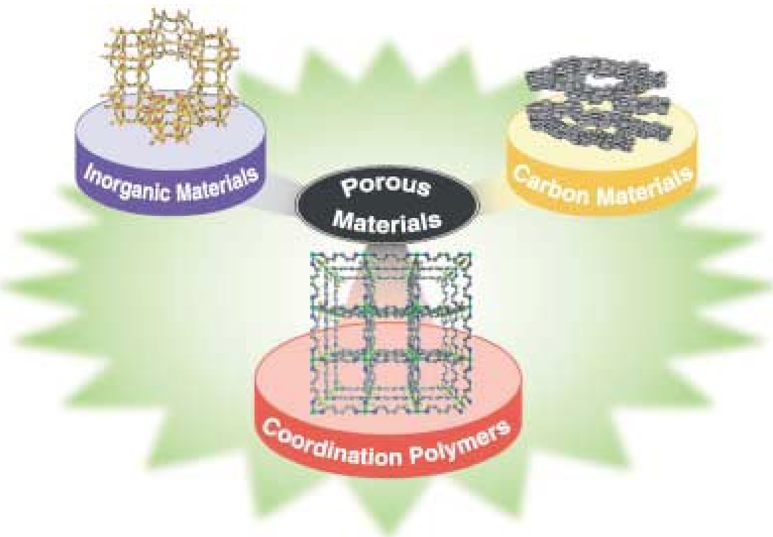
The influence of diamagnetic substrates absorption on magnetic properties of porous coordination polymers

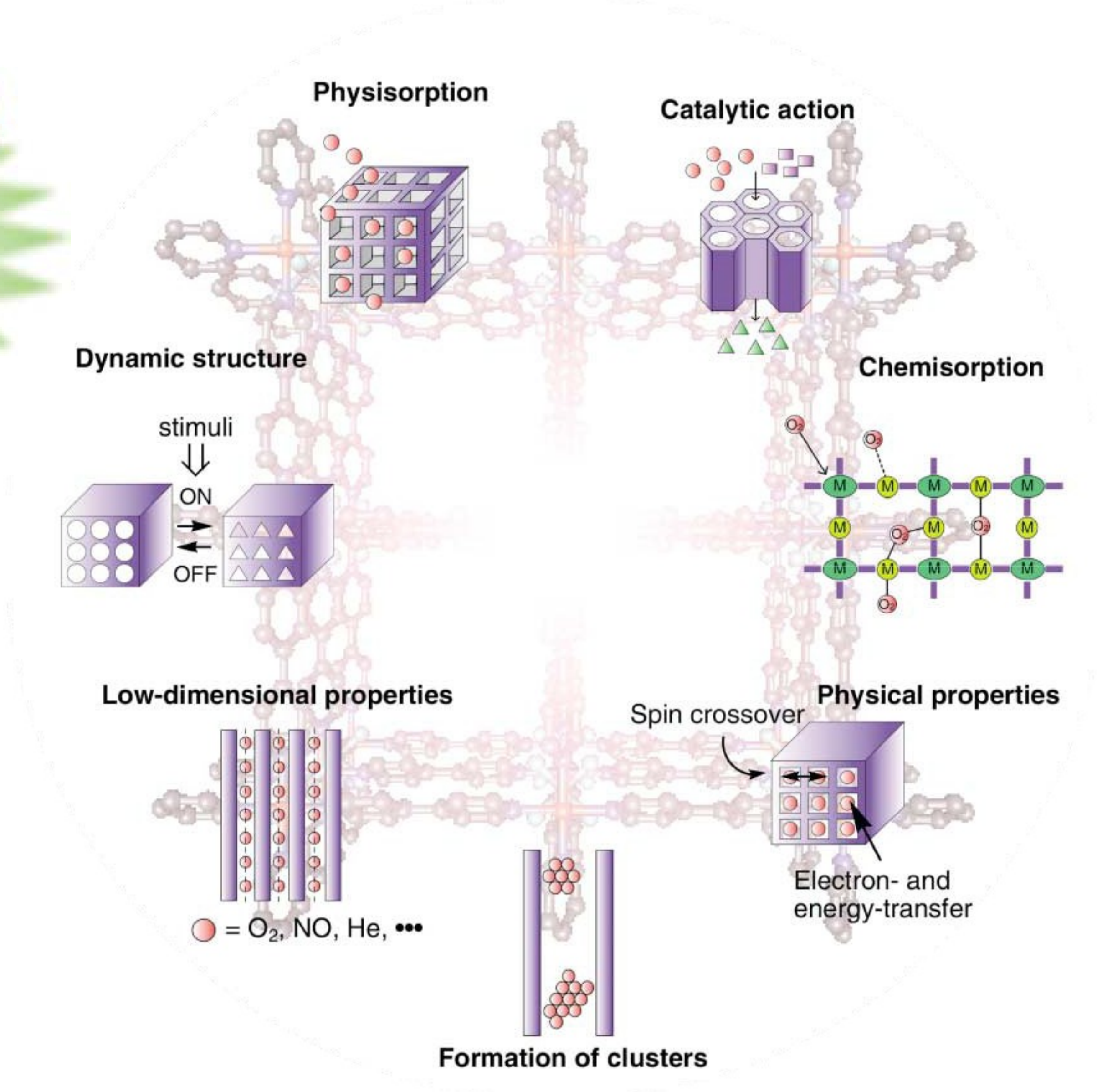
Mikhail Kiskin, Sergey Kolotilov,
Vladimir Novotortsev, Igor Eremenko

April 21, 2014

MSU



- Gas storage
- Catalysis
- Magnetic materials
- Luminescent materials
- Sensors
- Polyfunctional materials



S. Kitagawa, R. Kitaura, and S. Noro. Functional Porous Coordination Polymers.
Angew. Chem. Int. Ed. 2004, 43, 2334

PCP – porous coordination polymer

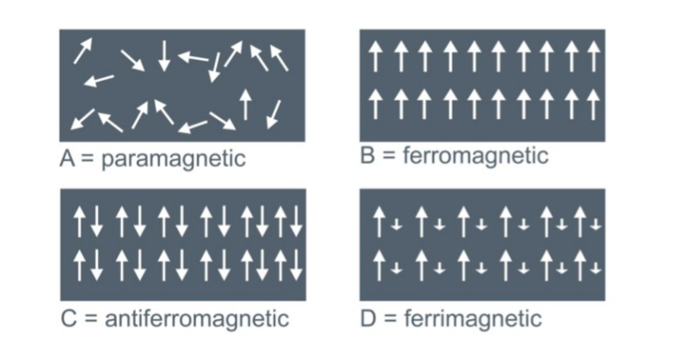
Interactions with different types of substrates: adsorption, absorption, chemisorption

Dynamics of structure:

mutual arrangement of the elements of the crystal lattice (gates opening, breathing)

interaction with substrate (coordination on the metal atom, H-bonding)

PCP with paramagnetic ions → magnetic properties



→ Spin crossover effect, Magnetic ordering, Hysteresis loop …

Modulation of the magnetic properties of PCP in the interaction with diamagnetic substrates

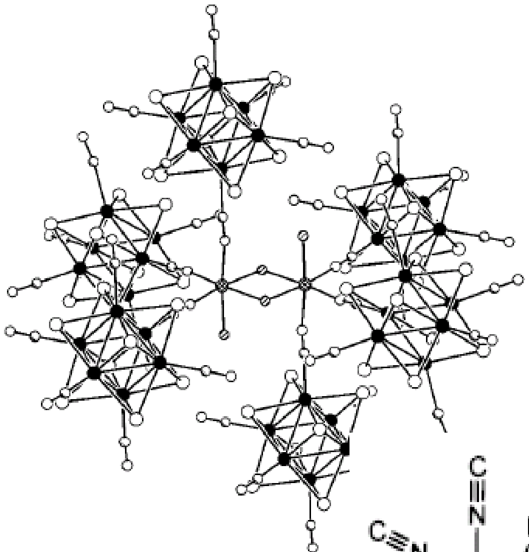
1. Change of coordination environment of paramagnetic metal ion
2. Formation or breaking of bond in the group, which transmits exchange interactions
3. Change of bond lengths and angles without new bonds formation or bonds breaking in coordination polymer

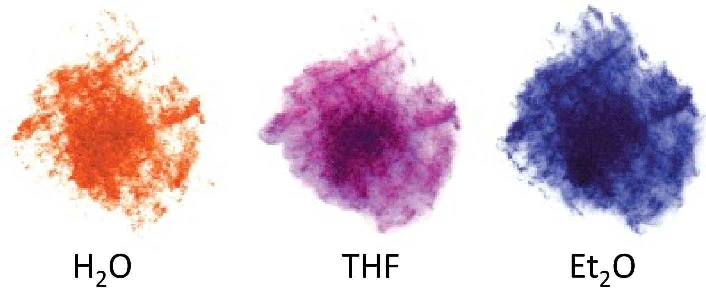
1. **Change of coordination environment of paramagnetic metal ion**

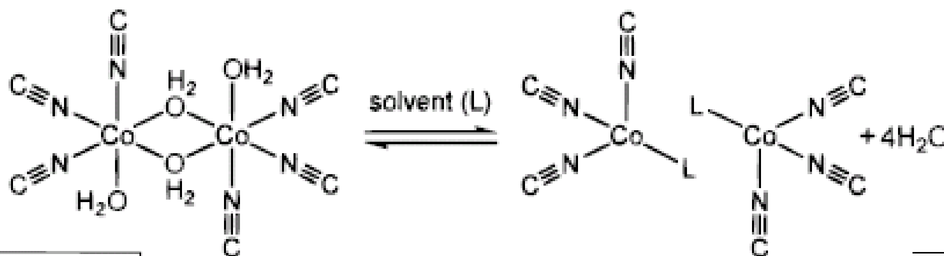
2. Formation or breaking of bond in the group, which transmits exchange interactions

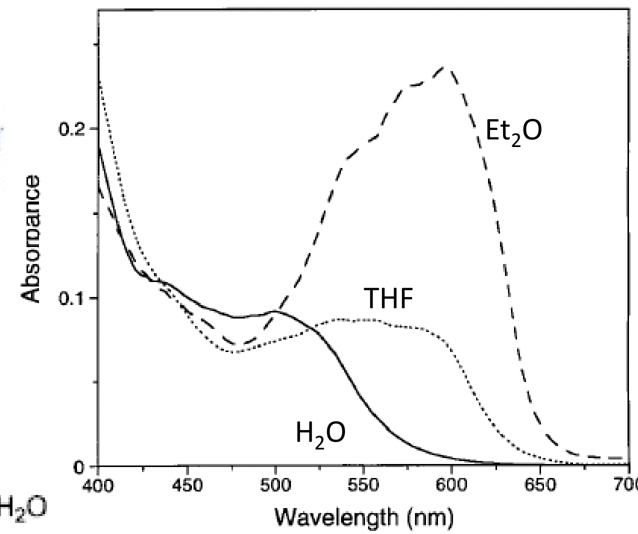
3. Change of bond lengths and angles without new bonds formation or bonds breaking in coordination polymer

$[Co_2(H_2O)_4][Re_6S_8(CN)_6]\cdot 10H_2O$

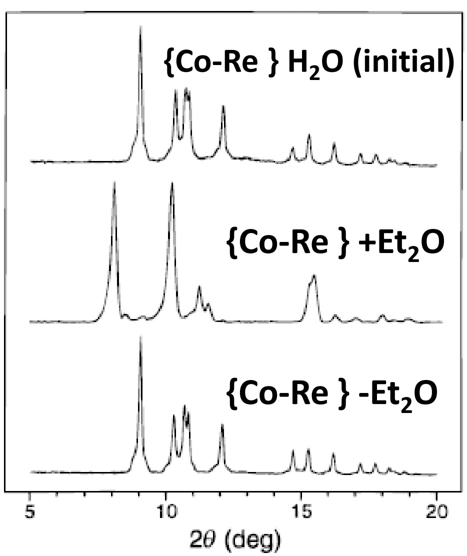


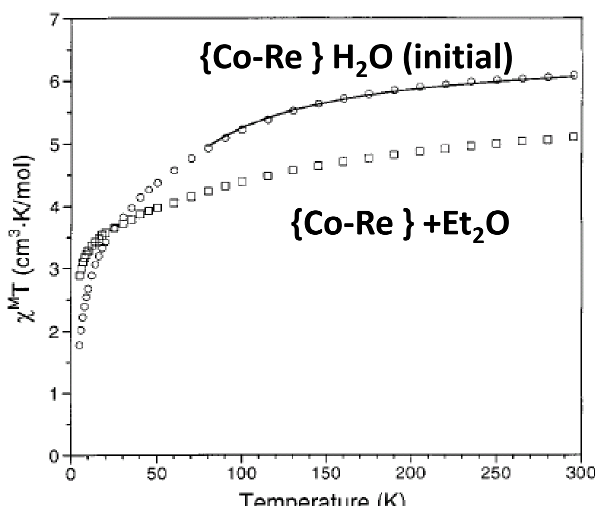






solvent	A_{596}/A_{434}	apparent color
as-prepared (water)	0.053(9)	orange
methanol	0.3(1)	orange
cyclohexane	0.4(1)	orange
acetonitrile	0.4(1)	orange
methyl *tert*-butyl ether	0.40(3)	orange
dichloromethane	0.46(9)	orange
ethanol	0.5(1)	orange-red
dimethylformamide	0.51(6)	orange-red
triethylamine	0.55(7)	orange-red
nitromethane	0.64(3)	red-violet
tetrahydrofuran	0.7(1)	red-violet
acetone	0.8(1)	violet
propionitrile	1.03(3)	violet
n-octanol	1.09(6)	violet
n-propanol	1.61(4)	violet
ethyl acetate	1.7(1)	violet
i-propanol	2.2(4)	blue-violet
diethyl ether	2.3(1)	blue-violet

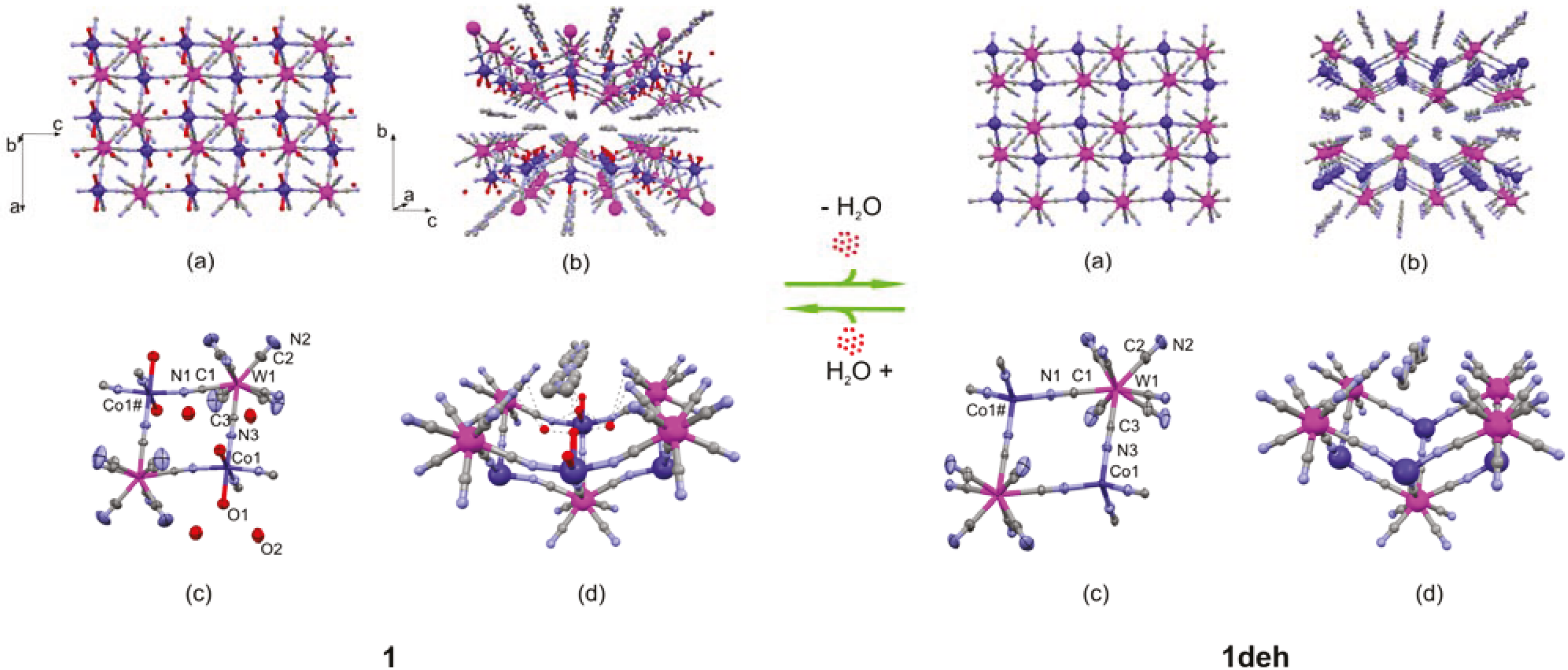




≈ 20 % decrease of $\chi_M T$ at T > 100 K

L.G. Beauvais, M.P. Shores, J.R. Long. *J. Am. Chem. Soc.* 2000. 122. 2763–2772.

$(tetrenH_5)_{1.6}\{Co(H_2O)_2[W(CN)_8]\}_4\cdot 12H_2O$ (tetren = tetraethylenepentaamine)



Podgajny, R.; Choraży, S.; Nitek, W.; Budziak, A.; Rams, M.; Gómez-García, C.J.; Oszajca, M.; Łasocha, W.; Sieklucka, B. *Cryst. Growth Des.* **2011**, *11*, 3866–3876.

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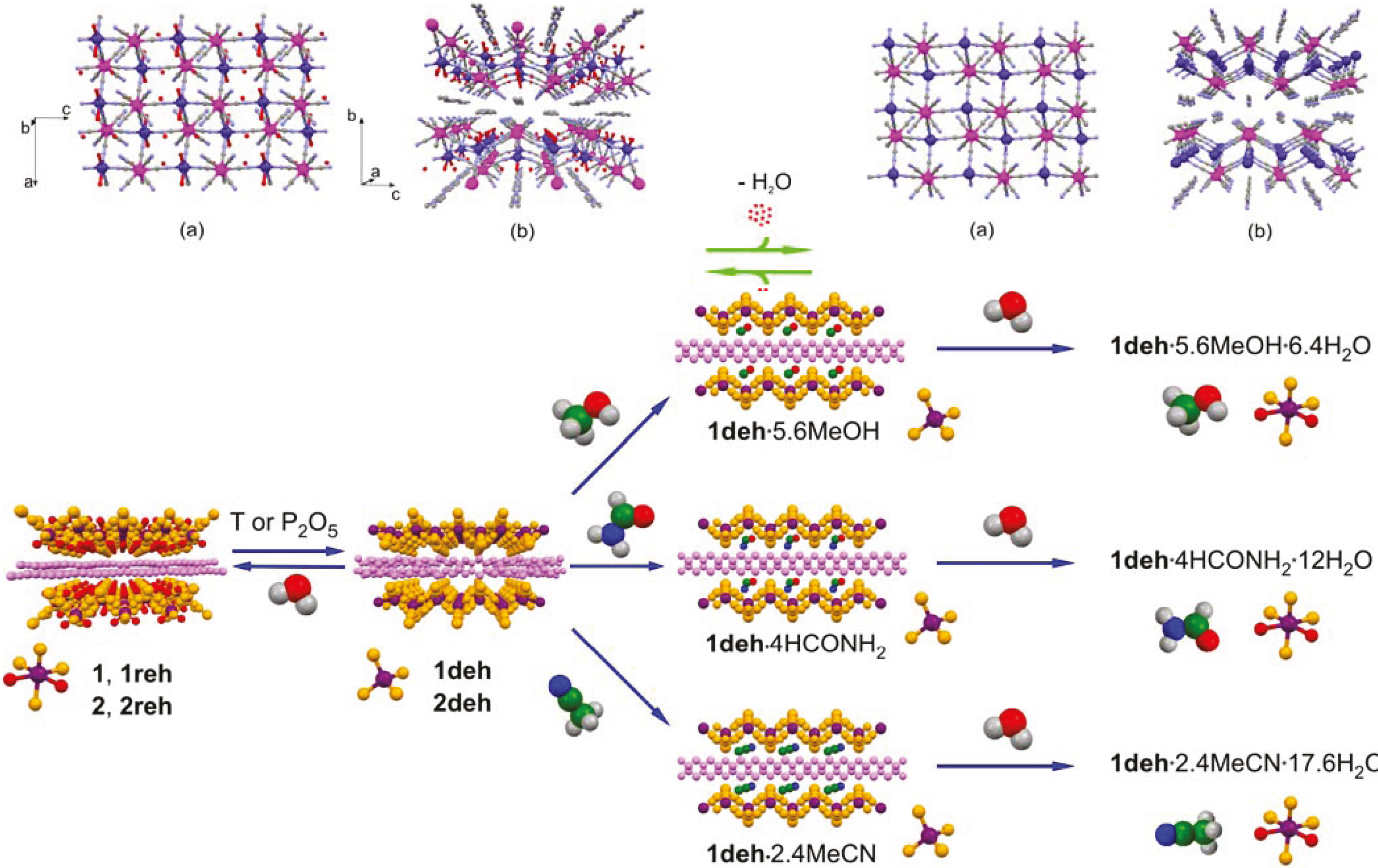

Podgajny, R.; Chorażу, S.; Nitek, W.; Budziak, A.; Rams, M.; Gómez-García, C.J.; Oszajca, M.; Łasocha, W.; Sieklucka, B. *Cryst. Growth Des.* **2011**, *11*, 3866–3876.

