Supporting Material

Reversible Solvatomagnetic Effect in Novel Tetranuclear Cubane-Type Ni_4 Complexes and Magnetostructural Correlations for the $[Ni_4(\mu_3\text{-}O)_4]$ Core

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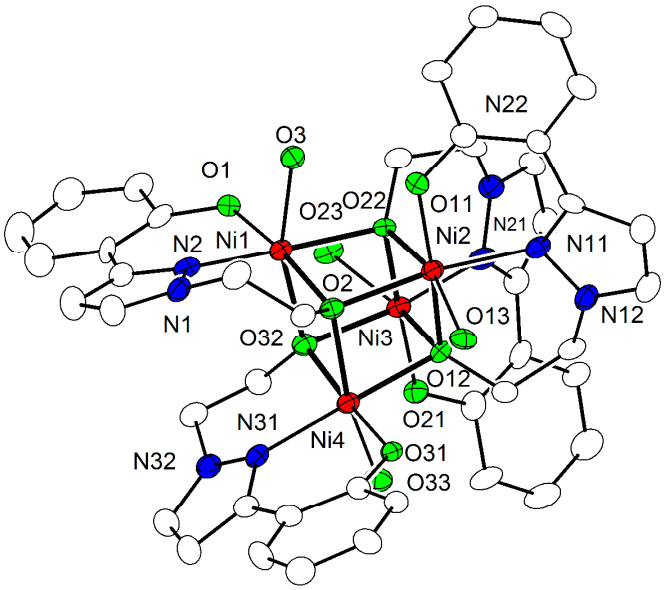

Figure S1a. Molecular structure of **2·CH_2Cl_2** (thermal ellipsoids drawn at the 30% probability level). Hydrogen atoms and all solvent molecules have been omitted. Only one of the two crystallographically independent molecules is shown.

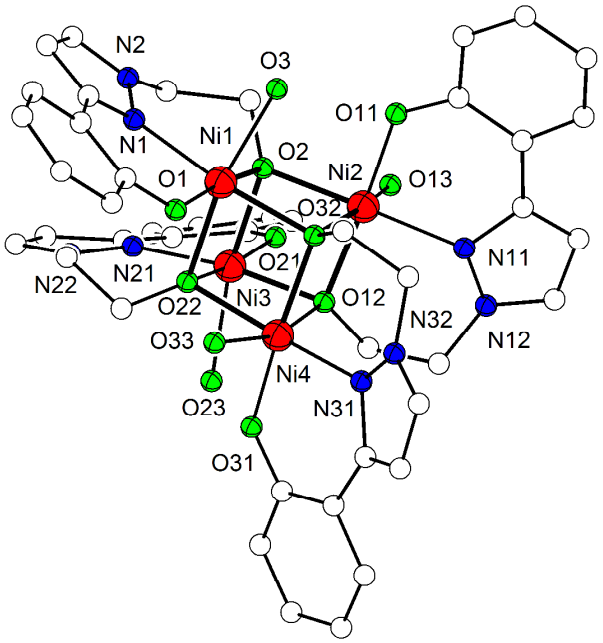

Figure S1b. Molecular structure of **2·H_2O**. Hydrogen atoms and all solvent molecules have been omitted. Crystal Data: a = 11.6970 Å, b= 9.3284 Å, c = 20.9717 Å, α = γ = 90°, β = 103.020°, V = 2229.5(3) $Å^3$, space group = Pc, Z =2.

Table S1. Selected Bond Lengths [Å] for **1·H_2O**.

atoms	bond lengths	atoms	bond lengths
Ni1–O1	1.9846(12)	Ni1–O2''	2.0666(9)
Ni1–O2	2.0199(11)	Ni1–O2'''	2.1118(10)
Ni1–N1	2.0257(13)	Ni1–O3	2.1445(13)

Symmetry operations used to generate equivalent atoms: ('') –0.25+*y*, 1.25–*x*, 1.25–*z*; (''') 1–*x*, 1.5–*y*, *z*.

Table S2. Selected Bond Lengths [Å] for **2·4C_3H_6O**.

atoms	bond lengths	atoms	bond lengths
Ni1–O1	1.9809(15)	Ni2–N11	2.0430(16)
Ni1–O2	2.0156(14)	Ni2–O2	2.0782(13)
Ni1–N1	2.0313(16)	Ni2–O12'	2.1069(14)
Ni1–O12'	2.0615(13)	Ni2–O13	2.1189(15)
Ni1–O2'	2.1494(15)	O2–Ni1'	2.1494(15)
Ni1–O3	2.1723(16)	O12–Ni1'	2.0615(13)
Ni2–O11	1.9919(15)	O12–Ni2'	2.1069(14)
Ni2–O12	2.0333(15)		

Symmetry operation used to generate equivalent atoms: (') 1–*x*, *y*, 0.5–*z*.

