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Supplementary Information

A New Nitrogen Rich Open Chain Diazine Ligand System: Synthesis, Coordination Chemistry and Magneto-Structural Studies

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Table S1: Crystal Structure Data for Complexes 1 – 5.

	1	**2**	**3**	**4**	**5**
Formula	$C_{30}H_{30}Cl_4Cu_3N_{10}O_{20}$	$C_{26}H_{20}Cl_4Cu_3N_8O_2$	$C_{24}H_{16}Cu_3N_{12}O_{14}$	$C_{26.33}H_{30.66}Cl_4Mn_3N_{10}O_6$	$C_{65}H_{66.5}F_{18}Fe_4N_{17.5}O_{29}S_6$
FW	1183.06	808.92	887.11	889.85	2314.61
Temp. (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/c	*I*2/*a*	*C*2/c	*P-1*	*P-1*
a/Å	14.859(3)	13.099 (3)	15.0153 (7)	10.3696 (5)	15.2861 (10)
b/Å	18.703(4)	13.734 (3)	14.1311 (7)	12.7637 (6)	18.7512 (11)
c/Å	15.719(3)	15.973 (7)	14.3905 (7)	14.6867 (6)	19.8454 (12)
α/°	90	90	90	75.3919 (17)	79.965 (2)
β/°	102.99(3)	106.33 (3)	98.110 (2)	70.8407 (17)	76.015 (2)
γ/°	90	90	90	75.991 (2)	68.805 (2)
V/Å^3	4256.6(16)	2757.6 (15)	3022.9 (3)	1749.63 (14)	5122.6 (6)
Z	4	4	4	2	2
D_{C}/Mg m^{-3}	1.846	1.948	1.949	1.689	1.501
μ(MoKα)/ cm^{-1}	1.83	2.73	2.19	1.43	0.79
Unique reflns	4356	2764	3079	5930	18011
Reflns [$I>2\sigma(I)$]	3650	2185	2742	4944	12925
R_{int}	0.053	0.024	0.096	0.049	0.054
R_1[a], wR_2[b]	0.029, 0.077	0.037, 0.116	0.035, 0.098	0.042, 0.117	0.068, 0.208
Max/min residual *e*$^-$ density (*e*Å^{-3})	+0.48, -0.75	+0.85, -0.73	+0.76, -0.54	+0.64, -0.87	+1.15, -0.67
CCDC	1579185	1579186	1579187	1579188	1579189

[a] $I > 2\sigma(I)$, [b] all data

Table S2: Selected bond lengths (Å) and angles (º) for **1**

Bonds	**Distances**	**Bond**	**Distances**
Cu1—N1i	1.937 (2)	Cu2—N1T	1.961 (2)
Cu1—N1	1.937 (2)	Cu2—N4	2.017 (2)
Cu1—N2i	2.003 (2)	Cu2—O4	2.0329 (19)
Cu1—N2	2.003 (2)	Cu2—O2	2.215 (2)
Cu2—N3	1.942 (2)		
Bond	**Angles**	**Bond**	**Angles**
N1i—Cu1—N1	79.62 (12)	N3—Cu2—O2	94.50 (8)
N1i—Cu1—N2i	79.99 (8)	N1T—Cu2—O2	95.90 (9)
N1—Cu1—N2i	158.05 (8)	N4—Cu2—O2	96.40 (9)
N1i—Cu1—N2	158.05 (8)	O4—Cu2—O2	92.07 (8)
N1—Cu1—N2	80.00 (8)	C6—O4—Cu2	109.41 (15)
N2i—Cu1—N2	121.24 (11)	C1—N1—Cu1	117.83 (16)
N3—Cu2—N1T	169.49 (9)	C5—N1—Cu1	118.31 (17)
N3—Cu2—N4	80.24 (8)	C7—N3—Cu2	118.16 (16)
N1T—Cu2—N4	97.10 (9)	N2—N3—Cu2	116.27 (14)
N3—Cu2—O4	79.38 (7)	C6—N2—Cu1	113.37 (16)
N1T—Cu2—O4	101.69 (8)	N3—N2—Cu1	134.93 (15)
N4—Cu2—O4	158.47 (8)		

