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"*Quasi-isotropic SMMs: slow relaxation of the magnetization in polynuclear $Cu^{II}/Mn^{II}$ complexes*"

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# 1-Instrumental measurements

**Physical measurements**: Magnetic susceptibility measurements were carried out on powdered fresh crystals samples with a MPMS5 Quantum Design susceptometer working in the range 30-300 K under magnetic fields of 0.3 T and under a field of 0.03T in the 30 – 2 K range to avoid saturation effects at low temperature. Diamagnetic corrections were estimated from Pascal Tables. Samples for analysis were vacuum dried to remove crystallization solvents. Infrared spectra (4000-400 cm–1) were recorded from KBr pellets on a Bruker IFS-125 FT-IR spectrophotometer.

# 2-Syntheses and characterization.

**[CuL1] metalloligand**: the $Cu^{II}$ complex [CuL1] derived from the unsymmetrical di-Schiff base ligand ($H_2L$ = N-(α-methylsalicylidene)-N′-(salicylidene)-2,2-dimethyl-1,3-propanediamine) was synthesized following the reported method[1] by replacing the 1,3-propanediamine with 2,2-dimethyl-1,3-propanediamine.

**N,N'-Ethylene-bis(3-ethoxysalicylaldiimine) (L2)** The Schiff base was synthesized following reported methods[2] mixing an ethanolic solution (15 mL) of ethylenediamine (3 mmols/0.18 g)) and o-vanillin (6 mmol/0.91 g). The solution was stirred at room temperature during two hours and the formed yellow solid was collected by filtration and air dried. Yield 80%.

**Synthesis of $[(Cu^{II}L1)_2Mn^{II}(N_3)_2]\cdot 2H_2O$ ($1\cdot 2H_2O$).** $Mn(ClO_4)_2\cdot H_2O$ (0.361 g, 1 mmol) was dissolved in a 10 ml of MeOH and to it a 2 ml aqueous solution of $NaN_3$ (0.130 g, 2 mmol) and a 30 ml methanolic solution of the metalloligand [CuL1] (0.772 g, 2 mmol) were added to it with stirring. After ~ 30 min of stirring, the light green solution was filtered to remove any suspended particles. Brown coloured diffraction quality single crystals were formed within a few days on slow evaporation of solvent. The crystals were collected after 5 days. Yield: 61%. $C_{40}H_{44}Cu_2MnN_{10}O_4$. Calcd: C, 52.74; H, 4.87; N, 15.38. Found C, 52.61; H, 4.99; N, 15.50.

**$[\{Cu^{II}(L2)Mn^{II}(H_2O)_2(MeOH)\}\text{-}\{Cu^{II}(L2)\}_2](ClO_4)_2\cdot MeOH$ (2·MeOH)** To a yellowish methanolic solution (10 ml) of the Schiff base L (0.8 mmol/0.3 g), an aqueous solution (5 ml) of $Cu(OAc)_2\cdot 4H_2O$ (0.8 mmol/0.159 g) was added. The reaction mixture was placed into a microwaves furnace at 80˚C for 30 minutes. The precursor $[Cu^{II}(L)]$ was formed as a green precipitate that was filtered and air dried. The freshly formed powder of $[Cu^{II}(L)]$ was dissolved in 20 ml of $CH_2Cl_2$ and of MeOH (1:1) and $Mn(ClO_4)_2\cdot 6H_2O$ (0.25 mmol/0.064 g) was added. The solution was heated in the microwaves furnace for 15 min. at 70˚C, resulting a clear dark solution. After 2 days brown crystals, suitable for X-ray diffraction, were formed by layering with diethylether. Yield: 70%. $C_{55}H_{61}Cl_2Cu_3MnN_6O_{23}$. Calcd: C, 44.32; H, 4.12; N, 5.64. Found C, 44.6; H, 4.4; N, 5.4.

**$[(\mu_{1,1}\text{-}N_3)_2\{Cu^{II}(L2)Mn^{II}\}\text{-}\{Cu^{II}(L2)Na^{I}(MeOH)(N_3)\}_2](ClO_4)_2$ (3)** The complex was prepared following the same procedure than complex **2** but adding $NaN_3$ (0.4 mmol/0.026 g) to the $[Cu^{II}(L)]$ / $Mn(ClO_4)_2\cdot 6H_2O$ dissolution. The mixture was introduced to microwaves for 15 min. at 70˚C. After two days brown crystals, suitable for X-ray diffraction, were formed by vapor diffusion of diethylether. Yield: 40%. $C_{74}H_{80}Cl_2Cu_4Mn_2N_{20}Na_2O_{26}$. Calcd: C, 41.41; H, 3.75; N, 13.05. Found C, 41.0; H, 3.7; N, 13.1.