Table S3. Selected Bond Lengths [Å] for **2·CH_2Cl_2**.

atoms	bond lengths	atoms	bond lengths
Ni2-O11	1.977(6)	Ni6-O51	1.984(5)
Ni2-O12	2.034(5)	Ni6-O52	2.001(5)
Ni2-N11	2.043(7)	Ni6-N51	2.013(6)
Ni2-O2	2.053(5)	Ni6-O42	2.066(5)
Ni2-O22	2.111(5)	Ni6-O62	2.117(5)
Ni2-O13	2.190(5)	Ni6-O53	2.182(6)
Ni3-O21	1.993(5)	Ni7-O61	1.992(5)
Ni3-O22	2.017(5)	Ni7-O62	2.011(5)
Ni3-N21	2.029(7)	Ni7-N61	2.035(6)
Ni3-O32	2.071(5)	Ni7-O72	2.087(5)
Ni3-O12	2.084(5)	Ni7-O52	2.088(5)
Ni3-O23	2.192(5)	Ni7-O63	2.179(5)
Ni4-N31	2.010(6)	Ni8-N71	2.001(6)
Ni4-O31	2.032(5)	Ni8-O71	2.017(6)
Ni4-O32	2.038(5)	Ni8-O72	2.057(6)

Ni4-O12	2.074(5)	Ni8-O52	2.080(5)
Ni4-O2	2.110(5)	Ni8-O73	2.113(6)
Ni4-O33	2.114(5)	Ni8-O42	2.132(6)
Ni1-N2	1.970(7)	Ni5-N41	2.010(6)
Ni1-O1	2.035(5)	Ni5-O41	2.035(5)
Ni1-O2	2.063(5)	Ni5-O42	2.056(5)
Ni1-O22	2.087(5)	Ni5-O62	2.079(5)
Ni1-O3	2.109(5)	Ni5-O43	2.116(5)
Ni1-O32	2.169(5)	Ni5-O72	2.132(6)

Table S4. Selected Bond Angles [°] for **1·H$_2$O**.

atoms	bond angles	atoms	bond angles
O1–Ni1–O2	171.78(5)	O2–Ni1–O2'''	79.65(4)
O1–Ni1–N1	90.80(6)	N1–Ni1–O2'''	104.77(4)
O2–Ni1–N1	92.44(5)	O2–Ni1'''–O2''	81.43(4)
O1–Ni1–O2''	94.00(4)	O1–Ni1–O3	96.20(5)
O2–Ni1–O2''	83.67(4)	O2–Ni1–O3	91.43(5)
N1–Ni1–O2'''	172.03(5)	N1–Ni1–O3	88.90(5)
O1–Ni1–O2'''	92.21(5)		

Symmetry operations used to generate equivalent atoms: (') –0.25+*y*, 1.25–*x*, 1.25–*z*; (''') 1–*x*, 1.5–*y*, *z*.

Table S5. Selected Bond Angles [°] for **2·4C$_3$H$_6$O**.

atoms	bond angles	atoms	bond angles
O1–Ni1–O2	171.01(7)	O11–Ni2–O12	170.60(6)
O1–Ni1–N1	90.43(6)	O11–Ni2–N11	89.70(6)
O2–Ni1–N1	92.26(6)	O12–Ni2–N11	92.21(6)
O1–Ni1–O12'	94.36(5)	O11–Ni2–O2	95.54(6)
O2–Ni1–O12'	84.16(5)	O12–Ni2–O2	83.69(5)
N1–Ni1–O12'	171.04(6)	N11–Ni2–O2	171.60(6)
O1–Ni1–O2'	91.75(6)	O11–Ni2–O12'	90.66(6)
O2–Ni1–O2'	79.27(6)	O12–Ni2–O12'	79.96(6)
N1–Ni1–O2'	106.20(6)	N11–Ni2–O12'	105.04(6)
O12–Ni1'–O2'	81.26(5)	O2–Ni2–O12'	81.53(5)
O1–Ni1–O3	96.69(6)	O11–Ni2–O13	97.28(6)
O2–Ni1–O3	92.07(6)	O12–Ni2–O13	91.96(6)
N1–Ni1–O3	85.42(6)	N11–Ni2–O13	88.82(6)
O12–Ni1'–O3	86.50(6)	O2–Ni2–O13	84.00(6)
O2–Ni1'–O3	165.63(5)	O12–Ni2'–O13	164.10(5)

Symmetry operation used to generate equivalent atoms: (') 1–*x*, *y*, 0.5–*z*.

Table S6. Selected Bond Angles [°] for **2·CH_2Cl_2**.

atoms	bond angles	atoms	bond angles
O11-Ni2-O12	172.1(2)	O51-Ni6-O52	172.9(2)
O11-Ni2-N11	89.8(2)	O51-Ni6-N51	90.4(2)
O12-Ni2-N11	92.6(2)	O52-Ni6-N51	92.3(2)
O11-Ni2-O2	94.4(2)	O51-Ni6-O42	93.9(2)
O12-Ni2-O2	84.3(2)	O52-Ni6-O42	84.3(2)
N11-Ni2-O2	170.7(2)	N51-Ni6-O42	171.7(3)
O11-Ni2-O22	92.9(2)	O51-Ni6-O62	93.6(2)
O12-Ni2-O22	79.28(19)	O52-Ni6-O62	79.4(2)
N11-Ni2-O22	105.7(2)	N51-Ni6-O62	104.0(2)
O2-Ni2-O22	82.4(2)	O42-Ni6-O62	82.8(2)
O11-Ni2-O13	97.5(2)	O51-Ni6-O53	96.7(2)
O12-Ni2-O13	90.2(2)	O52-Ni6-O53	89.9(2)
N11-Ni2-O13	85.9(2)	N51-Ni6-O53	89.1(2)
O2-Ni2-O13	85.3(2)	O42-Ni6-O53	83.4(2)
O22-Ni2-O13	164.5(2)	O62-Ni6-O53	163.3(2)
O21-Ni3-O22	174.0(2)	O61-Ni7-O62	175.7(2)
O21-Ni3-N21	89.7(2)	O61-Ni7-N61	90.6(2)
O22-Ni3-N21	92.5(2)	O62-Ni7-N61	92.0(2)
O21-Ni3-O32	94.0(2)	O61-Ni7-O72	93.5(2)
O22-Ni3-O32	84.6(2)	O62-Ni7-O72	84.3(2)
N21-Ni3-O32	171.6(2)	N61-Ni7-O72	172.3(3)
O21-Ni3-O12	93.7(2)	O61-Ni7-O52	96.2(2)
O22-Ni3-O12	80.3(2)	O62-Ni7-O52	79.9(2)
N21-Ni3-O12	104.8(2)	N61-Ni7-O52	104.2(2)
O32-Ni3-O12	82.5(2)	O72-Ni7-O52	81.9(2)
O21-Ni3-O23	97.7(2)	O61-Ni7-O63	95.7(2)
O22-Ni3-O23	88.0(2)	O62-Ni7-O63	87.9(2)
N21-Ni3-O23	88.4(2)	N61-Ni7-O63	87.0(2)
O32-Ni3-O23	83.7(2)	O72-Ni7-O63	86.1(2)
O12-Ni3-O23	162.6(2)	O52-Ni7-O63	163.6(2)
N31-Ni4-O31	89.3(2)	N71-Ni8-O71	87.3(2)
N31-Ni4-O32	92.9(2)	N71-Ni8-O72	93.0(2)
O31-Ni4-O32	173.8(2)	O71-Ni8-O72	174.2(2)
N31-Ni4-O12	173.8(2)	N71-Ni8-O52	173.7(2)

