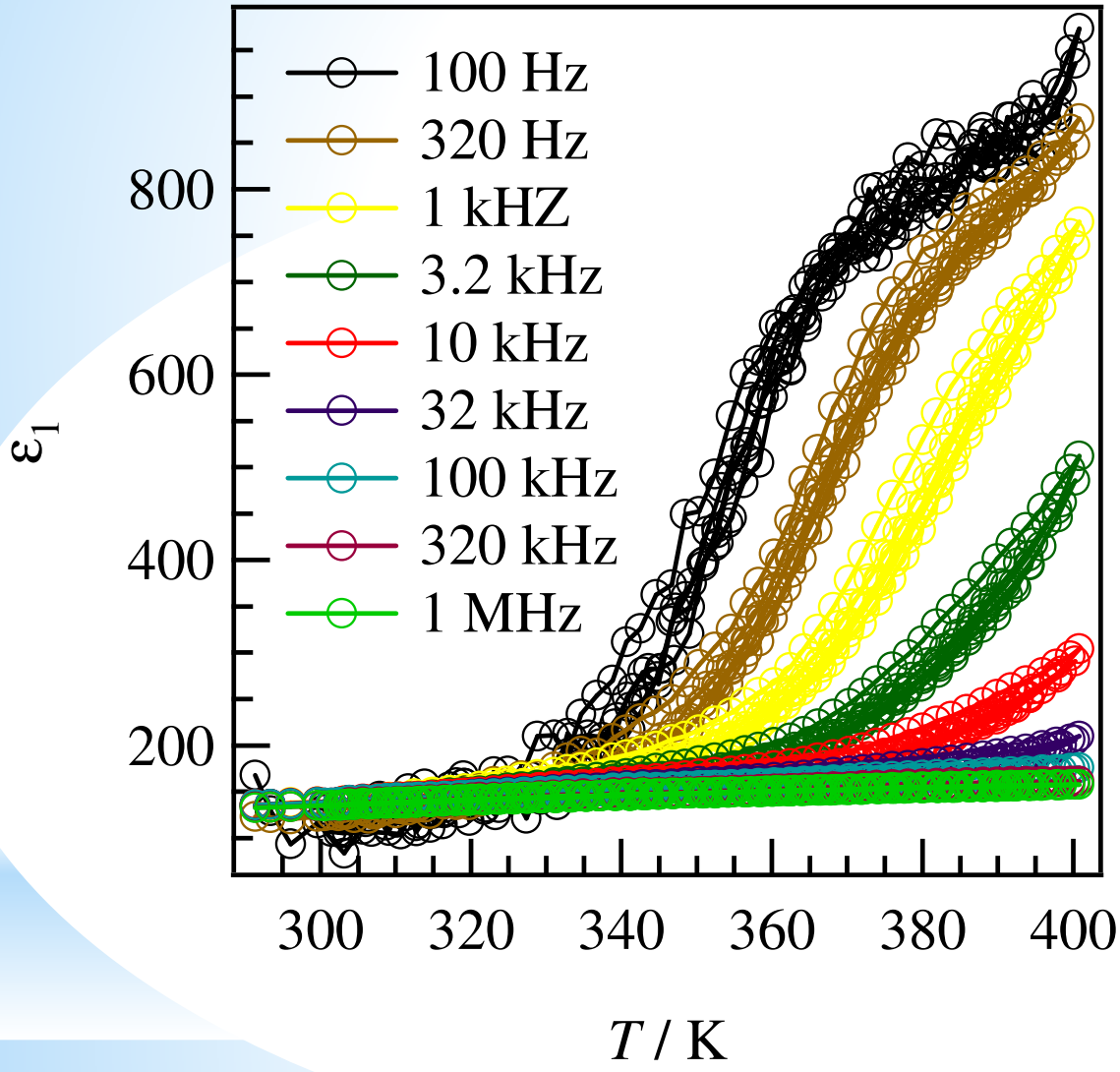


motion A motion B



Small energy barrier for the pendulum motion B

Temperature and field dependence dielectric constants of (anilinium)(benzo[18]crown-6) $[Mn^{II}Cr^{III}(oxalate)_3]^-$ (2)



The flip-flop motion of anilinium$^+$ dose not cause an inversion of the dipole-moment.

These large dielectric responses would correspond to the pendulum motions.

