

Electronic Supplementary Material (ESI) for Dalton Trans.

*"Occurrence of slow relaxation of the magnetization in a family of copper(II)/manganese(II) quasi-isotropic complexes with different ground spin states."*

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**3- Magnetic data.**

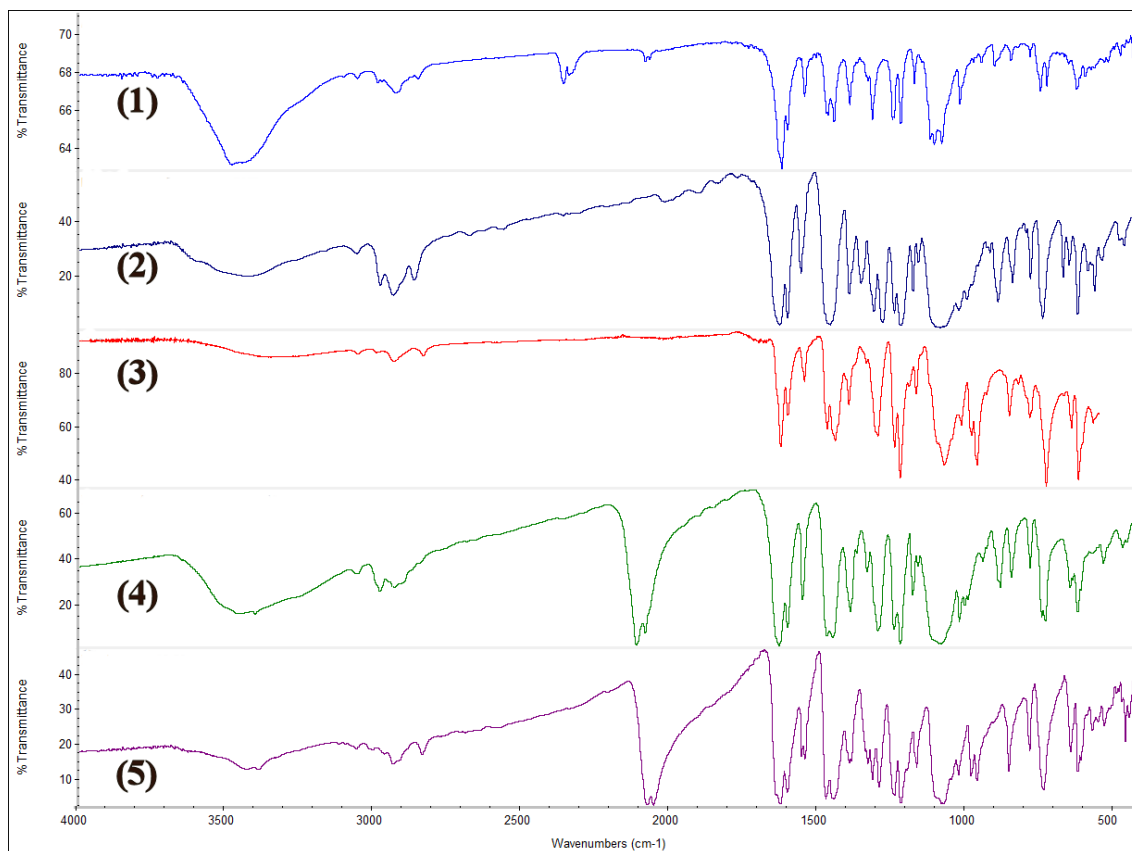
**Fig. S3.**  $\chi_M''$  dependence of the transverse field for complexes **2** (top), **3** (middle) and **5** (bottom).

**Fig. S4.** Plot of  $\ln(1/2\pi\nu)$  vs.  $T^{-1}$  from the  $\chi_M''(T)$  data for complexes **2, 3** and **5**.

**Fig. S5.**  $\chi_M''(T)$  for complexes **2, 3** and **5** showing the lower frequencies and high frequencies out-of-phase response.

