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Supporting Information

Structural Snapshots in the Copper(II) Induced Azide-Nitrile Cycloaddition: Effect of Peripheral Ligand Substituents on the Formation of Unsupported $\mu_{1,1}$-Azido vs. $\mu_{1,4}$-Tetrazolato Bridged Complexes

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Table S 1: Crystallographic details.

	$1·1.5CH_3CN$	$2·CH_3CN$	3	$4·0.5CH_3CN·0.5H_2O$	$6·C_2H_5CN·C_4H_{10}O$	$5·4CH_3CN$	$7·2C_4H_{10}O·5C_2H_5CN$
Chemical formula sum	$C_{66}H_{69}Cl_2Cu_2N_{29}O_8$	$C_{29}H_{27}ClCuN_{14}O_4$	$C_{45}H_{60}ClCuN_{13}O_4$	$C_{122}H_{123}Cl_6Cu_4N_{47}O_{25}$	$C_{55}H_{80}Cl_2CuN_{12}O_9$	$C_{100}H_{111}Cl_3Cu_2N_{28}O_{12}$	$C_{116}H_{167}Cl_3Cu_2N_{29}O_{14}$
M_r	1594.48	734.64	946.05	3114.53	1187.75	2130.60	2139.27
T (K)	110(2)	140(2)	140(2)	100(2)	118(2)	140(2)	100(2)
λ (Å)	0.71073	0.71073	0.71069	0.71073	0.71073	0.71069	1.54178
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic
Space group	P2(1)/n	P-1	P2(1)/c	P2(1)/c	P b c a	P-1	P-1
a, b, c (Å)	11.9577(6)	7.762(3)	22.312(5)	16.848(4)	20.631(2)	16.768(5)	15.7730(7)
	25.9892(14)	9.934(4)	16.019(5)	15.524(4)	23.395(2)	18.962(5)	16.4587(7)
	12.0161(6)	21.094(7)	13.436(5)	27.236(6)	26.182(2)	19.579(5)	26.440(1)
α,β, γ (deg)	90	81.671(7)	90	90	90	93.974(5)	88.921(2)
	91.070(3)	80.955(7)	100.679(5)	102.622(5)	90	99.507(5)	89.865(2)
	90	87.227(7)	90	90	90	93.995(5)	71.279(2)
V (Å^3)	3733.6(3)	1588.8(9)	4719(3)	6952(3)	12636(2)	6104(3)	6499.6(5)
Z	2	2	4	2	8	2	2
D_{calc} (g cm^{-3})	1.418	1.536	1.332	1.488	1.249	1.159	1.093
μ (mm^{-1})	0.715	0.832	0.576	0.806	0.490	0.477	1.447
meas. Θ-range (deg)	1.57-28.40	0.99-25.19	0.93-25.43	1.24-25.10	2.294-25.394	1.06-26.44	2.835-68.511
Indexbereich	-14<h<15	-9<h<8	-26<h<26	-20<h<20	-22<h<24	-19<h<20	-18<h<18
	-34<k<34	-11<k<11	-19<k<19	-18<k<13	-28<k<28	-23<k<23	-19<k<19
	-16<l<16	-25<l<24	-15<l<16	-29<l<32	-30<l<31	-24<l<24	-31<l<31
F(000)	1648	754	1996	3204	5032	2224	2556
meas. refl	67219	17407	51599	45566	123313	56577	81650
indep. refl.	9319	5654	8548	12289	11591	24109	23699
data / restraints / param.	9319/0/498	5654/6/443	8548/0/586	12289/0/938	11591/0/755	24109/33/1370	23699/21/1423
Goodness-of-fit on F^2	1.046	1.051	1.151	1.070	0.991	1.059	1.051
R_1 [$F^2 > 2\sigma(F^2)$]	0.0435	0.0557	0.0654	0.0541	0.0544	0.0632	0.0746
wR_2 (F^2)	0.1173	0.1175	0.2088	0.1467	0.1318	0.1887	0.2187
R_{int}	0.0318	0.0734	0.0736	0.0387	0.0694	0.0221	0.0364
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	1.601; -0.445	0.624; -0.782	1.161; -1.047	0.952; -0.597	0.919; -0.900	1.645; -1.286	1.205; -0.523
CCDC	966777	972217	1482435	966775	1482436	1482437	1482438

Table S 2. Selected bond lengths of Cu(TBTA)N_3 ·1.5CH3CN (**1**·1.5CH3CN)**.**

bond	d / Å
Cu1-N1	2.120(2)
Cu1-N10	2.037(2)
Cu1-N20	2.045(2)
Cu1-N30	2.088(2)
Cu1-N2	1.935(2)
N2-N3	1.204(3)
N3-N4	1.142(3)
Cu1- plane (tz-Ns)	0.376(1)

Table S 3. Selected angles in Cu(TBTA)N_3 ·1.5CH3CN (**1**·1.5CH3CN)**.**

angle	∡ / °
N1-Cu1-N10	79.4(1)
N1-Cu1-N20	80.5(1)
N1-Cu1-N30	78.5(1)
N1-Cu1-N2	175.2(1)
N2-Cu1-N10	95.9(1)
N2-Cu1-N20	102.8(1)
N2-Cu1-N30	103.4(1)
N10-Cu1-N20	119.7(1)
N20-Cu1-N30	110.2(1)
N30-Cu1-N10	120.5(1)
Cu1-N2-N3	120.1(2)
N2-N3-N4	176.4(3)