Table S3: Selected bond lengths (Å) and angles (º) for **2**

Bonds	**Distances**	**Bond**	**Distances**
Cu1—N1	1.975 (3)	Cu2—N3	1.966 (3)
Cu1—N1i	1.975 (3)	Cu2—O1	1.992 (3)
Cu1—N2	2.138 (3)	Cu2—N4	1.993 (3)
Cu1—N2i	2.138 (3)	Cu2—Cl2	2.2273 (15)
Cu1—Cl1i	2.7314 (16)	Cu2—Cl1ii	2.5488 (14)
Cu1—Cl1	2.7314 (16)	Cl1—Cu2ii	2.5488 (14)
Bonds	**Angles**	**Bond**	**Angles**
N1—Cu1—N1i	77.71 (19)	N3—Cu2—Cl2	161.65 (11)
N1—Cu1—N2	78.22 (12)	O1—Cu2—Cl2	98.96 (9)
N1i—Cu1—N2	155.12 (13)	N4—Cu2—Cl2	100.64 (11)
N1—Cu1—N2i	155.12 (13)	N3—Cu2—Cl1ii	94.56 (11)
N1i—Cu1—N2i	78.22 (12)	O1—Cu2—Cl1ii	94.55 (9)
N2—Cu1—N2i	126.33 (17)	N4—Cu2—Cl1ii	86.72 (11)
N1—Cu1—Cl1i	83.34 (10)	Cl2—Cu2—Cl1ii	103.78 (5)
N1i—Cu1—Cl1i	99.77 (10)	Cu2ii—Cl1—Cu1	144.79 (5)
N2—Cu1—Cl1i	83.59 (10)	C6—O1—Cu2	110.8 (3)
N2i—Cu1—Cl1i	94.62 (10)	C5—N1—Cu1	118.8 (3)
N1—Cu1—Cl1	99.76 (10)	C1—N1—Cu1	119.2 (3)
N1i—Cu1—Cl1	83.34 (10)	C6—N2—Cu1	110.5 (2)
N2—Cu1—Cl1	94.62 (10)	N3—N2—Cu1	138.0 (2)
N2i—Cu1—Cl1	83.59 (10)	C7—N3—Cu2	117.5 (3)
Cl1i—Cu1—Cl1	176.05 (5)	N2—N3—Cu2	116.1 (2)
N3—Cu2—O1	79.18 (12)	C13—N4—Cu2	126.7 (3)
N3—Cu2—N4	80.29 (14)	C9—N4—Cu2	112.3 (3)
O1—Cu2—N4	159.46 (13)		

Table S4: Selected bond lengths (Å) and angles (°) for 3

Bonds	Distances	Bonds	Distances
Cu1—N2	1.934 (2)	Cu1—O5	2.204 (2)
Cu1—O4	1.937 (2)	Cu2—N4i	1.935 (2)
Cu1—N1	2.053 (2)	Cu2—N4	1.935 (2)
Cu1—O1	2.122 (2)	Cu2—N3i	1.969 (2)
Cu1—O5A	2.204 (2)	Cu2—N3	1.969 (2)
Bonds	**Angles**	**Bonds**	**Angles**
N2—Cu1—O4	173.37 (9)	N4—Cu2—N3i	157.50 (10)
N2—Cu1—N1	79.75 (9)	N4i—Cu2—N3	157.50 (10)
O4—Cu1—N1	100.69 (9)	N4—Cu2—N3	80.21 (9)
N2—Cu1—O1	77.48 (9)	N3i—Cu2—N3	121.39 (14)
O4—Cu1—O1	100.33 (9)	C6—O1—Cu1	108.01 (17)
N1—Cu1—O1	153.20 (8)	N5—O4—Cu1	109.85 (17)
N2—Cu1—O5A	102.96 (9)	N6—O5—Cu1	120.4 (8)
O4—Cu1—O5A	83.18 (9)	N6A—O5A—Cu1	117.9 (4)
N1—Cu1—O5A	109.45 (10)	C12—N1—Cu1	129.5 (2)
O1—Cu1—O5A	89.40 (9)	C8—N1—Cu1	111.73 (18)
N2—Cu1—O5	102.96 (9)	C7—N2—Cu1	119.29 (19)
O4—Cu1—O5	83.18 (9)	N3—N2—Cu1	118.09 (17)
N1—Cu1—O5	109.45 (10)	C6—N3—Cu2	114.78 (18)
O1—Cu1—O5	89.40 (9)	N2—N3—Cu2	133.79 (18)
N4i—Cu2—N4	79.30 (14)	C5—N4—Cu2	118.99 (18)
N4i—Cu2—N3i	80.21 (9)		