Section 3: Summary and future works

Development of multifunctional materials based on the MOF system with the supramolecular cations.

·(organic ammonium)([18]crown-6 derivative)[MnCr(oxalate)$_3$] were synthesized.

· Salt 2 exhibits a ferromagnetic transition at 5.0 K.

· Dielectric responses were observed due to the pendulum motion of anilinium in the solid state of **2**.

· **Crystal 2 is a model compound for the molecular multifunctional materials.**

Future Plan

(anilinium)(bebzo[18]crown-6)[MnCr(oxalate)$_3$] (**2**)

A good candidate for the multifunctional materials with coexistence of ferromagnetism and ferroelectricity such as multiferroic materials.

Future plans:

·Development of the multifunctional materials such as multiferroic compounds based on the molecular system.

Acknowledgement

Professor Takayoshi Nakamura (Hokkaido University)
Professor Tomoyuki Akutagawa (Tohoku University)
Professor Shin-ichiro Noro (Hokkaido University)
Professor Sadamu Takeda (Hokkaido University)

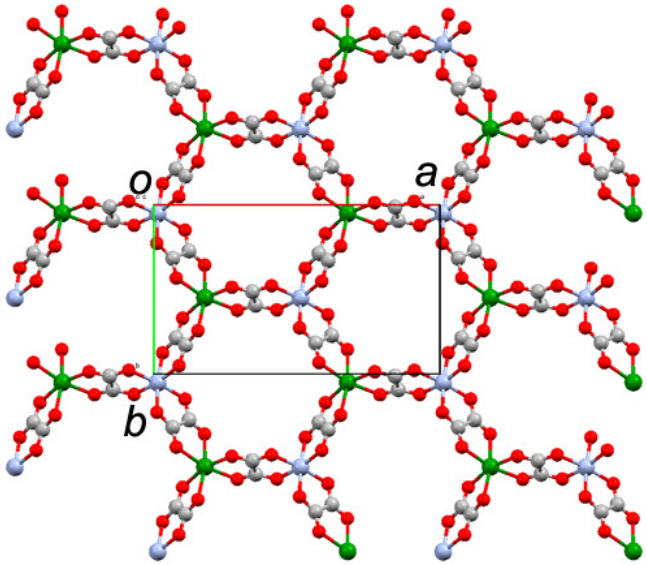
Dr. Toru Endo (Chisso Cooperation, Hokkaido University)

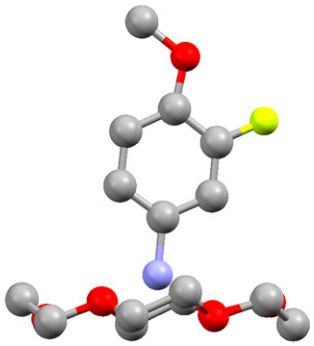
Mr. Masashi Yoshitake (Hokkaido University)

Professor Kunio Awaga (Nagoya University)
Dr. Hirofumi Yoshikawa (Nagoya University)

Professor Jun Kawamata (Yamaguchi University)
Professor Sadafumi Nishihara (Hiroshima University)
Dr. Yasutaka Suzuki (Yamaguchi University)
Dr. Ryo Tsunashima (Yamaguchi University)

Crystal structure of (3-fluoro-4-methoxy-anilinium)([18]crown-6) $[Mn^{II}Cr^{III}(oxalate)_3]^-$ $(CH_3OH)_2$ (1)