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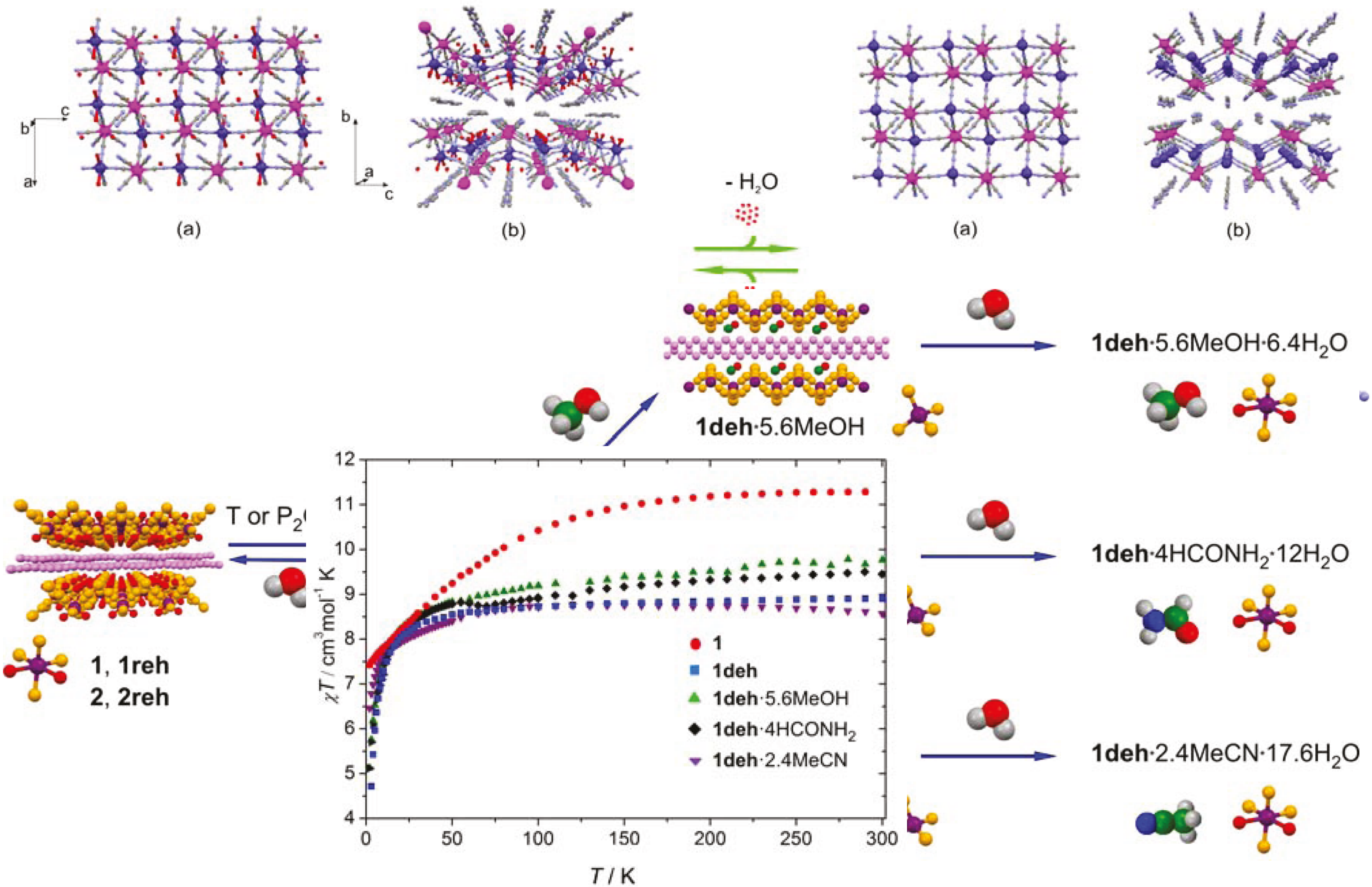
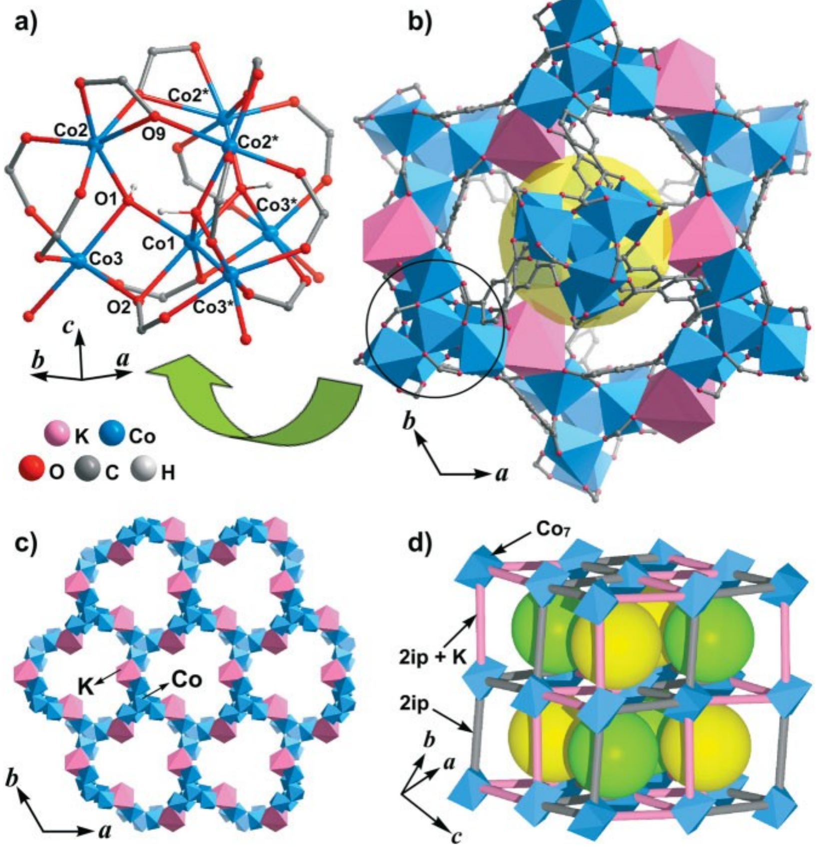
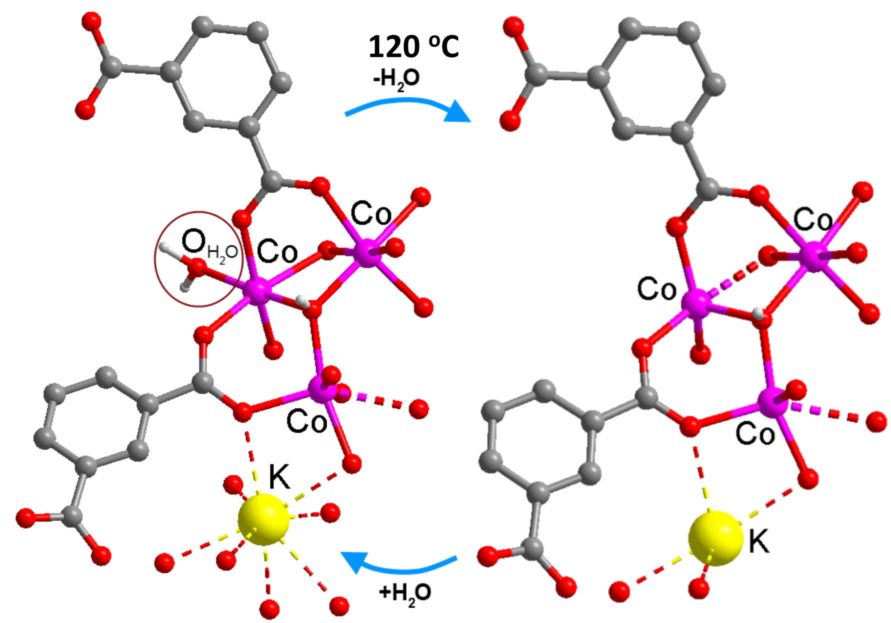


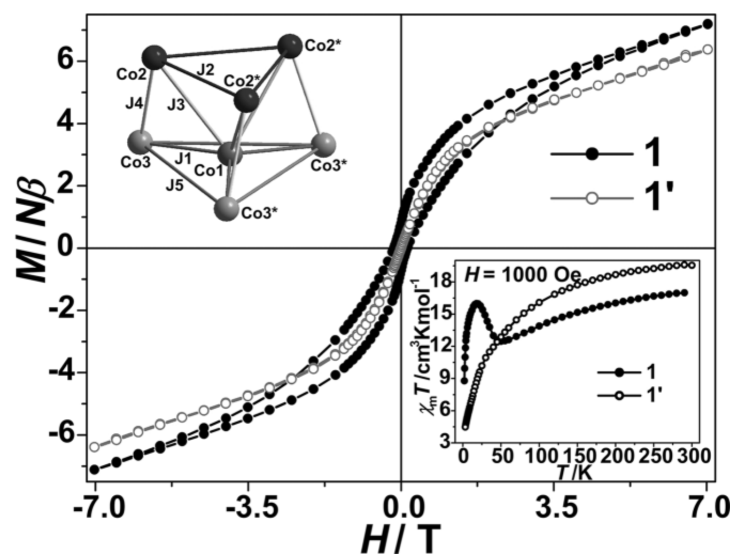
≈ 20 % decrease of $\chi_M T$ at room temperature

Podgajny, R.; Chorazy, S.; Nitek, W.; Budziak, A.; Rams, M.; Gómez-García, C.J.; Oszajca, M.; Łasocha, W.; Sieklucka, B. *Cryst. Growth Des.* **2011**, *11*, 3866–3876.

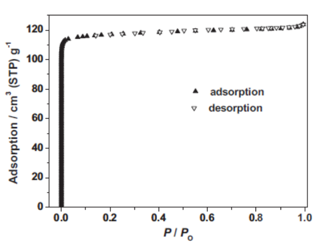
$KCo_7(OH)_3(1,3\text{-bdc})_6(H_2O)_4 \cdot 12H_2O \leftrightarrow KCo_7(OH)_3(1,3\text{-bdc})_6$ (1,3-bdc = 1,3-benzenedicarboxylate)







$KCo_7(OH)_3(1,3\text{-bdc})_6$: $S_L = 510\ m^2/g$ (N_2, 77 K)



Cheng, X.-N.; Zhang, W.-X.; Lin, Y.-Y.; Zheng, Y.-Z.; Chen, X.-M.
A *Adv. Mater.* **2007**, *19*, 1494–1498

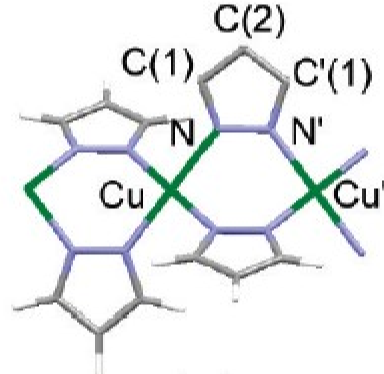
$[Cu(pz)_2(NH_3)] \leftrightarrow [Cu(pz)_2] \leftrightarrow [Cu(pz)_2(H_2O)]$

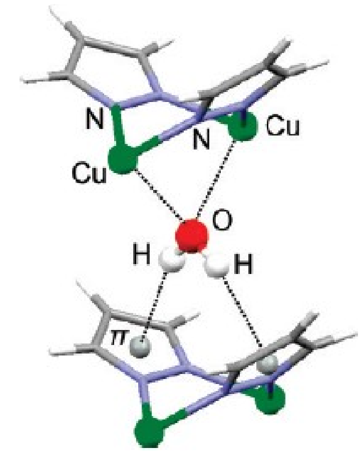
$$n\,Cu(NO_3)_2 + 2n\,Hpz \xrightarrow{28\%\ NH_{3(aq)}} [Cu(pz)_2(NH_3)]_n + 2n\,NH_4NO_3$$
1

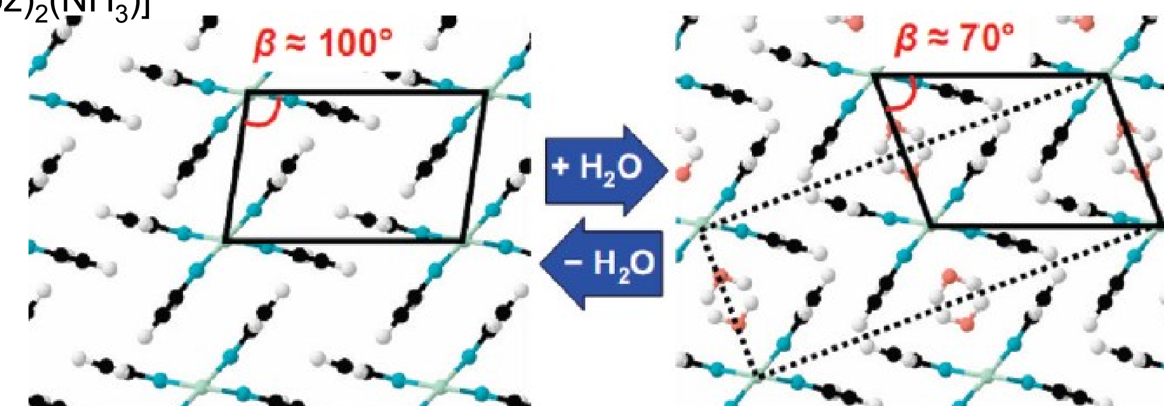
$$[Cu(pz)_2(NH_3)]_n \underset{NH_3}{\overset{90°C,\ 0.1\ mm\ Hg}{\rightleftharpoons}} \beta\text{-}[Cu(pz)_2]_n$$
2

$$\beta\text{-}[Cu(pz)_2]_n \underset{90°C,\ 0.1\ mm\ Hg}{\overset{H_2O}{\rightleftharpoons}} [Cu(pz)_2(H_2O)]_n$$
3

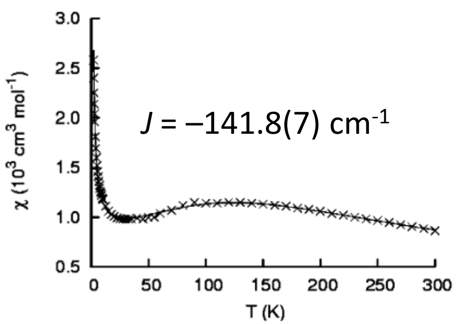
$[Cu(pz)_2]$ $[Cu(pz)_2(H_2O)]$ $[Cu(pz)_2(NH_3)]$



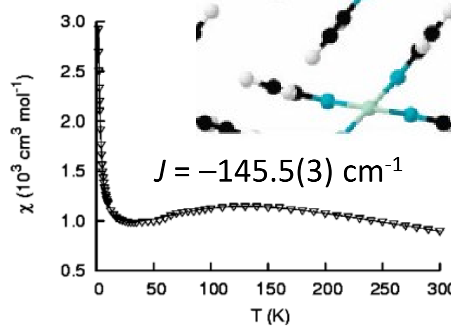




$H = -J\Sigma S_i S_{i+1}$



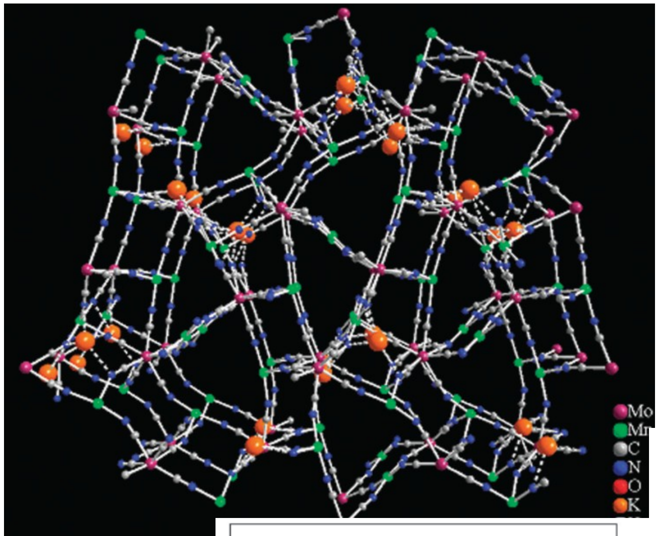
$[Cu(pz)_2]$

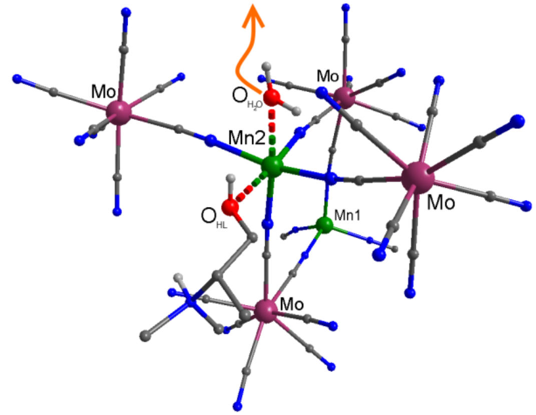


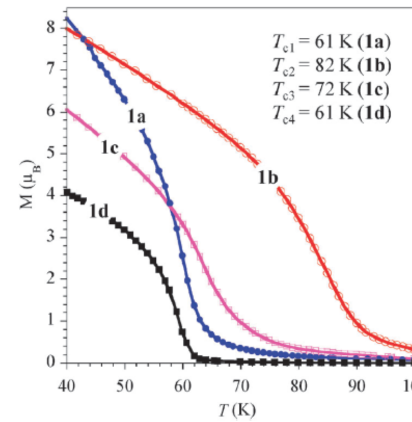
$[Cu(pz)_2(H_2O)]$

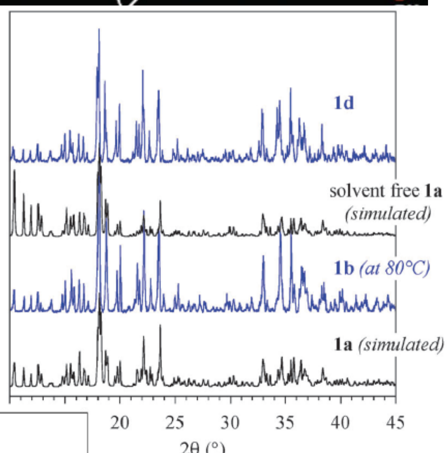
Bencini, A.; Casarin, M.; Forrer, D.; Franco, L.; Garau, F.; Masciocchi, N.; Pandolfo, L.; Pettinari, C.; Ruzzi, M.; Vittadini, A. *Inorg. Chem.* **2009**, *48*, 4044–4051

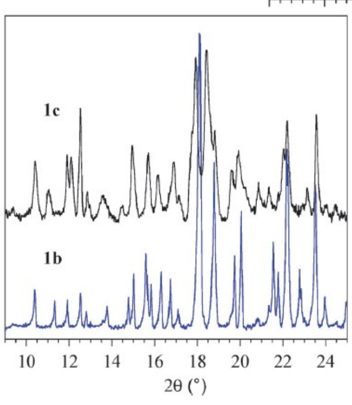
$[K_2(H_2O)_4Mn_5(H_2O)_8(MeCN)\{Mo(CN)_7\}_3]\cdot 2H_2O \leftrightarrow [K_2Mn_5\{Mo(CN)_7\}_3]$