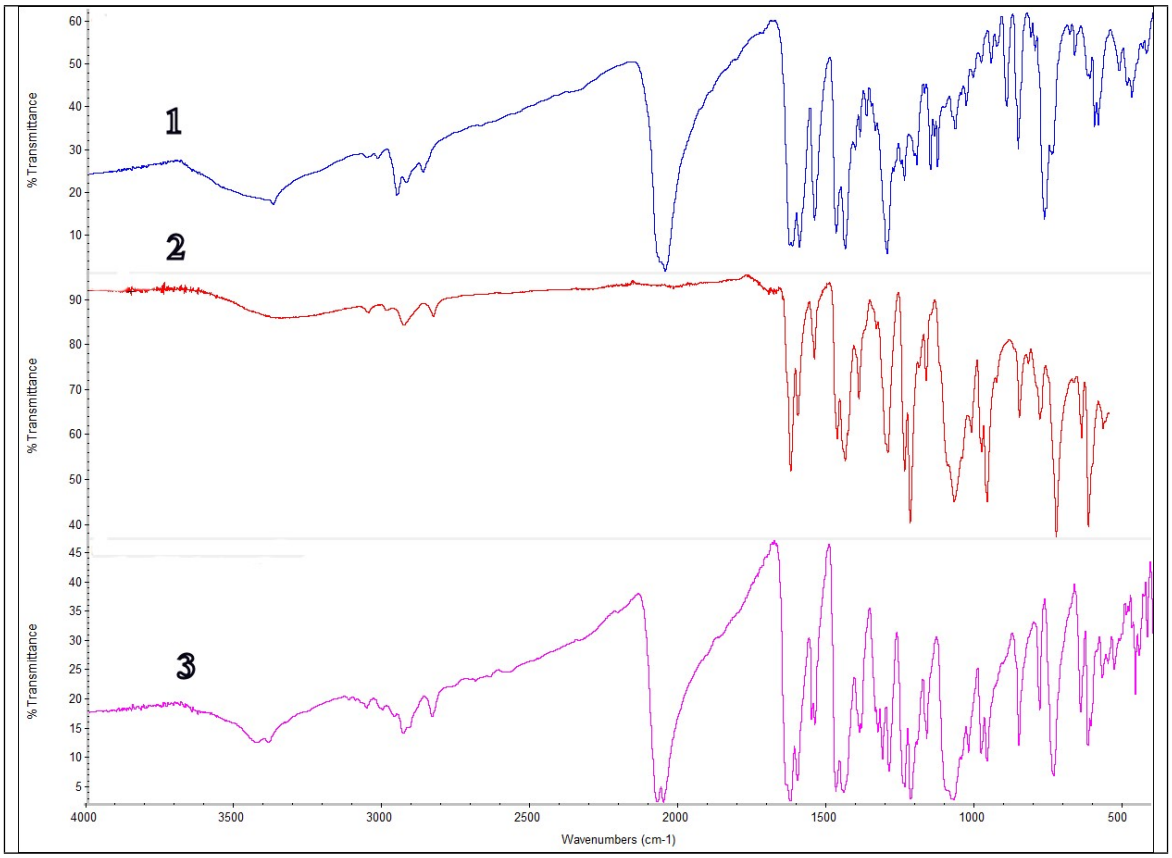


**Figure S1**. IR spectra for complexes **1** - **3**. Characteristic bands: st. C-H 3000-2800 $cm^{-1}$; N=C iminic ~1600 $cm^{-1}$; for **2** and **3**, st. $ClO_4^-$ 1075 $cm^{-1}$; δ $ClO_4^-$ 620 $cm^{-1}$. The stretching for the terminal and end-to-end azides for **3** appears differentiated at 2074 and 2055 $cm^{-1}$ respectively.

# 3-Structural aspects.

**Table S1**. Crystal data and structure refinement for complexes **1**, **2** and **3.**

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{40}H_{45}Cu_2MnN_{10}O_5$ | $C_{56}H_{66}Cl_2Cu_3MnN_6O_{24}$ | $C_{74}H_{80}Cl_2Cu_4Mn_2N_{20}Na_2O_{26}$ |
| FW | 927.88 | 1523.60 | 2146.5 |
| System | Monoclinic | Monoclinic | Triclinic |
| Space group | C2/c | P21/c | P-1 |
| *a*/Å | 16.839(2) | 15.4787(6) | 12.3500(6) |
| b/Å | 16.637(2) | 22.7556(9) | 13.0272(7) |
| *c*/Å | 16.478(2) | 17.7148(7) | 13.9308(7) |
| $\alpha$/deg. | 90 | 90 | 107.897(2) |
| ß/deg. | 99.467(2) | 97.002(1) | 91.793(2) |
| $\gamma$/deg. | 90 | 90 | 94.147(2) |
| *V*/ Å$^3$ | 4553.3(9) | 6193.1(4) | 2123.9(2) |
| *Z* | 4 | 4 | 1 |
| *T*, K | 296(2) | 100(2) | 100(2) |
| $\lambda$(MoK$\alpha$), Å | 0.71073 | 0.71073 | 0.71073 |
| $\rho_{calc}$, g·cm$^{-3}$ | 1.354 | 1.634 | 1.678 |
| $\mu$(MoK$_\alpha$), mm$^{-1}$ | 1.250 | 1.389 | 1.435 |
| *R* | 0.0609 | 0.0513 | 0.0334 |
| $\omega R^2$ | 0.1774 | 0.1188 | 0.0889 |