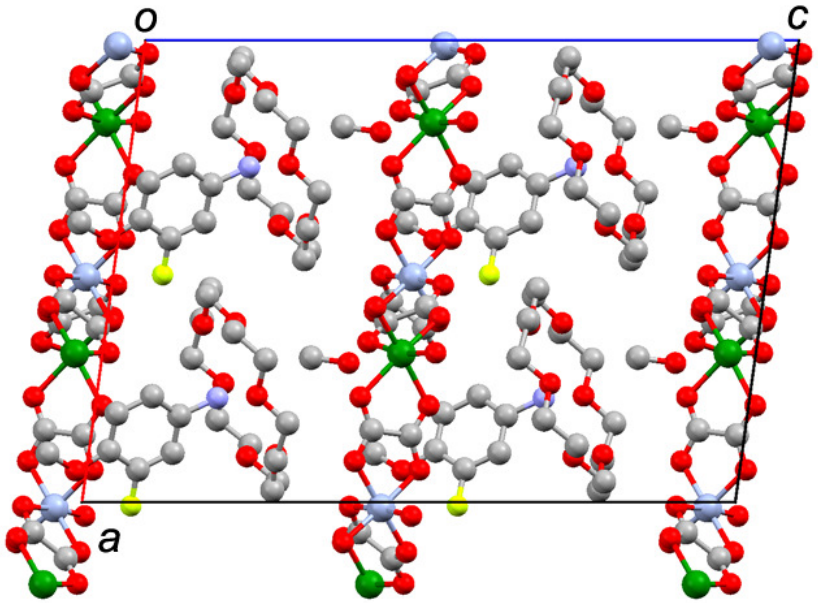




Shortest N···O distance of 2.810 Å

A mean plane of the six oxygen atoms of the crown ether was close to right angle (89.32°)

Hydrogen bonds between N and O atoms
Formation of the supramolecular cation

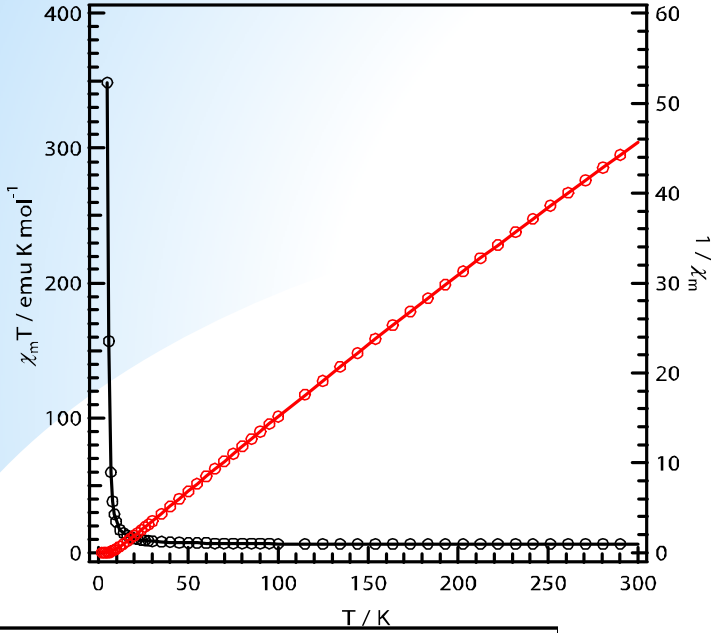


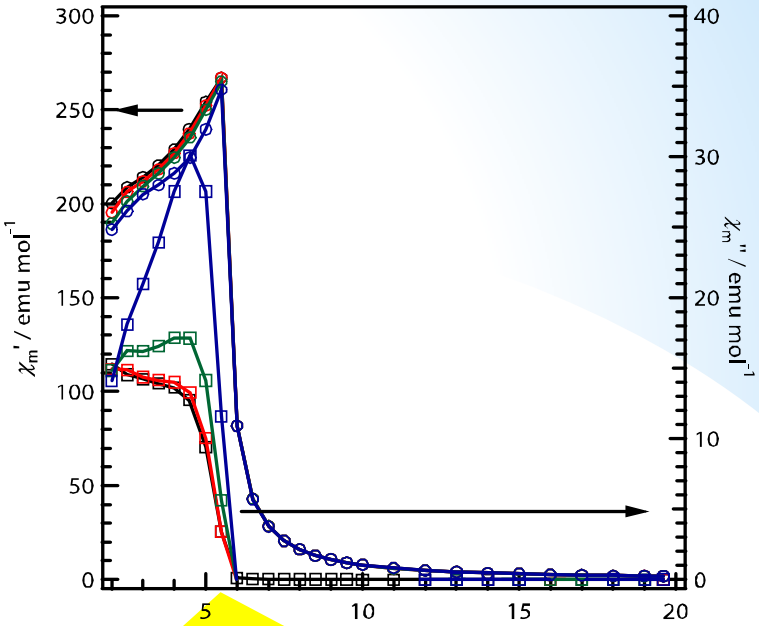
The two dimensional honeycomb structure
Diameter of the ring ca. 10 Å
Distance between the layers ca. 13 Å

Crystal data of **1**
Monoclinic; Space group, C_c; a = 16.1878(10) Å; b = 9.4716(5) Å; c = 22.6967(13) Å; b = 97.847(2)°; V = 3447.4(3) Å^3; Z = 4.