O31-Ni4-O12	94.7(2)	O71-Ni8-O52	97.4(2)
O32-Ni4-O12	83.6(2)	O72-Ni8-O52	82.80(19)
N31-Ni4-O2	102.6(2)	N71-Ni8-O73	91.1(3)
O31-Ni4-O2	92.8(2)	O71-Ni8-O73	97.2(2)
O32-Ni4-O2	81.1(2)	O72-Ni8-O73	88.6(2)
O12-Ni4-O2	82.0(2)	O52-Ni8-O73	84.2(2)
N31-Ni4-O33	90.0(2)	N71-Ni8-O42	103.2(2)
O31-Ni4-O33	96.8(2)	O71-Ni8-O42	93.8(2)
O32-Ni4-O33	88.9(2)	O72-Ni8-O42	80.5(2)
O12-Ni4-O33	84.8(2)	O52-Ni8-O42	80.75(19)
O2-Ni4-O33	164.3(2)	O73-Ni8-O42	162.4(2)
N2-Ni1-O1	87.2(2)	N41-Ni5-O41	88.6(2)
N2-Ni1-O2	92.4(2)	N41-Ni5-O42	92.5(2)
O1-Ni1-O2	171.5(2)	O41-Ni5-O42	172.5(2)
N2-Ni1-O22	172.4(2)	N41-Ni5-O62	173.6(2)
O1-Ni1-O22	98.5(2)	O41-Ni5-O62	95.6(2)
O2-Ni1-O22	82.7(2)	O42-Ni5-O62	84.00(19)
N2-Ni1-O3	91.1(2)	N41-Ni5-O43	90.6(3)
O1-Ni1-O3	97.5(2)	O41-Ni5-O43	97.0(2)
O2-Ni1-O3	91.0(2)	O42-Ni5-O43	90.3(2)
O22-Ni1-O3	83.2(2)	O62-Ni5-O43	84.1(2)
N2-Ni1-O32	104.2(2)	N41-Ni5-O72	103.2(2)
O1-Ni1-O32	92.7(2)	O41-Ni5-O72	92.1(2)
O2-Ni1-O32	79.2(2)	O42-Ni5-O72	80.5(2)
O22-Ni1-O32	80.60(19)	O62-Ni5-O72	81.5(2)
O3-Ni1-O32	162.0(2)	O43-Ni5-O72	163.7(2)

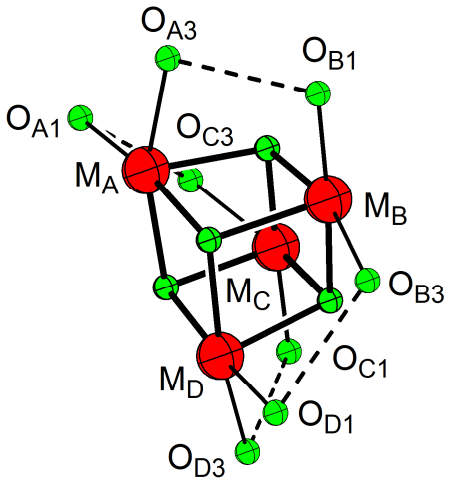

Figure S2. Emphasis of probable hydrogen bonding interactions in **1·H$_2$O**, **2·4C$_3$H$_6$O**, and **2·CH$_2$Cl$_2$**. **1·H$_2$O**: M_A= Ni1, O_{A1} = O1, O_{A3} = O3, M_B = Ni1', O_{B1} = O1', O_{B3} = O3', M_C = Ni1'', O_{C1} = O1'', O_{C3} = O3'', M_D = Ni1''', O_{D1} = O1''', O_{D3} = O3'''; **2·4C$_3$H$_6$O**: M_A = Ni1, O_{A1} = O1, O_{A3} = O3, M_B = Ni2, O_{B1} = O11, O_{B3} = O13, M_C = Ni2', O_{C1} = O11', O_{C3} = O13', M_D = Ni1', O_{D1} = O1', O_{D3} = O3' ; **2·CH$_2$Cl$_2$** (two crystallographically independent molecules): M_A = Ni1/5, O_{A1} = O1/41, O_{A3} = O3/43, M_B = Ni2/6, O_{B1} = O11/51, O_{B3} = O13/53, M_C = Ni3/7, O_{C1} = O21/61, O_{C3} = O23/63, M_D = Ni4/8, O_{D1} = O31/71, O_{D3} = O33/73. Symmetry operations used to generate equivalent atoms of **1·H$_2$O**: (') 1.25–*y*, 0.25+*x*, 1.25–*z*; ('') –0.25+*y*, 1.25–*x*, 1.25–*z*; (''') 1–*x*, 1.5–*y*, *z*. Symmetry operation used to generate equivalent atoms of **2·4C$_3$H$_6$O**: (') 1–*x*, *y*, 0.5–*z*.