**Table S2**. Selected bond distances (Å) and angles (°) for compound **1**.

| **Bond lengths (Å)** | | | |
|---|---|---|---|
| Cu1 – O11 | 1.880(3) | Mn(1) – O(11) | 2.322(3) |
| Cu1 – O31 | 1.893(3) | Mn(1) – O(31) | 2.138(3) |
| Cu1 – N19 | 1.912(4) | Mn(1) – N(35) | 2.163(15) |
| Cu1 – N23 | 1.929(5) | Mn(1) – N(35)$^{\#}$ | 2.070(15) |
| | | | |
| O11 – Cu1 – O31 | 83.9(1) | O31 – Cu1 – N19 | 168.3(2) |
| O11 – Cu1 – N19 | 94.8(2) | O31 – Cu1 – N23 | 90.8(2) |
| O11 – Cu1 – N23 | 162.7(2) | N19 – Cu1 – N23 | 93.6(2) |
| O11 – Mn1 – O31 | 68.8(1) | O31 – Mn1 – N35 | 98.3(6) |
| O11 – Mn1 – N35 | 83.3(4) | O31 – Mn1 – O31$^{\#}$ | 142.5(2) |
| O11 – Mn1 – O11$^{\#}$ | 81.7(2) | O31 – Mn1 – N35$^{a}$ | 102.3(6) |
| O11 – Mn1 – O31$^{\#}$ | 82.9(1) | N35 – Mn1 – N35$^{\#}$ | 112.5(7) |
| O11 – Mn1 – N35$^{\#}$ | 163.3(4) | | |
| | | | |

**Table S3**. Selected bond distances (Å) and angles (°) for compound **2**.

| *d* Å | | | |
|---|---|---|---|
| Cu2-O6 | 1.894(3) | Cu2-N3 | 1.919(3) |
| Cu2-O7 | 1.898(3) | Cu2-N4 | 1.908(3) |
| Mn-O6 | 2.192(2) | Mn-O13 | 2.153(3) |
| Mn-O7 | 2.191(3) | Mn-O14 | 2.141(3) |
| Mn-O23 | 2.164(3) | | |
| Mn-O5 | 2.585(3) | Mn-O8 | 2.624(2) |
| Cu1-O2 | 1.905(3) | Cu1-N1 | 1.942(3) |
| Cu1-O3 | 1.916(3) | Cu1-N2 | 1.931(3) |
| Cu3-O10 | 1.908(3) | Cu3-N5 | 1.941(3) |
| Cu3-O11 | 1.904(3) | Cu3-N6 | 1.939(3) |
| Angles (º) | | | |
| O6-Mn-O7 | 69.71(9) | O7-Mn-O23 | 143.7(1) |
| O6-Mn-O23 | 145.1(1) | O13-Mn-O14 | 173.1(1) |
| O7-Mn-O8 | 63.78(8) | O8-Mn-O23 | 81.30(9) |
| O5-Mn-O23 | 81.77(9) | O5-Mn-O6 | 64.16(8) |
| Cu2-O6-Mn | 103.9(1) | Cu2-O7-Mn | 103.7(1) |

**Table S4**. Selected bond distances (Å) and angles (°) for compound **3**.

| *d* Å | | | |
|---|---|---|---|
| Cu2-O6 | 1.894(1) | Cu2-N3 | 1.921(1) |
| Cu2-O7 | 1.897 (1) | Cu2-N4 | 1.911(2) |
| Mn-O6 | 2.222(1) | Mn-N8 | 2.180(2) |
| Mn-O7 | 2.179(1) | Mn-N8’ | 2.269(2) |
| Mn-N5 | 2.146(2) | | |
| Mn-O5 | 2.546(1) | Mn-O9 | 2.597(1) |
| Cu1-O2 | 1.898(1) | Cu1-N1 | 1.923(2) |
| Cu1-O3 | 1.892(1) | Cu1-N2 | 1.931(1) |
| | | | |
| Na-O1 | 2.680(1) | Na-O6 | 2.910(1) |
| Na-O2 | 2.326(1) | Na-O8 | 2.314(2) |
| Na-O3 | 2.344(1) | Na-N5 | 2.494(2) |
| Na-O4 | 2.681(1) | | |
| Angles (º) | | | |
| O6-Mn-O7 | 69.69(4) | O6-Mn-N8 | 143.98(5) |
| O7-Mn-N8 | 138.48(6) | N5-Mn-N8’ | 171.89(6) |
| O5-Mn-O6 | 63.68(4) | O5-Mn-N8 | 84.81(5) |
| O7-Mn-O9 | 64.06(5) | O9-Mn-N8 | 82.96(5) |
| Cu2-O6-Mn | 102.46(5) | Cu1-O7-Mn | 103.96(5) |
| Mn-N8-Mn’ | 104.55(6) | | |