**Fig. S6.** Cole-Cole plots for complexes **2, 3** and **5**.

## 1- IR spectra.

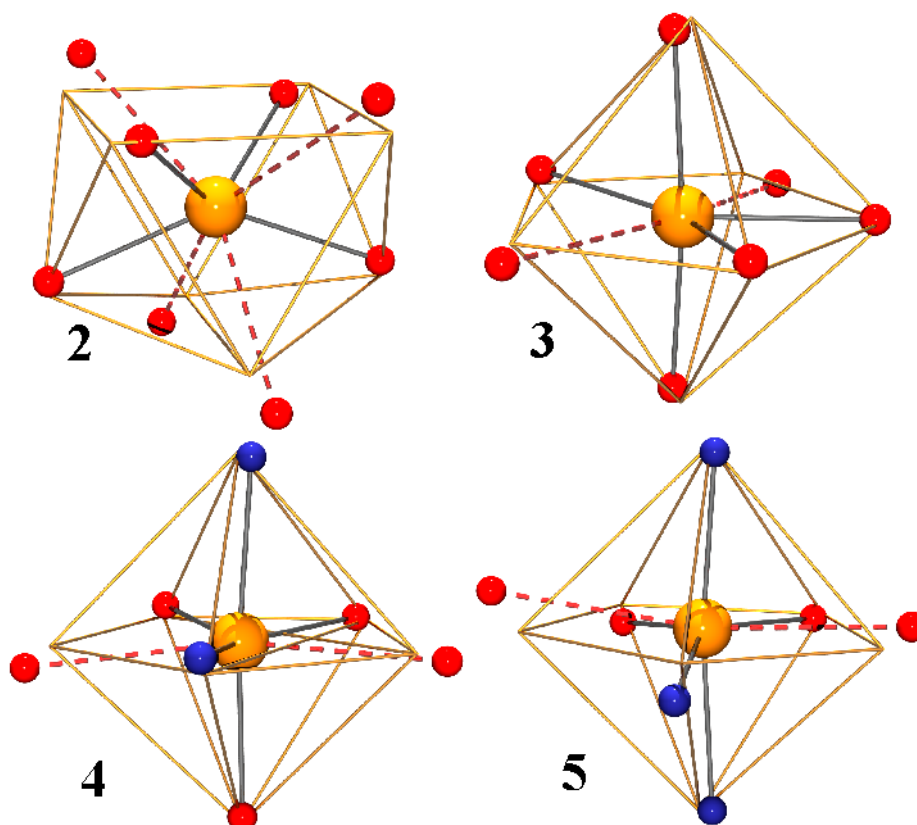


**Fig. S1.** IR spectra for complexes **1** - **5**. Characteristic bands: st. C-H 3000-2800 cm<sup>-1</sup>; N=C iminic ~1600 cm<sup>-1</sup>; C-O st. ClO<sub>4</sub><sup>-</sup> 1075 cm<sup>-1</sup>; δ ClO<sub>4</sub><sup>-</sup> 620 cm<sup>-1</sup>. Stretching for the azido ligands for **4** and **5** appears between 2050-2100 cm<sup>-1</sup>. **2RR** and **2SS** exhibit superimposable spectra and only one spectrum is shown.

## 2-Structural aspects.

**Table S1.** Crystal data and structure refinement for complexes **1** - **5**.

	<b>1</b>	<b>2SS</b> 2CH <sub>2</sub> Cl <sub>2</sub> ·0.5MeOH	<b>3</b> ·MeOH	<b>4</b> ·2MeOH	<b>5</b>
Formula	C <sub>21</sub> H <sub>26</sub> ClCu N <sub>2</sub> NaO <sub>9</sub>	C <sub>101</sub> H <sub>128</sub> Cl <sub>8</sub> Cu <sub>4</sub> Mn <sub>2</sub> N <sub>8</sub> O <sub>35</sub>	C <sub>56</sub> H <sub>66</sub> Cl <sub>2</sub> Cu <sub>3</sub> MnN <sub>6</sub> O <sub>24</sub>	C <sub>82</sub> H <sub>100</sub> Cl <sub>2</sub> Cu <sub>4</sub> Mn <sub>2</sub> N <sub>14</sub> O <sub>28</sub>	C <sub>74</sub> H <sub>80</sub> Cl <sub>2</sub> Cu <sub>4</sub> Mn <sub>2</sub> N <sub>20</sub> Na <sub>2</sub> O <sub>26</sub>
FW	572.42	2661.75	1523.60	2164.69	2146.5
System	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P21/c	P 1	P21/c	P-1	P-1
<i>a</i> /Å	8.0671(4)	12.2722(6)	15.4787(6)	9.876(1)	12.3500(6)
<i>b</i> /Å	21.2492(9)	14.5327(7)	22.7556(9)	14.787(2)	13.0272(7)
<i>c</i> /Å	14.0782(7)	17.2926(8)	17.7148(7)	16.663(2)	13.9308(7)
<i>α</i> /deg.	90	101.148(2)	90	73.292(5)	107.897(2)
<i>β</i> /deg.	103.285(2)	100.531(2)	97.002(1)	83.822(5)	91.793(2)
<i>γ</i> /deg.	90	111.062(2)	90	70.888(5)	94.147(2)
<i>V</i> /Å <sup>3</sup>	2348.7(2)	2714.5(2)	6193.1(4)	2201.8(5)	2123.9(2)
<i>Z</i>	4	1	4	1	1
<i>T</i> , K	100(2)	100(2)	100(2)	100(2)	100(2)
<i>λ</i> (MoK $\alpha$ ), Å	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{\text{calc}}$ , g·cm <sup>-3</sup>	1.619	1.628	1.634	1.633	1.678
$\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	1.118	1.279	1.389	1.376	1.435
Flack param.	----	0.02(1)	----	----	----
<i>R</i>	0.0340	0.0481	0.0479	0.0490	0.0334
$\omega R^2$	0.0718	0.1328	0.1094	0.1328	0.0889



