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The synthesis of Three New Cu_5, Cu_8 and Cu_{12} Clusters via the Use of a Semi-Flexible Aminotriazine-Based Bis-Methylpyridine Ligand

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Table 1S. Selected bond distances (Å) and angles (°) for complexes **1–3**.

	1		
Cu(1)-O(2)#1	1.987(3)	Cu(2)-N(5)	2.071(3)
Cu(1)-O(2)	1.987(3)	Cu(2)-O(5)	2.574(4)
Cu(1)-O(1)#1	2.032(2)	Cu(2)-O(9)#1	2.706(3)
Cu(1)-O(1)	2.032(2)	Cu(3)-O(2)	1.905(3)
Cu(1)-N(1)	2.333(3)	Cu(3)-N(6)	1.965(3)
Cu(1)-N(1)#1	2.333(3)	Cu(3)-O(4)	1.994(3)
Cu(2)-O(1)	1.906(3)	Cu(3)-N(7)	2.110(3)
Cu(2)-N(4)	1.974(3)	Cu(3)-O(6)	2.565(3)
Cu(2)-O(3)	1.984(3)	Cu(3)-O(9)	2.636(3)
O(2)#1-Cu(1)-O(2)	180.00(14)	N(5)-Cu(2)-O(5)	94.28(13)
O(2)#1-Cu(1)-O(1)#1	93.20(10)	O(1)-Cu(2)-O(9)#1	83.94(10)
O(2)-Cu(1)-O(1)#1	86.80(10)	N(4)-Cu(2)-O(9)#1	100.15(12)
O(2)#1-Cu(1)-O(1)	86.80(10)	O(3)-Cu(2)-O(9)#1	94.48(12)
O(2)-Cu(1)-O(1)	93.20(10)	N(5)-Cu(2)-O(9)#1	77.00(12)
O(1)#1-Cu(1)-O(1)	180.0	O(5)-Cu(2)-O(9)#1	171.24(12)
O(2)#1-Cu(1)-N(1)	89.42(11)	O(2)-Cu(3)-N(6)	173.16(14)
O(2)-Cu(1)-N(1)	90.58(11)	O(2)-Cu(3)-O(4)	92.77(12)
O(1)#1-Cu(1)-N(1)	88.43(11)	N(6)-Cu(3)-O(4)	93.71(15)
O(1)-Cu(1)-N(1)	91.58(11)	O(2)-Cu(3)-N(7)	91.79(12)
O(2)#1-Cu(1)-N(1)#1	90.58(11)	N(6)-Cu(3)-N(7)	81.96(14)
O(2)-Cu(1)-N(1)#1	89.42(11)	O(4)-Cu(3)-N(7)	173.10(13)
O(1)#1-Cu(1)-N(1)#1	91.58(11)	O(2)-Cu(3)-O(6)	96.06(10)
O(1)-Cu(1)-N(1)#1	88.42(11)	N(6)-Cu(3)-O(6)	81.98(13)
N(1)-Cu(1)-N(1)#1	180.0	O(4)-Cu(3)-O(6)	88.15(12)
O(1)-Cu(2)-N(4)	172.01(12)	N(7)-Cu(3)-O(6)	96.52(11)
O(1)-Cu(2)-O(3)	91.36(12)	O(2)-Cu(3)-O(9)	82.86(10)
N(4)-Cu(2)-O(3)	95.13(13)	N(6)-Cu(3)-O(9)	98.57(13)
O(1)-Cu(2)-N(5)	92.81(12)	O(4)-Cu(3)-O(9)	96.46(12)
N(4)-Cu(2)-N(5)	81.53(13)	N(7)-Cu(3)-O(9)	78.97(12)
O(3)-Cu(2)-N(5)	170.06(13)	O(6)-Cu(3)-O(9)	175.31(10)
O(1)-Cu(2)-O(5)	95.84(12)	Cu(2)-O(1)-Cu(1)	126.88(14)
N(4)-Cu(2)-O(5)	79.06(13)	Cu(3)-O(2)-Cu(1)	128.50(14)
O(3)-Cu(2)-O(5)	94.27(13)		