**Table S5**. SHAPE measures for the $Mn^{II}$ cations of complexes **1-3** parametrized. *S*(*P*) = 0 corresponds to a structure fully coincident in shape with the reference polyhedron P, regardless of size and orientation. The closest polyhedron to the corresponding coordination sphere is highlighted in red.

| | **(1)** | **(2)** | **(3)** |
|---|---|---|---|
| *S*(vOC-5) | -- | 7.00 | 5.89 |
| *S*(TBPY-5) | -- | 6.88 | 6.98 |
| *S*(SPY-5) | -- | 6.94 | 5.84 |
| *S*(JTBPY-5) | -- | 8.86 | 8.50 |
| *S*(OC-6) | **2.03** | -- | -- |
| *S*(TPR-6) | 11.85 | -- | -- |
| *S*(PBPY-7) | -- | **1.85** | **2.84** |
| *S*(COC-7) | -- | 7.74 | 5.77 |
| *S*(CTPR-7) | -- | 6.07 | 4.48 |
| *S*(JPBPY-7) | -- | 4.00 | 5.59 |

**Ideal $ML_5$ polyhedra:** vOC-5 ($C_4v$) Vacant octahedron; TBPY-5 ($D_3h$) Trigonal bipyramid; SPY-5 ($C_4v$) Spherical square pyramid; JTBPY-5 ($D_3h$) Johnson trigonal bipyramid J12.
**Ideal $ML_6$ polyhedra:** OC-6 (Oh) octahedron; TPR-6 ($D_3h$) trigonal prism
**Ideal $ML_7$ polyhedra:** PBPY-7 (D5h) Pentagonal bipyramid; COC-7 (C3v) Capped octahedron; CTPR-7 (C2v) Capped trigonal prism; JPBPY-7 (D5h) Johnson pentagonal bipyramid J13; JETPY-7 (C3v) Johnson elongated triangular pyramid J7.

