Supporting information

Field-assiated slow relaxation of magnetization in Cu(II) complexes with a pentaheterocyclic triphenodioxazine ligands: quasi-one-dimensional versus binuclear case

D.V. Korchagin,*[a] E.P. Ivakhnenko,[b] O.P. Demidov,[c] P.A. Knyazev[b], N.N. Efimov, [d]
R.B. Morgunov,[a] A.G. Starikov,[b] A.V. Palii,[a] V.I. Minkin,[b] and S.M. Aldoshin[a]

[a.] *Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, 1 Acad. Semenov Av., 142432 Chernogolovka, Russia; korden@icp.ac.ru*

[b.] *Institute of Physical and Organic Chemistry, Southern Federal University. 194/2 Stachki St. Rostov on Don, Russian Federation, 344090*

[c.] *North Caucasus Federal University.1 Pushkin st., Stavropol, Russian Federation, 355017*

[d] *Kurnakov Institute of General and Inorganic Chemistry, 31 Leninskii prosp. Moscow, Russian Federation, 119071,*

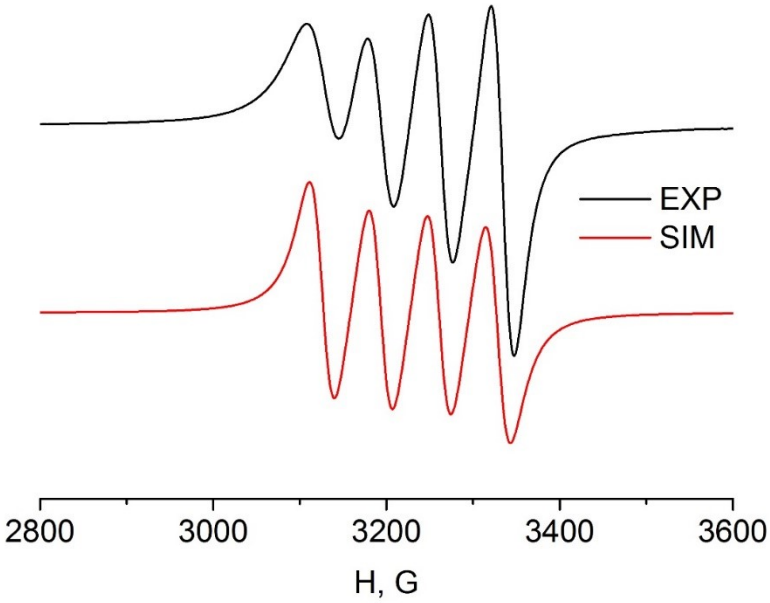
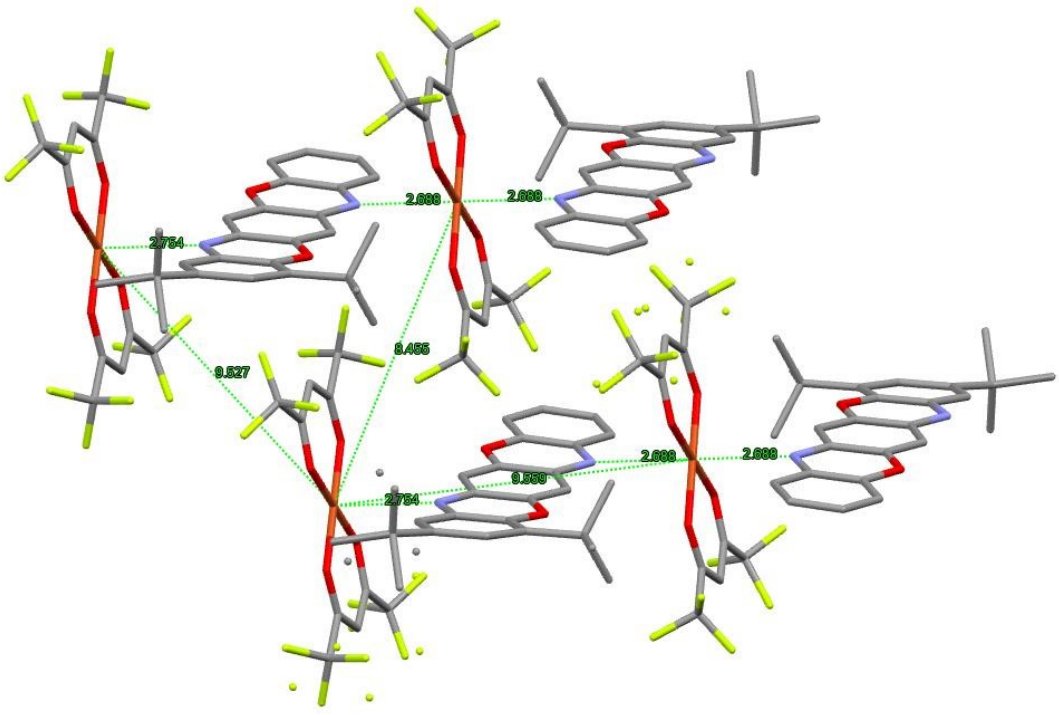
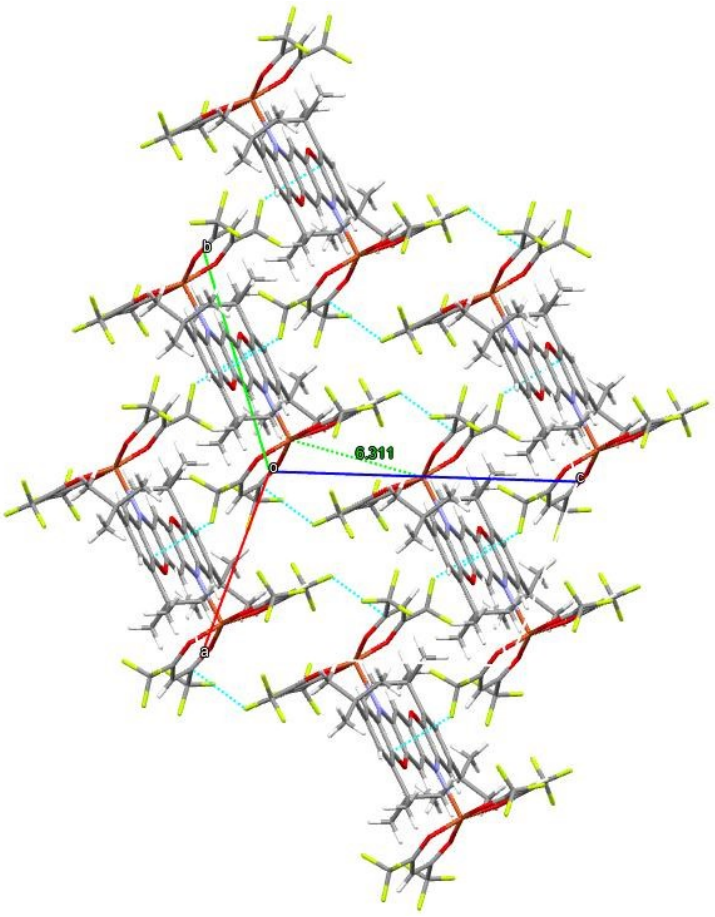