2			
Cu(1)-N(1)	2.013(5)	Cu(3)-N(8)	1.987(6)
Cu(1)-O(1)	1.915(5)	Cu(3)-O(2)	1.955(4)
Cu(1)-O(1)#1	1.948(5)	Cu(3)-O(6)	1.924(4)
Cu(1)-O(2)	2.017(4)	Cu(3)-O(12)	2.272(6)
Cu(1)-O(3)	2.283(4)	Cu(4)-O(2)	2.001(5)
Cu(2)-N(4)	2.128(5)	Cu(4)-O(3)	1.931(4)
Cu(2)-N(5)	1.964(6)	Cu(4)-O(5)	1.915(5)
Cu(2)-O(3)	1.904(5)	Cu(4)-O(7)	1.909(5)
Cu(2)-O(4)	1.947(4)	Cu(4)-O(8)	2.430(5)
Cu(3)-N(7)	2.082(5)	Cu(1)-Cu(1)#1	2.9128(14)
N(1)-Cu(1)-Cu(1)#1	129.75(14)	N(7)-Cu(3)-O(12)	87.7(2)
N(1)-Cu(1)-O(2)	92.53(19)	N(8)-Cu(3)-N(7)	80.6(2)
N(1)-Cu(1)-O(3)	92.51(18)	N(8)-Cu(3)-O(12)	97.2(2)
O(1)#1-Cu(1)-Cu(1)#1	40.65(15)	O(2)-Cu(3)-N(7)	90.50(19)
O(1)-Cu(1)-Cu(1)#1	41.48(15)	O(2)-Cu(3)-N(8)	164.2(2)
O(1)-Cu(1)-N(1)	168.34(19)	O(2)-Cu(3)-O(12)	95.4(2)
O(1)#1-Cu(1)-N(1)	89.6(2)	O(6)-Cu(3)-N(7)	170.9(2)
O(1)-Cu(1)-O(1)#1	82.1(2)	O(6)-Cu(3)-N(8)	90.7(2)
O(1)-Cu(1)-O(2)	96.0(2)	O(6)-Cu(3)-O(2)	98.61(19)
O(1)#1-Cu(1)-O(2)	177.35(19)	O(6)-Cu(3)-O(12)	90.9(2)
O(1)-Cu(1)-O(3)	97.07(18)	O(2)-Cu(4)-O(8)	86.52(18)
O(1)#1-Cu(1)-O(3)	100.58(18)	O(3)-Cu(4)-O(2)	87.04(18)
O(2)-Cu(1)-Cu(1)#1	137.43(14)	O(3)-Cu(4)-O(8)	81.68(18)
O(2)-Cu(1)-O(3)	77.77(17)	O(5)-Cu(4)-O(2)	177.2(2)
O(3)-Cu(1)-Cu(1)#1	101.76(11)	O(5)-Cu(4)-O(3)	94.16(19)
N(5)-Cu(2)-N(4)	81.9(2)	O(5)-Cu(4)-O(8)	96.17(19)
O(3)-Cu(2)-N(4)	88.7(2)	O(7)-Cu(4)-O(2)	94.44(19)
O(3)-Cu(2)-N(5)	170.6(2)	O(7)-Cu(4)-O(3)	172.7(2)
O(3)-Cu(2)-O(4)	96.87(19)	O(7)-Cu(4)-O(5)	84.0(2)
O(4)-Cu(2)-N(4)	174.0(2)	O(7)-Cu(4)-O(8)	105.56(19)
O(4)-Cu(2)-N(5)	92.5(2)		