Table S5: bond lengths (Å) and angles (°) for **4**

Bonds	**Distances**	**Bonds**	**Distance**
Mn1—O4	2.201 (3)	Mn2—N1	2.323 (3)
Mn1—O6	2.208 (3)	Mn2—Cl1	2.3686 (12)
Mn1—N4	2.295 (3)	Mn2—Cl2	2.3900 (12)
Mn1—N5	2.297 (3)	Mn3—N7	2.121 (3)
Mn1—O3	2.303 (3)	Mn3—O2	2.204 (3)
Mn1—O2	2.306 (2)	Mn3—N8	2.294 (3)
Mn1—O1	2.359 (2)	Mn3—Cl6B	2.360 (5)
Mn2—N2	2.116 (3)	Mn3—Cl5	2.3844 (12)
Mn2—O1	2.225 (2)	Mn3—Cl6A	2.393 (3)
Bonds	**Angles**	**Bonds**	**Angles**
O4—Mn1—O6	89.67 (11)	O2—Mn1—O1	151.37 (9)
O4—Mn1—N4	96.91 (10)	N2—Mn2—O1	72.50 (10)
O6—Mn1—N4	143.99 (11)	N2—Mn2—N1	71.10 (12)
O4—Mn1—N5	98.33 (10)	O1—Mn2—N1	142.10 (11)
O6—Mn1—N5	145.14 (11)	N2—Mn2—Cl1	129.92 (10)
N4—Mn1—N5	68.87 (10)	O1—Mn2—Cl1	101.53 (7)
O4—Mn1—O3	173.93 (10)	N1—Mn2—Cl1	93.77 (9)
O6—Mn1—O3	84.41 (10)	N2—Mn2—Cl2	113.60 (9)
N4—Mn1—O3	88.69 (10)	O1—Mn2—Cl2	104.91 (7)
N5—Mn1—O3	85.84 (10)	N1—Mn2—Cl2	98.99 (9)
O4—Mn1—O2	81.74 (10)	Cl1—Mn2—Cl2	115.85 (5)
O6—Mn1—O2	78.23 (10)	N7—Mn3—O2	72.34 (10)
N4—Mn1—O2	137.71 (10)	N7—Mn3—N8	72.27 (12)
N5—Mn1—O2	69.54 (9)	O2—Mn3—N8	144.52 (11)
O3—Mn1—O2	95.70 (9)	N7—Mn3—Cl6B	128.27 (18)
O4—Mn1—O1	85.88 (9)	O2—Mn3—Cl6B	98.40 (16)
O6—Mn1—O1	75.97 (9)	N8—Mn3—Cl6B	105.26 (16)
N4—Mn1—O1	69.29 (9)	N7—Mn3—Cl5	121.97 (9)
N5—Mn1—O1	138.16 (10)	O2—Mn3—Cl5	99.17 (7)
O3—Mn1—O1	93.96 (9)	N8—Mn3—Cl5	97.29 (9)