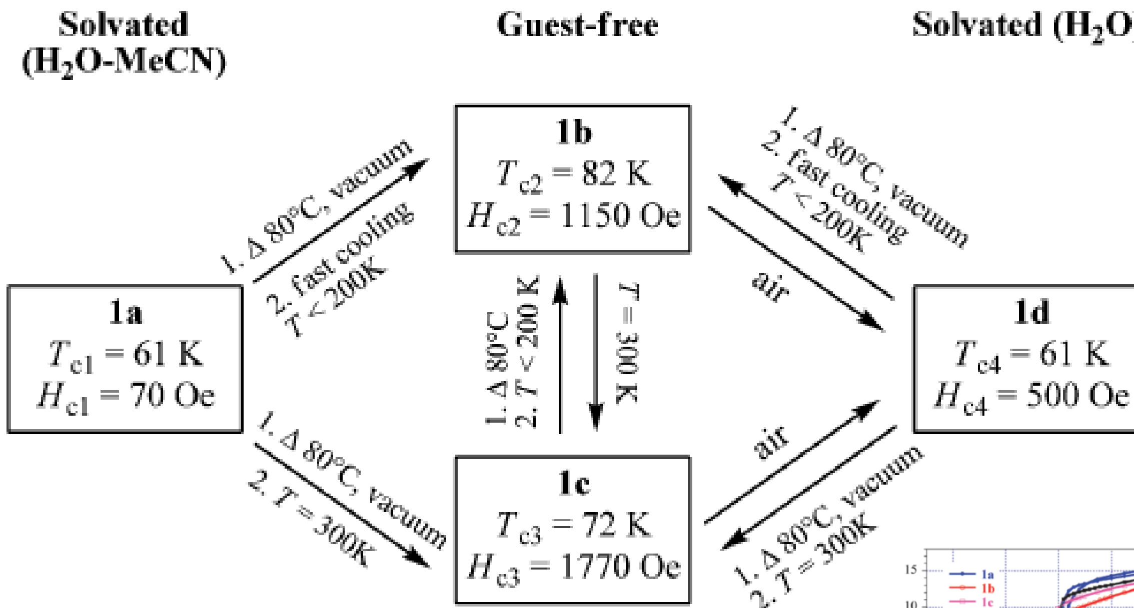


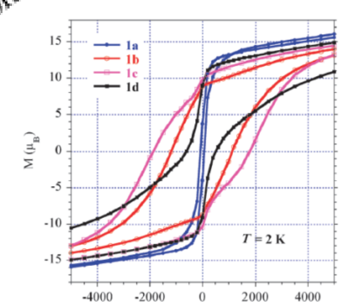






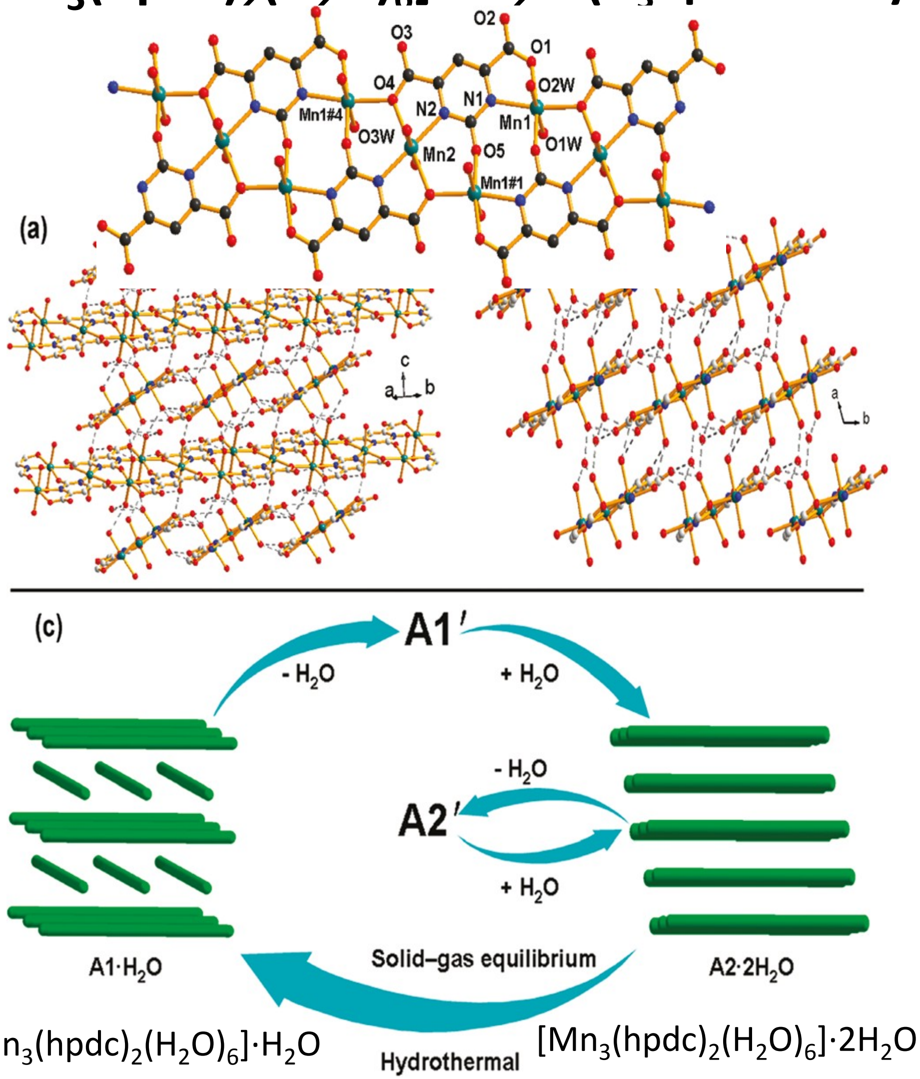


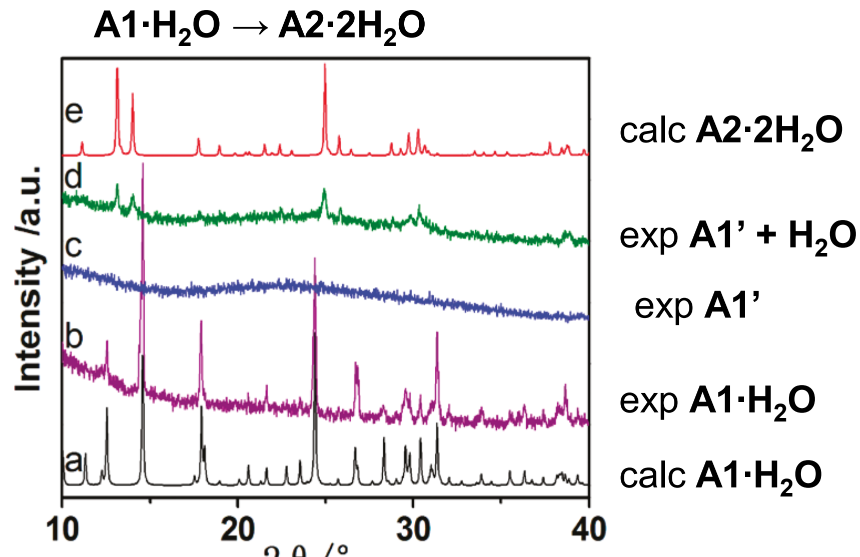


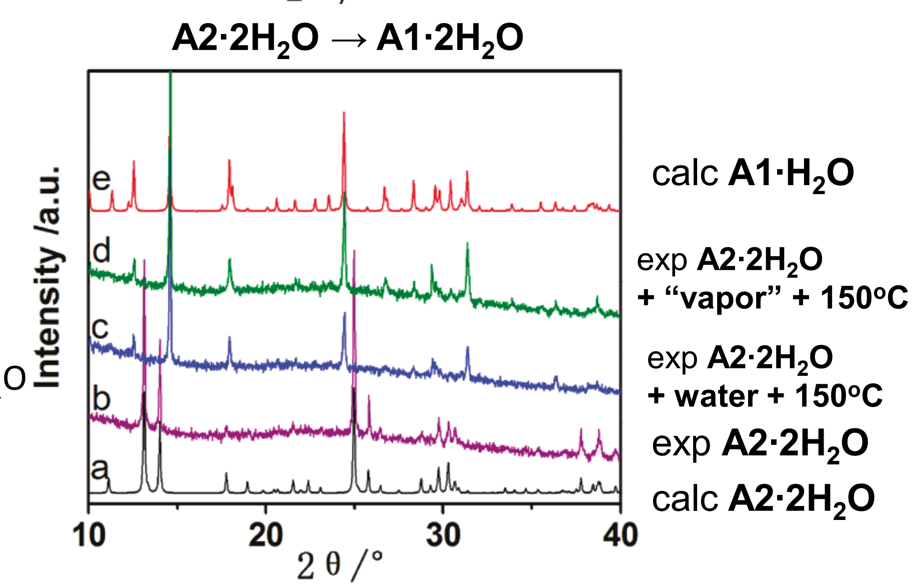


Milon, J.; Guionneau, P.; Duhayon, C.; Sutter, J.-P. *New J. Chem.* **2011**, *35*, 1211–1218

$[Mn_3(hpdc)_2(H_2O)_6]\cdot xH_2O$ (H_3hpdc = 2-hydroxypyrimidine-4,6-dicarboxylic acid)



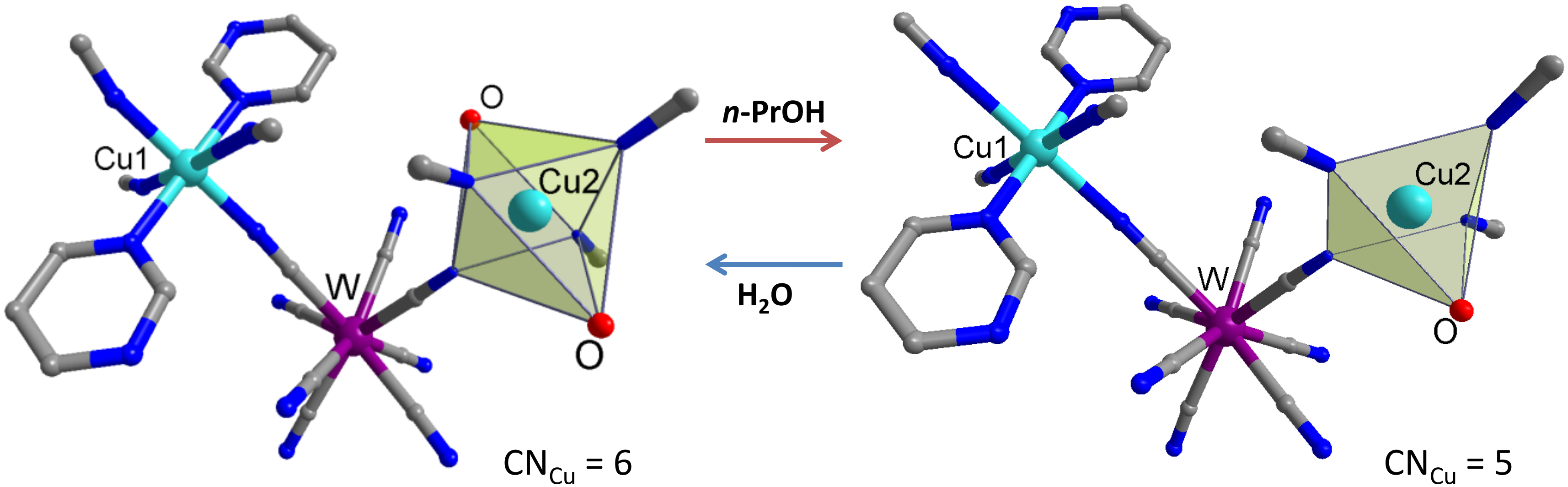




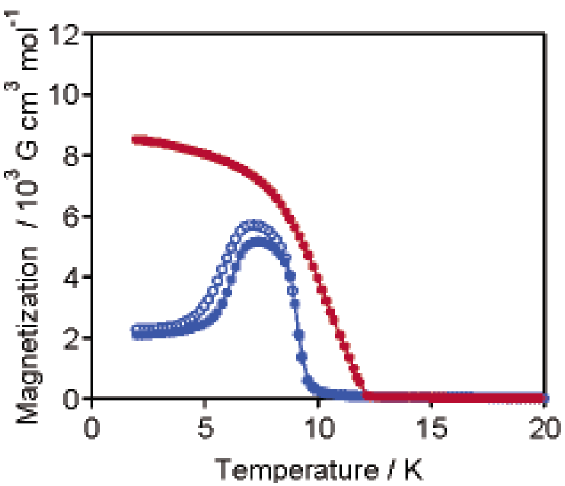
	J (in absolute value), cm^{-1}	zJ', cm^{-1}
$A1\cdot H_2O$	–0.88	–1.57
$A2\cdot 2H_2O$	+0.02	–0.47

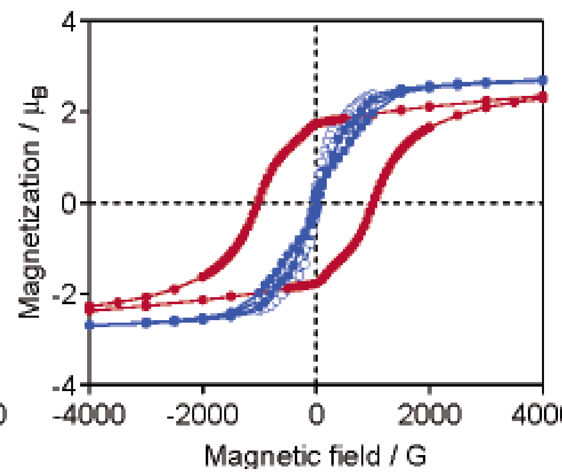
Jian-Ke Sun, Xu-Hui Jin, Chao Chen, and Jie Zhang, Inorg. Chem. **2010**, 49, 7046–7051

$Cu_3[W(CN)_8]_2(pym)_2 \cdot 8H_2O \leftrightarrow Cu_3[W(CN)_8]_2(pym)_2 \cdot 3/2PrOH \cdot 9/4H_2O$



T_C = 9.5 K





T_C = 12 K

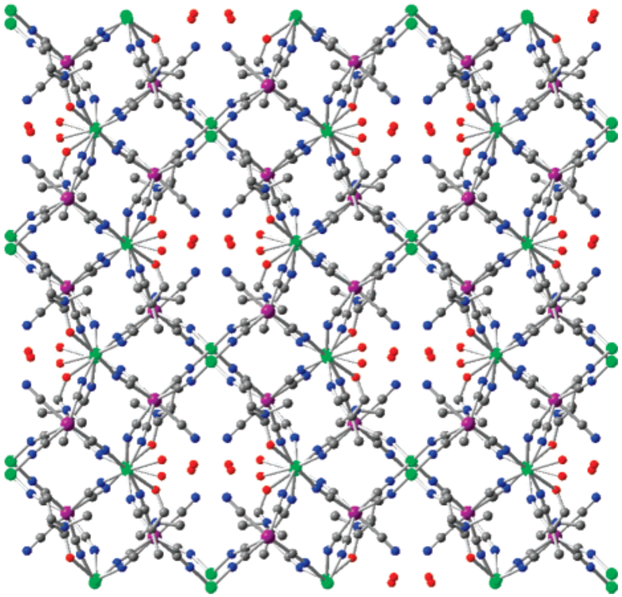
$\chi_M T$ (293 K) = 2.22 cm^3 K mol^{-1}

$\chi_M T$ (293 K) = 1.99 cm^3 K mol^{-1}

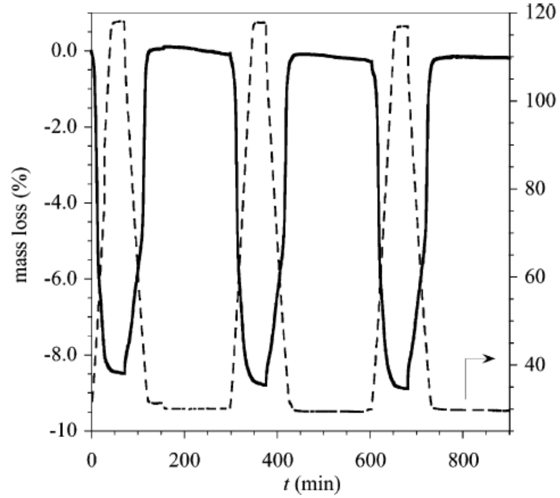
10 % decrease of $\chi_M T$ at 293 K

Ohkoshi, S.; Tsunobuchi, Y.; Takahashi, H.; Hozumi, T.; Shiro, M.; Hashimoto, K. Synthesis and Alcohol Vapor Sensitivity of a Ferromagnetic Copper–Tungsten Bimetallic Assembly. *J. Am. Chem. Soc.* **2007**, *129*, 3084–3085

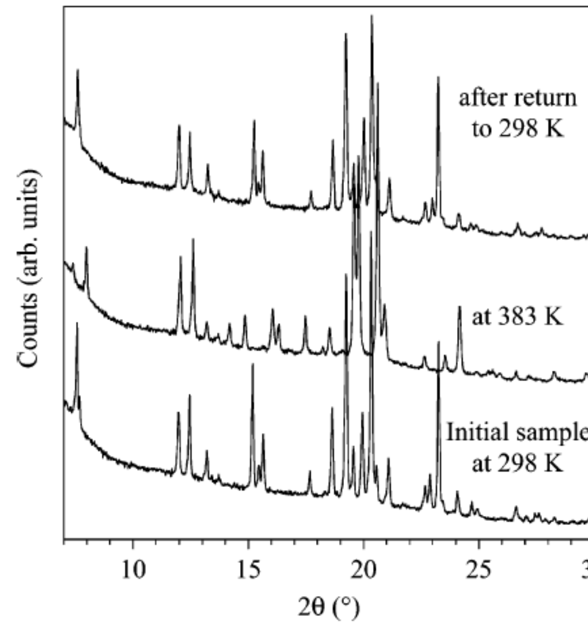
[{Mn(Hdmal)(H_2O)}$_2$Mn{Mo(CN)$_7$}$_2$]·2H_2O (L = N,N-dimethylalaninol)

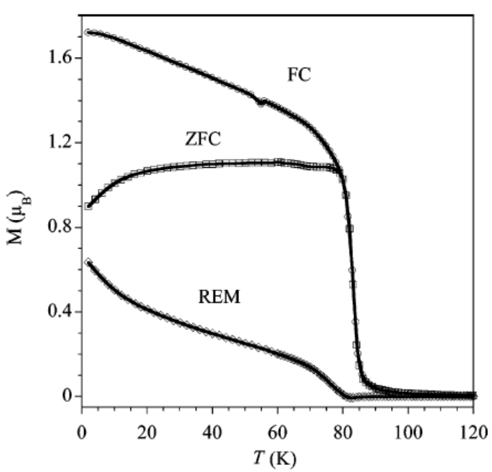


S_{BET} = 15 m^2/g



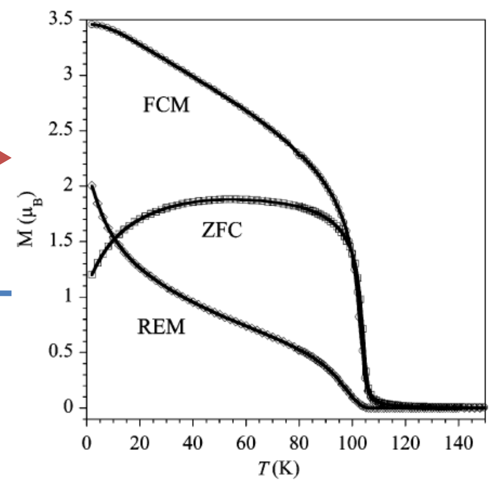
Loss of 4.7H_2O at 120 °C.
Fully reversible process.





120 °C

H_2O

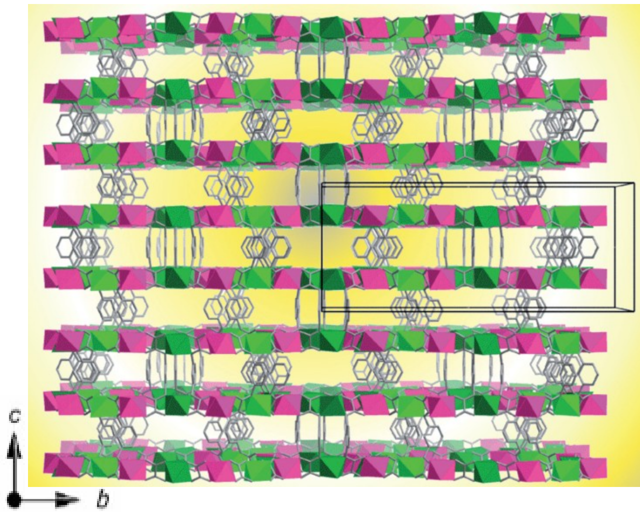


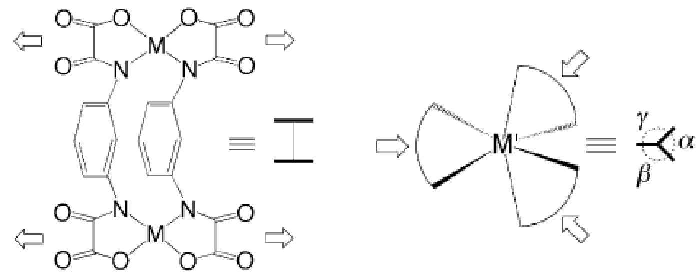
T_C = 85 K. **T_C = 106 K.**

Milon, J.; Daniel, M.-C.; Kaiba, A.; Guionneau, P.; Brandès, S.; Sutter, J.–P. Nanoporous Magnets of Chiral and Racemic [{Mn(HL)}$_2$Mn{Mo(CN)$_7$}$_2$] with Switchable Ordering Temperatures (T_C = 85 K ↔ 106 K) Driven by H_2O Sorption (L = N,N-Dimethylalaninol). *J. Am. Chem. Soc.* **2007**, *129*, 13872–13878

$[Na(H_2O)_4]_4[Mn_4\{Cu_2(mpba)_2(H_2O)_4\}_3]\cdot 56.5H_2O$

($mpba^{2-}$ = N,N’-1,3-phenylenebis(oxamate))