Table S 4. Selected bond lengths of [Cu(TPTA)(N_3)]ClO_4·CH_3CN (**2**·CH_3CN).

bond	d / Å
Cu1-N2	1.908(4)
Cu1-N10	1.972(4)
Cu1-N20	2.046(4)
Cu1-N30	2.047(4)
Cu1-N1	2.154(4)
N2-N3	1.179(6)
N3-N4	1.144(7)
Cu1-plane (tz-Ns)	0.367

Table S 5. Selected angles in [Cu(TPTA)(N_3)]ClO_4·CH_3CN (**2**·CH_3CN).

angle	∡ / °
N3-N2-Cu1	125.5(4)
N2-Cu1-N1	177.0(2)
N2-Cu1-N10	102.8(2)
N2-Cu1-N20	97.2(2)
N2-Cu1-N30	101.2(2)
N10-Cu1-N1	79.2(2)
N20-Cu1-N1	79.8(1)
N30-Cu1-N1	79.6(2)
N20-Cu1-N10	123.8(2)
N20-Cu1-N30	107.6(2)
N30-Cu1-N10	118.8(2)

Table S 6. Selected bond lengths of [Cu(TDTA)(N_3)]ClO_4 (**3**).

bond	d / Å
Cu1-N2	1.909(4)
Cu1-N10	2.006(4)
Cu1-N20	2.008(4)
Cu1-N30	2.086(4)
Cu1-N1	2.105(4)
N2-N3	1.184(6)
N3-N4	1.133(6)
Cu1-plane (tz-Ns)	0.347

Table S 7. Selected angles in [Cu(TDTA)(N_3)]ClO_4 (**3**).

angle	∡ / °
N3-N2-Cu1	120.1(3)
N2-Cu1-N1	176.6(2)
N2-Cu1-N10	97.8(2)
N2-Cu1-N20	98.8(2)
N2-Cu1-N30	103.7(2)
N10-Cu1-N1	80.6(2)
N20-Cu1-N1	80.0(2)
N30-Cu1-N1	79.8(1)
N20-Cu1-N10	128.3(2)
N20-Cu1-N30	109.4(2)
N30-Cu1-N10	113.5(2)

Table S 8. Selected bond lengths of $[Cu_2(TBTA)_2(\mu_{1,1}\text{-}N_3)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5CH_3CN$ (**4** $\cdot 0.5CH_3CN\cdot 0.5H_2O$).

bond	d / Å
Cu1-N2	1.959(3)
Cu1-N5	2.083(3)
Cu1-N40	2.026(3)
Cu1-N50	2.079(3)
Cu1-N60	2.043(3)
Cu2-N2	1.963(3)
Cu2-N1	2.116(3)
Cu2-N10	2.076(3)
Cu2-N20	2.046(3)
Cu2-N30	2.010(3)
N2-N3	1.250(5)
N3-N4	1.152(5)
Cu1-Cu2	3.470(1)
Cu1-plane (tz-Ns)	0.340(1)
Cu2-plane (tz-Ns)	0.342(1)

Table S 9. Selected angles in $[Cu_2(TBTA)_2(\mu_{1,1}\text{-}N_3)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5CH_3CN$ (**4** $\cdot 0.5CH_3CN\cdot 0.5H_2O$).

angle	∡ / °
Cu1-N2-Cu2	124.4(2)
N3-N2-Cu1	111.1(3)
N3-N2-Cu2	119.4(3)
N4-N3-N2	177.6(5)
N2-Cu1-N5	174.3(1)
N2-Cu1-N40	67.8(1)
N2-Cu1-N50	100.7(2)
N2-Cu1-N60	102.9(2)
N40-Cu1-N5	79.6(1)
N50-Cu1-N5	80.5(2)
N60-Cu1-N5	81.3(2)
N40-Cu1-N50	109.9(2)
N40-Cu1-N60	124.5(2)
N50-Cu1-N60	117.4(2)
N2-Cu2-N1	176.8(2)
N2-Cu2-N10	102.5(1)
N2-Cu2-N20	101.2(2)
N2-Cu2-N30	95.9(2)
N10-Cu2-N1	79.1(2)
N20-Cu2-N1	80.8(2)
N30-Cu2-N1	80.9(2)
N30-Cu2-N20	129.1(2)
N30-Cu2-N10	113.8(2)
N10-Cu2-N20	108.7(2)

Table S 10. Selected bond lengths of $[Cu_2(TDTA)_2(\mu_{1,4}$-(5-methyltetrazolate))]$(ClO_4)_3 \cdot 4CH_3CN$ (**5**·$4CH_3CN$).