		3	
Cu(1)-O(1)	1.921(2)	Cu(3)-N(9)	2.009(3)
Cu(1)-O(3)	1.9246(5)	Cu(4)-N(7)	1.924(3)
Cu(1)-O(4)	1.960(3)	Cu(4)-O(5)	1.939(3)
Cu(1)-N(1)	1.963(3)	Cu(4)-O(3)	1.9474(5)
Cu(1)-Cu(4)#1	2.7429(6)	Cu(4)-N(8)	1.979(3)
Cu(1)-Cu(4)	2.7543(6)	Cu(4)-Cu(1)#1	2.7428(6)
Cu(1)-Cu(5)	2.8658(6)	Cu(5)-O(1)	1.932(2)
Cu(1)-Cu(3)	2.9529(6)	Cu(5)-O(2)	1.951(2)
Cu(2)-O(7)	1.938(2)	Cu(5)-N(5)	1.956(3)
Cu(2)-O(1)	1.939(2)	Cu(5)-N(6)	1.972(3)
Cu(2)-O(2)	1.949(2)	Cu(6)-O(9)	1.930(3)
Cu(2)-O(8)	1.951(3)	Cu(6)-N(12)	1.978(3)
Cu(2)-Cu(5)	2.9150(6)	Cu(6)-N(13)	2.018(3)
Cu(3)-O(1)	1.931(2)	Cu(6)-O(10)	2.093(2)
Cu(3)-N(10)	1.968(3)	Cu(6)-O(2)	2.202(3)
Cu(3)-O(6)	1.972(2)		
O(1)-Cu(1)-Cu(4)#1	127.61(7)	N(9)-Cu(3)-Cu(1)	121.07(8)
O(3)-Cu(1)-Cu(4)#1	45.235(16)	N(7)-Cu(4)-O(5)	163.99(12)
O(4)-Cu(1)-Cu(4)#1	105.51(8)	N(7)-Cu(4)-O(3)	96.83(12)
N(1)-Cu(1)-Cu(4)#1	84.64(8)	O(5)-Cu(4)-O(3)	92.05(12)
O(1)-Cu(1)-Cu(4)	142.64(7)	N(7)-Cu(4)-N(8)	84.16(12)
O(3)-Cu(1)-Cu(4)	44.991(16)	O(5)-Cu(4)-N(8)	92.83(12)
O(4)-Cu(1)-Cu(4)	83.47(8)	O(3)-Cu(4)-N(8)	157.06(10)
N(1)-Cu(1)-Cu(4)	89.57(8)	N(7)-Cu(4)-Cu(1)#1	81.58(8)
Cu(4)#1-Cu(1)-Cu(4)	89.698(17)	O(5)-Cu(4)-Cu(1)#1	95.68(8)
O(1)-Cu(1)-Cu(5)	42.08(6)	O(3)-Cu(4)-Cu(1)#1	44.563(15)
O(3)-Cu(1)-Cu(5)	145.94(3)	N(8)-Cu(4)-Cu(1)#1	156.33(9)
O(4)-Cu(1)-Cu(5)	86.49(8)	N(7)-Cu(4)-Cu(1)	114.64(9)
N(1)-Cu(1)-Cu(5)	84.78(8)	O(5)-Cu(4)-Cu(1)	80.92(8)
Cu(4)#1-Cu(1)-Cu(5)	164.85(2)	O(3)-Cu(4)-Cu(1)	44.323(15)
Cu(4)-Cu(1)-Cu(5)	101.042(17)	N(8)-Cu(4)-Cu(1)	114.66(9)
O(1)-Cu(1)-Cu(3)	40.09(6)	Cu(1)#1-Cu(4)-Cu(1)	88.524(17)
O(3)-Cu(1)-Cu(3)	134.83(4)	O(1)-Cu(5)-O(2)	82.22(10)
O(4)-Cu(1)-Cu(3)	115.00(8)	O(1)-Cu(5)-N(5)	99.13(10)
N(1)-Cu(1)-Cu(3)	71.17(8)	O(2)-Cu(5)-N(5)	173.99(11)
Cu(4)#1-Cu(1)-Cu(3)	90.786(17)	O(1)-Cu(5)-N(6)	173.98(11)
Cu(4)-Cu(1)-Cu(3)	160.60(2)	O(2)-Cu(5)-N(6)	95.29(11)
Cu(5)-Cu(1)-Cu(3)	75.527(15)	N(5)-Cu(5)-N(6)	83.92(12)