Table S6: bond lengths (Å) and angles (°) for **5**

Bonds	Distances	Bonds	Distances
Fe1—O7	2.105 (4)	Fe3—O10	2.097 (4)
Fe1—N16	2.153 (5)	Fe3—N8	2.154 (5)
Fe1—N5	2.190 (4)	Fe3—N13	2.189 (4)
Fe1—N15	2.198 (4)	Fe3—N7	2.193 (4)
Fe1—N4	2.226 (4)	Fe3—N12	2.226 (4)
Fe1—N6	2.385 (4)	Fe3—N14	2.352 (4)
Fe2—O4	1.902 (4)	Fe4—O2	1.917 (4)
Fe2—O1	2.010 (4)	Fe4—O3	2.007 (3)
Fe2—O6	2.036 (4)	Fe4—O9	2.023 (4)
Fe2—O5	2.043 (4)	Fe4—O8	2.034 (4)
Fe2—N2	2.069 (4)	Fe4—N10	2.079 (4)
Fe2—N1	2.135 (4)	Fe4—N9	2.145 (4)
Bonds	**Angles**	**Bonds**	**Angles**
O7—Fe1—N16	168.58 (16)	N2—Fe2—N1	74.93 (18)
O7—Fe1—N5	93.41 (16)	O10—Fe3—N8	166.23 (16)
N16—Fe1—N5	97.55 (17)	O10—Fe3—N13	93.67 (16)
O7—Fe1—N15	98.52 (16)	N8—Fe3—N13	98.61 (16)
N16—Fe1—N15	74.50 (17)	O10—Fe3—N7	99.00 (16)
N5—Fe1—N15	142.88 (16)	N8—Fe3—N7	74.43 (16)
O7—Fe1—N4	90.27 (15)	N13—Fe3—N7	144.37 (16)
N16—Fe1—N4	89.99 (16)	O10—Fe3—N12	88.71 (16)
N5—Fe1—N4	72.51 (16)	N8—Fe3—N12	89.07 (16)
N15—Fe1—N4	141.87 (16)	N13—Fe3—N12	72.41 (15)
O7—Fe1—N6	94.30 (15)	N7—Fe3—N12	140.56 (15)
N16—Fe1—N6	92.54 (16)	O10—Fe3—N14	96.37 (15)
N5—Fe1—N6	69.37 (15)	N8—Fe3—N14	93.69 (16)
N15—Fe1—N6	74.76 (15)	N13—Fe3—N14	69.99 (15)
N4—Fe1—N6	141.79 (15)	N7—Fe3—N14	75.57 (15)
O4—Fe2—O1	109.23 (15)	N12—Fe3—N14	142.29 (15)
O4—Fe2—O6	91.20 (17)	O2—Fe4—O3	109.42 (15)
O1—Fe2—O6	90.84 (16)	O2—Fe4—O9	89.45 (16)
O4—Fe2—O5	87.54 (17)	O3—Fe4—O9	92.99 (15)
O1—Fe2—O5	92.21 (16)	O2—Fe4—O8	89.22 (17)
O6—Fe2—O5	176.94 (17)	O3—Fe4—O8	91.49 (16)
O4—Fe2—N2	173.99 (17)	O9—Fe4—O8	175.52 (17)
O1—Fe2—N2	75.56 (16)	O2—Fe4—N10	173.67 (16)
O6—Fe2—N2	92.38 (18)	O3—Fe4—N10	75.35 (15)
O5—Fe2—N2	88.64 (17)	O9—Fe4—N10	94.51 (17)
O4—Fe2—N1	100.34 (17)	O8—Fe4—N10	86.46 (17)
O1—Fe2—N1	150.43 (16)	O2—Fe4—N9	100.86 (16)
O6—Fe2—N1	88.61 (17)	O3—Fe4—N9	149.72 (16)
O5—Fe2—N1	88.87 (16)	O9—Fe4—N9	87.64 (17)
N10—Fe4—N9	74.42 (17)	O8—Fe4—N9	88.41 (18)

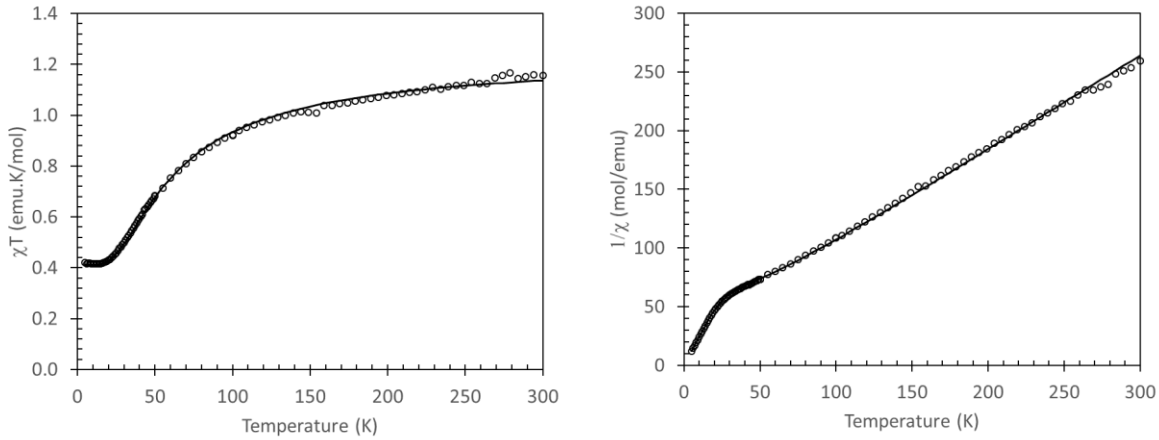

Figure 1S: Temperature dependence of χT (left) and 1/χ (right) for **1** with the solid line representing the fit to the linear trimer model (g = 2.096(3), and J/k = -35.3(3) K)