bond	d / Å
Cu1-N1	2.133(2)
Cu1-N100	1.972(2)
Cu1-N10	1.961(2)
Cu1-N20	1.979(2)
Cu1-N30	2.175(2)
Cu2-N2	2.100(2)
Cu2-N400	1.950(2)
Cu2-N70	2.082(2)
Cu2-N80	2.045(2)
Cu2-N90	2.044(2)
N100-N200	1.349(3)
N200-N300	1.295(3)
N300-N400	1.354(2)
N400-C200	1.331(3)
C200-N100	1.324(3)
Cu1-Cu2	6.021(1)
Cu1-plane (tz-Ns)	0.342(1)
Cu2-plane (tz-Ns)	0.370(1)
Cu1-Cu2(intermolecualar)	9.385(2)

Table S 11. Selected angles in $[Cu_2(TDTA)_2(\mu_{1,4}$-(5-methyltetrazolate))]$(ClO_4)_3 \cdot 4CH_3CN$ (**5**·$4CH_3CN$).

angle	∡ / °
Cu1-N100-C200	137.5(1)
C200-N400-Cu2	131.7(1)
N100-C200-N400	108.9(1)
N1-Cu1-N100	170.6(1)
N1-Cu1-N10	81.3(1)
N1-Cu1-N20	79.7(1)
N1-Cu1-N30	79.3(1)
N10-Cu1-N100	65.8(1)
N20-Cu1-N100	97.6(1)
N30-Cu1-N100	110.1(1)
N10-Cu1-N20	141.6(1)
N20-Cu1-N30	108.8(1)
N30-Cu1-N10	100.0(1)
N2-Cu2-N400	177.5(1)
N2-Cu2-N70	79.2(1)
N2-Cu2-N80	79.7(1)
N2-Cu2-N90	80.0(1)
N70-Cu2-N400	100.1(1)
N80-Cu2-N400	102.8(1)
N90-Cu2-N400	98.1(1)
N90-Cu2-N80	123.2(1)
N90-Cu2-N70	111.4(1)
N70-Cu2-N80	115.9(1)

Table S 12. Selected bond lengths of [Cu(TDTA)(C_2H_5CN)]ClO_4·C_2H_5CN·$C_4H_{10}O$ (**6**·C_2H_5CN·$C_4H_{10}O$).

bond	d / Å
Cu1-N2	1.949(3)
Cu1-N10	2.148(2)
Cu1-N20	2.004(2)
Cu1-N30	1.990(2)
Cu1-N1	2.082(2)
N2-C1	1.126(4)
Cu1-plane (tz-Ns)	0.313

Table S 13. Selected angles in [Cu(TDTA)(C_2H_5CN)]ClO_4·C_2H_5CN·$C_4H_{10}O$ (**6**·C_2H_5CN·$C_4H_{10}O$).

angle	∡ / °
C1-N2-Cu1	166.8(3)
N2-Cu1-N1	177.0(1)
N2-Cu1-N10	102.8(1)
N2-Cu1-N20	95.9(1)
N2-Cu1-N30	98.8(1)
N10-Cu1-N1	80.0(1)
N20-Cu1-N1	82.7(1)
N30-Cu1-N1	80.5(1)
N20-Cu1-N10	99.1(1)
N20-Cu1-N30	136.0(1)
N30-Cu1-N10	117.4(1)

Table S 14. Selected bond lengths of $[Cu_2(TDTA)_2(\mu_{1,4}$-(5-ethyltetrazolate))]$(ClO_4)_3 \cdot 2C_4H_{10}O \cdot 5C_2H_5CN$ (**7**$\cdot 2C_4H_{10}O \cdot 5C_2H_5CN$).

bond	d / Å
Cu1-N1	2.114(3)
Cu1-N100	1.944(3)
Cu1-N10	2.044(3)
Cu1-N20	2.068(3)
Cu1-N30	2.047(3)
Cu2-N2	2.103(3)
Cu2-N400	1.937(2)
Cu2-N70	2.076(3)
Cu2-N80	2.051(3)
Cu2-N90	2.004(3)
N100-N200	1.312(5)
N200-N300	1.290(6)
N300-N400	1.406(5)
N400-C400	1.296(4)
C400-N100	1.310(4)
Cu1-Cu2	5.991(1)
Cu1-plane (tz-Ns)	0.367(1)
Cu2-plane (tz-Ns)	0.355(1)

Table S 15. Selected angles in $[Cu_2(TDTA)_2(\mu_{1,4}$-(5-ethyltetrazolate))]$(ClO_4)_3 \cdot 2C_4H_{10}O \cdot 5C_2H_5CN$ (**7**$\cdot 2C_4H_{10}O \cdot 5C_2H_5CN$).

angle	∡ / °
Cu1-N100-C400	138.2(2)
C400-N400-Cu2	136.7(2)
N100-C200-N400	111.2(3)
N1-Cu1-N100	176.4(2)
N1-Cu1-N10	80.0(2)
N1-Cu1-N20	79.7(1)
N1-Cu1-N30	79.3(1)
N10-Cu1-N100	99.7(1)
N20-Cu1-N100	103.5(1)
N30-Cu1-N100	98.0(2)
N10-Cu1-N20	117.3(2)
N20-Cu1-N30	109.1(2)
N30-Cu1-N10	124.1(1)
N2-Cu2-N400	177.2(1)
N2-Cu2-N70	80.0(1)
N2-Cu2-N80	78.7(1)
N2-Cu2-N90	81.2(1)
N70-Cu2-N400	102.4(1)
N80-Cu2-N400	99.0(1)
N90-Cu2-N400	99.1(2)
N90-Cu2-N80	128.7(1)
N90-Cu2-N70	116.4(1)
N70-Cu2-N80	105.8(1)