O(7)-Cu(2)-O(1)	98.72(10)	O(1)-Cu(5)-Cu(1)	41.79(7)
O(7)-Cu(2)-O(2)	177.66(11)	O(2)-Cu(5)-Cu(1)	103.08(7)
O(1)-Cu(2)-O(2)	82.06(10)	N(5)-Cu(5)-Cu(1)	74.63(8)
O(7)-Cu(2)-O(8)	86.52(11)	N(6)-Cu(5)-Cu(1)	144.20(9)
O(1)-Cu(2)-O(8)	174.39(10)	O(1)-Cu(5)-Cu(2)	41.25(7)
O(2)-Cu(2)-O(8)	92.78(10)	O(2)-Cu(5)-Cu(2)	41.61(7)
O(7)-Cu(2)-Cu(5)	139.41(8)	N(5)-Cu(5)-Cu(2)	138.53(8)
O(1)-Cu(2)-Cu(5)	41.05(6)	N(6)-Cu(5)-Cu(2)	136.83(9)
O(2)-Cu(2)-Cu(5)	41.65(7)	Cu(1)-Cu(5)-Cu(2)	66.262(15)
O(8)-Cu(2)-Cu(5)	133.51(8)	O(9)-Cu(6)-N(12)	168.02(11)
O(1)-Cu(3)-N(10)	99.74(10)	O(9)-Cu(6)-N(13)	89.53(13)
O(1)-Cu(3)-O(6)	89.18(10)	N(12)-Cu(6)-N(13)	81.55(13)
N(10)-Cu(3)-O(6)	170.62(11)	O(9)-Cu(6)-O(10)	90.33(11)
O(1)-Cu(3)-N(9)	159.57(11)	N(12)-Cu(6)-O(10)	95.98(11)
N(10)-Cu(3)-N(9)	81.54(11)	N(13)-Cu(6)-O(10)	163.71(12)
O(6)-Cu(3)-N(9)	89.08(11)	O(9)-Cu(6)-O(2)	94.87(10)
O(1)-Cu(3)-Cu(1)	39.83(7)	N(12)-Cu(6)-O(2)	95.98(11)
N(10)-Cu(3)-Cu(1)	114.22(8)	N(13)-Cu(6)-O(2)	113.10(11)
O(6)-Cu(3)-Cu(1)	71.08(8)	O(10)-Cu(6)-O(2)	83.13(9)

Table 2S. Bond valence sums for Cu[a] and selected oxygen[b] atoms in **1–3**.

Complex **1**		
Atom	Cu(I)	Cu(II)
Cu1	1.66	1.93
Cu2	1.64	2.02
Cu3	1.64	2.01
	BVS	assignment
O1	0.86	OH^-
O2	0.91	OH^-
O3	0.41	H_2O
O4	0.40	H_2O

Complex **2**		
Atom	Cu(I)	Cu(II)
Cu1	1.68	1.96
Cu2	1.60	1.96
Cu3	1.66	2.03
Cu4	1.76	1.95
	BVS	assignment
O1	1.19	OH^-
O2	1.14	OH^-
O3	0.92	OH^-

Complex **3**		
Atom	Cu(I)	Cu(II)
Cu1	1.65	1.95
Cu2	1.62	1.80
Cu3	1.56	1.94
Cu4	1.66	2.07
Cu5	1.62	2.02
Cu6	1.63	2.02
	BVS	assignment
O1	1.87	O^{2-}
O2	1.10	OH^{-}
O3	1.84	O^{2-}

[a]The underlined value is the one closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the underlined value. [b]A BVS in the ~1.8–2.0, ~1.0–1.2, and ~0.2–0.4 ranges for an O atom is indicative of non-, single- and double-protonation, respectively, but can be altered somewhat by hydrogen bonding.