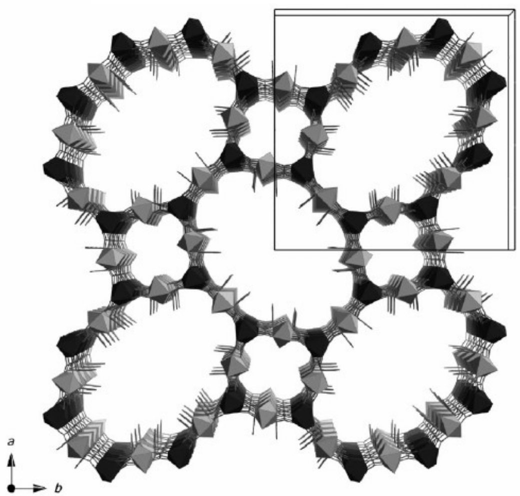


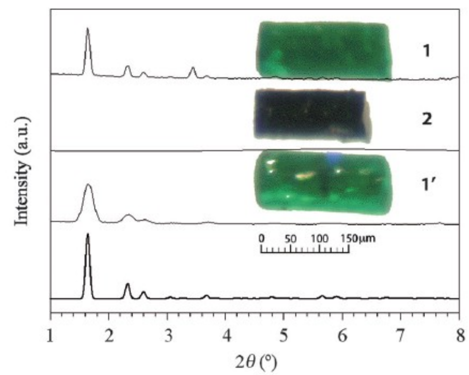
$Cu_2(mpba)_2$

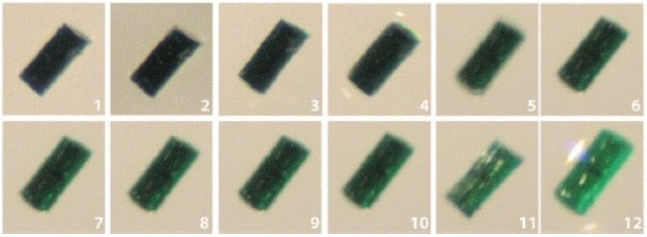
Δ

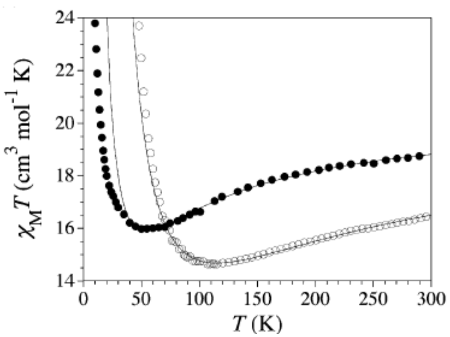
$-85H_2O$

$[Na_4Mn_4\{Cu_2(mpba)_2\}_3]$









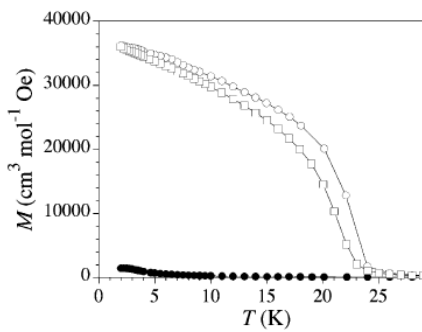
T_C = 22.5 K

J_{CuMn} = –31.1(2) cm^{-1}

Δ

J_{CuMn} = –13.4(3) cm^{-1}

T_C = 2.3 K



Ferrando-Soria, J.; Ruiz-García, R.; Cano, J.; Stiriba, S.-E.; Vallejo, J.; Castro, I.; Julve, M.; Lloret, F.; Amorós, P.; Pasán, J.; Ruiz-Pérez, C.; Journaux, Y.; Pardo, E. Reversible Solvatomagnetic Switching in a Spongelike Manganese(II)–Copper(II) 3D Open Framework with a Pillared Square/Octagonal Layer Architecture. *Chem. Eur. J.* **2012**, *18*, 1608

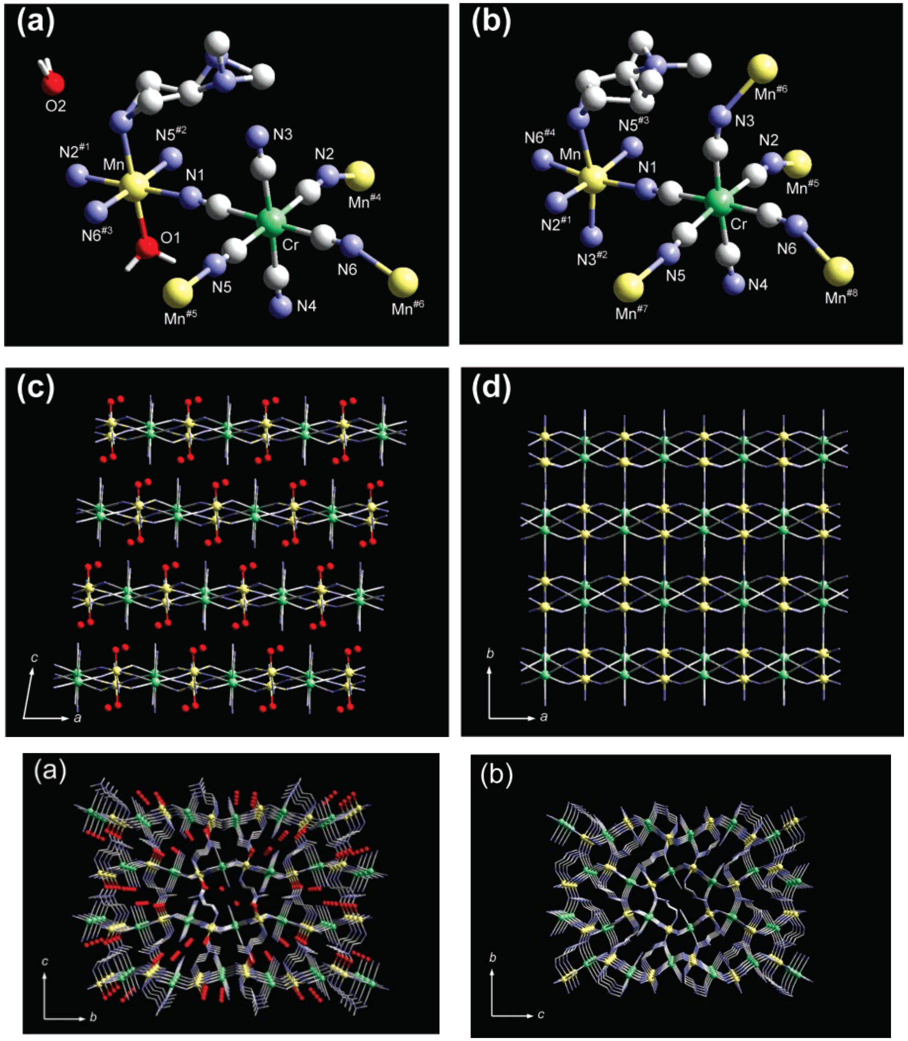
1. Change of coordination environment of paramagnetic metal ion

2. <u>Formation or breaking of bond in the group, which transmits exchange interactions</u>

3. Change of bond lengths and angles without new bonds formation or bonds breaking in coordination polymer

$[Mn(NNdmenH)(H_2O)][Cr(CN)_6]\cdot H_2O \leftrightarrow [Mn(NNdmenH)][Cr(CN)_6]$

(NNdmen = N,N-dimethylethylenediamine)

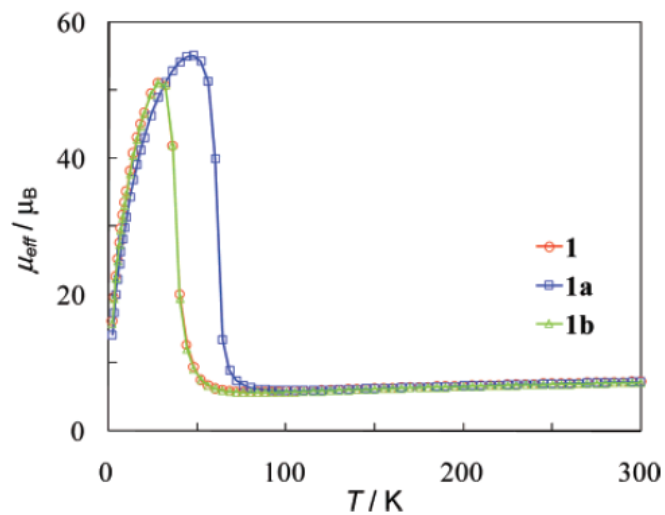


2D

$-2H_2O$

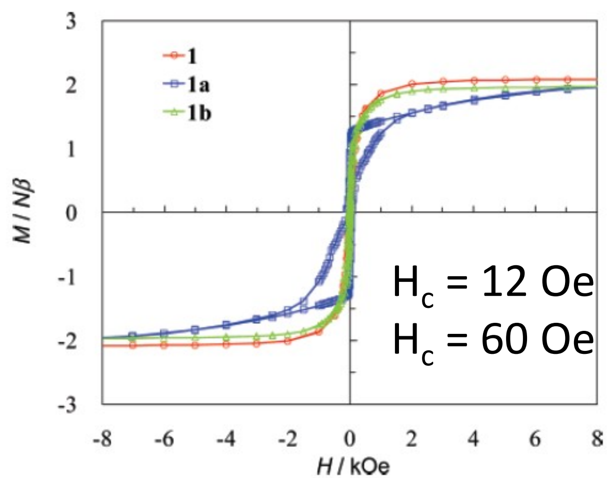
t = 100 °C

3D



T_c = 35.2 K for 2D

T_c = 60.4 K for 3D



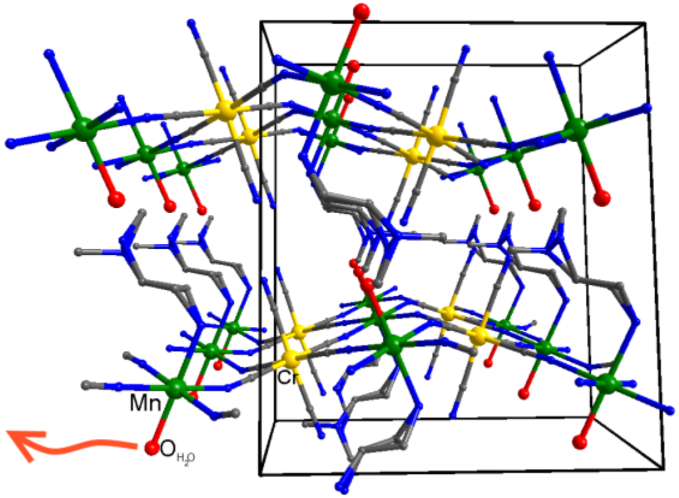
H_c = 12 Oe for 2D

H_c = 60 Oe for 3D

Kaneko, W.; Ohba, M.; Kitagawa, S. A Flexible Coordination Polymer Crystal Providing Reversible Structural and Magnetic Conversions. *J. Am. Chem. Soc.* **2007**, *129*, 13706–13712.

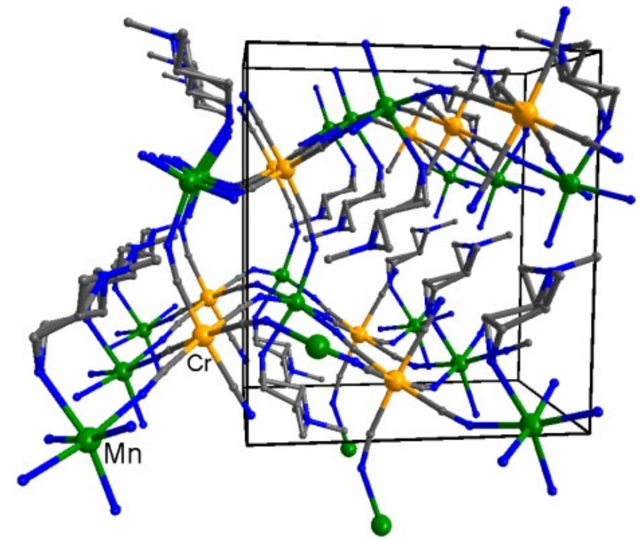
$[Mn(\textit{rac}\text{-}pnH)(H_2O)Cr(CN)_6]\cdot H_2O \leftrightarrow [Mn(\textit{rac}\text{-}pnH)(H_2O)Cr(CN)_6]\cdot H_2O$

(*rac*-pn = racemic 1,2-diaminopropane)



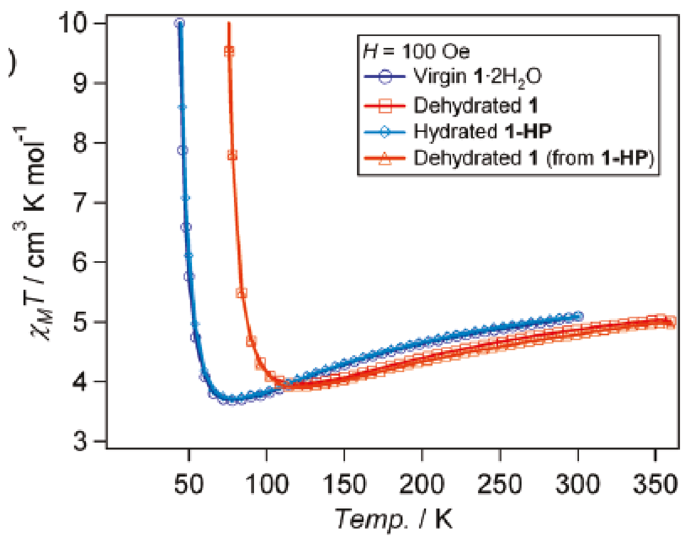
100 °C
$-2H_2O$

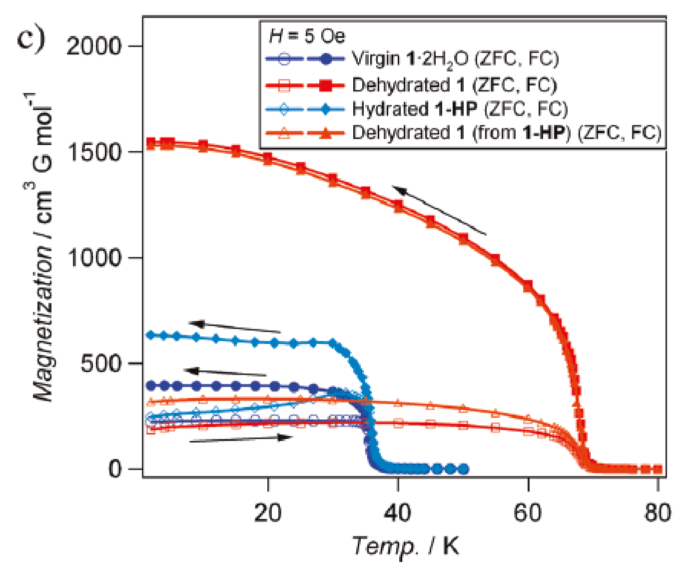
$+2H_2O$



2D↔3D

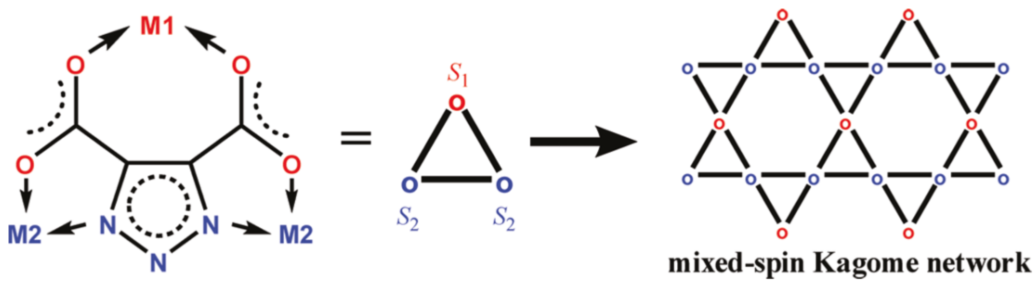
T_C = 36 K ↔ T_C = 70 K

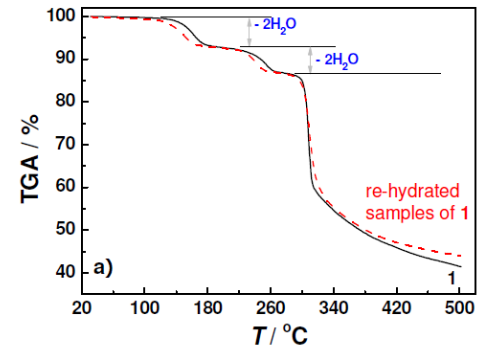


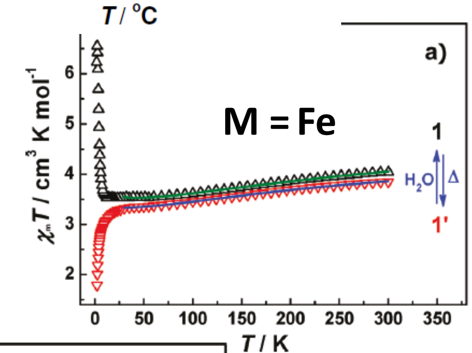


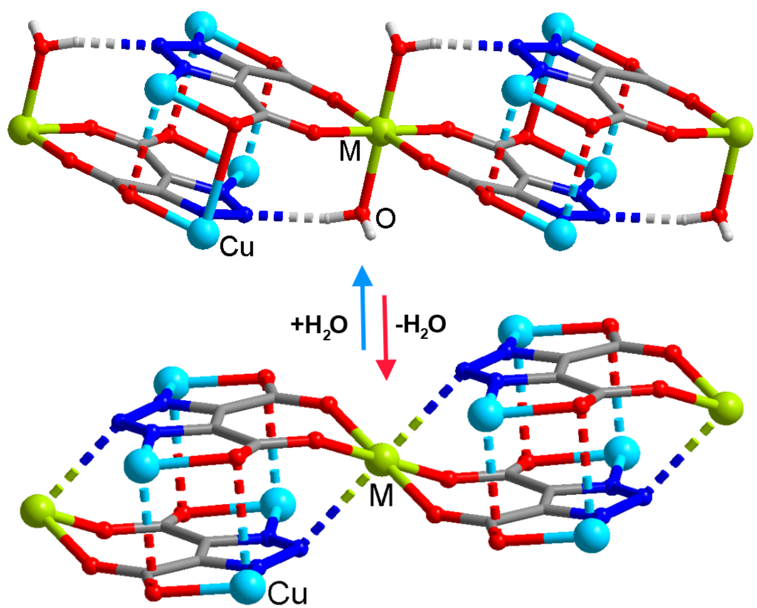
Yoshida, Y.; Inoue, K.; Kurmoo, M. Consecutive Irreversible Single-Crystal to Single-Crystal and Reversible Single-Crystal to Glass Transformations and Associated Magnetism of the Coordination Polymer, $[Mn^{II}(rac\text{-}pnH)(H_2O)Cr^{III}(CN)_6]\cdot H_2O$. *Inorg. Chem.* **2009**, *48*, 10726–10736

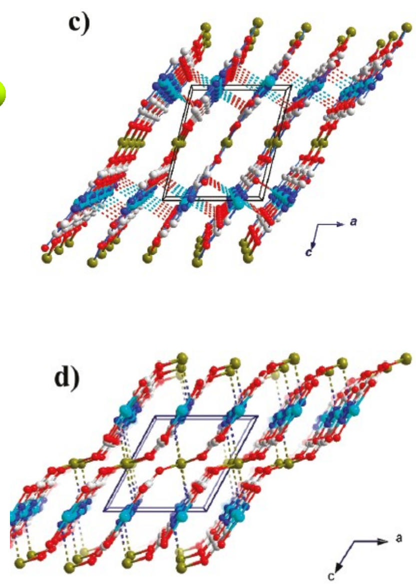
$[Cu_2M(tzdc)_2(H_2O)_2]\cdot 2H_2O$ (M^{II} = Fe or Mn, $tzdc^{3-}$ = 1,2,3-triazole-4,5-dicarboxylate)

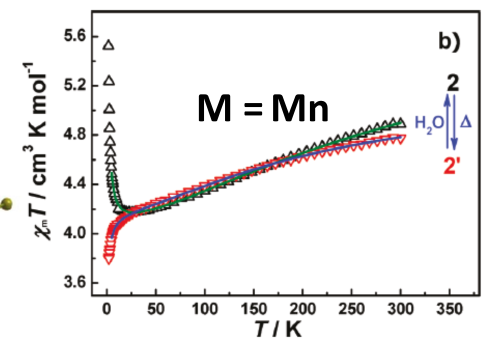












$$\chi_{tolal} = 2\chi(Cu^{II}\text{-Chain}) + \chi(M^{II})$$

Cu_2Fe: $J_{Cu\text{-}Cu(chain)} = -195(7)\ cm^{-1}$

$J_{Cu\text{-}Cu(chain)} = -182(6)\ cm^{-1}$

Cu_2Mn: $J_{Cu\text{-}Cu(chain)} = -174(4)\ cm^{-1}$

$J_{Cu\text{-}Cu(chain)} = -151(2)\ cm^{-1}$

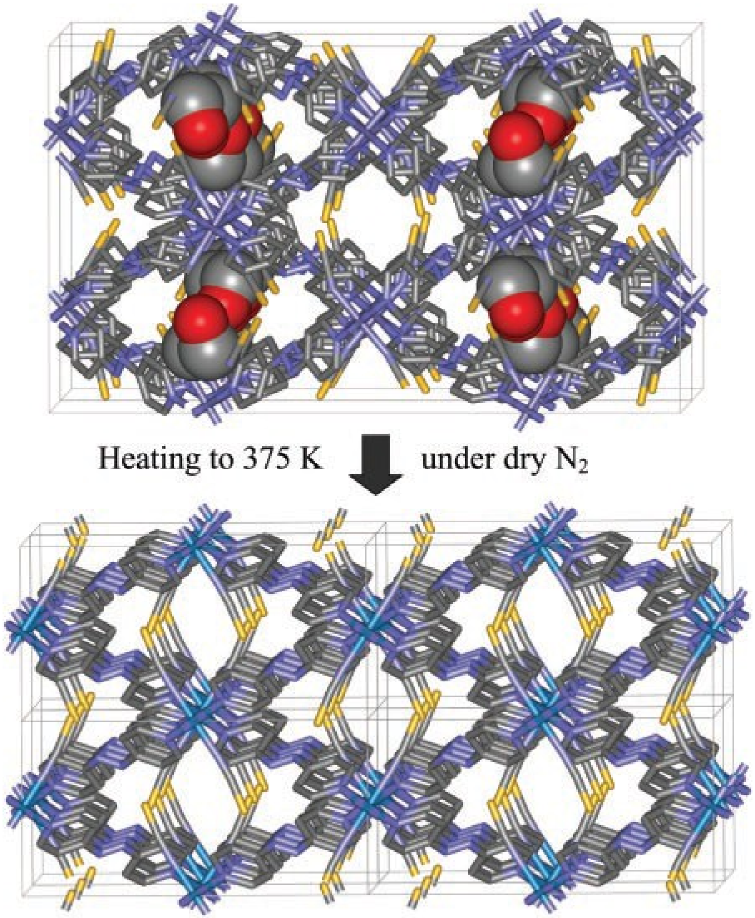
Zhang, W.-X.; Xue,W.; Chen, X.-M. Flexible Mixed-Spin Kagomé Coordination Polymers with Reversible Magnetism Triggered by Dehydration and Rehydration. *Inorg. Chem.* **2011**, *50*, 309–316.