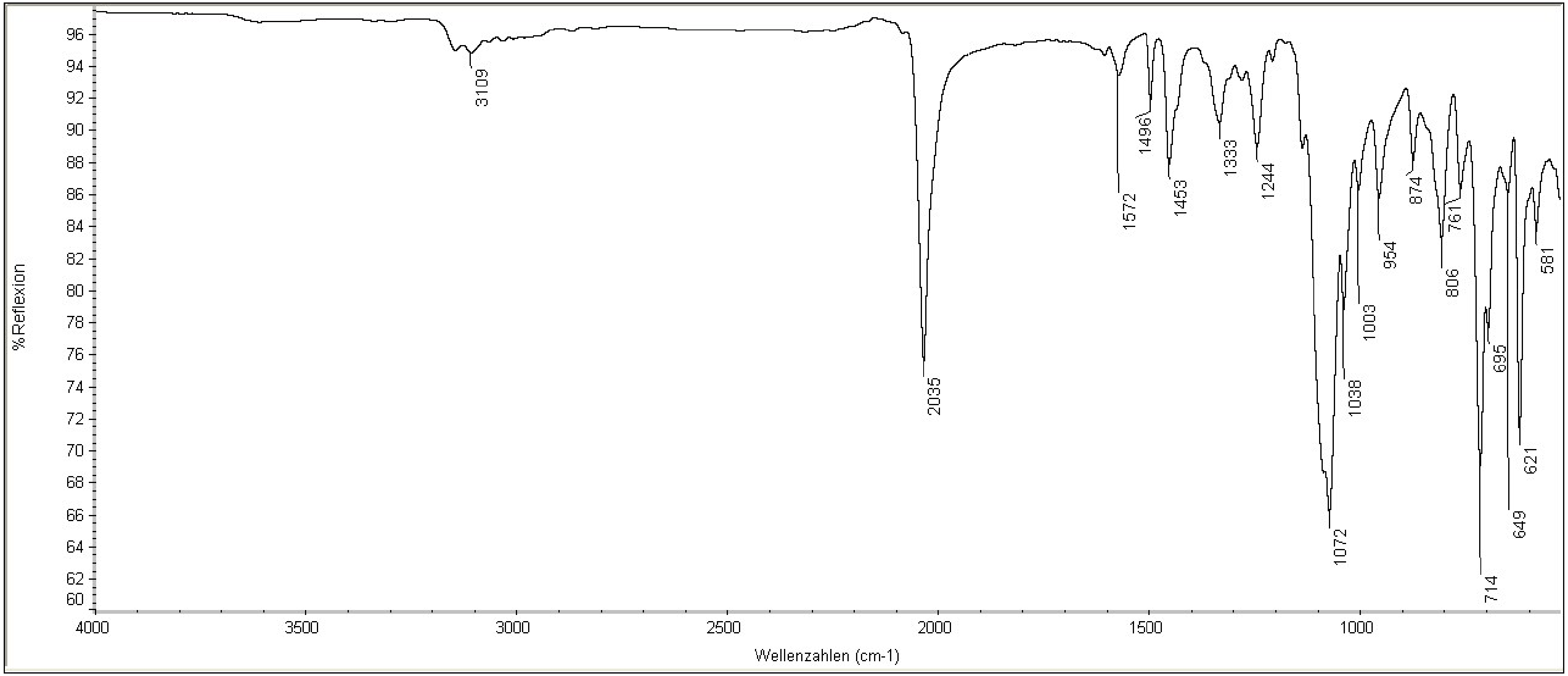

Fig. S1 IR-spectrum of Cu(TBTA)N_3 ·1.5CH3CN (**1**·1.5CH3CN).