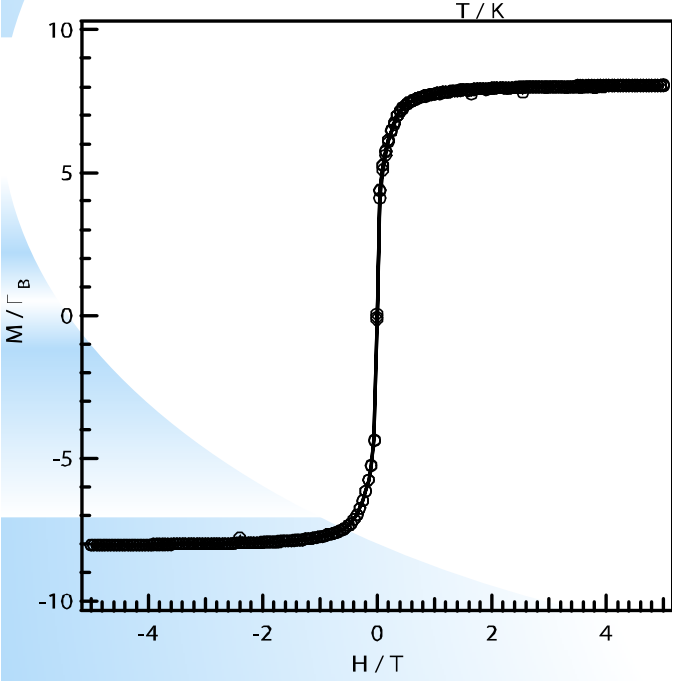
·Space group without inversion center
·No disorder of F and MeO groups

Magnetic susceptibility of (3-fluoro-4-methoxy-anilinium)([18]crown-6) $[Mn^{II}Cr^{III}(oxalate)_3]^-$ $(CH_3OH)_2$ (1)