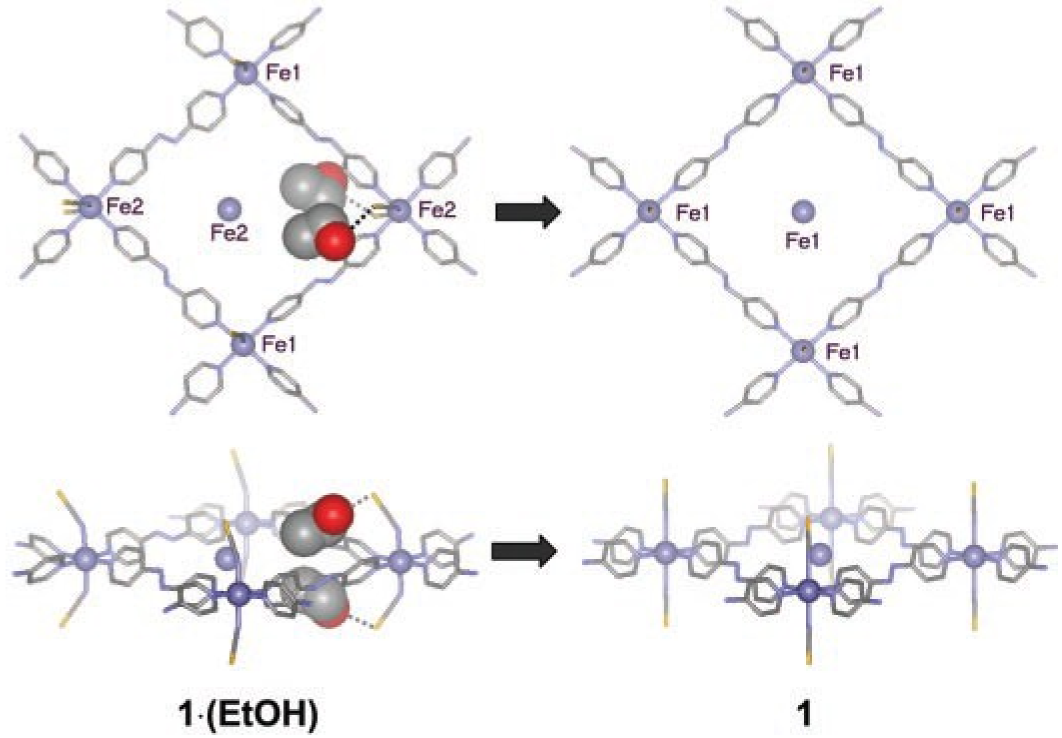
1. Change of coordination environment of paramagnetic metal ion

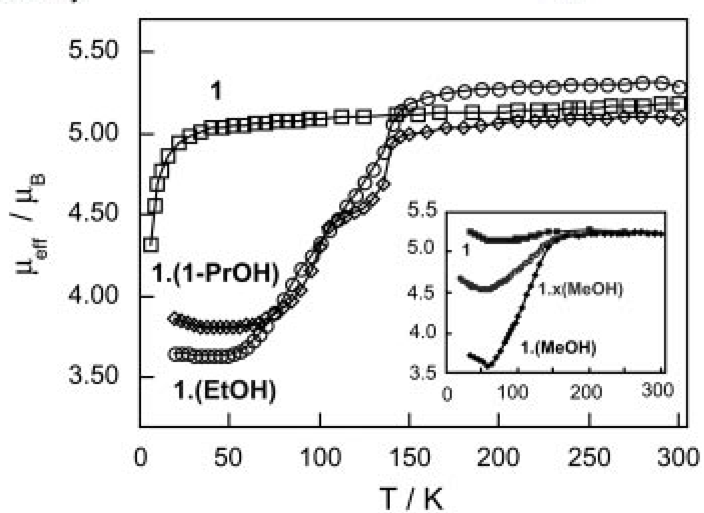
2. Formation or breaking of bond in the group, which transmits exchange interactions

3. <u>Change of bond lengths and angles without new bonds formation or bonds breaking in coordination polymer</u>

Guest-Dependent Spin Crossover in $Fe_2(azpy)_4(NCS)_4 \cdot Solv$ (azpy is *trans*-4,4'-azopyridine)

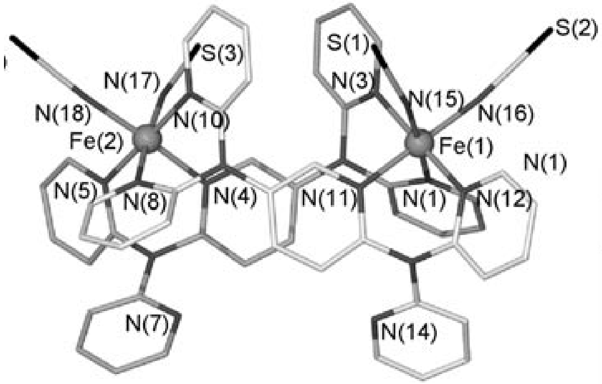




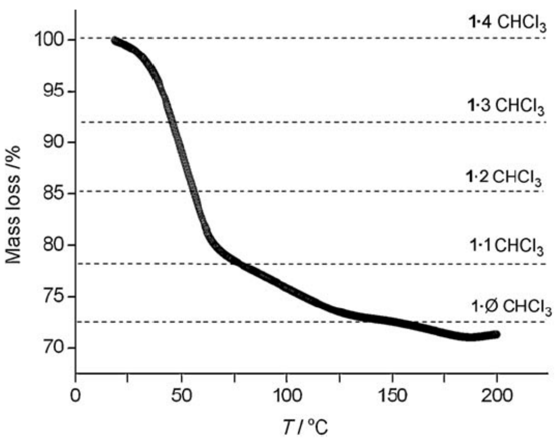


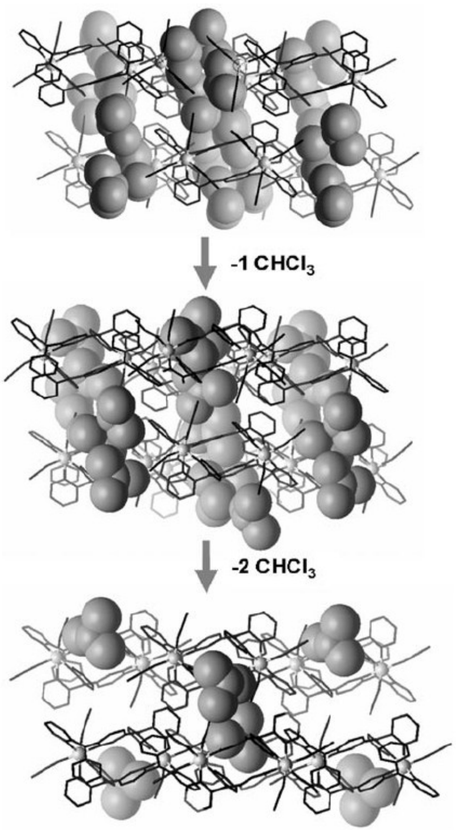
Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion J. D. Guest-Dependent Spin Crossover in a Nanoporous Molecular Framework Material. Science **2002**, *298*, 1762–1765

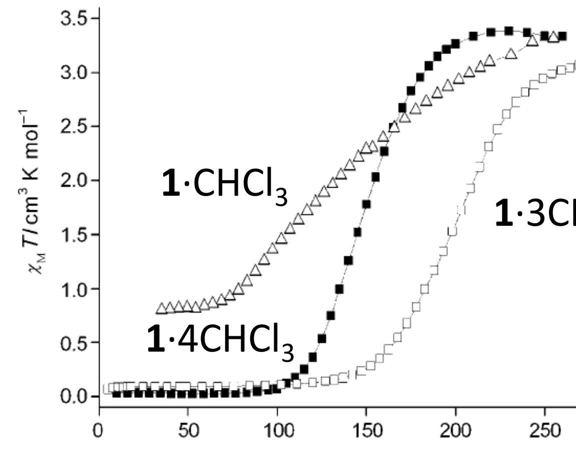
Thermal Induced Spin Crossover $[Fe^{II}_2(ddpp)_2(NCS)_4]\cdot 4CHCl_3$

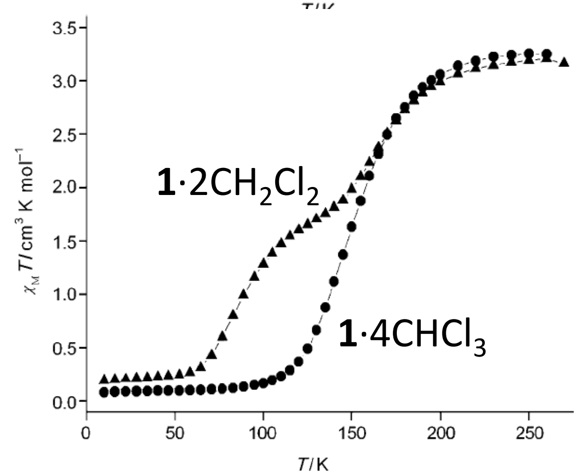


	1·4CHCl$_3$ 250 K	1·4CHCl$_3$ 123 K	1·3CHCl$_3$ 250 K	1·3CHCl$_3$ 110 K	1·CHCl$_3$ 250 K	1·CHCl$_3$ 110 K
spin state (Fe1-{Fe1/Fe2})	HS–HS	LS–LS	HS–HS	LS–LS	HS–HS	LS–HS
T [K]	250(2)	123(2)	250(2)	110(2)	250(2)	110(2)
$\langle d_{Fe(1)-N}\rangle$ [Å]	2.175(3)	2.004(5)	2.113(4)	1.977(3)	2.174(6)	1.984(4)
$\langle d_{Fe(2)-N}\rangle$ [Å]	–	–	2.173(4)	1.995(3)	2.179(6)	2.113(4)



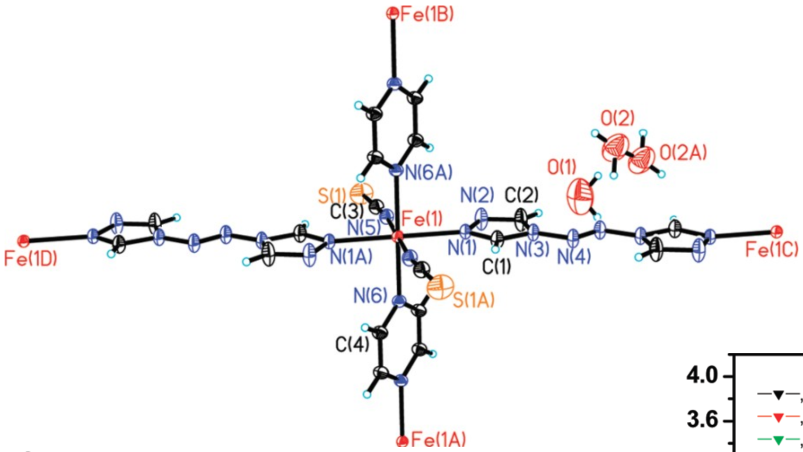


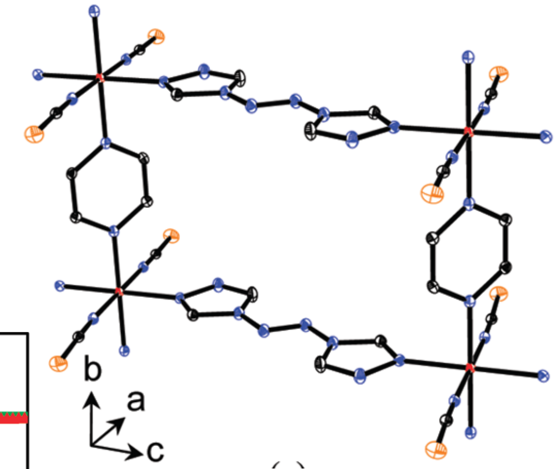


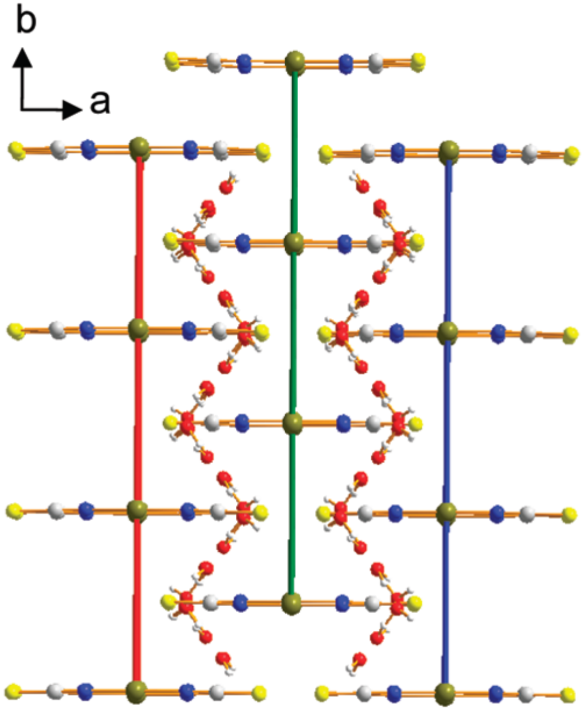


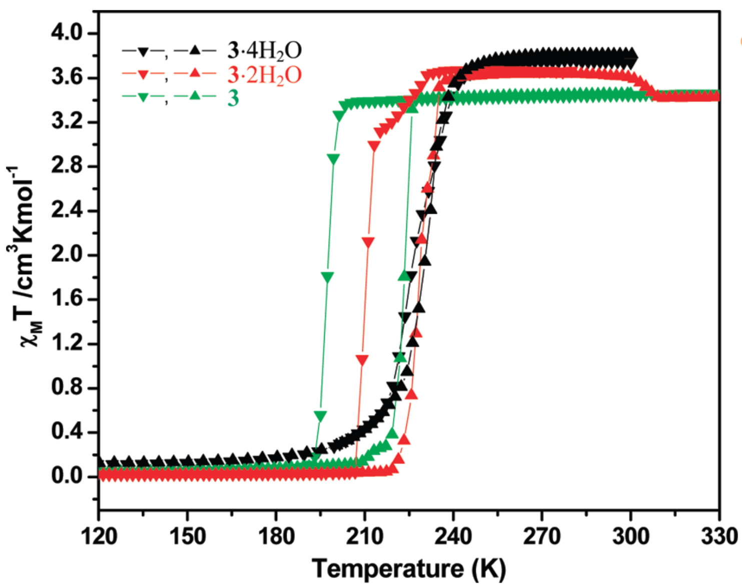
Amoore, J.J.M.; Neville, S.M.; Moubaraki, B.; Iremonger, S.S.; Murray, K.S.; Létard, J.-F.; Kepert, C.J. Thermal- and Light-Induced Spin Crossover in a Guest-Dependent Dinuclear Iron(II) System. *Chem. Eur. J.* **2010**, *16*, 1973–1982

$[Fe(\mu\text{-atrz})(\mu\text{-pyz})(NCS)_2]\cdot xH_2O$ (atrz = trans-4,4'-azo-1,2,4-triazole, x = 4, 2, 0)





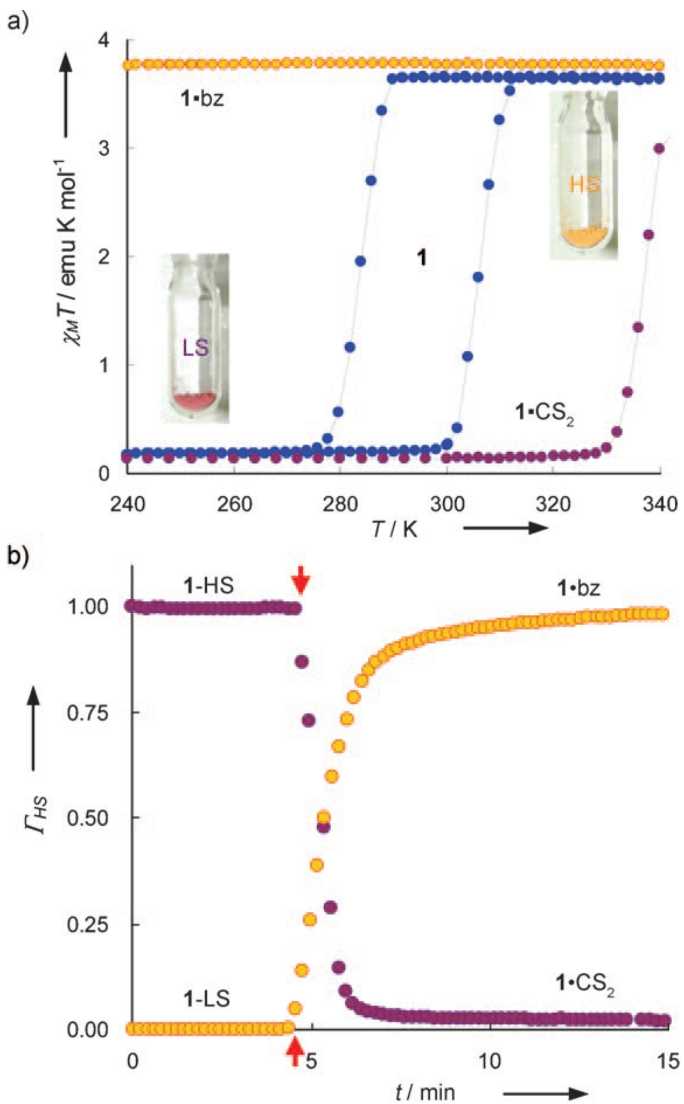


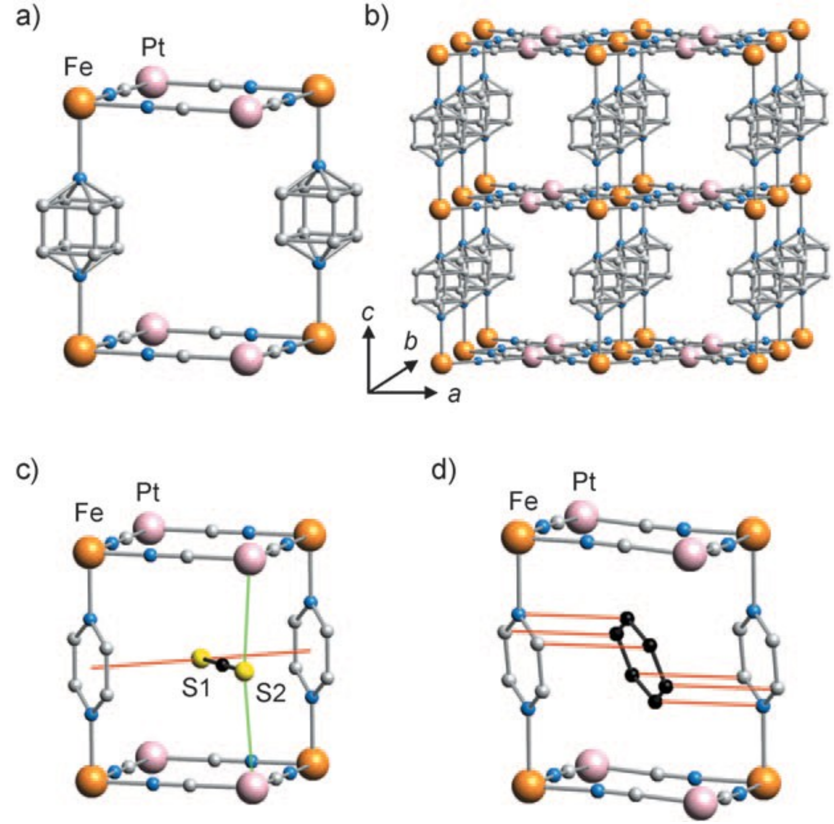


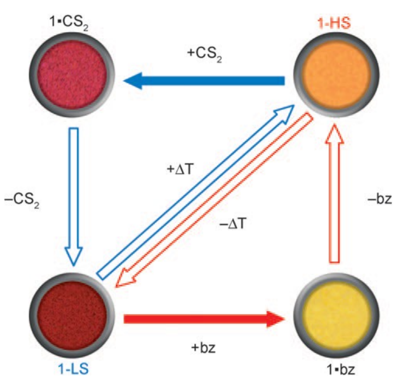
compound	$T_{1/2}\downarrow$ (K)	$T_{1/2}\uparrow$ (K)	hysteresis (K)
$3\cdot 4H_2O$	223	232	9
$3\cdot 2H_2O$	210	227	17
3	197	223	26

