Systematic investigations on copper(II) coordination polymers based on organic ligands with mixed carboxylic and nitrogen-based moieties

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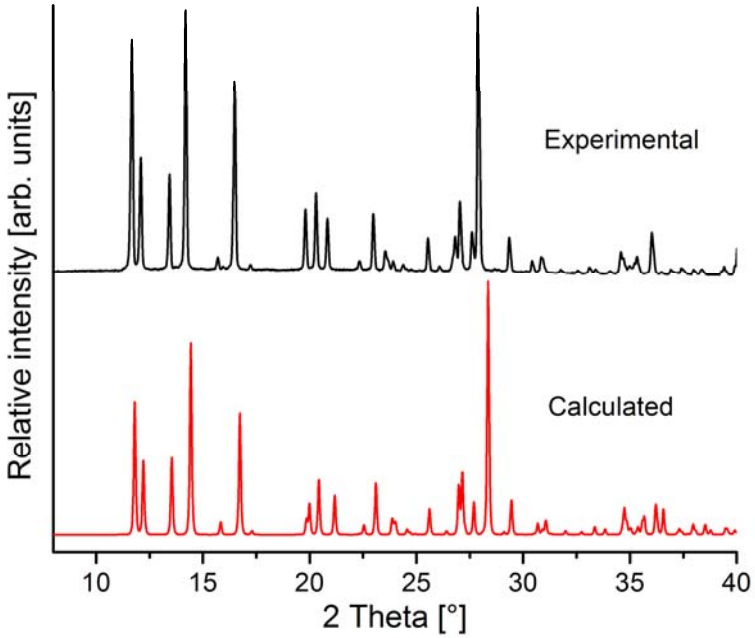

Fig. S1. Experimental XRPD pattern (top) and XRPD pattern calculated from single crystal data of compound **1** (bottom).

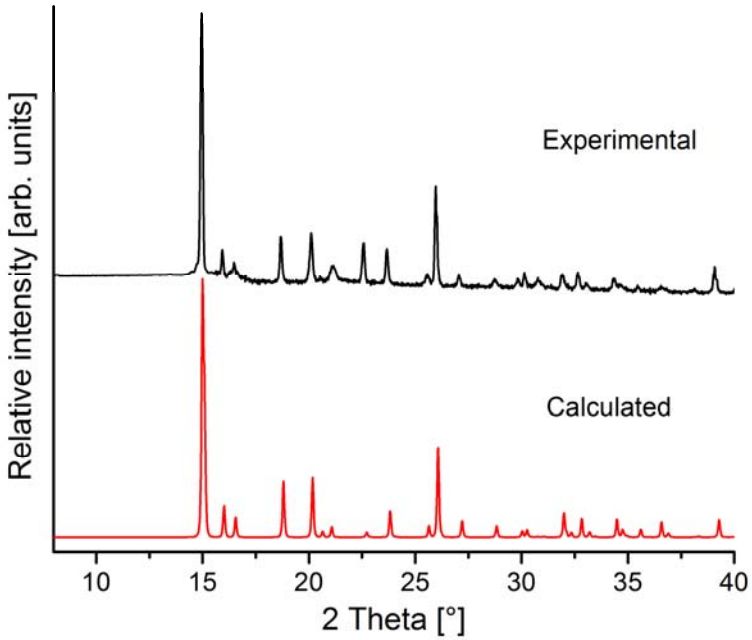

Fig. S2. Experimental XRPD pattern (top) and XRPD pattern calculated from single crystal data of compound **2** (bottom).