**Fig. S2.** Coordination environment for the Mn<sup>II</sup> cation in complexes **2SS**–**5**. Dashed red bonds show the large contacts Mn–O<sub>alkoxy</sub>. The ideal polyhedra (biapicited trigonal prism for **2SS** and pentagonal bipyramid for **3**–**5**) are shown in orange.

**Table S2.** Relevant donor-acceptor distances (Å) and donor-H···acceptor angles for the H-bonds present in complexes **1**, **3**, **4** and **5**. For **1** and **5** correspond to the intermolecular H-bonds that determines the 1D arrangement in the network whereas for **3** and **4** correspond to the intramolecular H-bonds between the central and the capping [CuL] fragments.

	D···A (Å)		D-H···A (deg.)		
Complex <b>1</b>	O9···O5'	2.831(2)	O9-H90···O5'	158.6(3)	Intermolecular
Complex <b>5</b>	O8···N7'	2.843(2)	O8-H8O···N7'	166(2)	
Complex <b>3</b>	O13···O9	2.955(4)	O13-H13B···O9	137(3)	Intramolecular
	O13···O10	2.806(3)	O13-H13B···O10	148(3)	
	O13···O11	2.752(3)	O13-H13A···O11	157(3)	
	O13···O12	2.975(4)	O13-H13A···O12	129(3)	
	O14···O1	3.024(4)	O14-H14A···O1	140(3)	
	O14···O2	2.762(4)	O14-H14A···O2	148(3)	
	O14···O3	2.809(3)	O14-H14B···O3	153(3)	
	O14···O4	3.059(4)	O14-H14B···O4	132(3)	
Complex <b>4</b>	O9···O5	2.963(3)	O9-H9B···O5	138(2)	
	O9···O6	2.820(2)	O9-H9B···O6	150(2)	
	O9···O7	2.872(3)	O9-H9A···O7	135(3)	
	O9···O8	2.971(3)	O9-H9A···O8	154(3)	