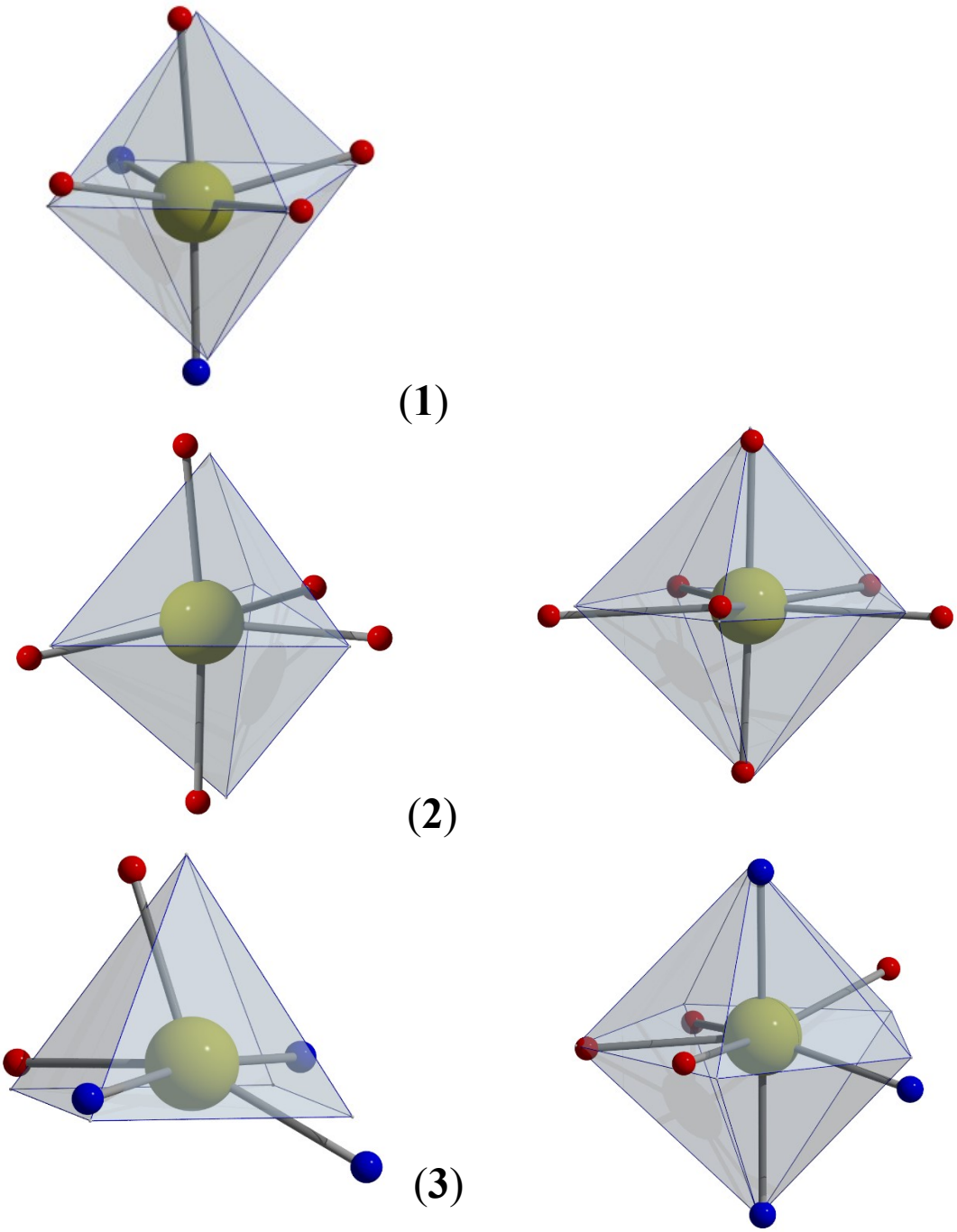


**Figure S2**. Plot of the coordination sphere for complexes **1-3**, referenced to the ideal polyhedron with lower *S*(*P*) value.