Chuang, Y.-C.; Liu, C.-T.; Sheu, C.-F.; Ho, W.-L.; Lee, G.-H.; Wang, C.-C.; Wang, Y. New Iron(II) Spin Crossover Coordination Polymers $[Fe(\mu\text{-atrz})_3]X_2\cdot 2H_2O$ ($X = ClO_4^-$, BF_4^-) and $[Fe(\mu\text{-atrz})(\mu\text{-pyz})(NCS)_2]\cdot 4H_2O$ with an Interesting Solvent Effect. *Inorg. Chem.* **2012**, *51*, 4663–4671

Chemo-Switching of Spin State in $[Fe(pyz)][Pt(CN)_4]\cdot xSolv$





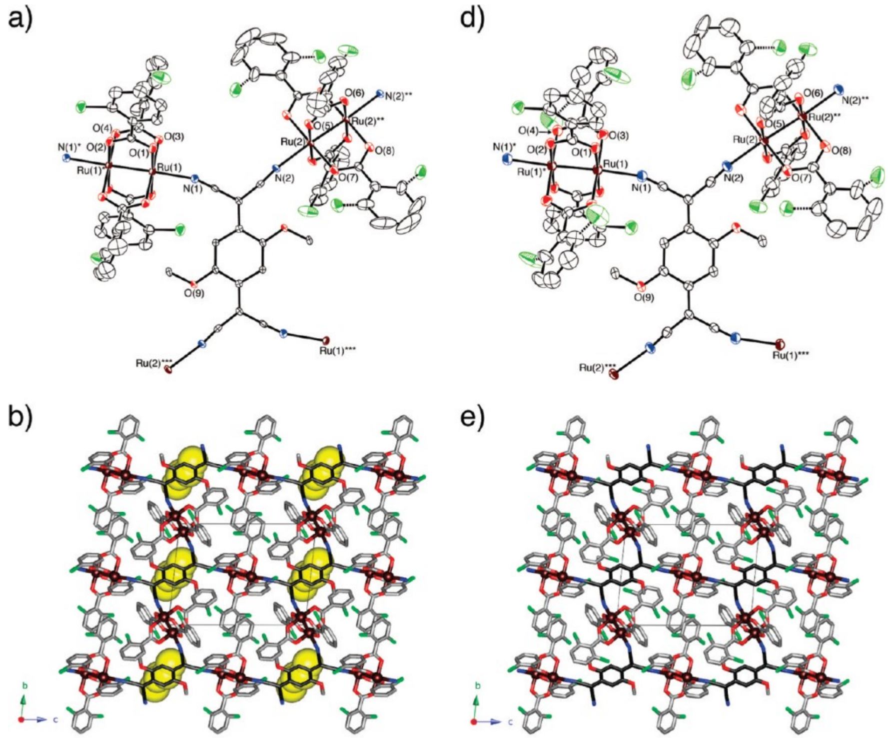


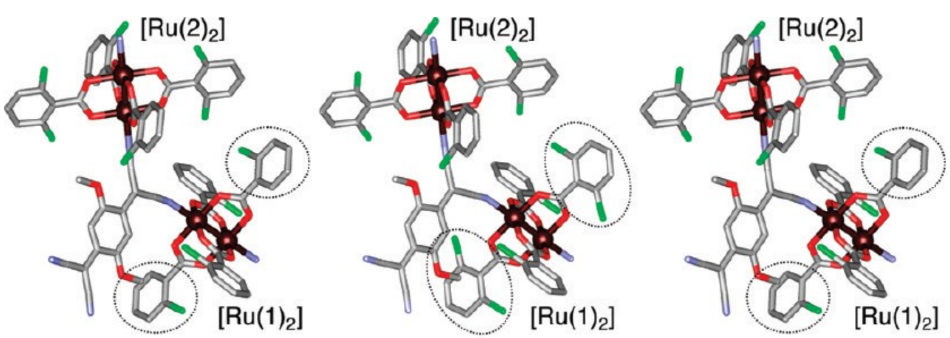
Guest molecule		Effect
CO_2, O_2	N_2,	None
H_2O, MeOH, 2-PrOH, Benzene, Toluene, Pyrrole, Furan,	D_2O, EtOH, Acetone, Pyrazine, Pyridine, Thiophene, THF	HS stabilized
CS_2		LS stabilized

Ohba, M.; Yoneda, K.; Agustí, G.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A.; Yamasaki, M.; Ando, H.; Nakao, Y.; Sakaki, S.; Kitagawa, S. Bidirectional Chemo-Switching of Spin State in a Microporous Framework. *Angew. Chem. Int. Ed.* **2009**, *48*, 4767–4771

$[\{Ru_2(O_2CPh\text{-}o\text{-}Cl)_4\}_2TCNQ(MeO)_2]\cdot CH_2Cl_2$

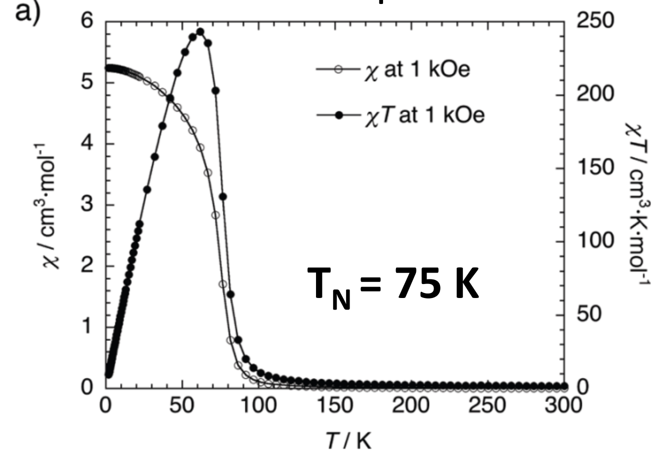
(o-$ClPhCO_2^-$ = *o*-chlorobenzoate; $TCNQ(MeO)_2$ = 2,5-dimethoxy-7,7,8,8-tetracyanoquinodimethane)



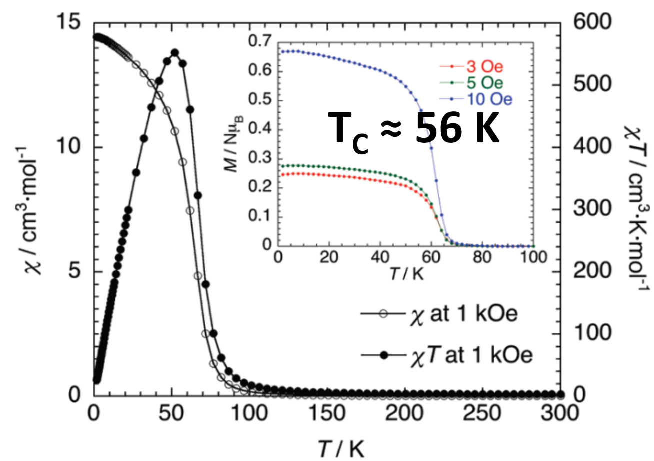


1 **1-dry** **1’**

solvated phase

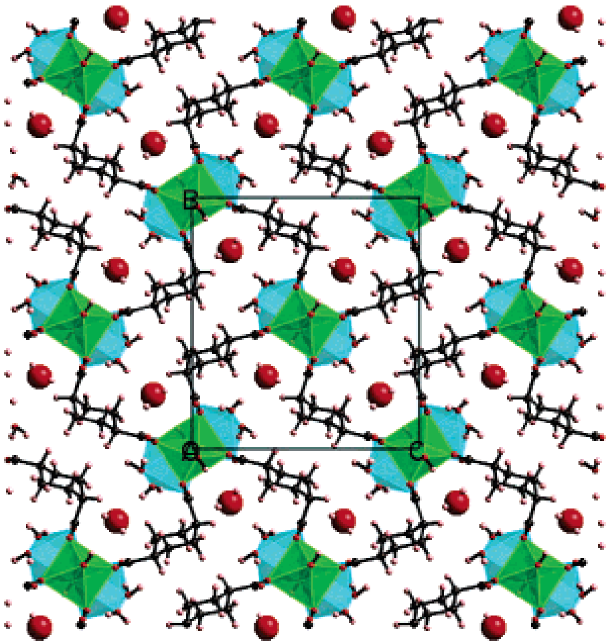


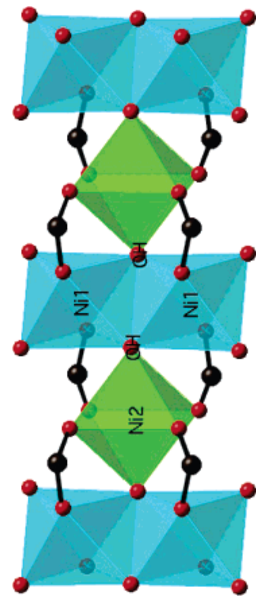
desolvated phase

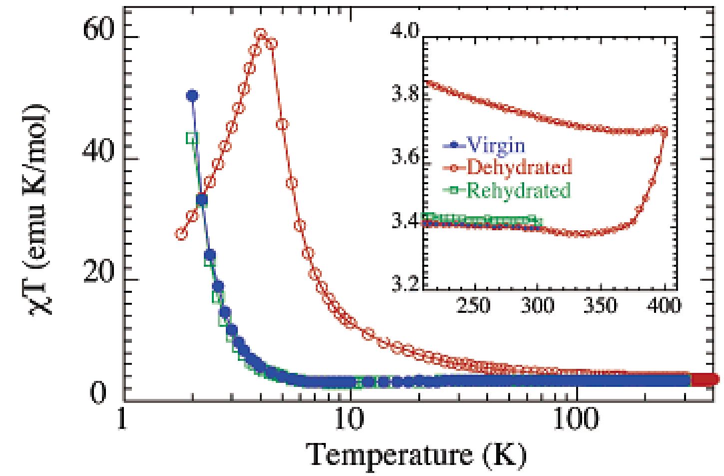


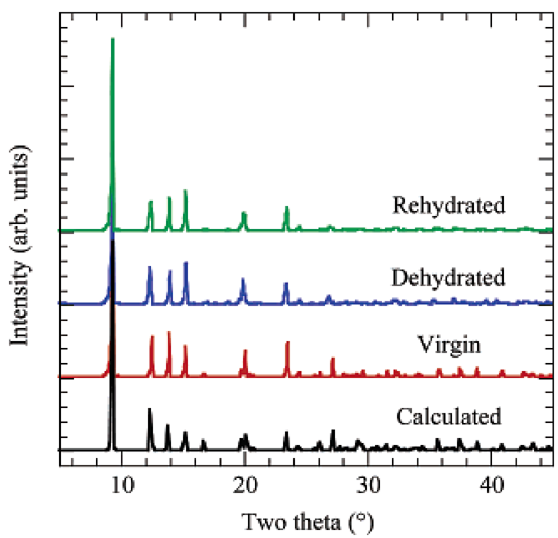
Motokawa, N.; Matsunaga, S.; Takaishi, S.; Miyasaka, H.; Yamashita, M.; Dunbar, K. R. Ferromagnet Related to Solvation/Desolvation in a Robust Layered $[Ru_2]_2$TCNQ Charge-Transfer System. *J. Am. Chem. Soc.* **2010**, *132*, 11943–11951

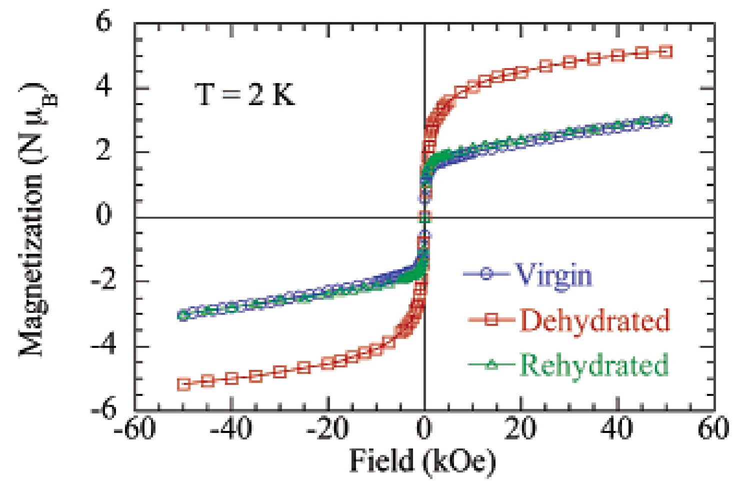
$[Ni_3(OH)_2($*cis*$\text{-}1,4\text{-chdc})_2(H_2O)_4]\cdot 2H_2O$ (1,4-chdc = 1,4-cyclohexanedicarboxylic)





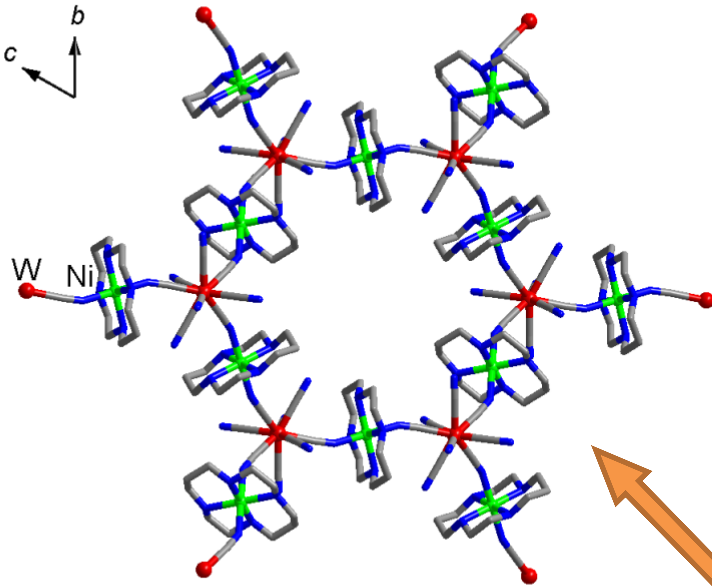


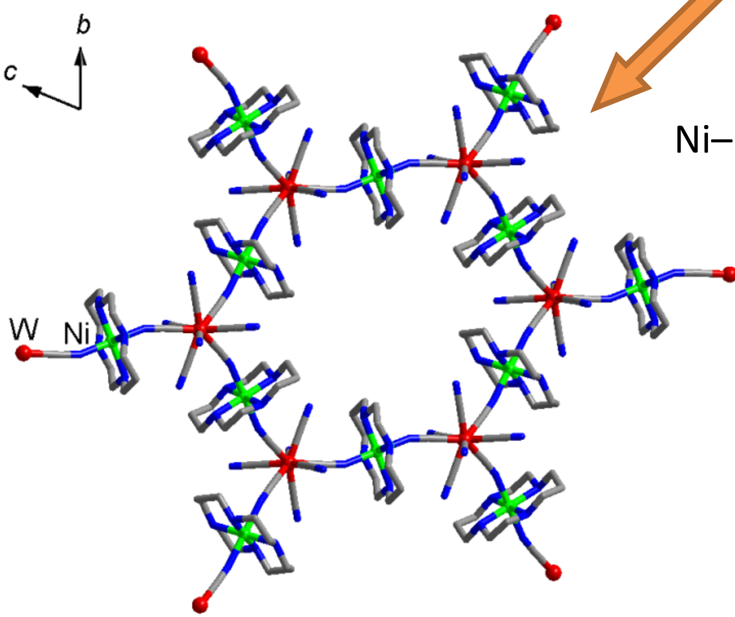


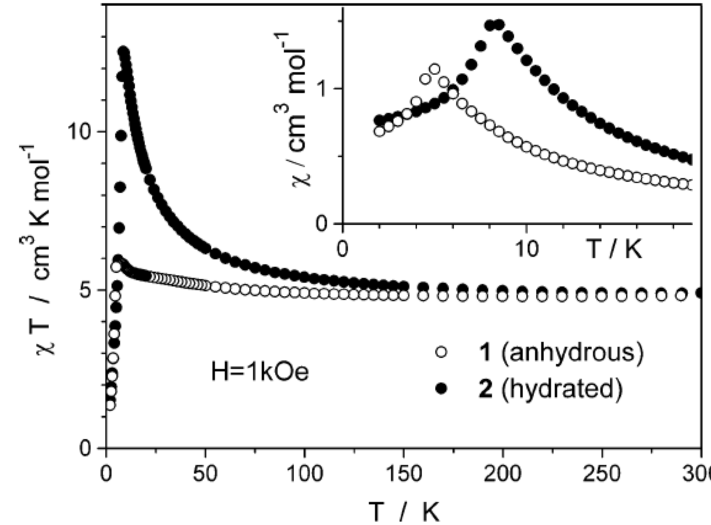


Kurmoo, M.; Kumagai, H.; Akita-Tanaka, M.; Inoue, K.; Takagi, S. Metal-Organic Frameworks from Homometallic Chains of Nickel(II) and 1,4-Cyclohexanedicarboxylate Connectors: Ferrimagnet-Ferromagnet Transformation. *Inorg. Chem.* **2006**, *45*, 1627–1637

$[Ni(cyclam)]_3[W(CN)_8]_2 \cdot 16H_2O \rightarrow [Ni(cyclam)]_3[W(CN)_8]_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane)







Hydration-dehydration reversible at 25-40 °C

T_N = 8.0 K

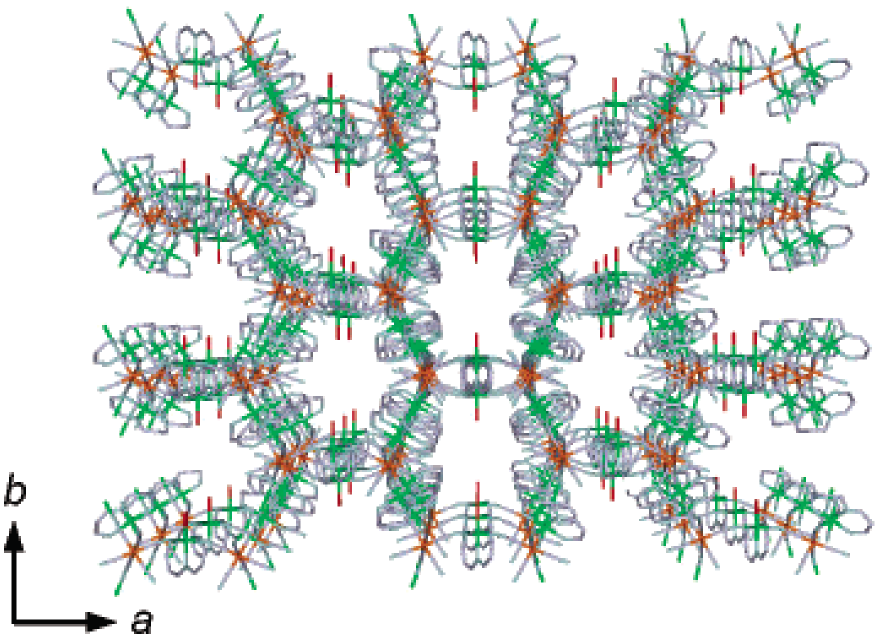
T_N = 5.0 K

Ni–N–C–W angles - 159.5 to 149.7

Nowicka, B.; Rams, M.; Stadnicka, K.; Sieklucka, B. Reversible Guest–Induced Magnetic and Structural Single–Crystal–to–Single–Crystal Transformation in Microporous Coordination Network $\{[Ni(cyclam)]_3[W(CN)_8]_2\}_n$. *Inorg. Chem.* **2007**, *46*, 8123–8125.