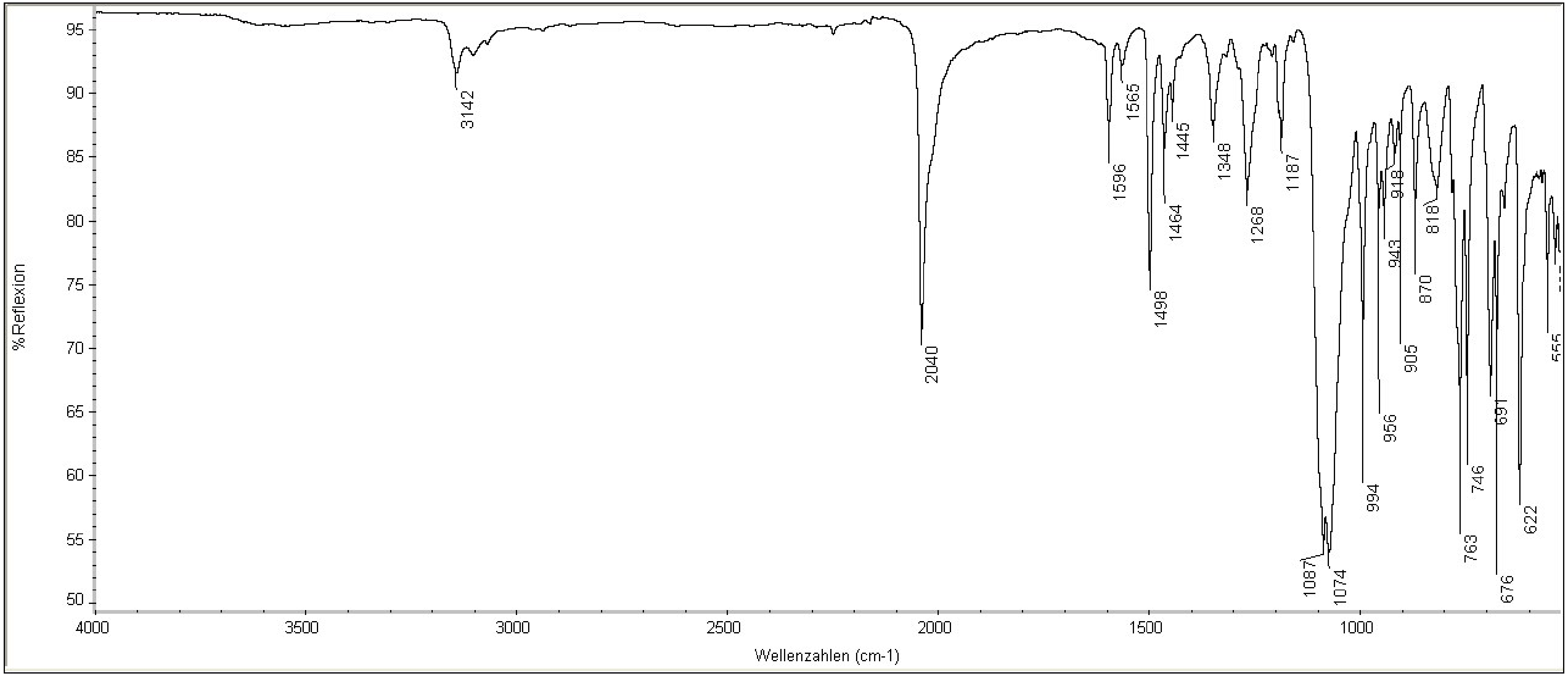

Fig. S2 IR-spectrum of $[Cu(TPTA)(N_3)]ClO_4 \cdot CH_3CN$ (**2**$\cdot CH_3CN$).

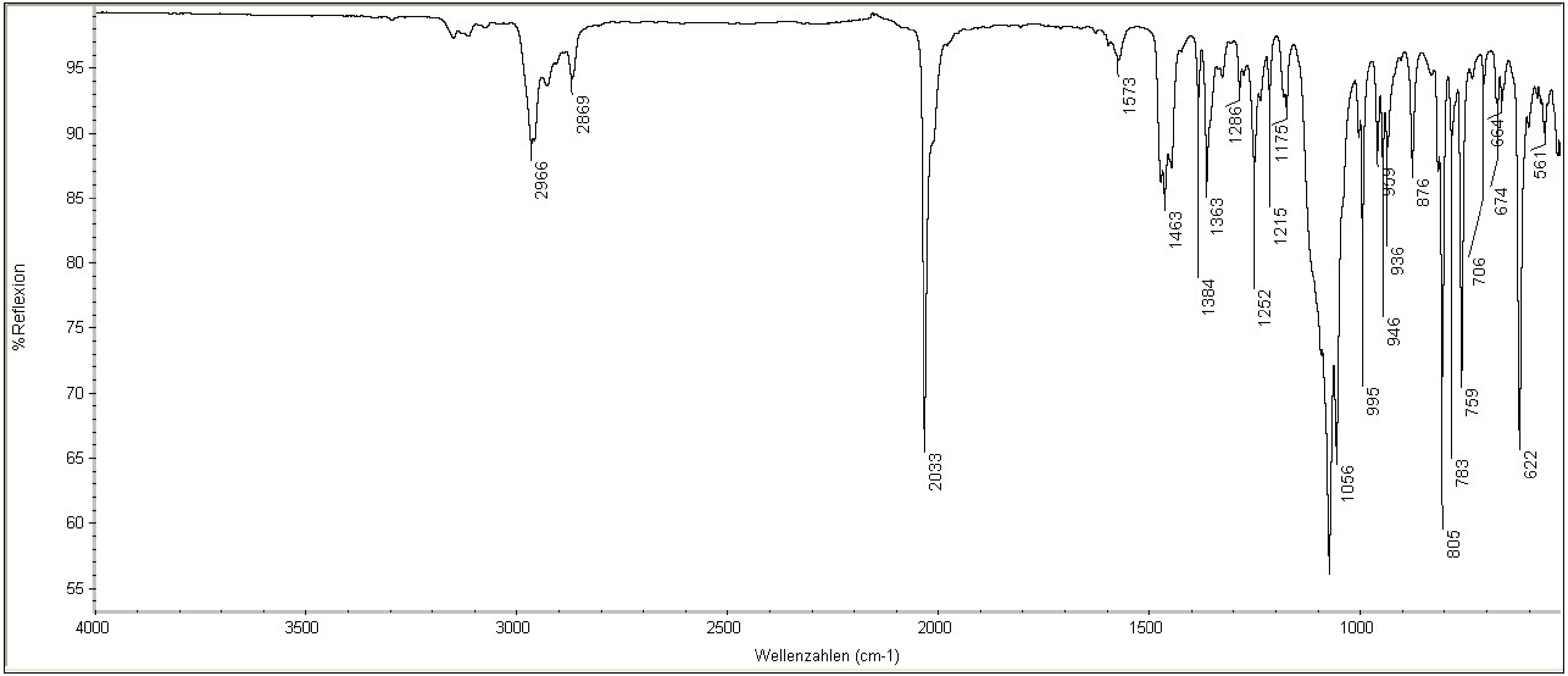

Fig. S3 IR-spectrum of $[Cu(TDTA)(N_3)]ClO_4$ (**3**).