Fig. S1. Experimental (black) and simulated (red) ESR spectra of $Cu(hfac)_2$ (toluene solution, 295K, g = 2.1352, a(Cu) = 67.45 G).

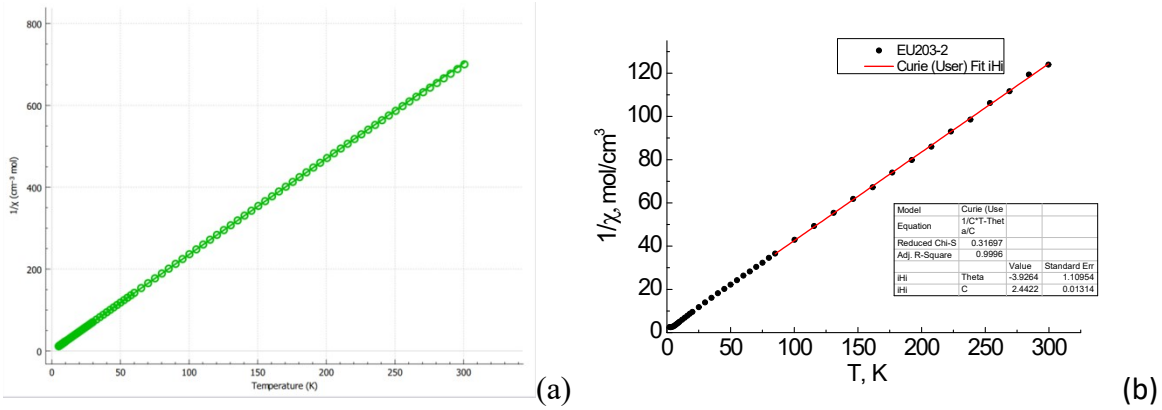


(a)



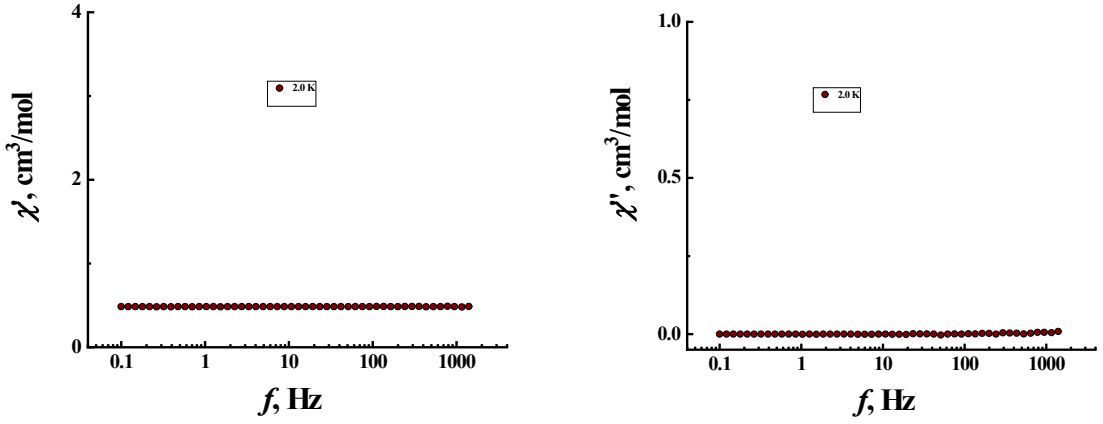
(b)

Fig.S2. Fragments of crystal packing of **1** (a) and **2**(b)



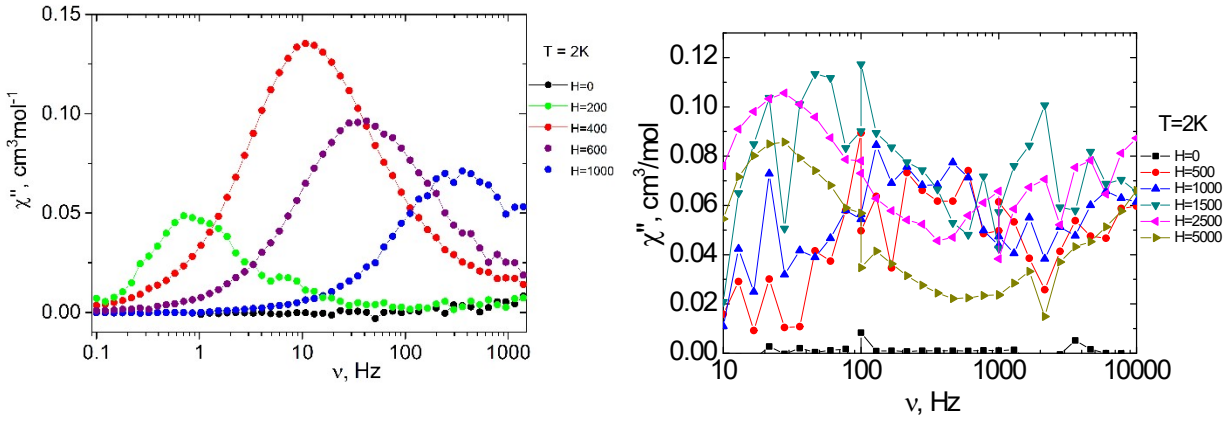
(a) (b)

Fig. S3. χ^{-1}(T) dependances for **1** (a) and **2** (b)(H = 1 and 5 кOe, respectively).