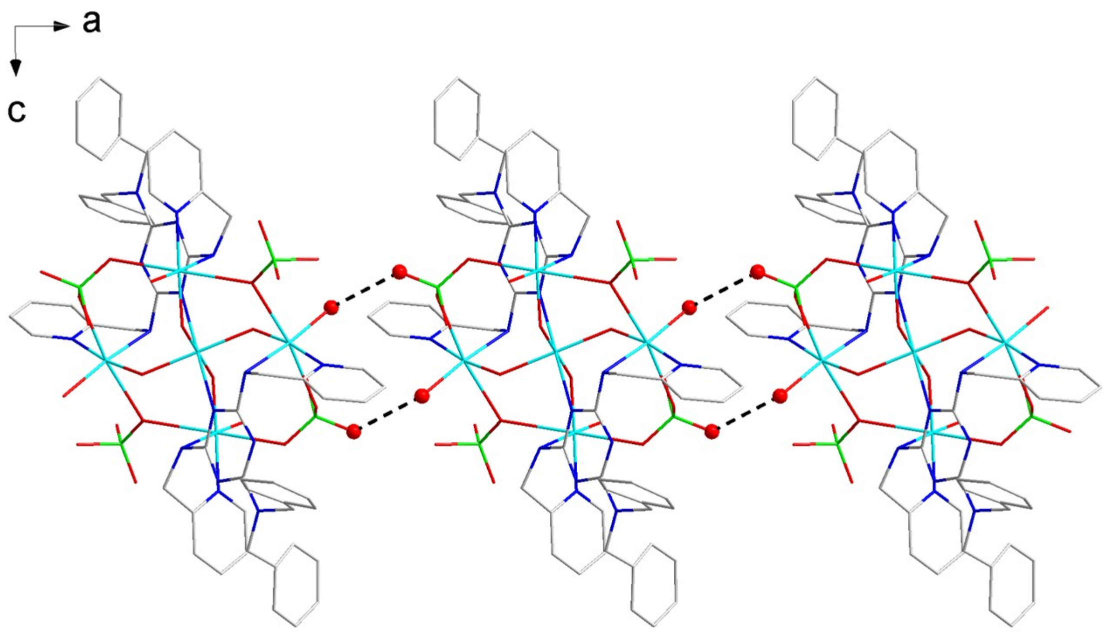

Fig. 1S. Representations of Cu_5-based 1D supramolecular structure of **1** showing along the *b* axis. Hydrogen atoms have been omitted for clarity.