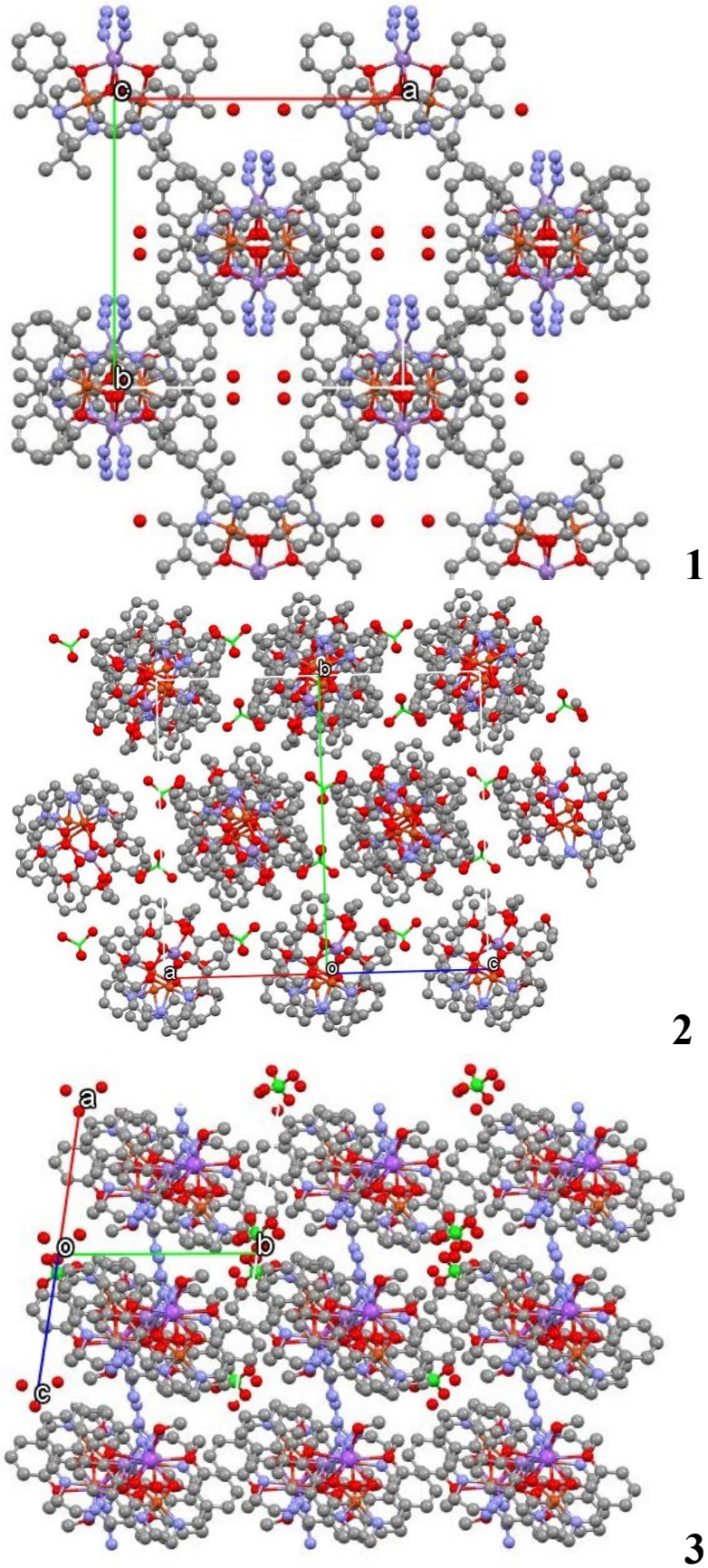


**Figure S3**. Plot of the network arrangement of complexes **1-3** viewed along the pillared clusters.

## 4-Magnetic data.

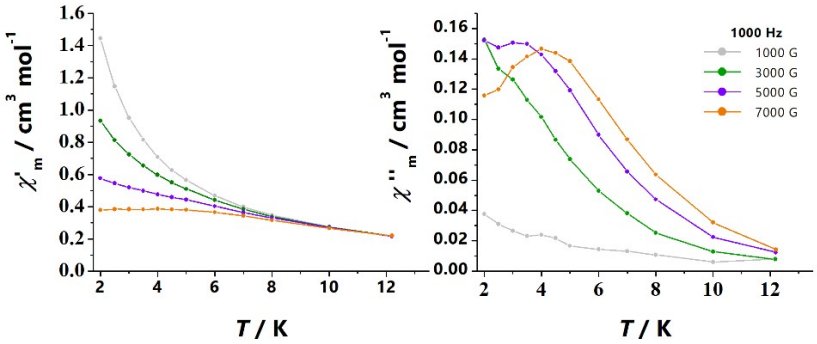


**Figure S4**. $\chi_M$'' dependence of the transverse field for complex **1**.

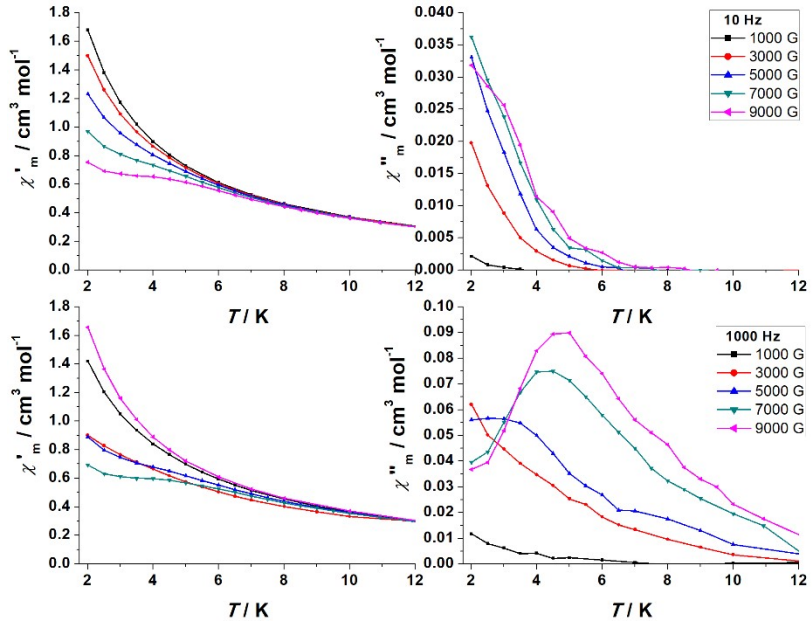


**Figure S5**. $\chi_M$'' dependence of the transverse field for complex **2**.

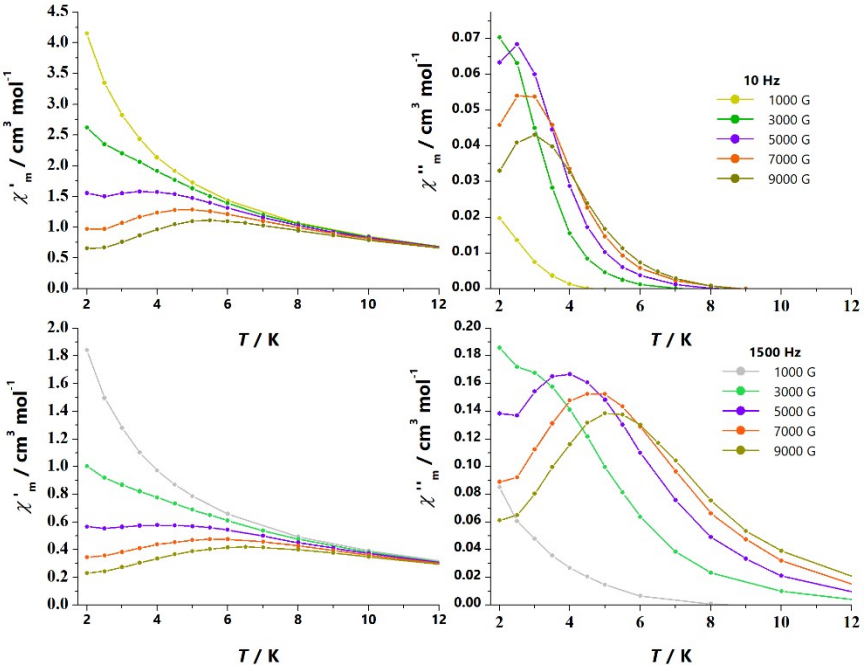


**Figure S6**. $\chi_M$'' dependence of the transverse field for complex **3**.

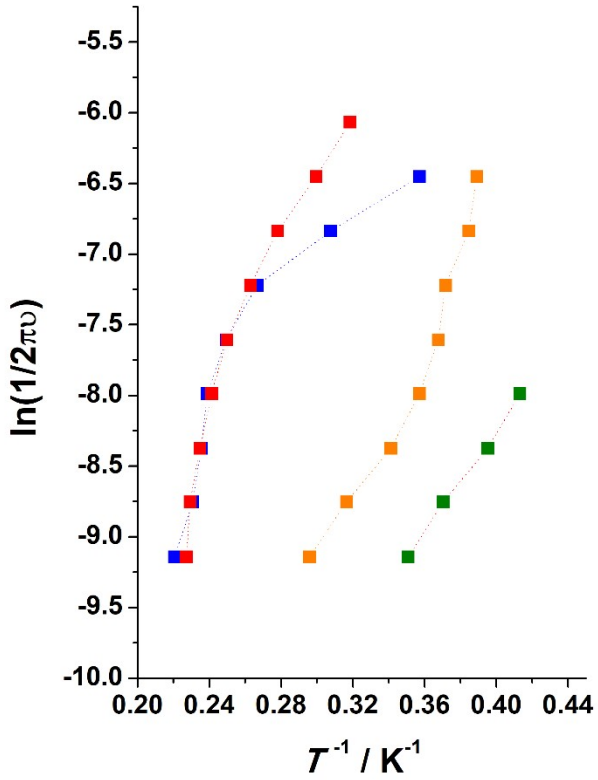