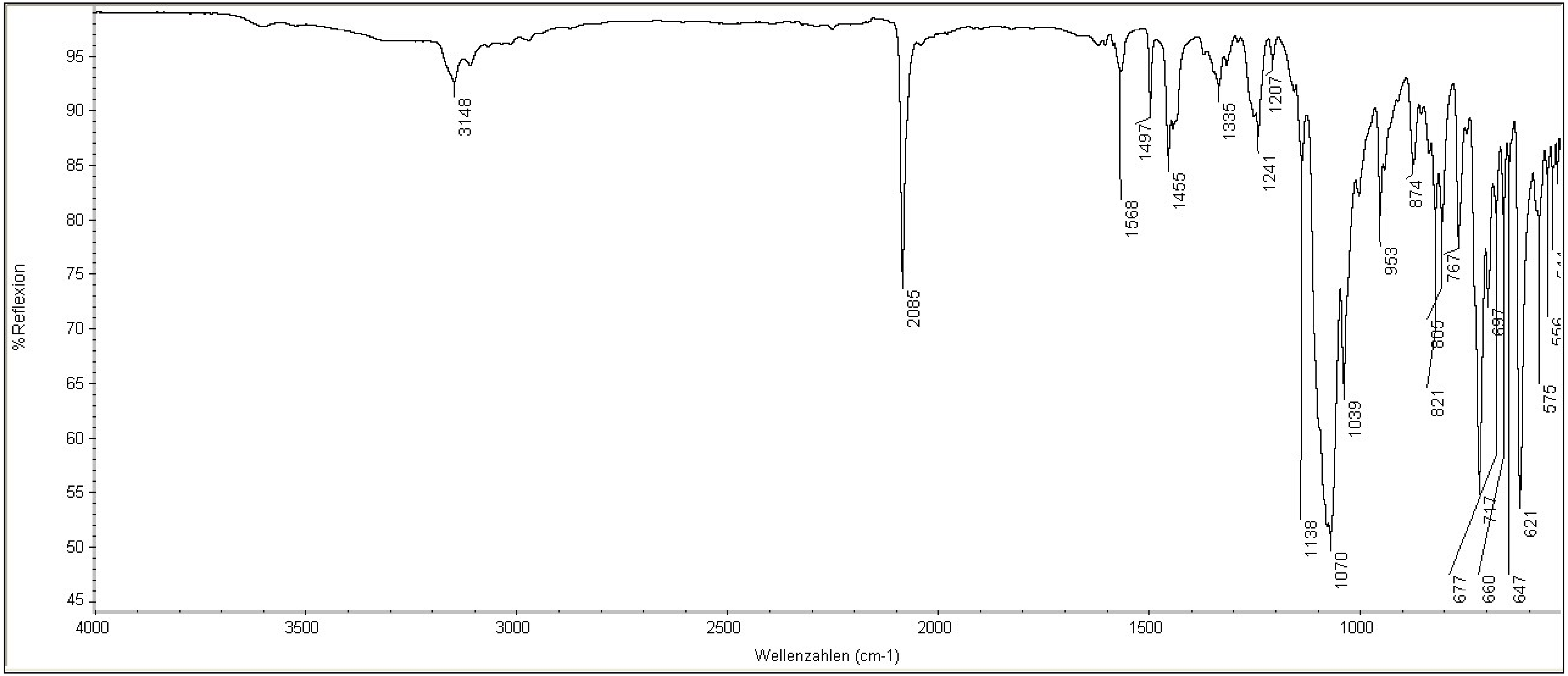

Fig. S4 IR-spectrum of $[Cu_2(TBTA)_2(\mu_{1,1}\text{-}N_3)](ClO_4)_3\cdot 0.5CH_3CN\cdot 0.5CH_3CN$ (**4** $\cdot 0.5CH_3CN\cdot 0.5CH_3CN$).