### 3-Magnetic data.

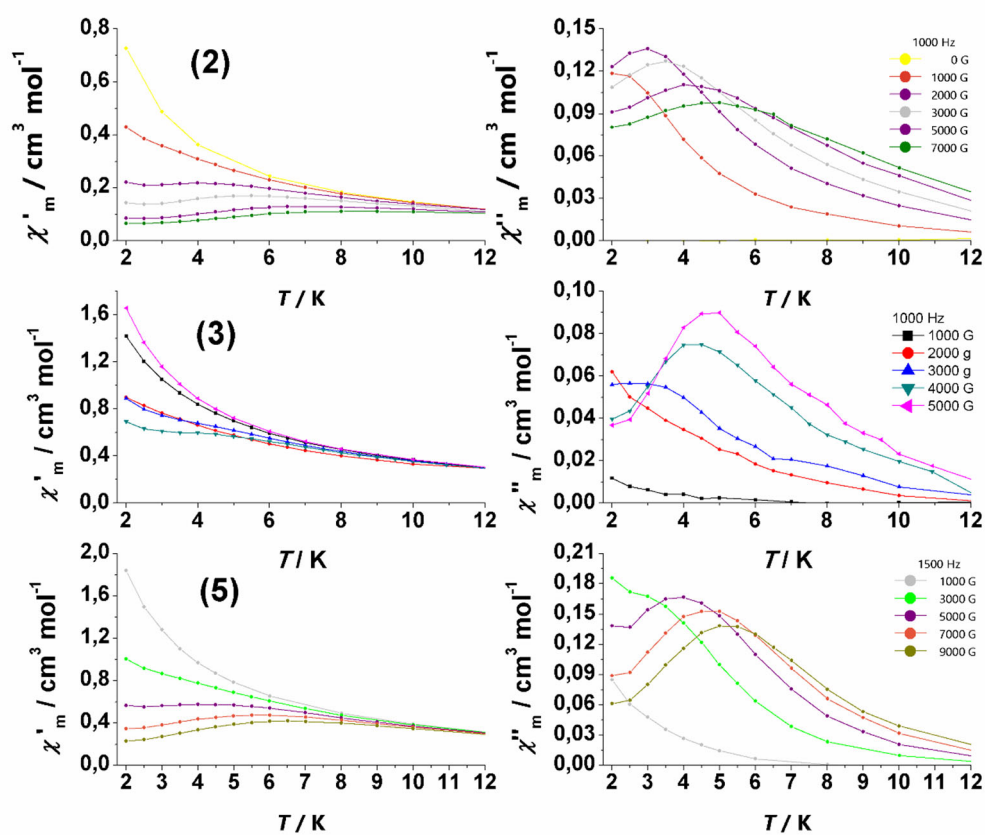
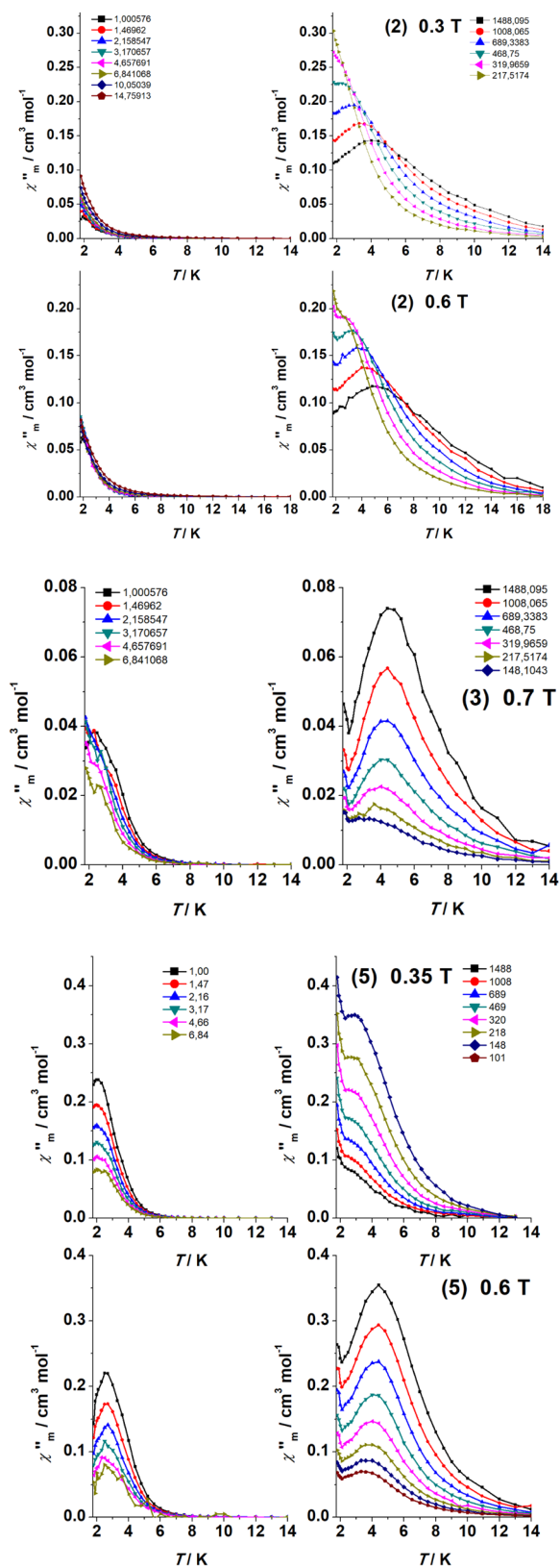
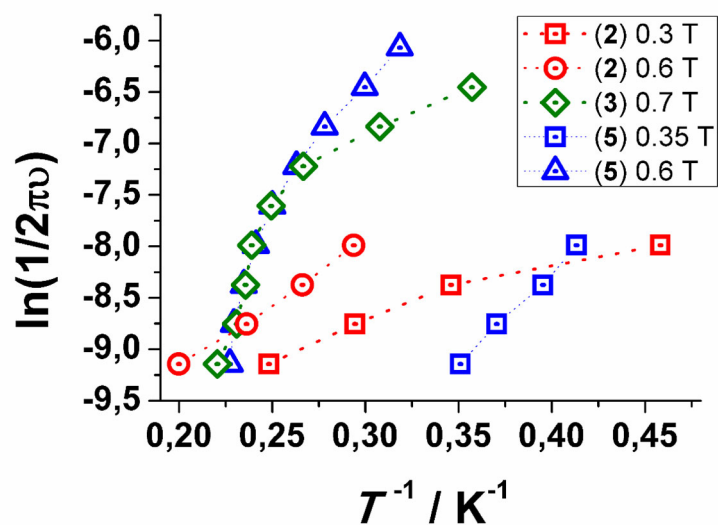