Table S7. Probable Hydrogen Bonding Interactions and Ni···Ni Distances in **1·H$_2$O**, **2·4C$_3$H$_6$O**, and **2·CH$_2$Cl$_2$**. (see Figure S2 for Numbering Scheme)

distances	**1·H$_2$O**	**2·4C$_3$H$_6$O**	**2·CH$_2$Cl$_2$**
O_{A3}···O_{B1}	2.636(2)	2.660(2)	2.621(7) / 2.660(7)
O_{B3}···O_{D1}	2.636(2)	2.695(2)	2.635(7) / 2.690(8)
O_{C3}···O_{A1}	2.636(2)	2.695(2)	2.682(8) / 2.672(8)
O_{D3}···O_{C1}	2.636(2)	2.660(2)	2.680(8) / 2.681(8)
M_A···M_B	3.0831(3)	3.0727(4)	3.0983(14) / 3.0837(14)
M_A···M_C	3.0831(3)	3.1078(4)	3.1124(14) / 3.0942(14)
M_A···M_D	3.1708(4)	3.2072(4)	3.2038(16) / 3.1945(16)
M_B···M_C	3.1708(4)	3.1697(4)	3.1623(13) / 3.1522(14)
M_B···M_D	3.0831(3)	3.1078(4)	3.0719(14) / 3.0892(14)
M_C···M_D	3.0831(3)	3.0727(4)	3.0786(14) / 3.1062(14)

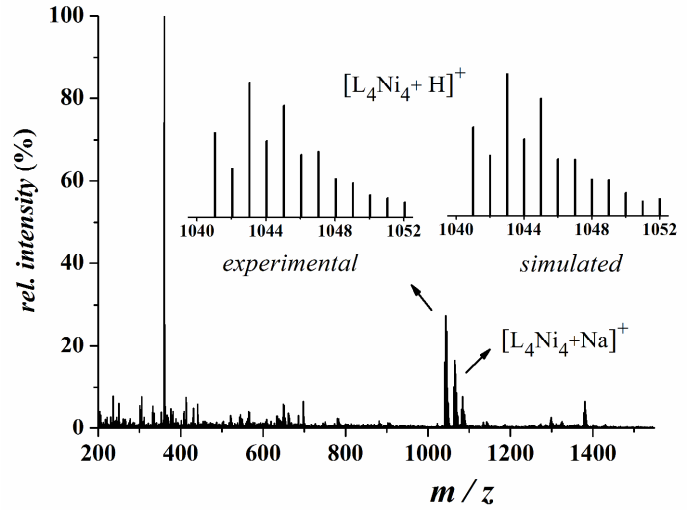

Figure S3. Positive ion ESI-MS spectrum of **1** in C_3H_6O solution. The inset shows the observed and calculated isotopic distribution pattern for the ion $[Ni_4L_4+H]^+$.

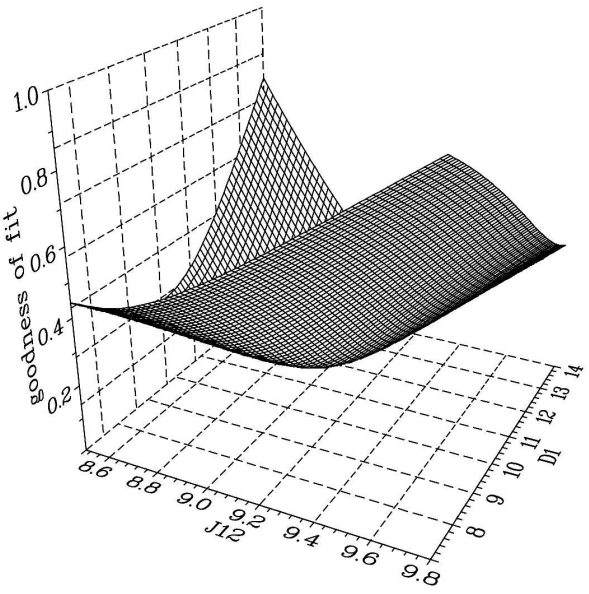

Figure S4. The 3D error surface for the pairs $J_1(J_{12})$–D for **1**·$\mathbf{H_2O}$.