$[Ni(dipn)]_2[Ni(dipn)(H_2O)][Fe(CN)_6]_2 \cdot 11H_2O$

(where dipn is *N*,*N*-di(3-aminopropyl)-amine)

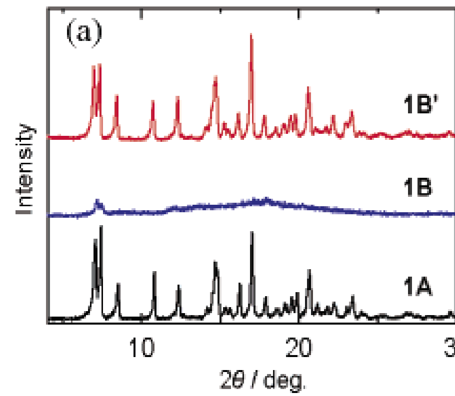


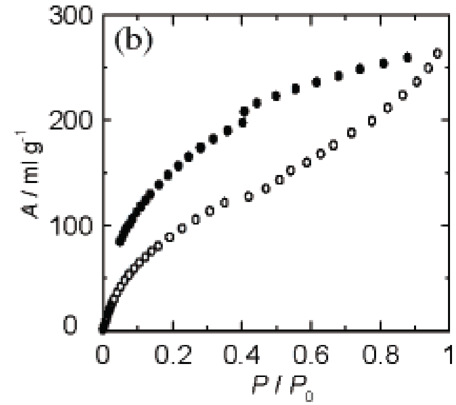
A - $[Ni(dipn)]_2[Ni(dipn)(H_2O)][Fe(CN)_6]_2 \cdot 11H_2O$

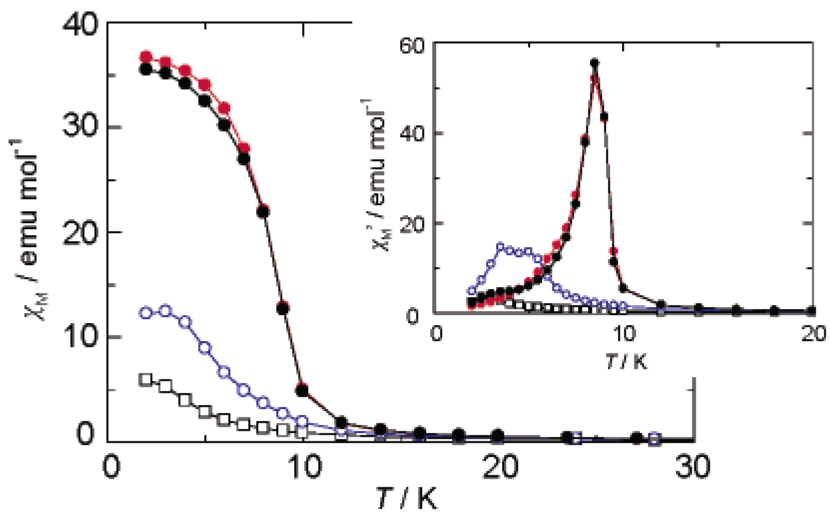
B - $[Ni(dipn)]_2[Ni(dipn)(H_2O)][Fe(CN)_6]_2 \cdot 2H_2O$
(dehydrated in vacuum at RT)

C - $[Ni(dipn)]_2[Ni(dipn)][Fe(CN)_6]_2$
(dehydrated in vacuum at 100 ^oC)

B' - $[Ni(dipn)]_2[Ni(dipn)(H_2O)][Fe(CN)_6]_2 \cdot 12H_2O$
(rehydrated from **B**)







A (   ) - T_c = 8.5 K, H_c = 350 Oe

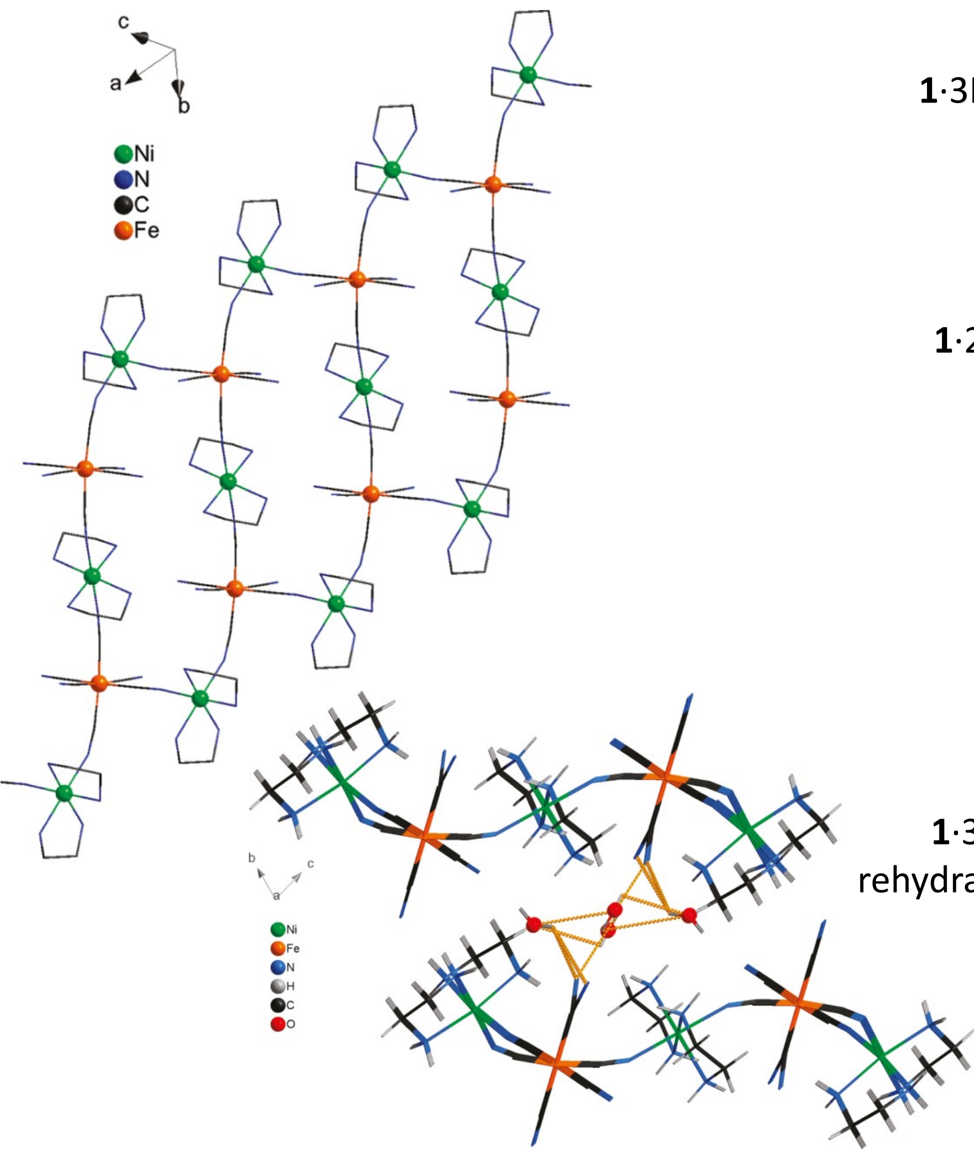
B (   ) - T_c = 6 K, H_c = 50 Oe

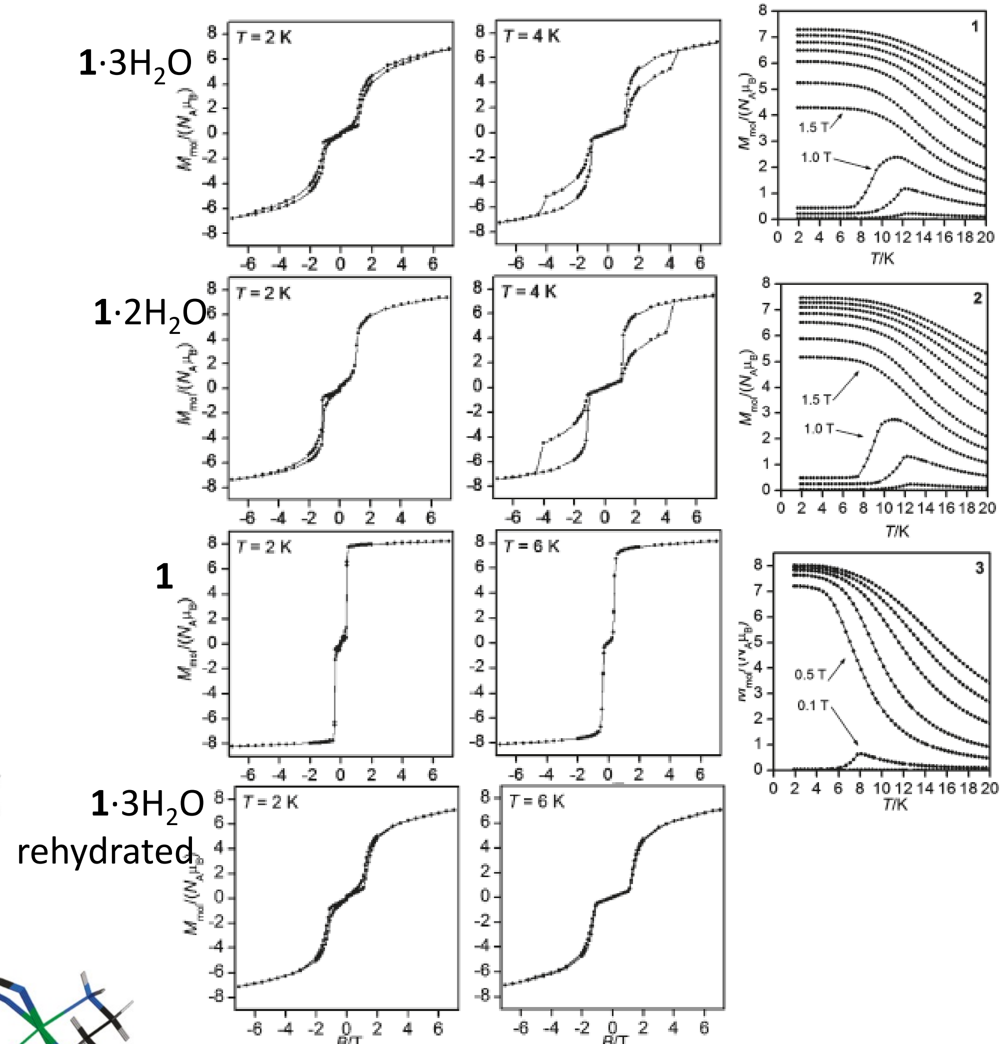
B' (   ) - T_c = 8.5 K, H_c = 350 Oe

C (   ) - no magnetic ordering

Yanai, N.; Kaneko, W.; Yoneda, K.; Ohba, M.; Kitagawa, S. Reversible Water-Induced Magnetic and Structural Conversion of a Flexible Microporous Ni(II)Fe(III) Ferromagnet. *J. Am. Chem. Soc.* **2007**, *129*, 3496–3497.

$[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot xH_2O$ (en = 1,2-ethylenediamine, x = 3, 2 and 0)





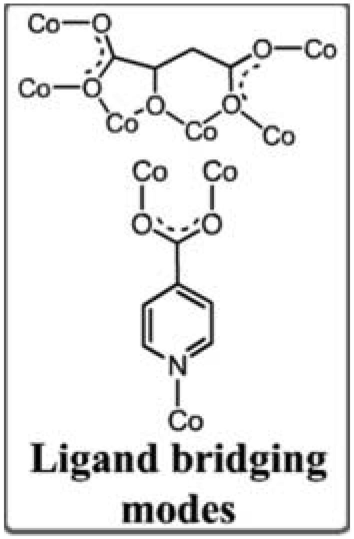
1$\cdot 3H_2O$: T_N = 13 K, B_C = 1.1 T (2K)

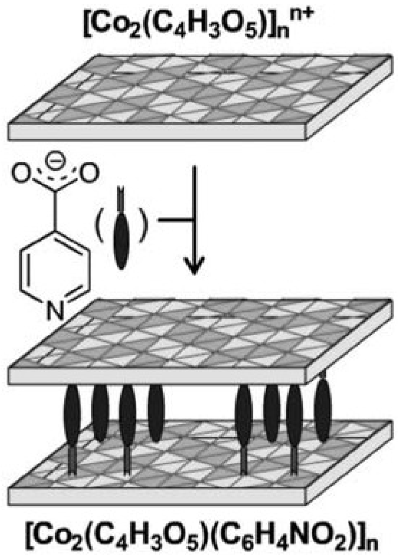
1$\cdot 2H_2O$: T_N = 13 K, B_C = 1.1 T (2K)

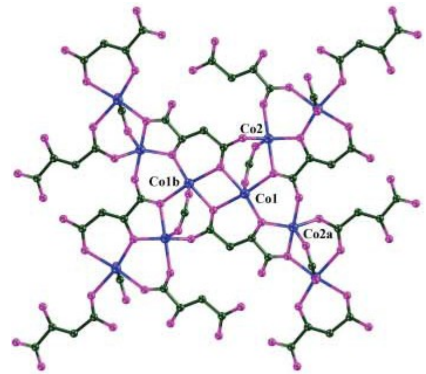
1: T_N = 8.4 K, B_C = 0.35 T (2K)

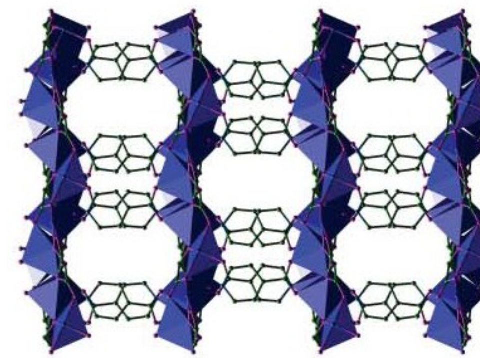
Herchel, R.; Tuček, J.; Trávníček, Z.; Petridis, D.; Zbořil, R. Crystal Water Molecules as Magnetic Tuners in Molecular Metamagnets Exhibiting Antiferro-Ferro-Paramagnetic Transitions. *Inorg. Chem.* **2011**, *50*, 9153–9163

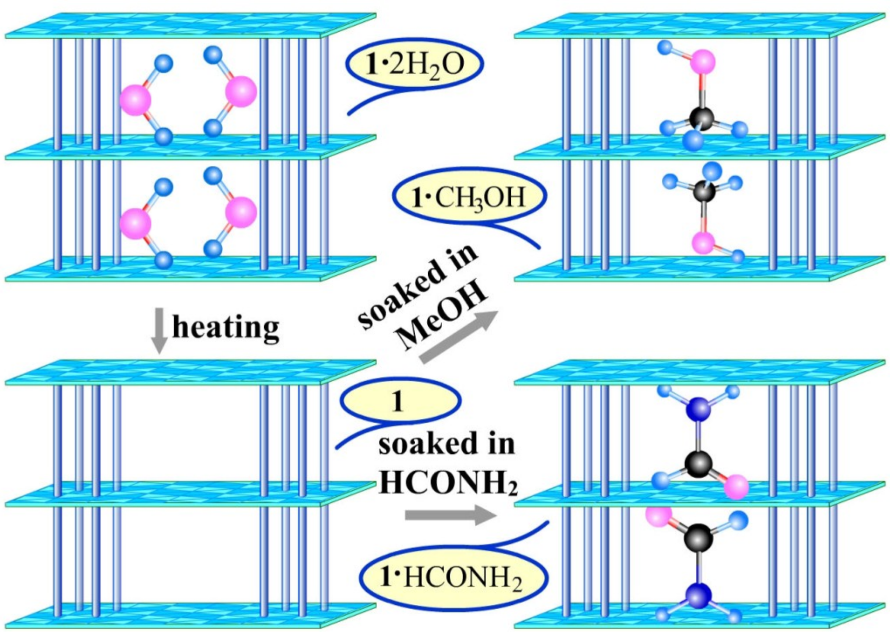
Transformation and guest modulation of cooperative magnetic properties Co_2(ma)(ina) (ma^{3-} = malate, ina^{-} = isonicotinate)

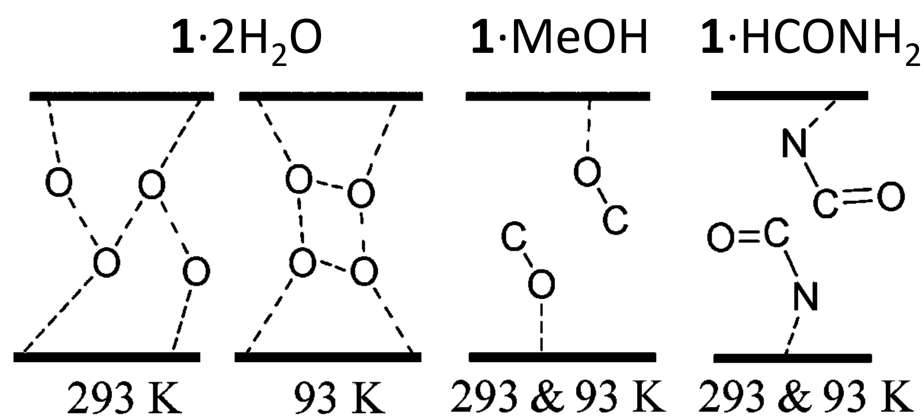








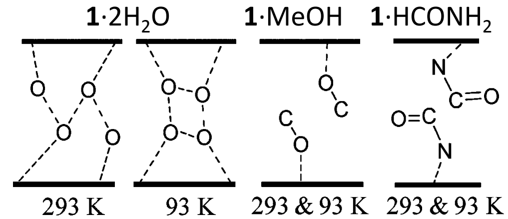




Zeng, M.-H.; Feng, X.-L.; Zhang, W.-X.; Chen, X.-M. A robust microporous 3D cobalt(II) coordination polymer with new magnetically frustrated 2D lattices: single-crystal transformation and guest modulation of cooperative magnetic properties. *Dalton Trans.*, **2006**, 5294–5303

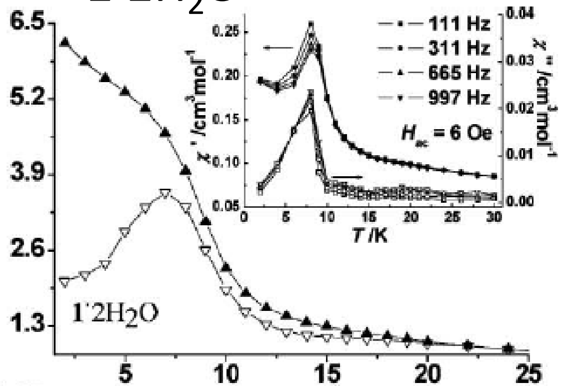
Transformation and guest modulation of cooperative magnetic properties Co_2(ma)(ina) (ma^{3-} = malate, ina^- = isonicotinate)

	$1\cdot 2H_2O$	$1\cdot MeOH$	$1\cdot HCONH_2$	1
$\mu_{eff\,(per\,Co2)}$	6.67	6.32	6.25	6.44
C	6.61	5.94	5.82	6.24
θ	−48.6	−45.2	−59.6	−60.2
T^*/K (ac 111 Hz)	8.0	3.6	3.6	—
M ($N\beta$/mol at 70 kOe, 2 K)	1.70	1.40	1.22	1.19
T_{div}(at FC–ZFC)	7.5	3.5	3.6	<2
$f = \lvert\theta\rvert/T_N$	6.1	12.9	16.6	>30

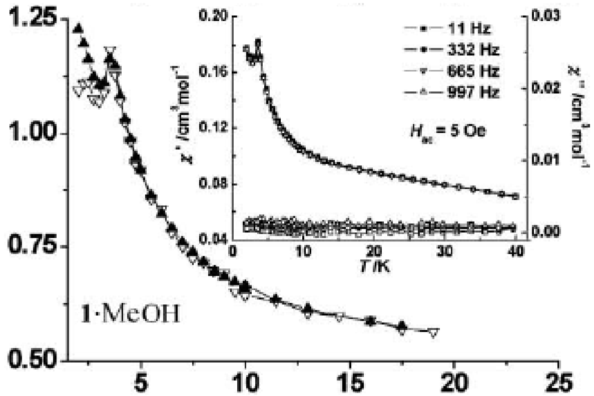


$1\cdot 2H_2O$ (293 K)	$1\cdot 2H_2O$ (93 K)	$1\cdot MeOH$ (293 K)	$1\cdot MeOH$ (93 K)	$1\cdot HCONH_2$ (293K)	$1\cdot HCONH_2$ (93 K)	1 (293 K)
9.238(1)	9.200(1)	9.231(1)	9.207(1)	9.240(1)	9.217(1)	9.227(1)
8.940(1)	8.946(1)	8.940(1)	8.923(1)	8.959(2)	8.952(1)	8.929(1)

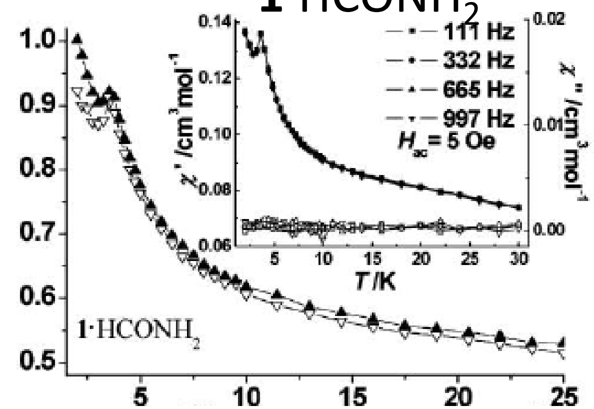
$1\cdot 2H_2O$

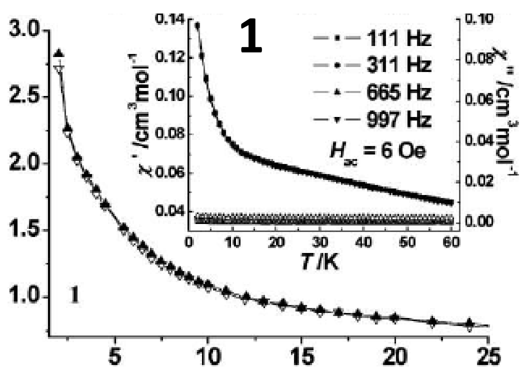


$1\cdot MeOH$



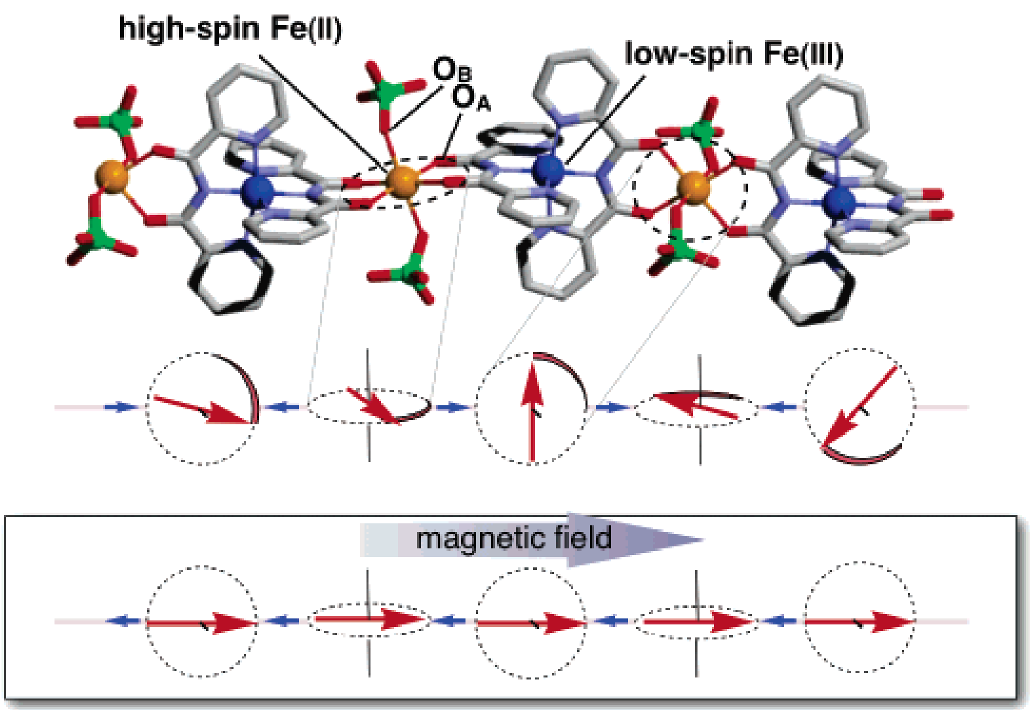
$1\cdot HCONH_2$



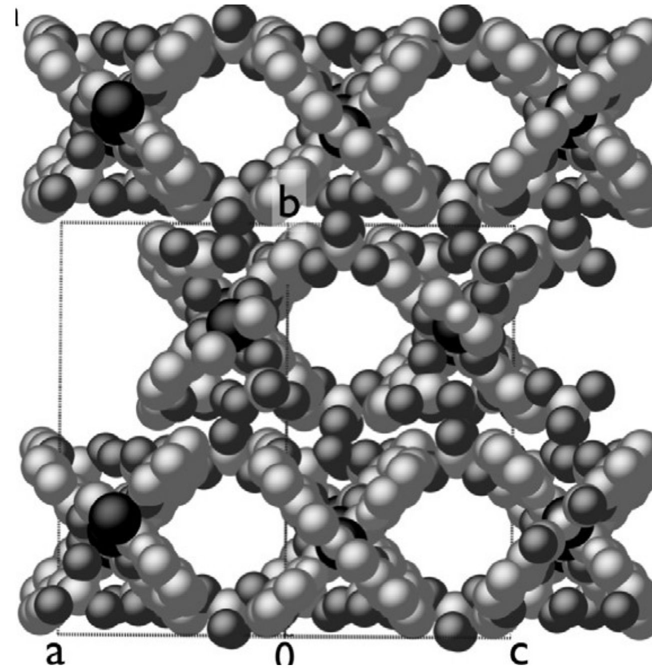


Zeng, M.-H.; Feng, X.-L.; Zhang, W.-X.; Chen, X.-M. A robust microporous 3D cobalt(II) coordination polymer with new magnetically frustrated 2D lattices: single-crystal transformation and guest modulation of cooperative magnetic properties. *Dalton Trans.*, **2006**, 5294–5303