**Figure S7**. Plot of ln(1/2πν) vs. $T^{-1}$ from the $\chi_M$''($T$) data for complexes **1** (orange) **2** (blue) and **3** (3500 G, green; 6000 G, red).The data is limited to the HF region for which the maxima of $\chi_M$'' can be observed.

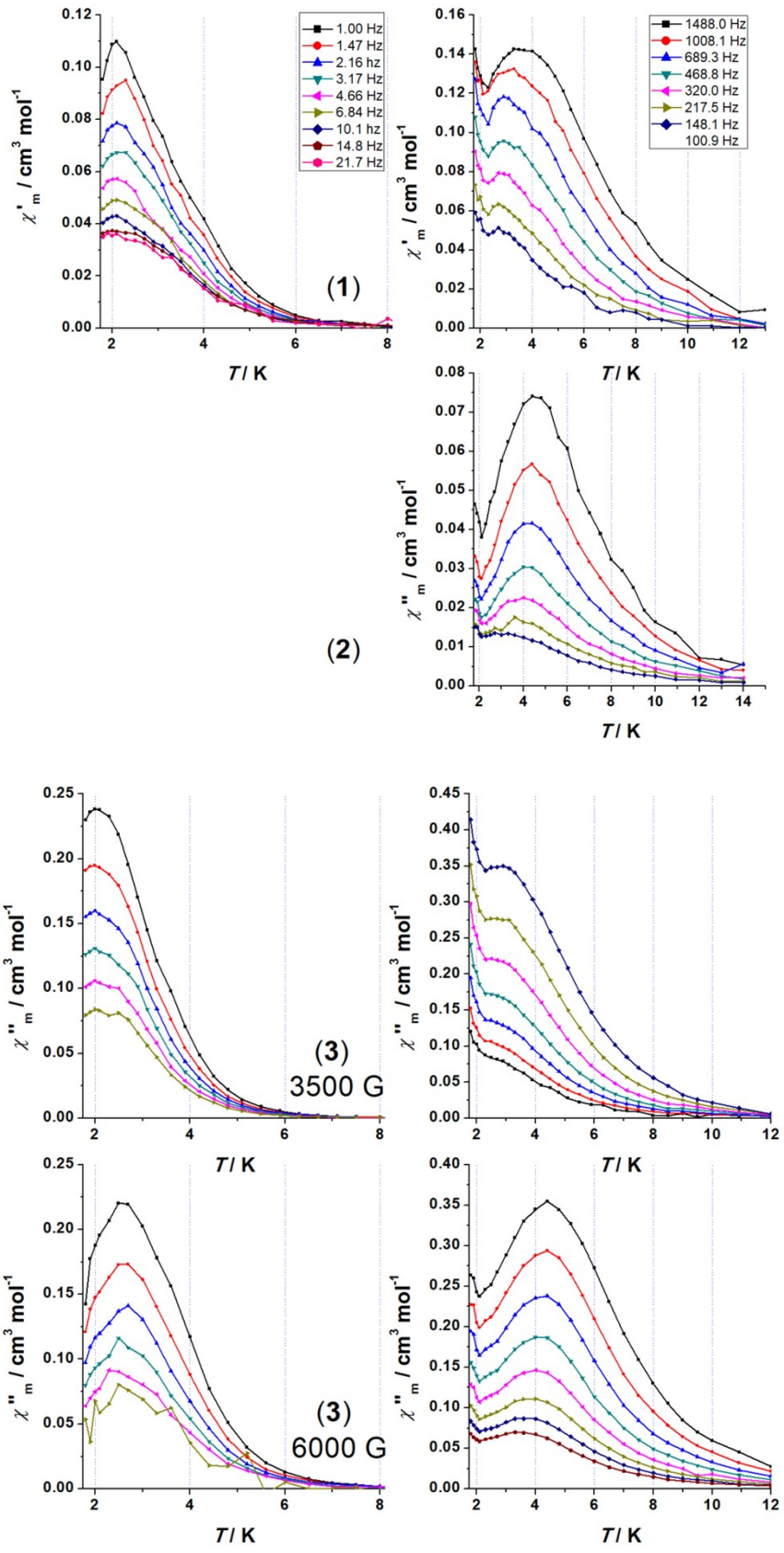


**Figure S8**. $\chi_M$''($T$) for complexes **1**, **2** amd **3** showing that the position of the maxima is temperature independent for the lower frequencies (left) and temperature dependent for the higher (right) frequencies. For the intermediate range of frequencies maxima are not defined.