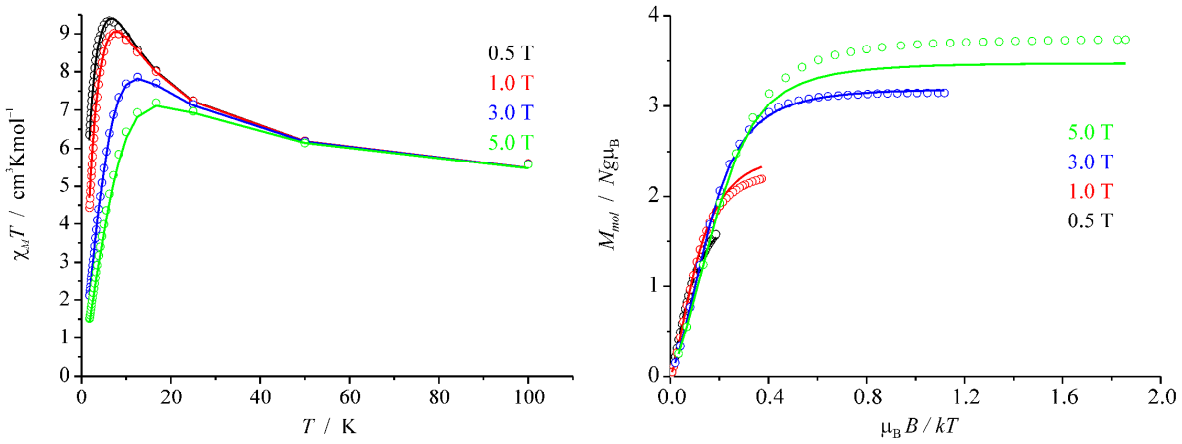

Figure S5. Variable temperature–variable field (VTVH) magnetization measurements for **1·H$_2$O** shown as $\chi_M T$ *versus* T (left) and M_{mol} *versus* B/T (right) in the field and temperature ranges 0.5 – 5 T and 1.8 – 100 K. The splitting of the isofield lines (right) confirms a high level of magnetic anisotropy. The best fit parameters are g = 2.13, J_1 = +9.43 cm^{-1}, J_2 = –5.63 cm^{-1} (fixed), D = +11.1 cm^{-1}.

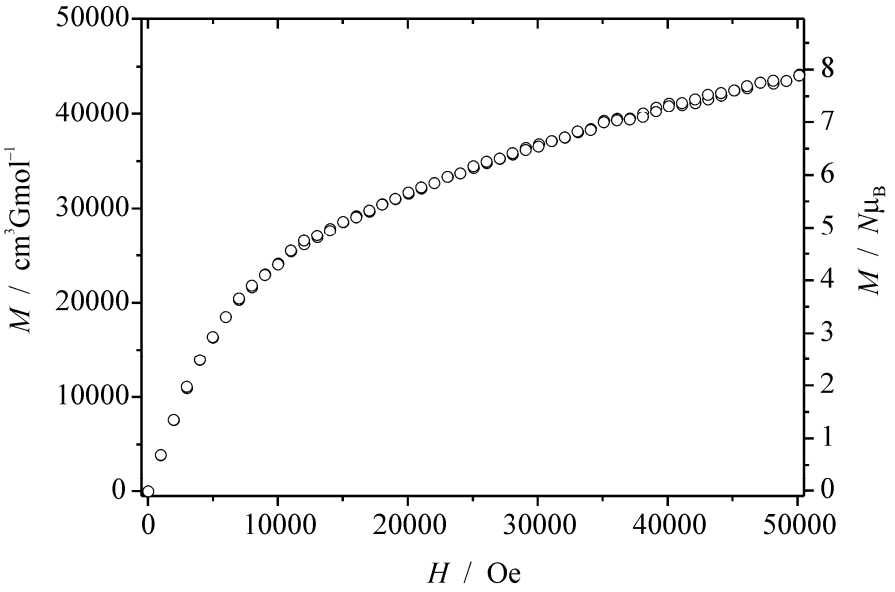

Figure S6. The magnetization measurement of **1**·**H_2O** at 2 K.

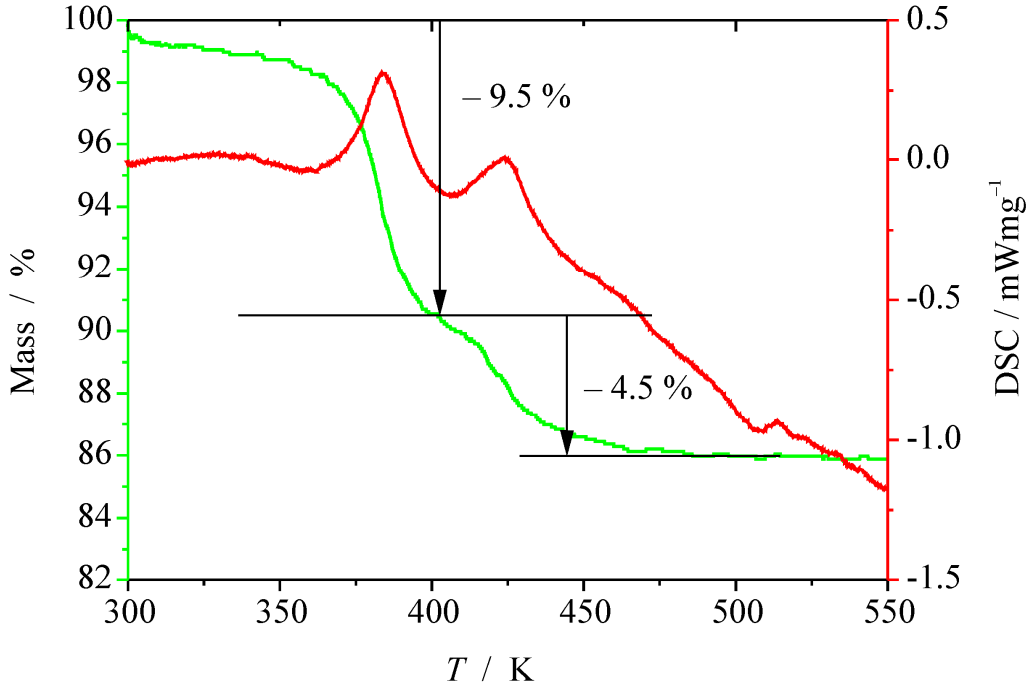

Figure S7. Thermogravimetric measurement of **2·2C$_3$H$_6$O**, fresh crystalline material powdered in air, scan rate: 5 K/min.