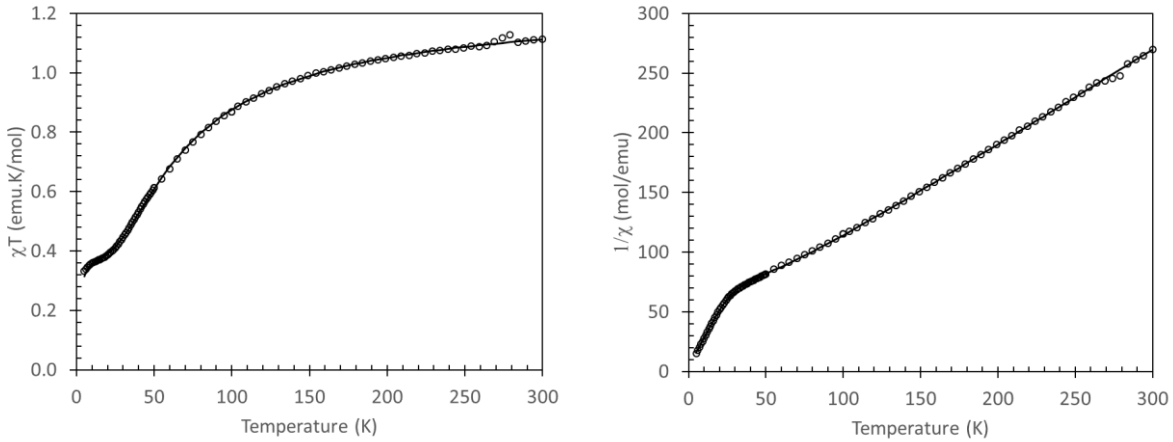

Figure 2S: Temperature dependence of χT (left) and 1/χ (right) for **2** with the solid line representing the fit to the linear trimer model (g = 2.098(2), and J/k = -38.9(2) K, θ = - 1.0 K)

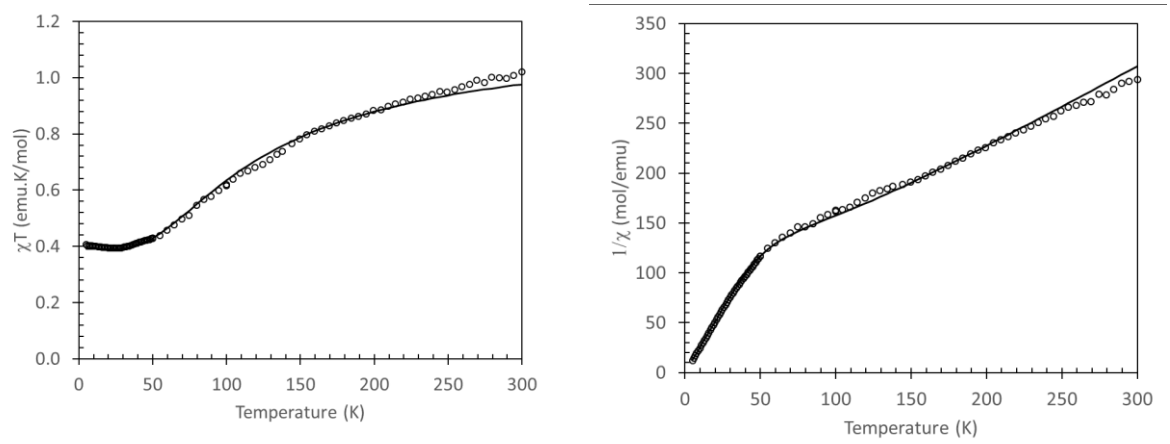

Figure 3S: Temperature dependence of χT (left) and 1/χ (right) for **3** with the solid line representing the fit to the linear trimer model (g = 2.03, and J/*k* = -72(1) K)