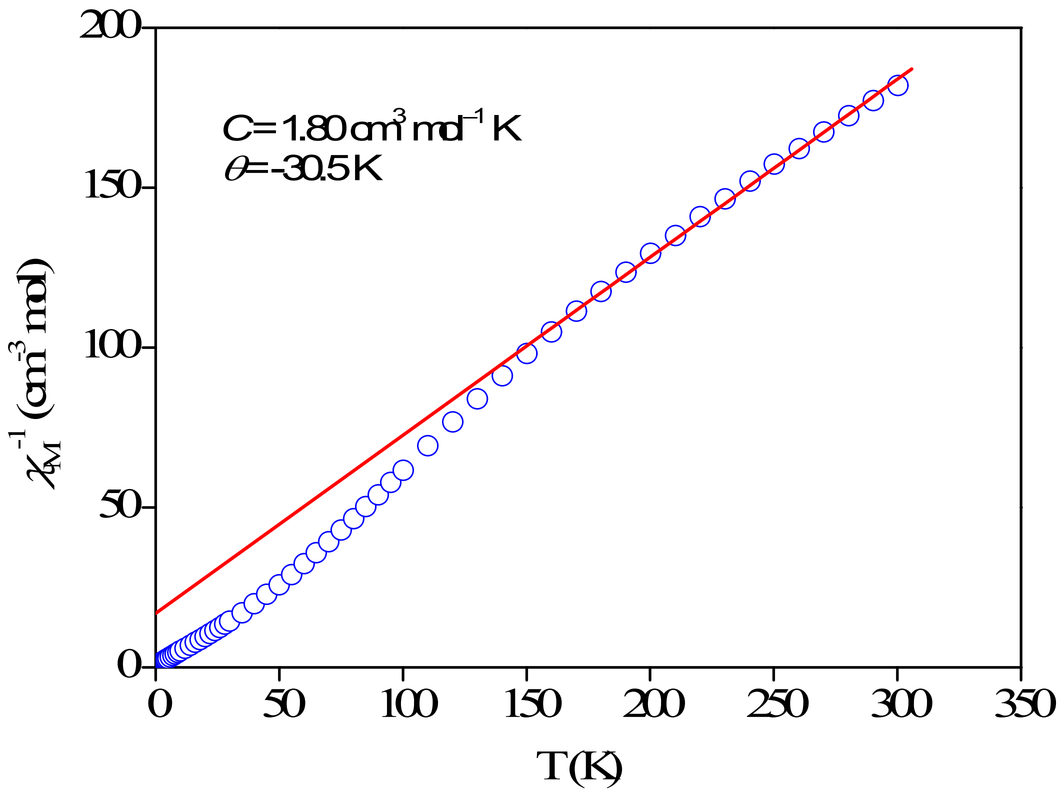

Fig. 2S. Plot of χ_M^{-1} (○) vs. temperature for a microcrystalline sample of complex **1**. The solid line represents the best fit χ_M^{-1} above 150 K with a Curie–Weiss law.

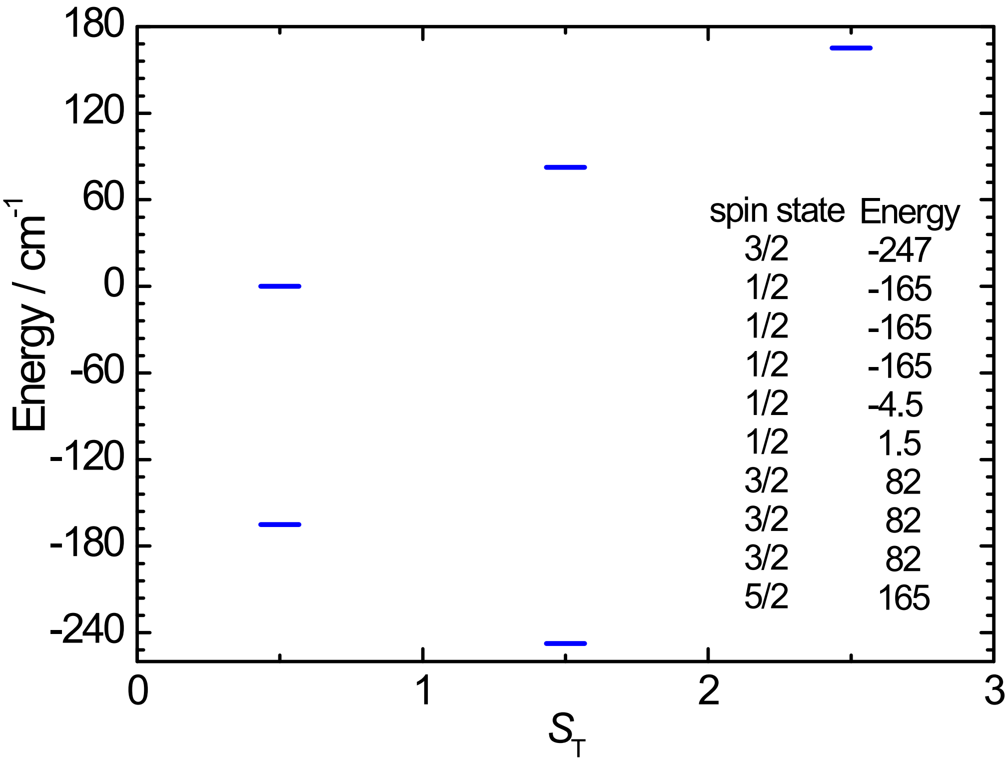

Fig. 3S. Diagram of all energy values for all S_T spin states of complex **1**.