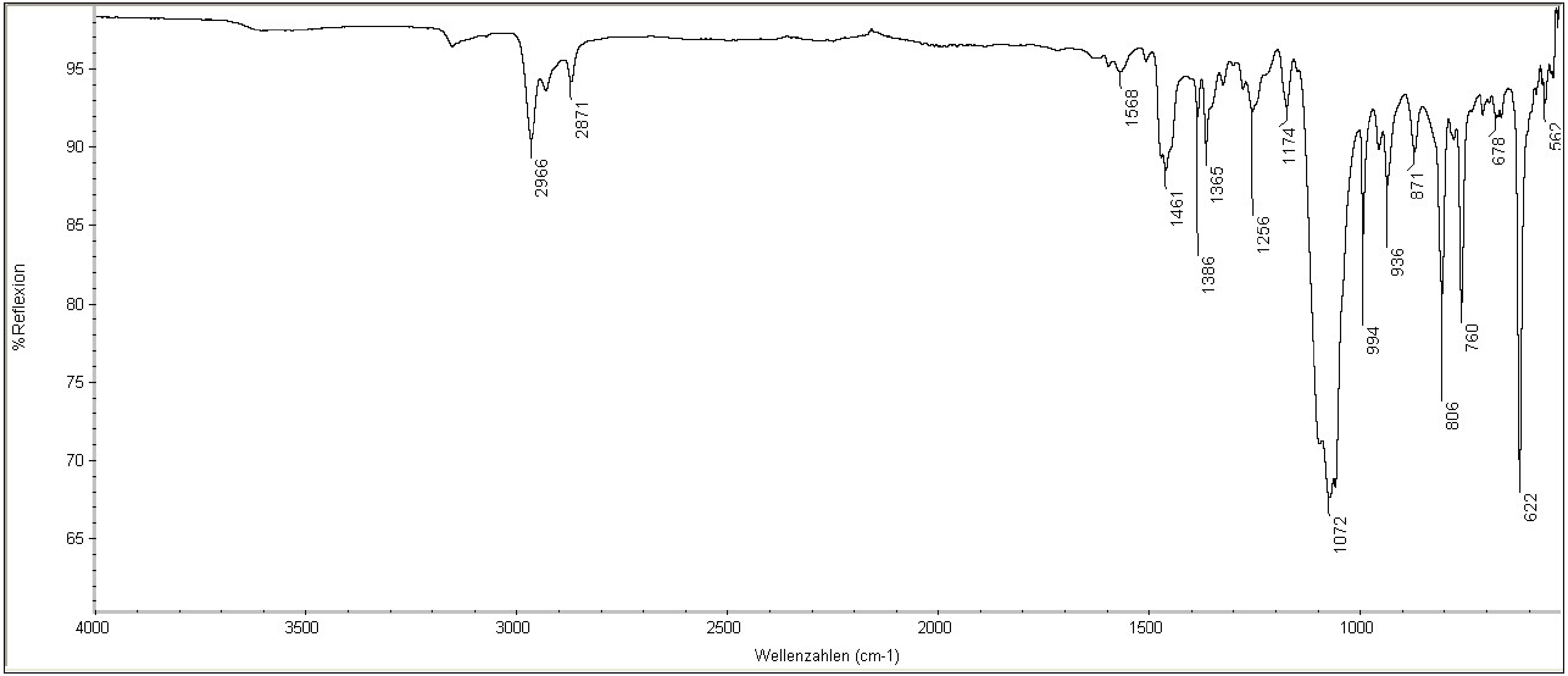

Fig. S5 IR-spectrum of $[Cu_2(TDTA)_2(\mu_{1,4}$-(5-methyltetrazolate))]$(ClO_4)_3 \cdot 4CH_3CN$ (**5**$\cdot 4CH_3CN$).

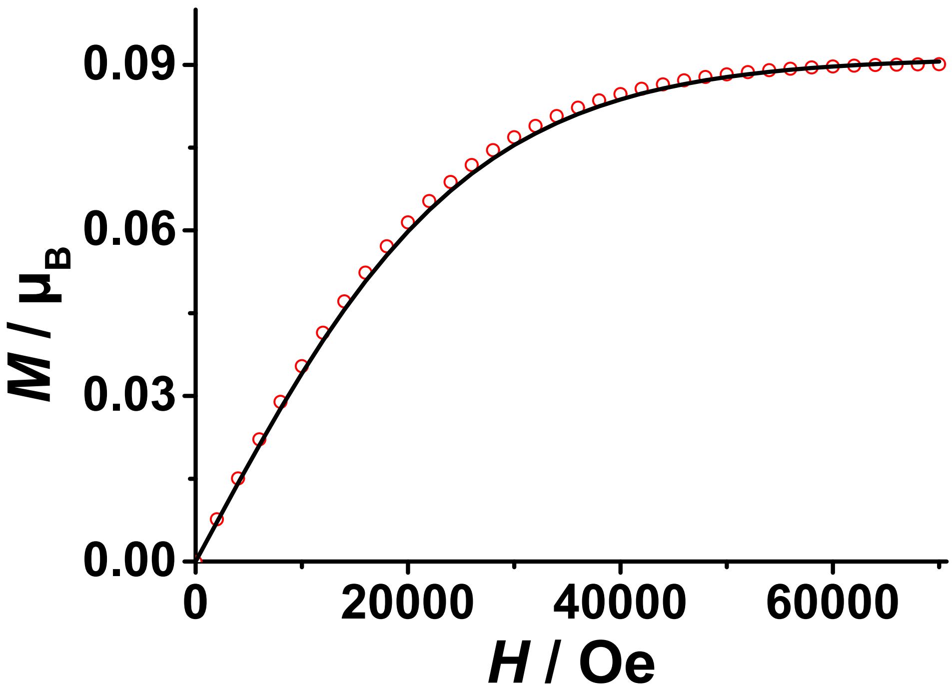

Fig. S6 Magnetization (red circles) and simulation (J = -26.0 cm^{-1}, g_{av} = 2.1, $H = -2J\hat{S}_1\hat{S}_2$; black line) **5** at 2 K with 4 % of uncoupled S = ½.