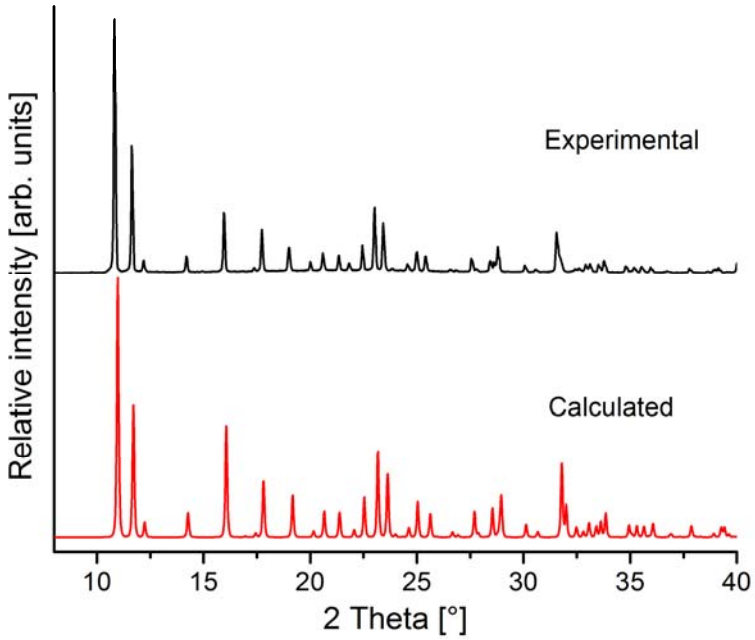

Fig. S3. Experimental XRPD pattern (top) and XRPD pattern calculated from single crystal data of compound **3** (bottom).

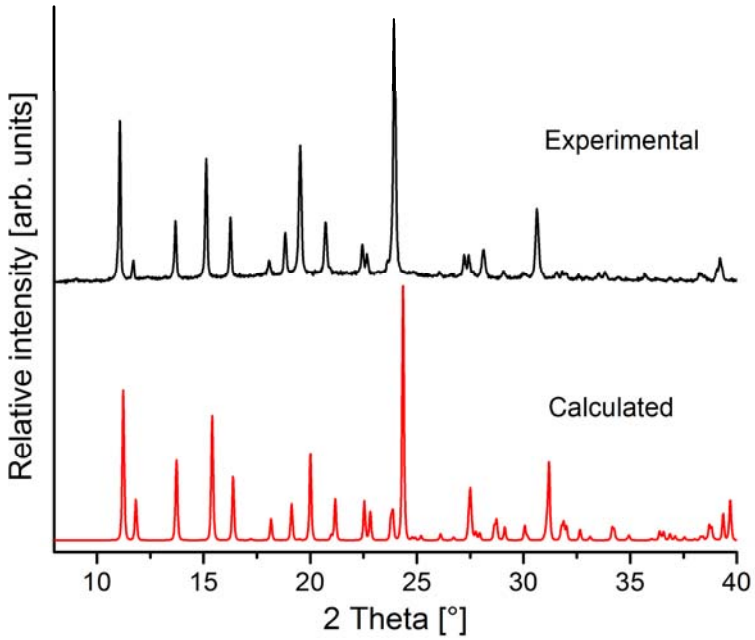

Fig. S4. Experimental XRPD pattern (top) and XRPD pattern calculated from single crystal data of compound **4** (bottom).

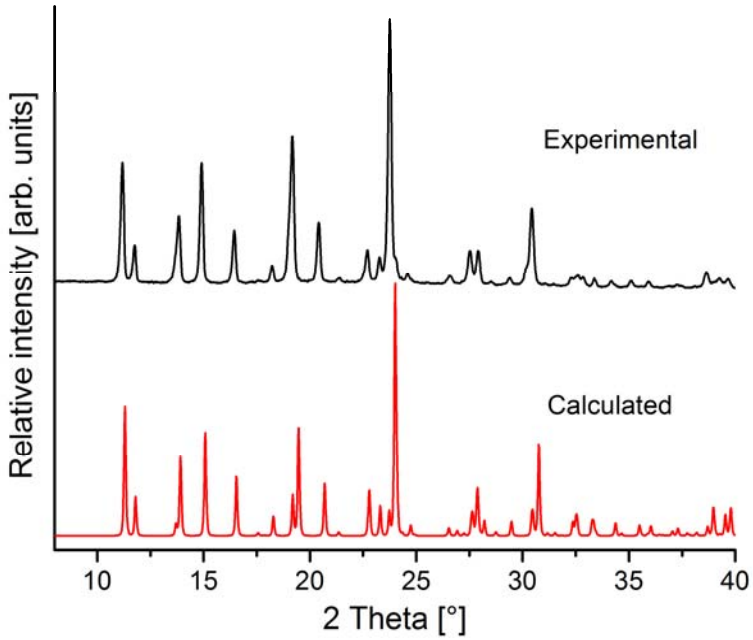

Fig. S5. Experimental XRPD pattern (top) and XRPD pattern calculated from single crystal data of compound **5** (bottom).