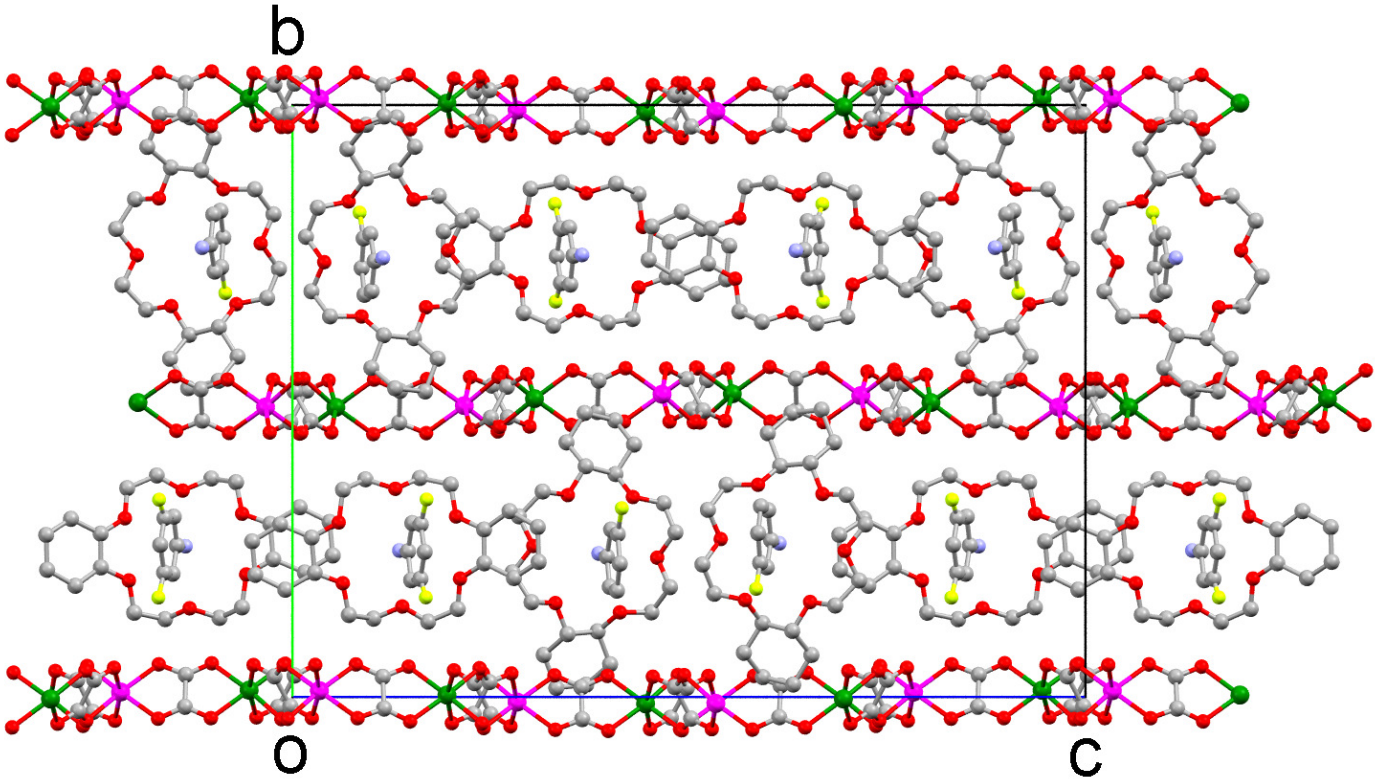
Ferromagnetic transition at 5.5 K



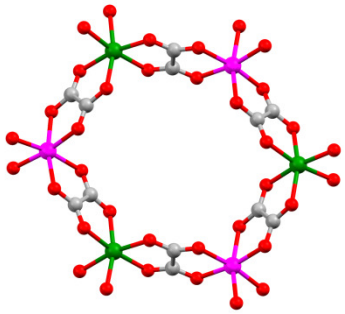
(1) Crystal **1** exhibits ferromagnetic behavior.
(2) Salt **1** is a good candidate of a multifunctional material with coexistence of a ferromagnetism and a ferroelectricity.

Crystal structure of (*m*-fluoroanilinium)(*trans-syn-trans*-DCH[18]crown-6)[MnCr(oxalate)$_3$] at 25 ºC

Crystal data of orthorhombic
$P2_12_12_1$
a = 9.1025(5)Å
b = 25.0202(12) Å
c = 33.5384(15) Å
V = 7638.2(7) Å^3
T = 25 °C



Two dimensional honeycomb structure including the supramolecular cations



Two dimensional honeycomb structure

⇩

Ferromagnetic behaviour

Pores of the anion layers are filled with cyclohexane moieties of the crown ethers