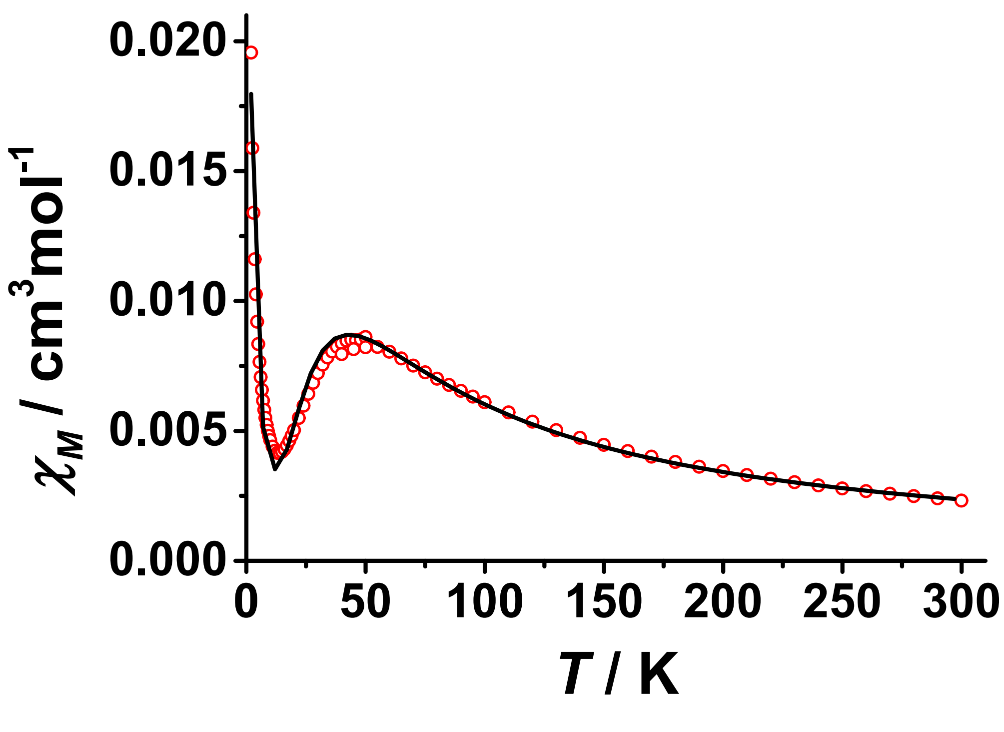

Fig. S7 Experimental (red circles) and simulated (J = -26.0 cm^{-1}, g_{av} = 2.1, $H = -2J\hat{S}_1\hat{S}_2$; black line) temperature dependence of χ_m of **5** with 4 % of uncoupled S = ½.

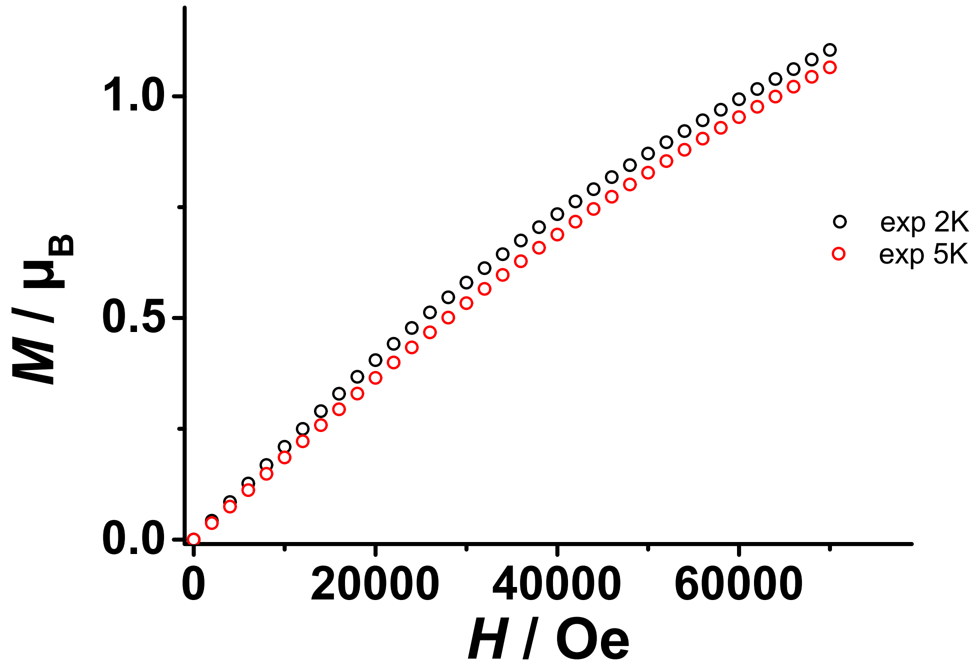

Fig. S8 Magnetization of **4** at 2 K and 5 K.