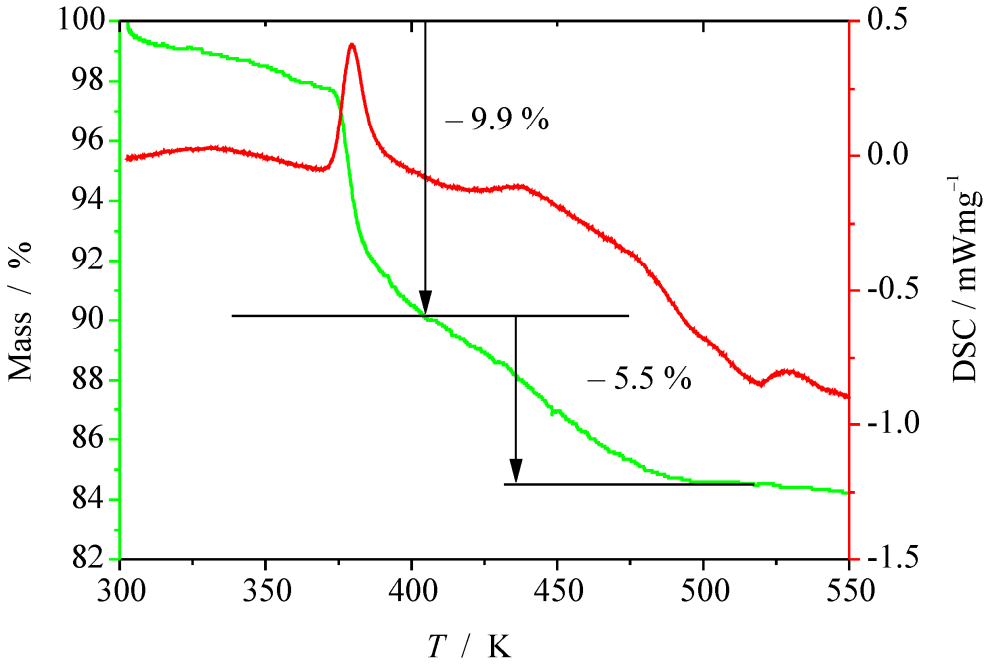

Figure S8. Thermogravimetric measurement of **2·2C$_3$H$_6$O**, powdered crystalline material dried in air over night, scan rate: 5 K/min.

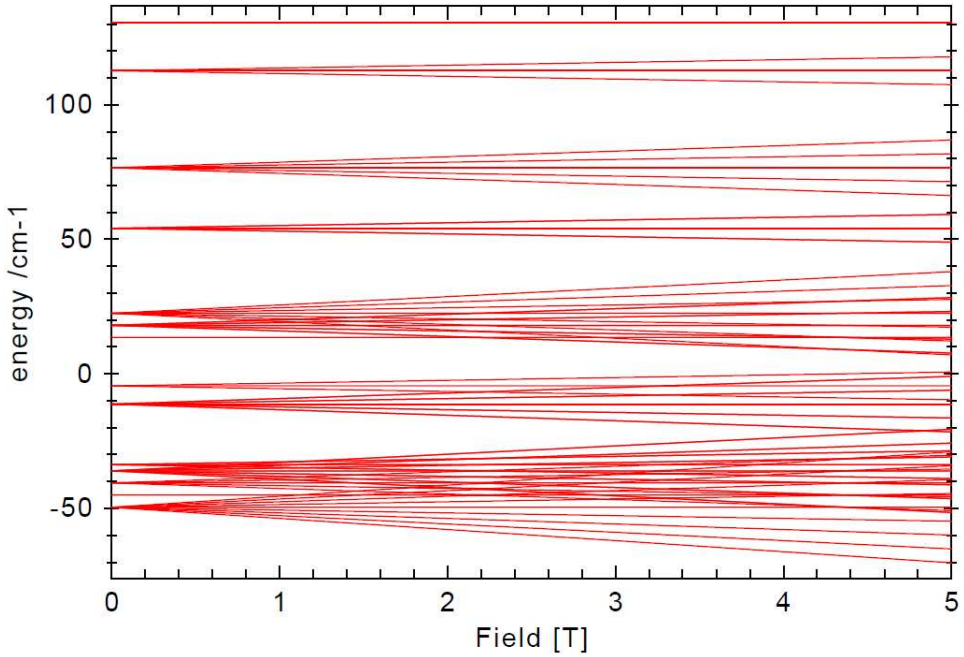

Figure S9. Energy level calculation for **1·H$_2$O** with parameters g = 2.22, J_1 = +8.90 cm^{-1}, J_2 = –5.63 cm^{-1}.