(a) (b)

Fig. S4. Frequency dependence of the in-phase χ' (a), out-of-phase χ'' (b) AC susceptibility χ_M for **1** at temperature T = 2K and H_{DC}=0 Oe.



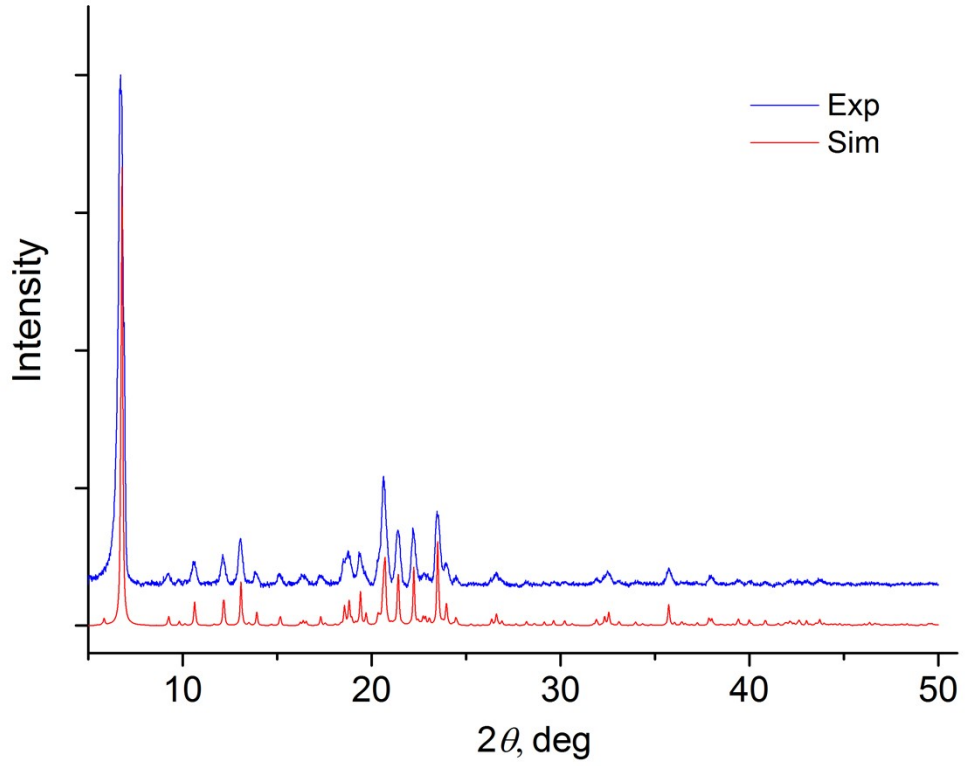
(a) (b)

Fig. S5. Frequency dependences of the out-of-phase (χ") AC susceptibility for **1** (a) and **2**(b) at different values of applied DC magnetic field and T = 2 K.