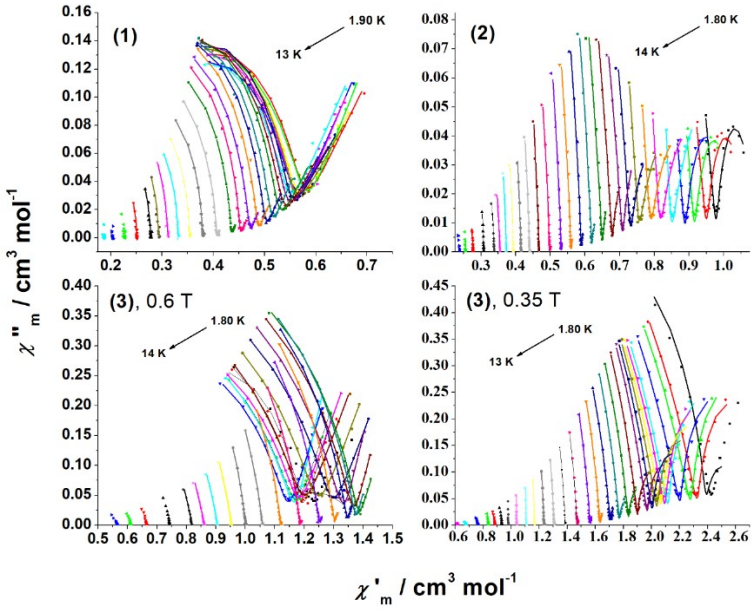


**Figure S9**. Cole-Cole plots for complexes **1**, **2** and **3.** Solid lines show the best fit of the experimental data.

**Table S6**. Best fit values for the ln($\tau$) *vs*. $T^{-1}$ plot ( $\frac{1}{\tau} = CT^n + AT + QT$ ) for complexes **1**-**3**.

| | ***C*** | ***n*** | ***QT*** | ***A*** | $E_a^*$ | $\tau_o^*$ |
|---|---|---|---|---|---|---|
| (**1**) | 2.011 | 4.38 | 9745 | -- | 13.5 | $2.9 \cdot 10^{-6}$ |
| (**2**) | 0.001 | 8.4 | -- | 20714 | 42.8 | $4.9 \cdot 10^{-8}$ |
| (**3**) - 3500 G | $2.9 \cdot 10^{-4}$ | 9.1 | -- | 1847 | 32.5 | $1.8 \cdot 10^{-8}$ |
| (**3**) - 6000 G | 0.95 | 5.23 | -- | 6232 | 45.2 | $6.7 \cdot 10^{-8}$ |

*Values extracted from the higher temperature data. Due to the limited number of points these values have a large degree of uncertain.

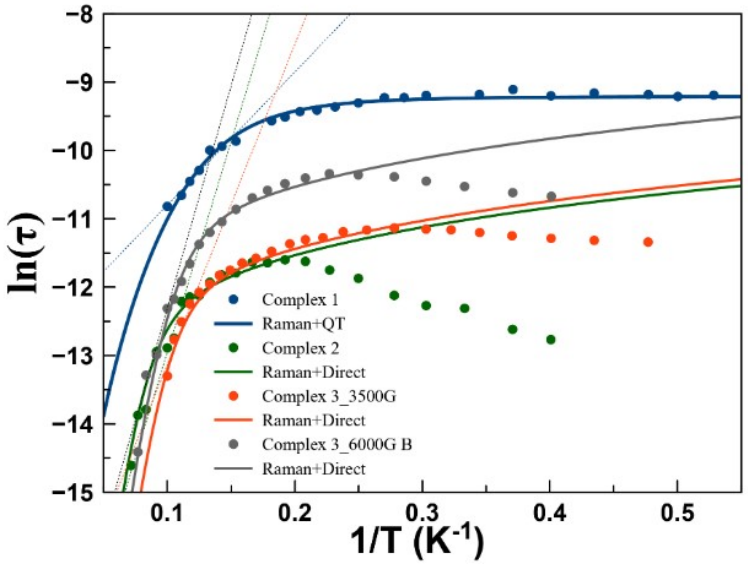


**Figure S10**. Plot of ln($\tau$) *vs*. $T^{-1}$ for complexes **1** – **3**. Solid lines show the best fit of the experimental data. For **2** and **3** the fit was performed for the increasing high temperature data. A after the maximum of the plot the decrease of ln($\tau$) at lower temperatures. Straigh solid lines (gray), shows the slope of the linear region at higher temperatures.

**References**


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2. I. Correia, J. C. Pessoa, M. T. Duarte, M. F. M.da Piedade, T. Jackush, T. Kiss, M. M. C. A. Castro, C. F. G. C. Geraldes and F. Avecilla, *Eur. J. Inorg. Chem*., 2005 , 732.