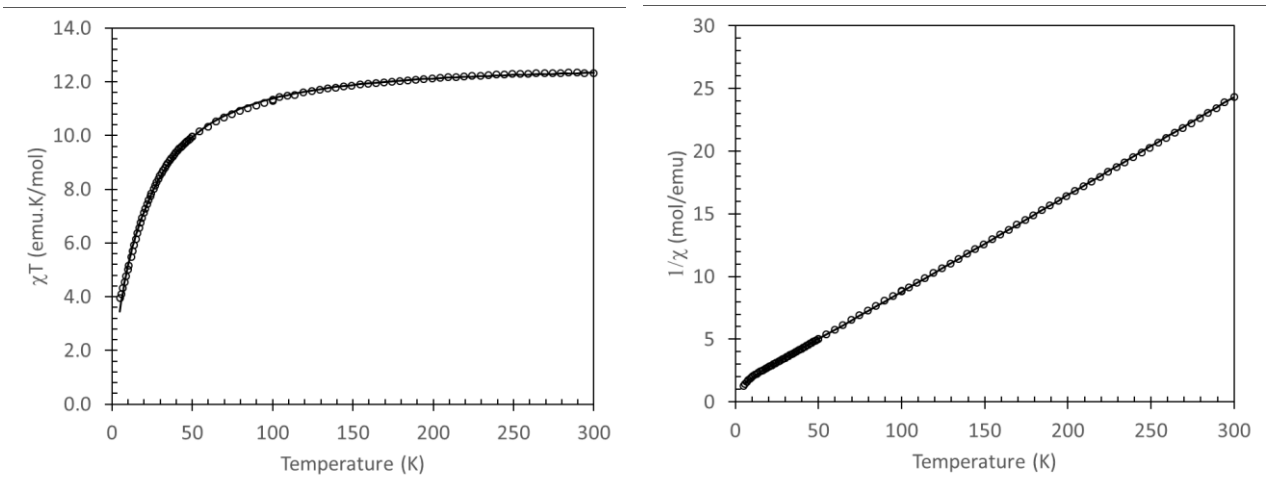

Figure 4S: Temperature dependence of χT (left) and 1/χ (right) for **4** with the solid line representing the fit to the linear trimer model (g = 1.963(2), and J/*k* = -0.66(1) K)

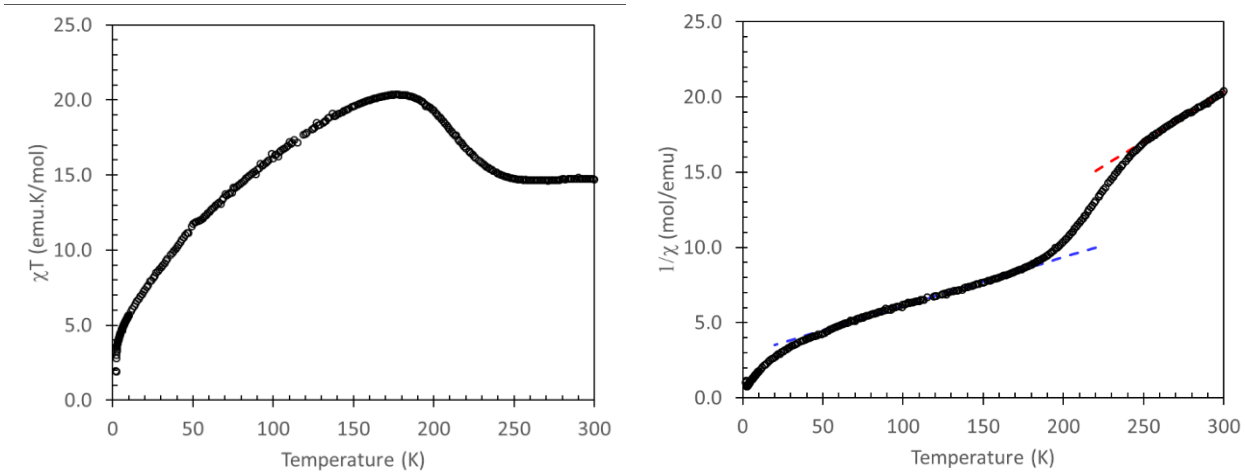

Figure 5S: Temperature dependence of χT (left) and 1/χ *vs* T (right) for **5**. The dotted lines represent the fit to Curie-Weiss behaviour in the selected regions; T > 250 K (C = 15.175 emu.K.mol^{-1}, θ = -9.0) and 20 < T < 230 K (C = 30.864 emu.K.mol^{-1} and θ = -96.6 K).