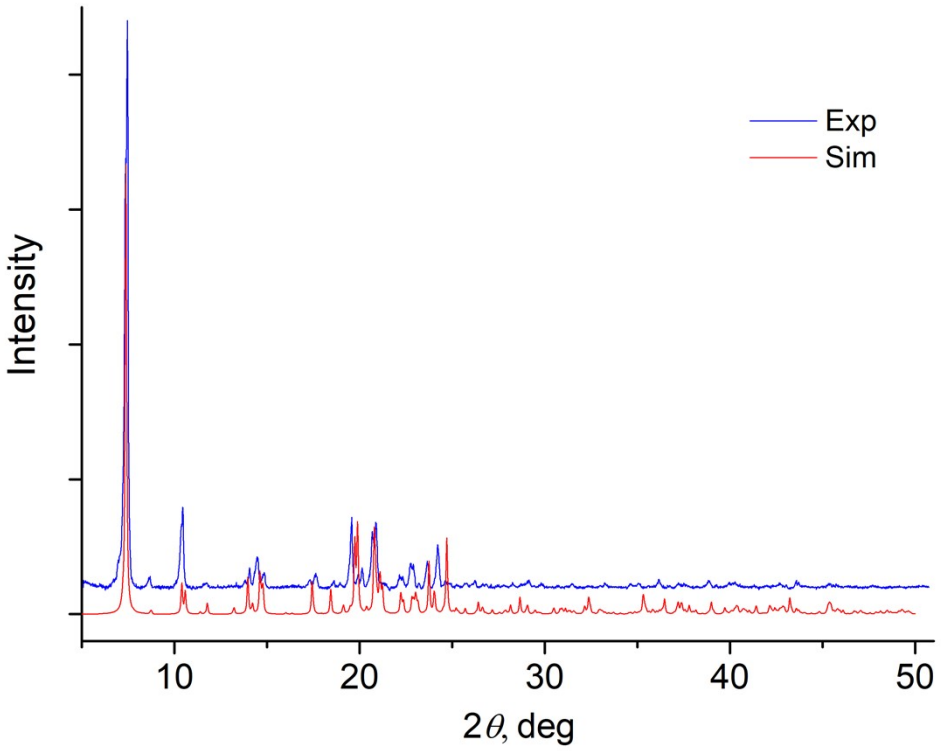
Table S1. Crystal data and structure refinement for **1** and **2**.

Parameters	**1**	**2**
Empirical formula	$C_{36}H_{28}CuF_{12}N_2O_6$	$C_{54}H_{46}Cu_2F_{24}N_2O_{10}$
Formula weight, g/mol	876.14	1466.01
Temperature, K	293(1)	100(1)
Crystal system; space group	Triclinic; P-1	Triclinic; P-1
a, Å	9.5270(2)	9.3736(5)
b, Å	13.6628(3)	13.0106(6)
c, Å	15.3279(2))	13.5156(7)
α, deg.	91.565(2)	99.681(4)
β, deg.	97.827(2)	103.799(4)
γ, deg.	106.988(2)	107.618(4)

Volume, Å^3	1885.58(7)	1473.32(14)
Z; ρ (calculated), g/cm^3	2; 1.543	2; 1.651
μ, mm^{-1}	1.789	2.115
F(000)	886	738
Crystal size, mm	0.29 x 0.18 x 0.05	0.24 x 0.17 x 0.11
θ range, deg.	2.917 to 67.684	3.487 to 67.684
Reflections collected	39179	24302
Reflections unique [R(int)]	7869 [0.0188]	6115 [0.0589]
N of param. (Constrains)	666(36)	421(0)
Goodness-of-fit on F^2	1.074	1.028
Final R_1; wR_2 [$I>2\sigma(I)$]	0.0386; 0.1177	0.0489; 0.1291
R_1; wR_2 (all data)	0.0458; 0.1269	0.0546; 0.1373
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e·Å^{-3}	0.280 and -0.505	0.936 and -0.731
CCDC	2296209	2296208

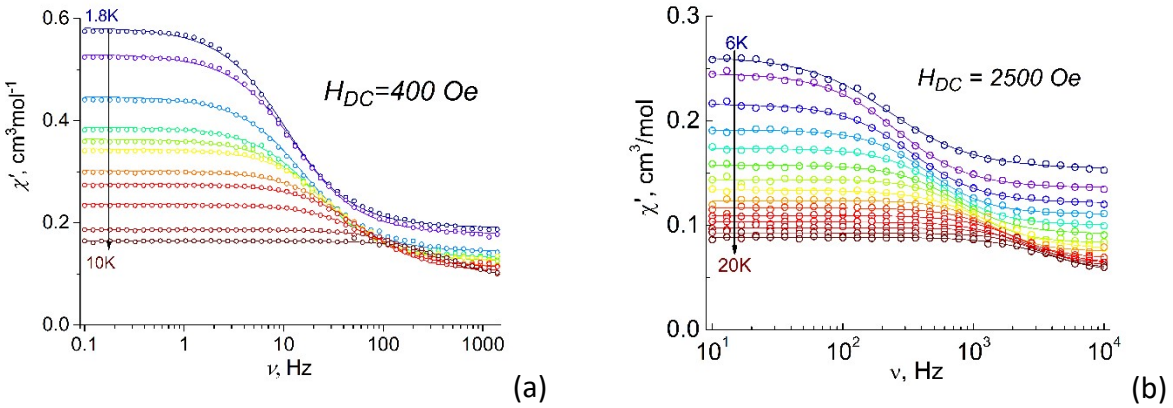


(a)



(b)

Fig. S6. Powder X-ray diffraction pattern of polycrystalline sample of **1** (a) and **2** (b): experimental (blue), and calculated from single crystal data (red).