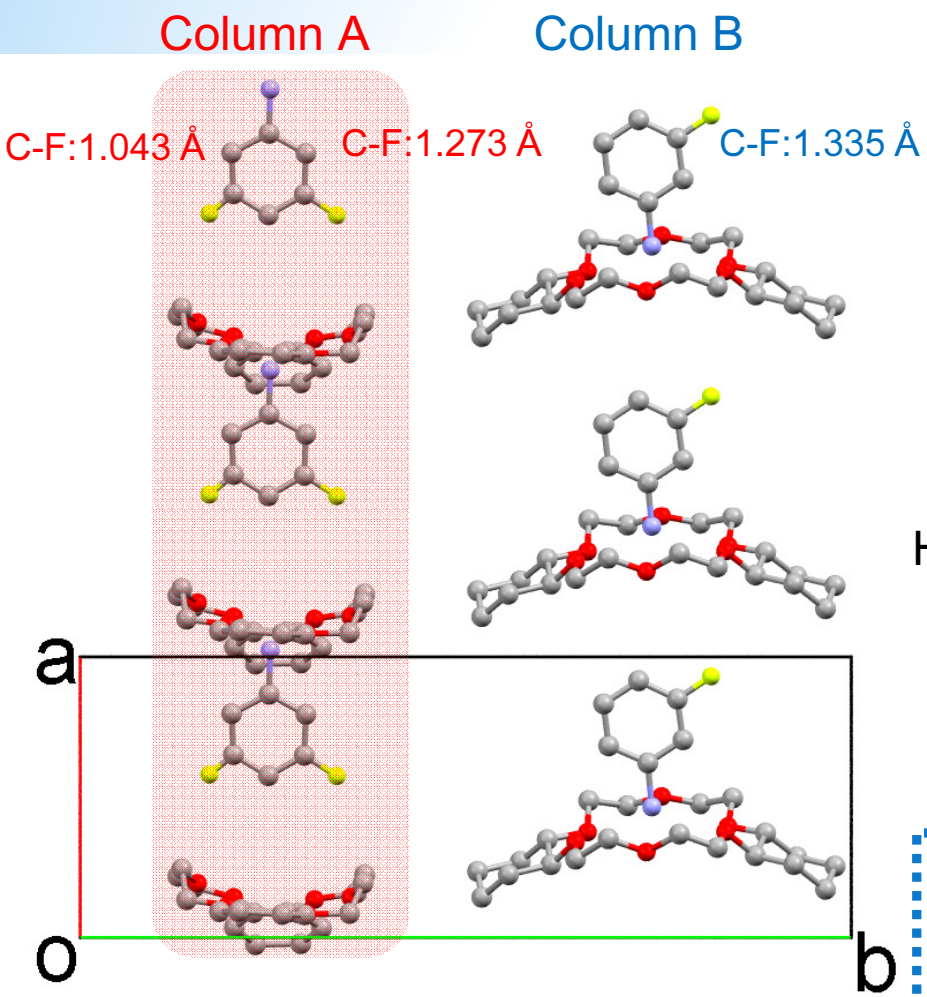
⇩

No solvent molecule in the salt

⇩

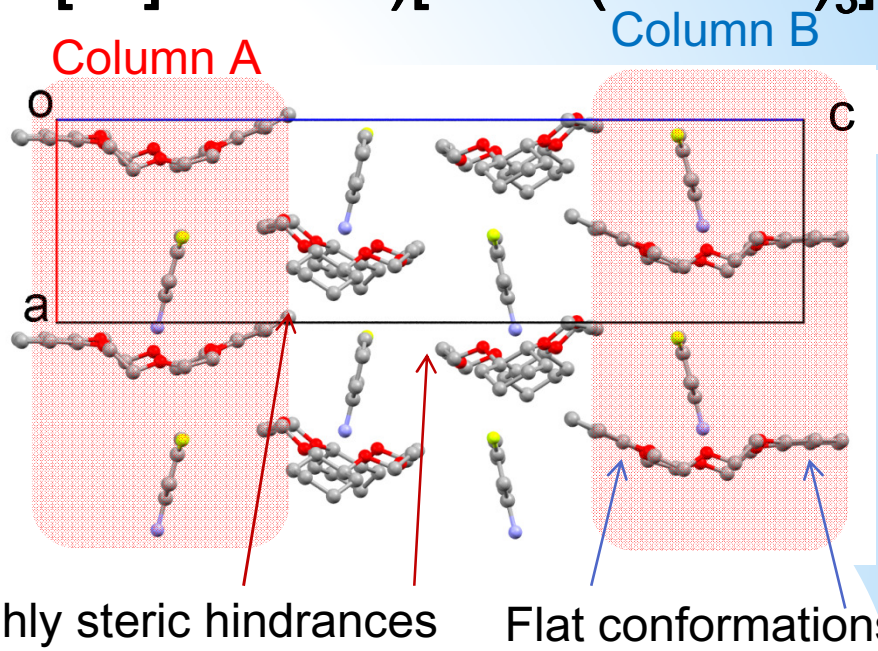
Air stable compound

Molecular arrangements of supramolecular cations of (*m*-fluoroanilinium)(*trans-syn-trans*-DCH[18]crown-6)[$MnCr(oxalate)_3$]



Two crystallographically independent supramolecular cations in this crystal

Disordered fluorine atoms on the cations



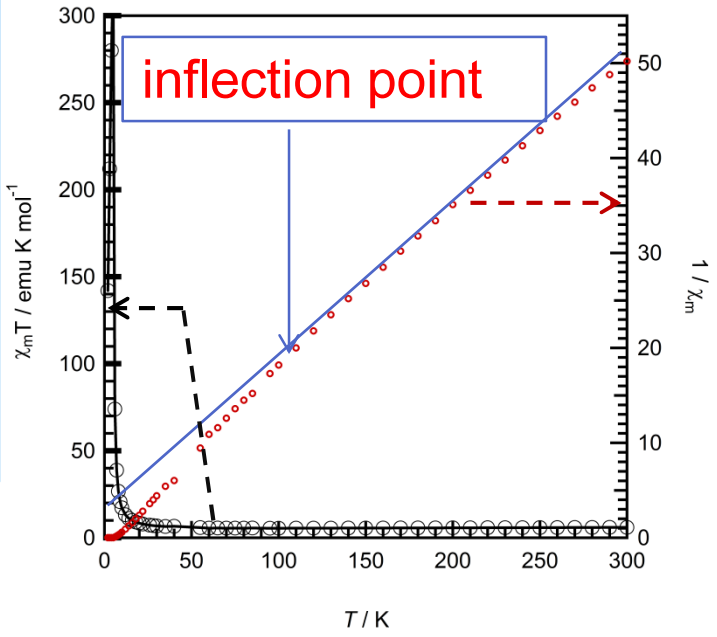
This complex is a good candidate for the multifunctional material coexisting a ferromagnetism and a ferroelectricity.