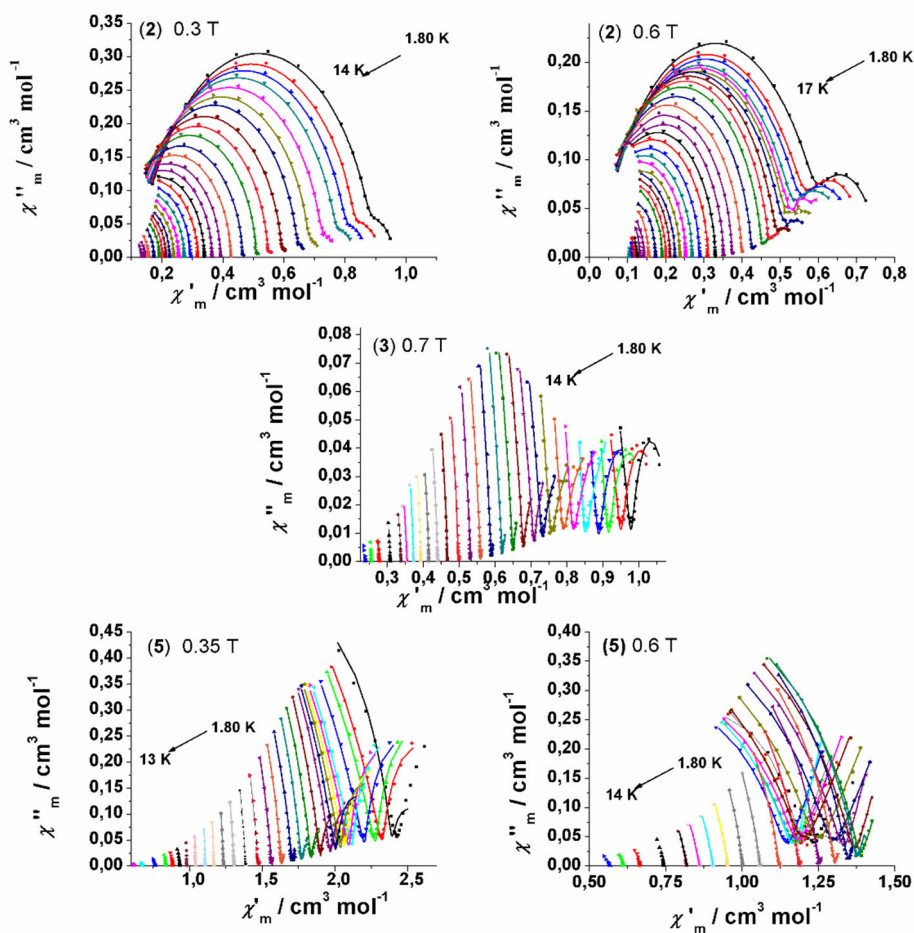
Fig. S3.  $\chi_M''$  dependence of the transverse field for complexes 2 (top), 3 (middle) and 5 (bottom).



**Fig. S4.**  $\chi''_m(T)$  for complexes 2, 3 and 5 showing the lower frequencies (left) and temperature dependent high frequencies (right) out-of-phase response. For the intermediate range of frequencies maxima are not defined.



**Fig. S5.** Plot of  $\ln(1/2\pi\nu)$  vs.  $T^{-1}$  from the  $\chi_M''(T)$  data for complexes **2** (red), **3** (green) and **5** (blue). The data is limited to the HF region for which the maxima of  $\chi_M''$  can be observed.



**Fig. S6.** Cole-Cole plots for complexes **2**, **3** and **5**. Solid lines show the best fit of the experimental data.