(a) (b)

Fig. S7. Frequency dependences of the in-phase χ' for **1** (a) and **2** (b) at different temperatures and H_{DC}=400 Oe and 2500 Oe, respectively (points – experiment, lines – fit by generalized Debye model).

Table S2. Best fit parameters of the one-component Debye model for the Cole-Cole plot of complex **1** at H_{DC} =400 Oe

T, K	χ_S,cm^3 mol^{-1}	χ_T,cm^3 mol^{-1}	τ, s	α	R_1 [a]
1.8	0.190	0.584	0.154E-01	0.171	0.223E-02

2.0	0.178	0.531	0.123E-01	0.166	0.150E-02
2.2	0.143	0.448	0.993E-02	0.170	0.289E-02
2.5	0.131	0.388	0.762E-02	0.157	0.257E-02
2.7	0.125	0.365	0.636E-02	0.161	0.248E-02
3.0	0.126	0.345	0.516E-02	0.153	0.145E-02
3.5	0.113	0.303	0.360E-02	0.164	0.118E-02
4.0	0.111	0.277	0.280E-02	0.158	0.115E-02
5.0	0.104	0.236	0.199E-02	0.148	0.870E-03
8.0	0.094	0.187	0.605E-03	0.123	0.187E-03
10.0	0.089	0.165	0.321E-03	0.082	0.171E-03

[a] The mean residual sum of squares, $R_1 = \frac{1}{n}\sum_{i=1}^{n}\frac{(Y_{exp} - Y_{calc})^2}{Y_{exp}^{\ 2}}$

Table S3. Best fit parameters of the one-component Debye model for the Cole-Cole plot of complex **2** at H_{DC} =2500 Oe

T, K	χ_S,cm^3 mol^{-1}	χ_T,cm^3 mol^{-1}	τ, s	α	R_1 [a]
6	0.153	0.262	0.678E-03	0.124	0.654E-03
7	0.136	0.244	0.608E-03	0.084	0.175E-03
8	0.121	0.216	0.465E-03	0.072	0.185E-03
9	0.110	0.191	0.355E-03	0.039	0.850E-04
10	0.100	0.173	0.276E-03	0.029	0.113E-03
11	0.090	0.158	0.212E-03	0.048	0.610E-03
12	0.084	0.144	0.179E-03	0.029	0.633E-03
13	0.079	0.133	0.135E-03	0.039	0.163E-03
14	0.073	0.124	0.110E-03	0.059	0.257E-03
15	0.068	0.116	0.893E-04	0.010	0.148E-03
16	0.065	0.109	0.721E-04	0.018	0.899E-04

17	0.062	0.103	0.660E-04	0.028	0.656E-04
18	0.059	0.098	0.523E-04	0.041	0.194E-03
19	0.056	0.092	0.459E-04	0.065	0.216E-03
20	0.053	0.088	0.400E-04	0.059	0.145E-03

[a] The mean residual sum of squares, $R_1 = \frac{1}{n}\sum_{i=1}^{n}\frac{(Y_{exp} - Y_{calc})^2}{Y_{exp}^{\ 2}}$

Table S4. Total energies (E_{tot}, a.u.) for the structures of compound **L1**, **L2**, **1a-1c**, **2-2b** and $Cu(hfac)_2$ optimized at the DFT B3LYP/6-311++G(d,p) level of theory.

Structure	E_{tot}
L1	-1266.696503
L2	-1581.285426
$Cu(hfac)_2$	-3522.415768
1a	-9578.264993
1b	-8311.561341
1c	-4789.131488
2	-8626.152444
2a	-5103.721477
2b	-6685.002512