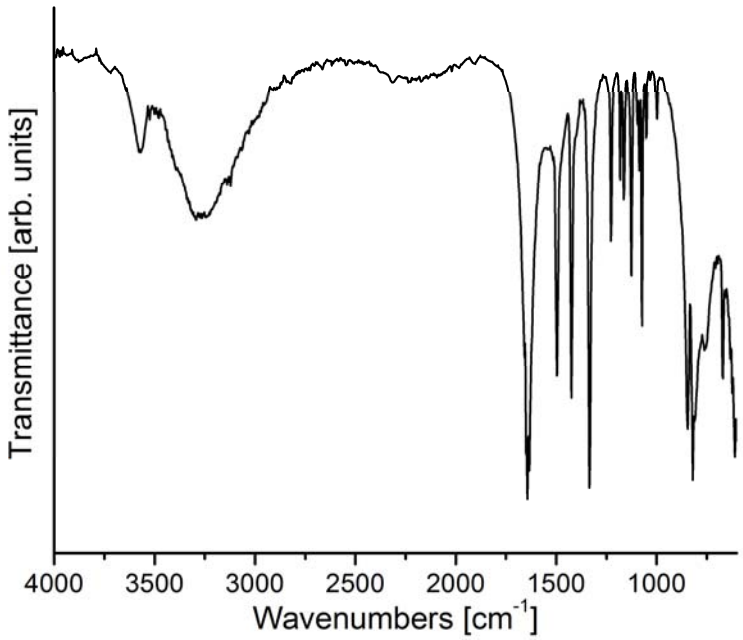

Fig. S6. IR spectroscopic data of compound **1**.

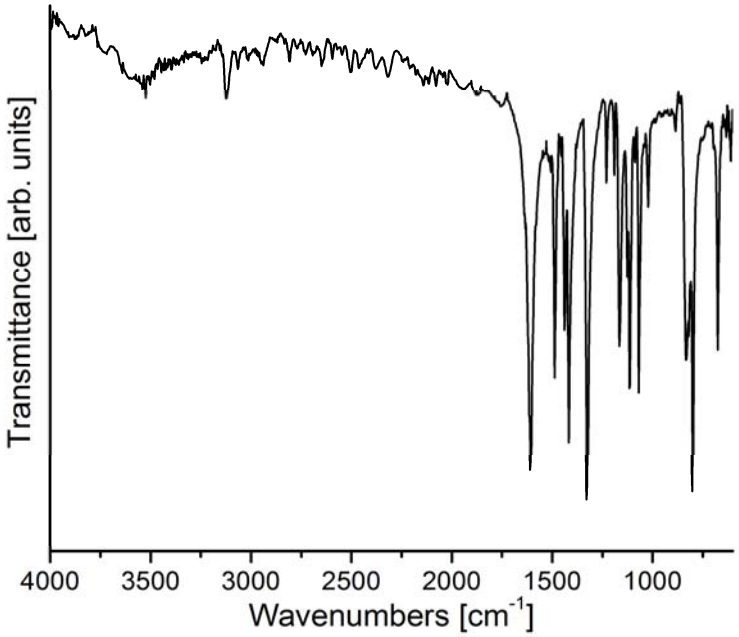

Fig. S7. IR spectroscopic data of compound **2**.