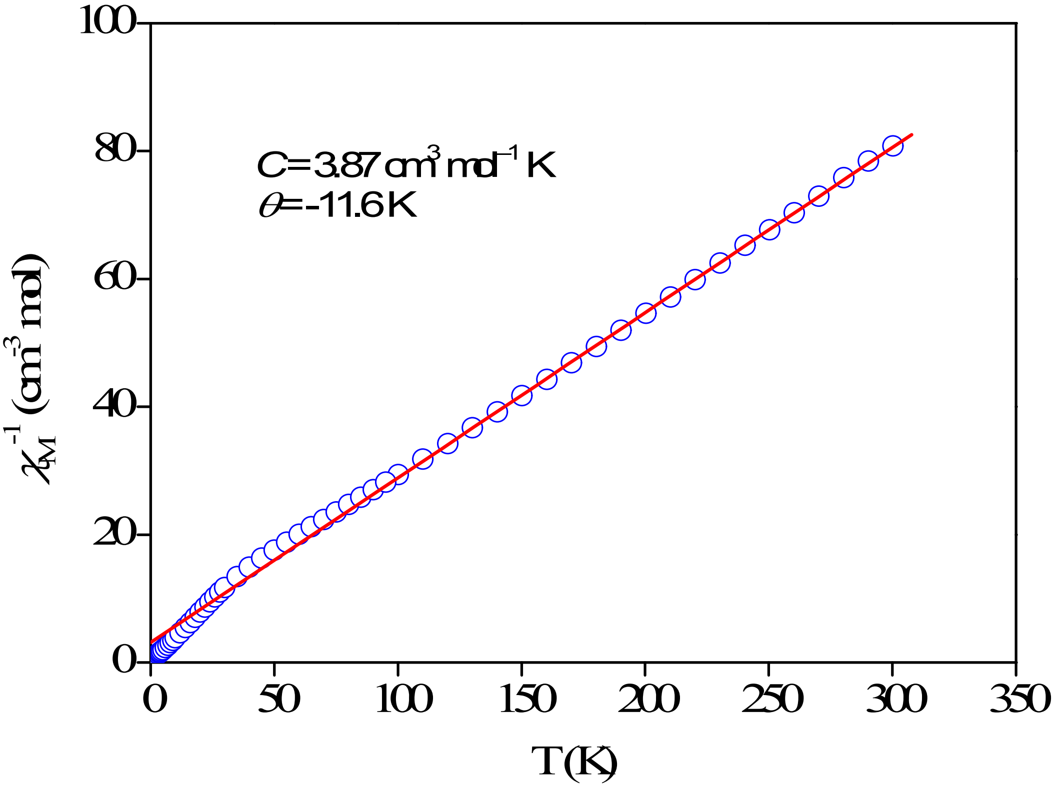

Fig. 4S. Plot of χ_M^{-1} (○) vs. temperature for a microcrystalline sample of complex **2**. The solid line represents the best fit χ_M^{-1} above 100 K with a Curie–Weiss law.