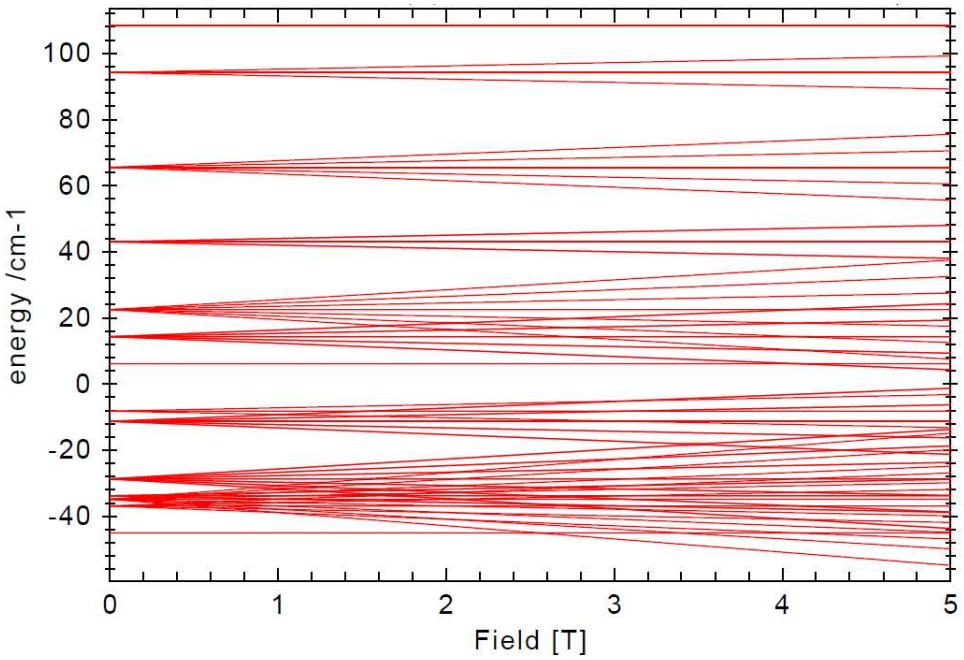

Figure S10. Energy level calculation for **2'·H_2O** with parameters g = 2.14, J_1 = +7.17 cm^{-1}, J_2 = –5.63 cm^{-1}.

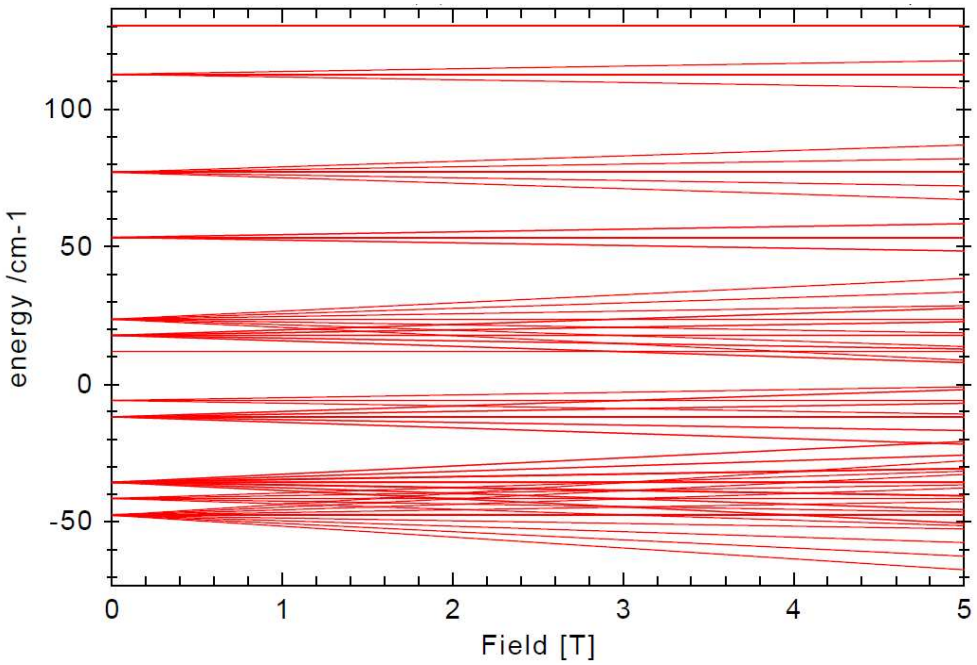

Figure S11. Energy level calculation for **2·4C$_3$H$_6$O** with parameters g = 2.12, J_1 = +8.90 cm^{-1}, J_2 = –5.91 cm^{-1}.