$[Fe^{II}(ClO_4)_2\{Fe^{III}(bpca)_2\}]ClO_4{\cdot}3CH_3NO_2$ (Hbpca = bis(2-pyridylcarbonyl)amine)



Loss $3CH_3NO_2$ at 30°C



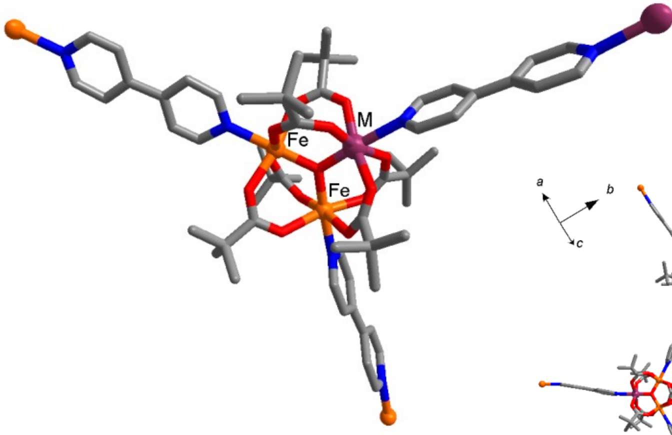
SCM

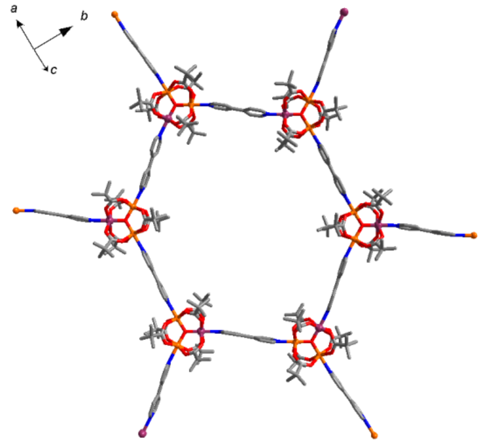
Solvated - Δ/k_B = 21.9(3) K

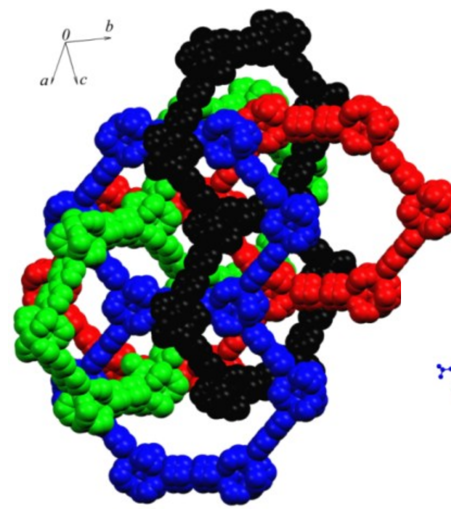
Desolvated - Δ/k_B to 26.0(9) K

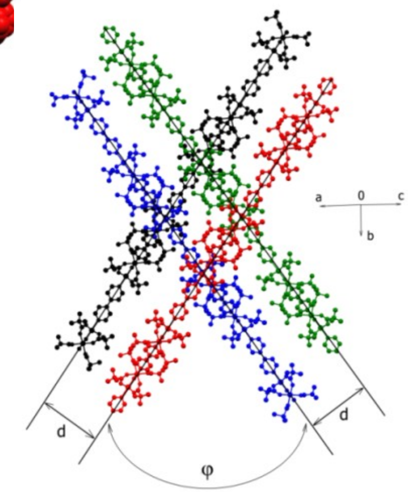
Kaneko, Y.; Kajiwara, T.; Yamane, H.; Yamashita, M. Solvent induced reversible change of magnetic properties in a Fe(II)–Fe(III) single chain magnet. *Polyhedron*, **2007**, *26*, 2074–2078

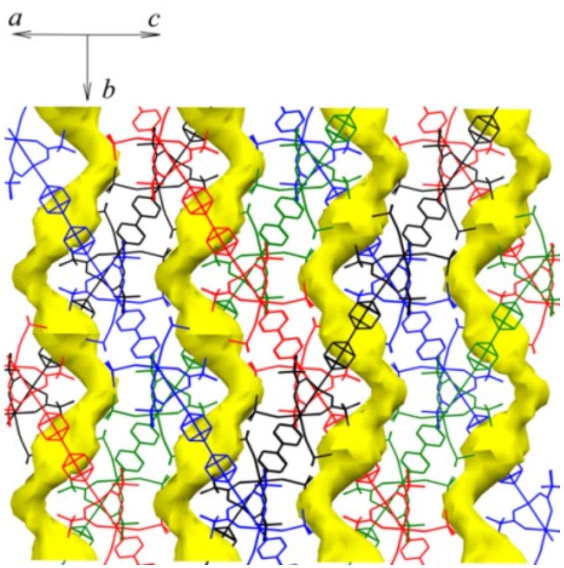
$[Fe_2MO(Piv)_6(4,4'\text{-}bpy)_{1.5}\cdot 2Solv]_n$ (M = Ni, Co)







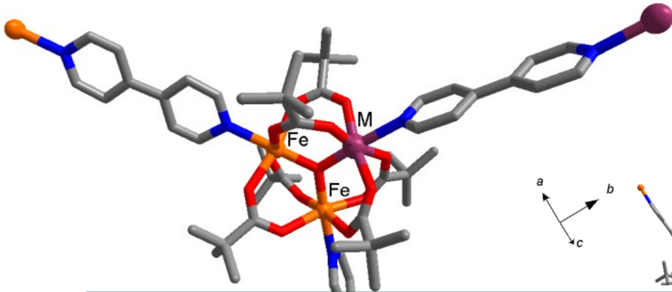


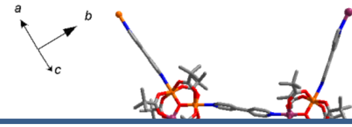


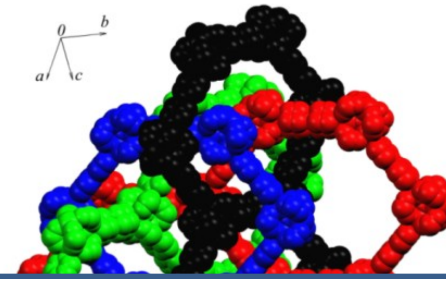
	T, K	d, Å	φ, deg	V, cm³/g	β, deg
DMF	120	10,800(5)	63,56(1)	0,21	91,755(1)
	150	10,849(5)	64,38(1)	0,22	91,96(4)
	160	10,930(5)	65,36(1)	0,22	93,470(6)
	260	11,242(8)	68,525(7)	0,27	95,72(1)
	296	11,277(4)	69,208(9)	0,27	96,22(1)
DEF	173	11,357(5)	71,51(5)	0,28	–
	260	11,447(5)	72,290(7)	0,30	–

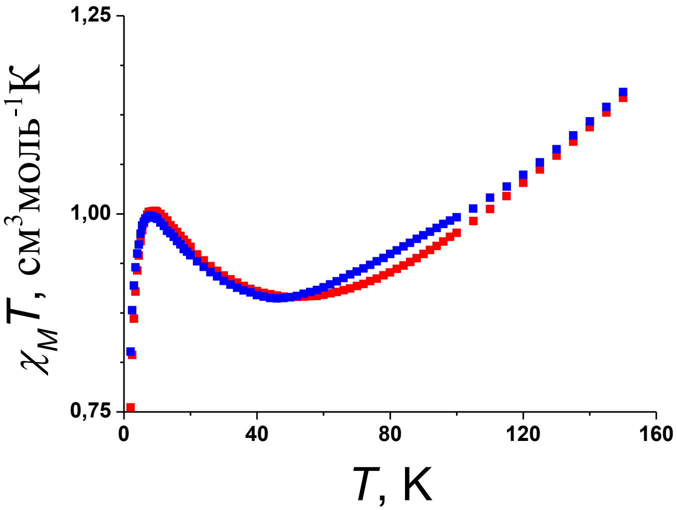
Polunin, R.A.; Kolotilov, S.V.; Kiskin, M.A.; Cador, O.; Golhen, S.; Shvets, O.V.; Ouahab, L.; Dobrokhotova, Z.V.; Ovcharenko, V.I.; Eremenko, I.L.; Novotortsev, V.M.; Pavlishchuk, V.V. Structural flexibility and sorption properties of 2D porous coordination polymers constructed from trinuclear heterometallic pivalates and 4,4'-bipyridine. *Eur. J. Inorg. Chem.*, **2011**, 4985–4992

$[Fe_2MO(Piv)_6(4,4'\text{-}bpy)_{1.5}\cdot 2Solv]_n$ (M = Ni, Co)



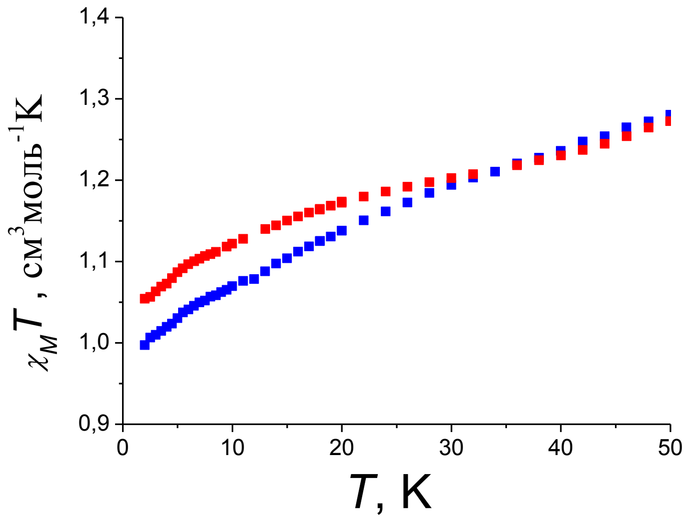






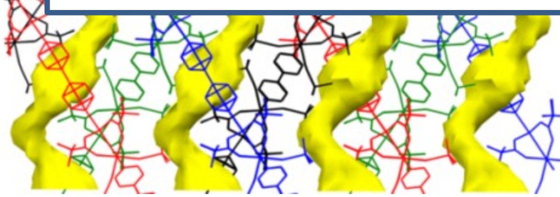
$[Fe_2NiO(Piv)_6(4,4'\text{-}bpy)_{1,5}\cdot 2DMF]_n$ ( ): **$D_{Ni} \approx 0$**

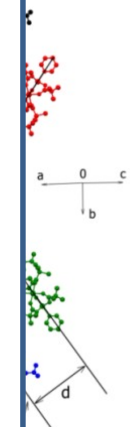
$[Fe_2NiO(Piv)_6(4,4'\text{-}bpy)_{1,5}]_n$ ( ): **D_{Ni} = 5.2(1) cm^{-1}**



$[Fe_2CoO(Piv)_6(4,4'\text{-}bpy)_{1,5}\cdot 2DMF]_n$ ( ): **D_{Co} = 40(2) cm^{-1}**

$[Fe_2CoO(Piv)_6(4,4'\text{-}bpy)_{1,5}]_n$ ( ): **D_{Co} = 58(3) cm^{-1}**





	160	**10,930(5)**	**65,36(1)**	**0,22**	**93,470(6)**
	260	**11,242(8)**	**68,525(7)**	**0,27**	**95,72(1)**
	296	**11,277(4)**	**69,208(9)**	**0,27**	**96,22(1)**
DEF	**173**	**11,357(5)**	**71,51(5)**	**0,28**	**–**
	260	**11,447(5)**	**72,290(7)**	**0,30**	**–**

Polunin, R.A.; Kolotilov, S.V.; Kiskin, M.A.; Cador, O.; Golhen, S.; Shvets, O.V.; Ouahab, L.; Dobrokhotova, Z.V.; Ovcharenko, V.I.; Eremenko, I.L.; Novotortsev, V.M.; Pavlishchuk, V.V. Structural flexibility and sorption properties of 2D porous coordination polymers constructed from trinuclear heterometallic pivalates and 4,4'-bipyridine. *Eur. J. Inorg. Chem.*, **2011**, 4985–4992

Compounds, magnetic properties of which are governed by properties of isolated ions

$[Co_2(H_2O)_4][Re_6S_8(CN)_6]\cdot 10H_2O$	≈ 20 % decrease of $\chi_M T$ at T > 100 K
$(tetrenH_5)_{1.6}\{Co(H_2O)_2[W(CN)_8]\}_4\cdot 12H_2O$	≈ 20 % decrease of $\chi_M T$ at room temperature

Compounds, magnetic properties of which are governed by exchange interactions, but which do not undergo ferro- or antiferromagnetic ordering

$Cu(pz)_2\cdot(H_2O)$	J_{Cu-Cu}, cm^{-1}: –145.5(3) → –141.8(7)
$[Mn_3(hpdc)_2(H_2O)_6]\cdot H_2O$	J_{Mn-Mn}, cm^{-1}: –0.88 → –1.57 zJ'- , cm^{-1}: +0.02 → –0.47
$[Cu_2Fe(tzdc)_2(H_2O)_2]\cdot 2H_2O$	J_{Cu-Cu}, cm^{-1}: –195(7) → –182(6) ϑ', K: 1.1(1) → 0.5(1)
$[Cu_2Mn(tzdc)_2(H_2O)_2]\cdot 2H_2O$	J_{Cu-Cu}, cm^{-1}: –174(4) → –151(2) ϑ', K: 0.51(1) → –0.26(1)
$Fe_2CoO(Piv)_6(4,4'\text{-bipy})_{1.5}\cdot 2DMF$	D_{Co}, cm^{-1}: 58(3) → 40(2) J_{Fe-Co}, cm^{-1}: –34.3(5) → –36.7
$[\{Fe_3O(HCOO)_6\}\{Mn(HCOO)_3(H_2O)_3\}]\cdot 3.5HCOOH$	zJ', cm^{-1}: –0.16(4) → –1.42(5)
$[Fe^{II}(ClO_4)_2\{Fe^{III}(bpca)_2\}]ClO_4\cdot 3CH_3NO_2$	Δ/k_B, K: 21.9(3) → 26.0(9)
$[Ni(en)_2]_3[Fe(CN)_6]_2\cdot 3H_2O$	B_C, T: 1.1 → 0.35
$Co_2(H_2O)_4(2,6\text{-ndc})_2(DMF)_2\cdot 2H_2O$	ϑ, K: –65.3 → –7.5
$[Co_3(IB)_2(BTEC)(H_2O)_2]\cdot 2H_2O$	D_{Co}, cm^{-1}: 80.15 → 65.38 zJ', cm^{-1}: 0.42 → 0.75

Compounds, which undergo magnetic ordering

$[\{Ru_2(O_2CPh\text{-}o\text{-}Cl)_4\}_2TCNQ(MeO)_2]\cdot CH_2Cl_2$	T_N = 75 K → T_C ≈ 56 K
$[Mn(pydz)(H_2O)_2][Mn(H_2O)_2][Nb(CN)_8]\cdot 2H_2O$	T_C, K: 44 → 68 → 100
$[K_2(H_2O)_4Mn_5(H_2O)_8(CH_3CN)\{Mo(CN)_7\}_3]\cdot 2H_2O$	T_C, K: = 82 → 72
$[Mn_3(4,4'\text{-bipy})_3(H_2O)_4][Cr(CN)_6]_2\cdot 2(4,4'\text{-bipy})\cdot 4H_2O$	T_C, K: = 80 → 45.3
$Cu_3[W(CN)_8]_2(pym)_2\cdot 8H_2O$	T_C, K: 9.5 → 12.0
$[\{Mn(Hdmal)(H_2O)\}_2Mn\{Mo(CN)_7\}_2]\cdot 2H_2O$	T_C, K: 85 → 106
$[Na(H_2O)_4]_4[Mn_4\{Cu_2(mpba)_2(H_2O)_4\}_3]\cdot 56.5H_2O$	T_C, K: 22.5 → 2.3
$[Mn(NNdmenH)(H_2O)][Cr(CN)_6]\cdot H_2O$	T_C, K: 35.2 → 60.4
$[Mn(rac\text{-}pnH)(H_2O)Cr(CN)_6]\cdot H_2O$	T_C, K: 36 → 70
$[Ni(dipn)]_2[Ni(dipn)(H_2O)][Fe(CN)_6]_2\cdot 11H_2O$	T_C, K: 8.5 → *ca.* 6 → no ordering at T > 2 K
$Co[Cr(CN)_6]_{2/3}\cdot zH_2O$	T_C, K: 28 → 22
$K_{0.2}Mn_{1.4}Cr(CN)_6\cdot 6H_2O$	T_C, K: 66 → 99
$K_2Mn_3(H_2O)_6[Mo(CN)_7]_2\cdot 6H_2O$	T_C, K: 39 → 72
$(Co_{0.41}Mn_{0.59})[Cr(CN)_6]_{2/3}\cdot zH_2O$	Disappearance of magnetic pole inversion effect
$[KCo_7(OH)_3(1,3\text{-bdc})_6(H_2O)_4]\cdot 12H_2O$	Disappearance of M *vs.* H hysteresis at 2 K
$[Ni(cyclam)]_3[W(CN)_8]_2\cdot 16H_2O$	T_N, K: 8.0 → 5.0
$Co_2(ma)(ina)\cdot 2H_2O$	T_N, K: 8 → < 2
$Co_2(ma)(ina)\cdot CH_3OH$	T_N, K: 3.5 → < 2
$Co_2(ma)(ina)\cdot HCONH_2$	T_N, K: 3.5 → < 2
$\{Fe(Tp)(CN)_3\}_4\{Fe(CH_3CN)(H_2O)_2\}_2\cdot 10H_2O\cdot 2CH_3CN$	ϑ, K: –2.95 → +7.43 No ordering → metamagnet
$[Co_3(CH_3OH)(\mu_3\text{-OH})_2(datrz)(sip)]\cdot 2.25H_2O$	Metamagnet (T_N = 4.3 K under 0.7 kOe or T_N = 5.3 K under 0.1 kOe) → antiferromagnet (T_N = 5.3 K)

Current Inorganic Chemistry, 2013, *3*, 144-160

The Influence of Diamagnetic Substrates Absorption on Magnetic Properties of Porous Coordination Polymers

Sergey V. Kolotilov[a,*], Mikhail A. Kiskin[b], Igor L. Eremenko[b] and Vladimir M. Novotortsev[b]

[a]*L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028, Ukraine*

[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prosp. 31, 119991 Moscow, GSP-1, Russian Federation*

Abstract: Reported cases of the influence of guest molecules absorption/desorption o
ordination polymers (PCP) of transition metals are reviewed. Interaction of PCPs wit
netic susceptibility in wide temperature range, as well as can lead to change of the r
temperature and other magnetic characteristics. The reasons of such influence can be
molecule coordination to metal ion or decoordination; formation or cleavage of bond
change interactions between metal ions; or change of bond lengths or angles in coord
lattice adaptation to the guest molecule.