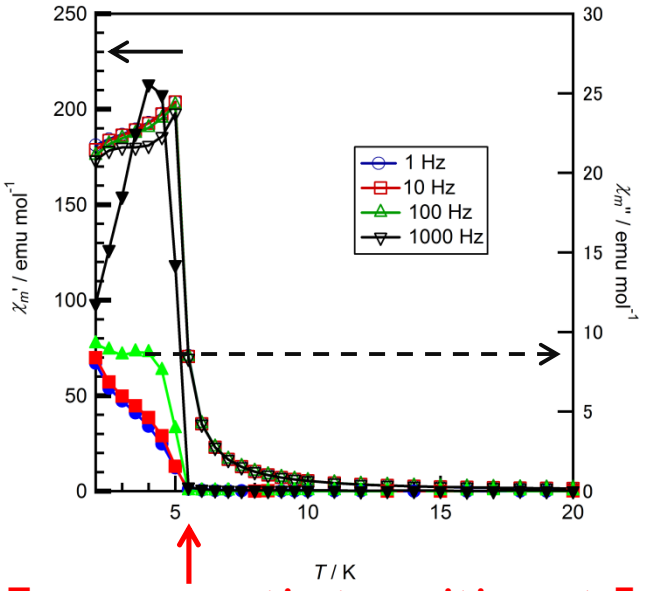
Debatable points

(1) The C-F Bond lengths in column A are shorter than the typical bond length.

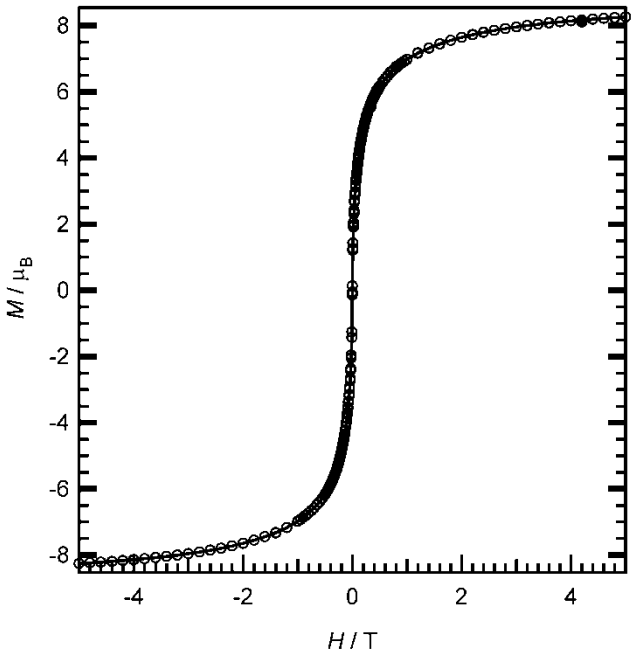
(2) The cyclohexane moieties in column A are not *trans-syn-trans* conformation.