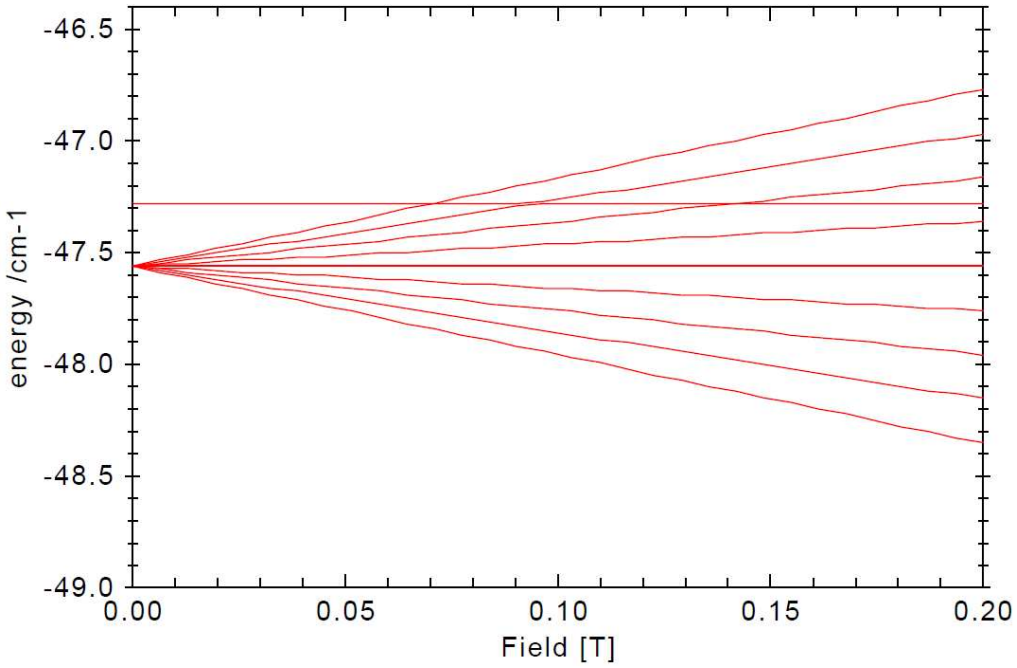

Figure S12. Zoomed view of the lowest energy levels (S_T = 4 and S_T = 0) for **2·4C$_3$H$_6$O** with parameters g = 2.12, J_1 = +8.90 cm^{-1}, J_2 = –5.91 cm^{-1}.

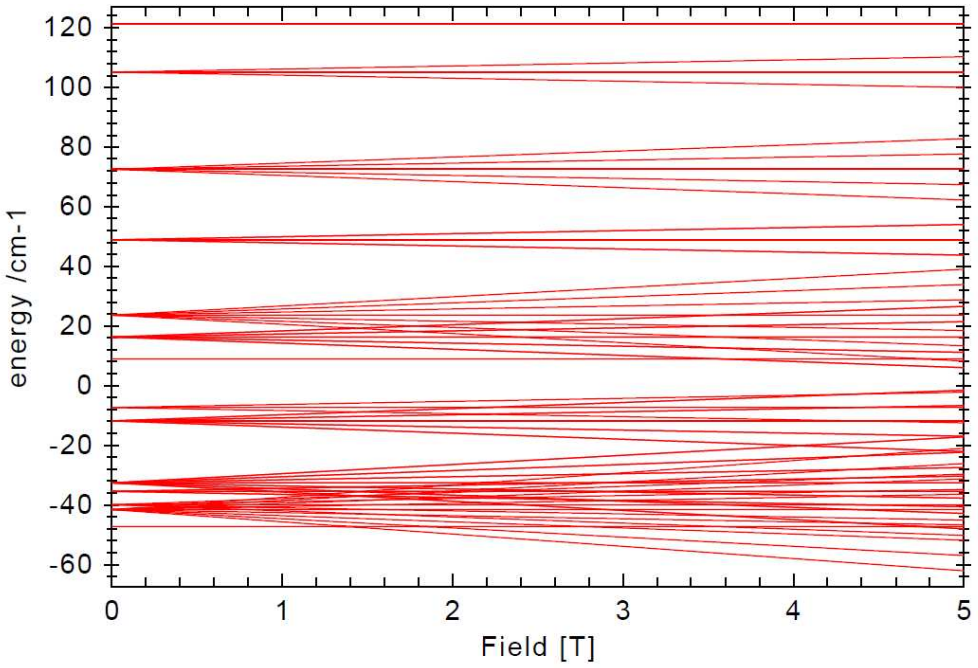

Figure S13. Energy level calculation for **2·2C_3H_6O** with parameters g = 2.20, J_1 = +8.15 cm^{-1}, J_2 = –5.91 cm^{-1}.

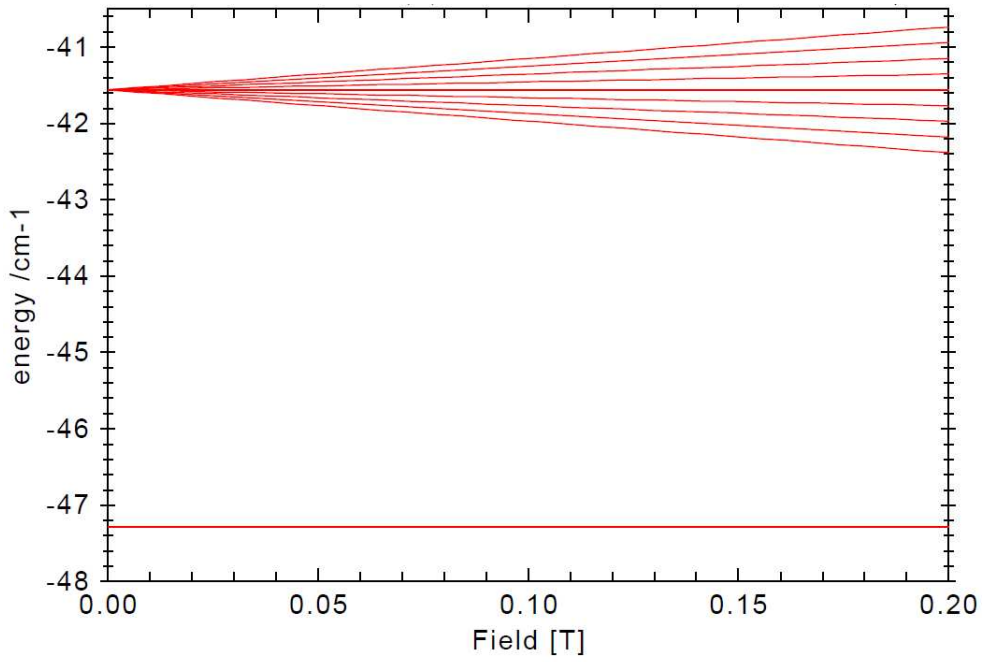

Figure S14. Zoomed view of the lowest energy levels (S_T = 0 and S_T = 4) for **2·2C_3H_6O** with parameters g = 2.20, J_1 = +8.15 cm^{-1}, J_2 = –5.91 cm^{-1}.