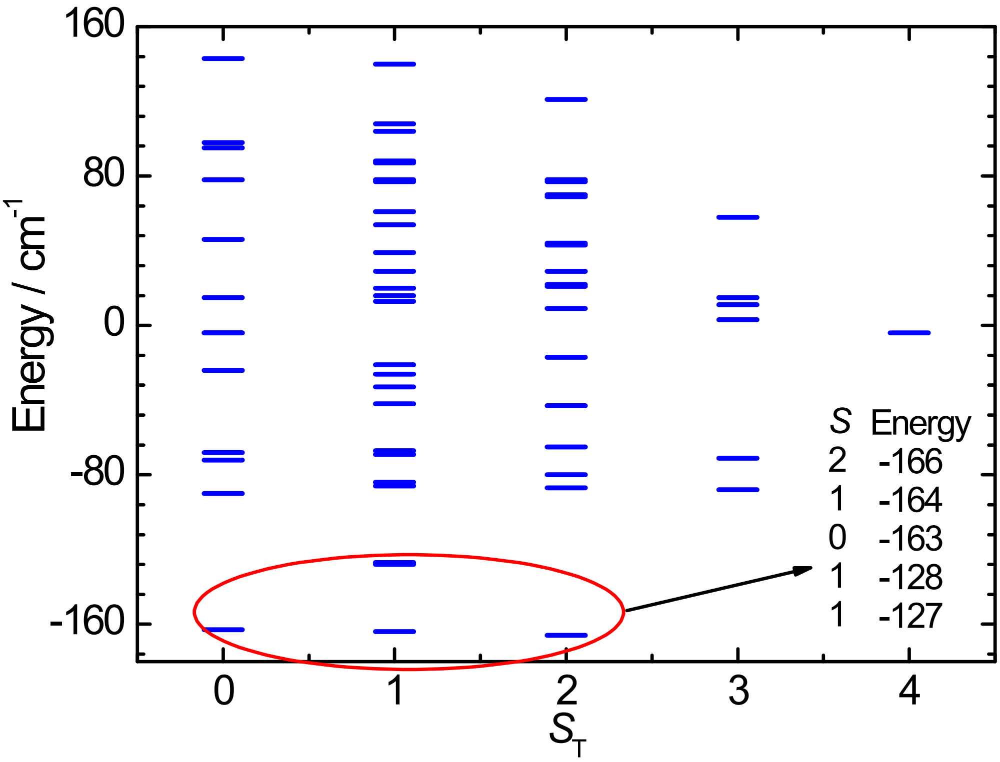

Fig. 5S. Diagram of all energy values for all S_T spin states of complex **2**.

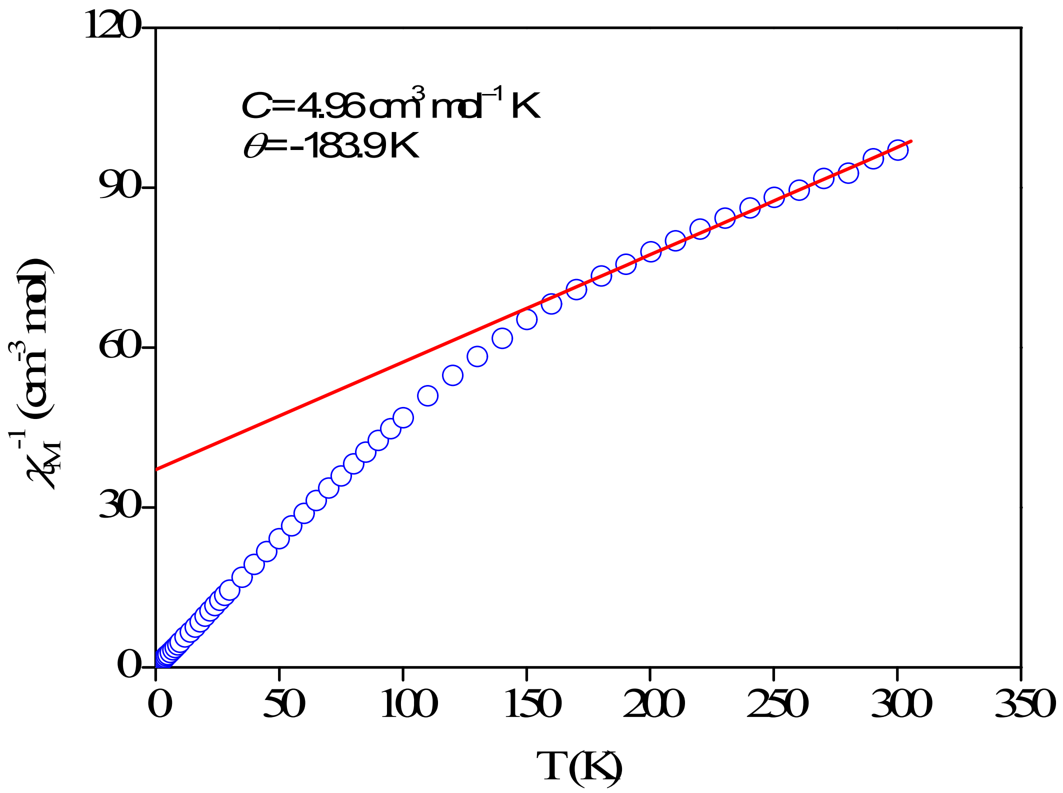

Fig. 6S. Plot of χ_M^{-1} (○) vs. temperature for a microcrystalline sample of complex **3**. The solid line represents the best fit χ_M^{-1} above 160 K with a Curie–Weiss law.