Magnetic susceptibility of the salt





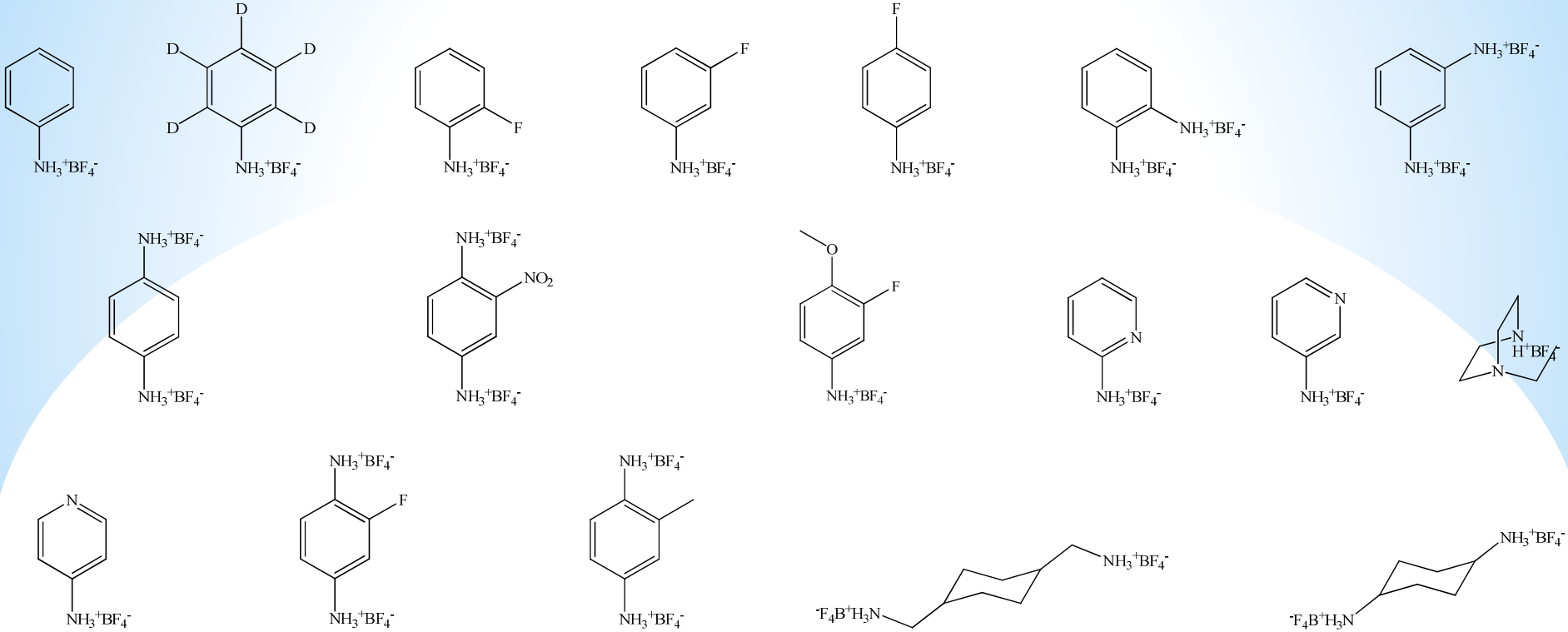
Ferromagnetic transition at 5.5 K



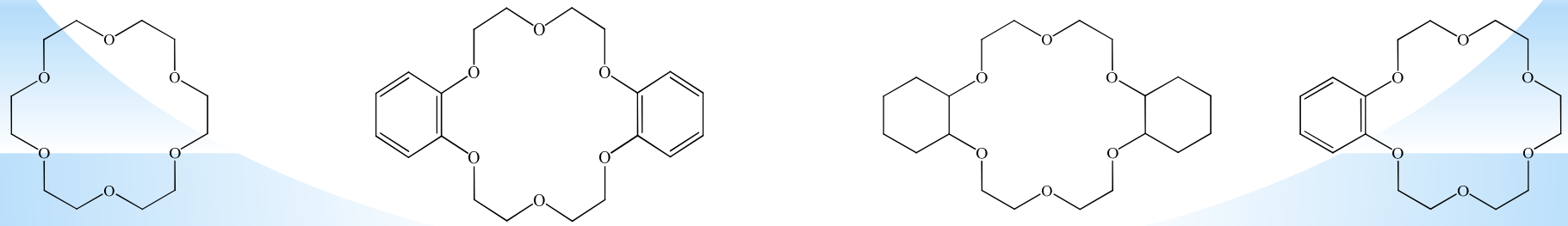
(1) The exhibits a ferromagnetic behavior.
(2) Ferromagnetic transition at 5.5 K
(3) Saturated magnetization of the salt is about 8 μ_B.
(4) In $1/\chi$ vs. T plot, inflection point was observed at 110 K.
→Interaction between the supramoleculer cation and the oxalete complex?

Organic ammonium and crown ether derivatives

Anilinium derivatives



[18]crown-6 derivatives



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