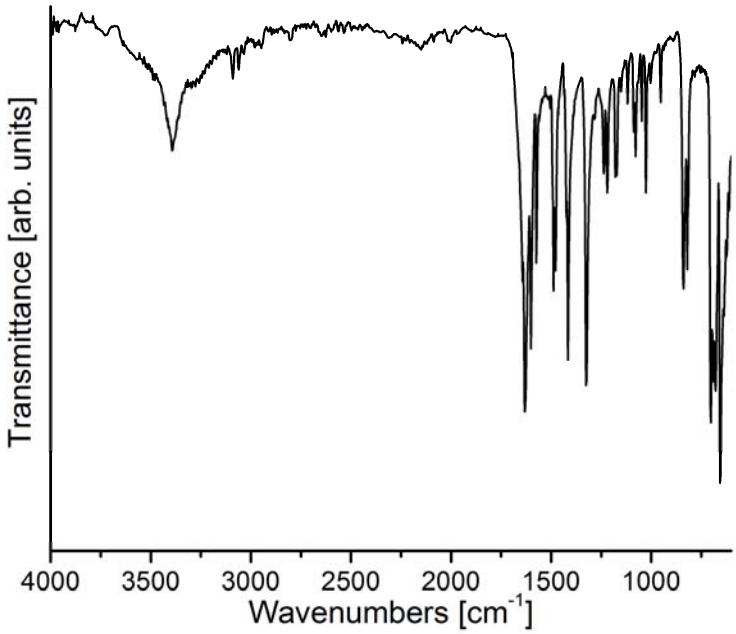

Fig. S8. IR spectroscopic data of compound **3**.

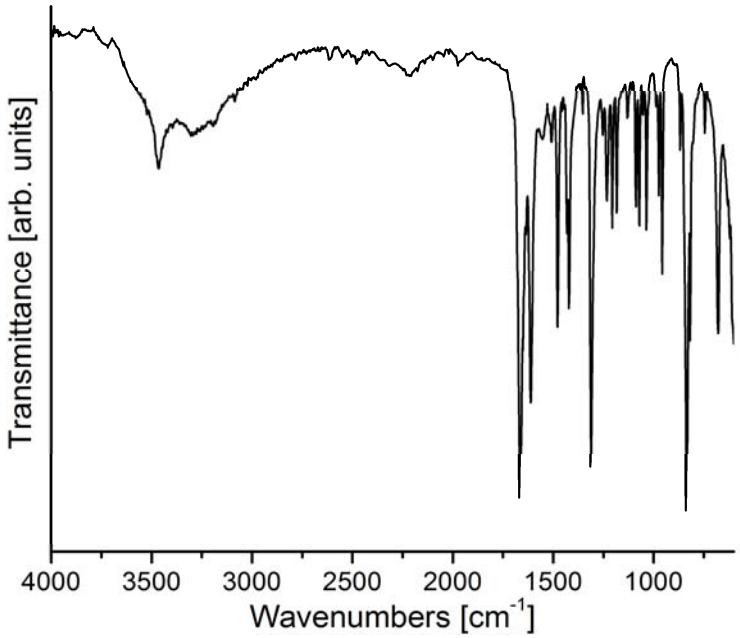

Fig. S9. IR spectroscopic data of compound **4**.

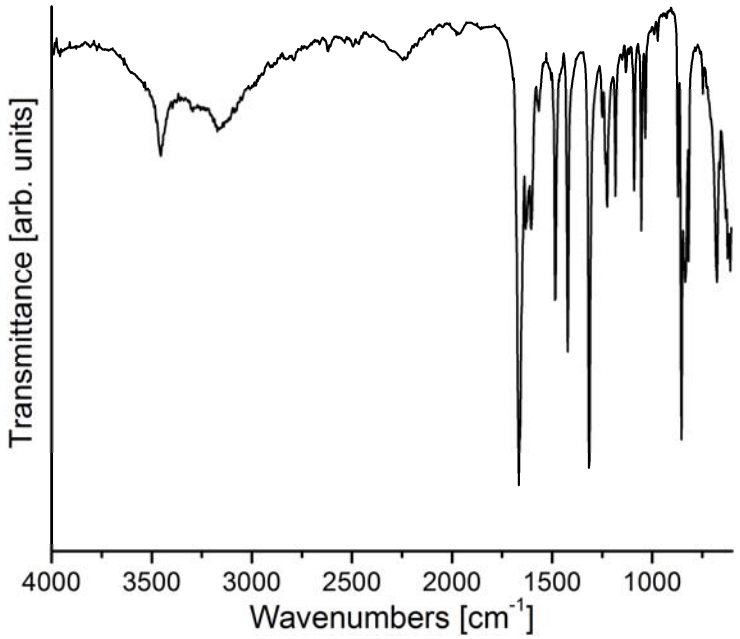

Fig. S10. IR spectroscopic data of compound **5**.

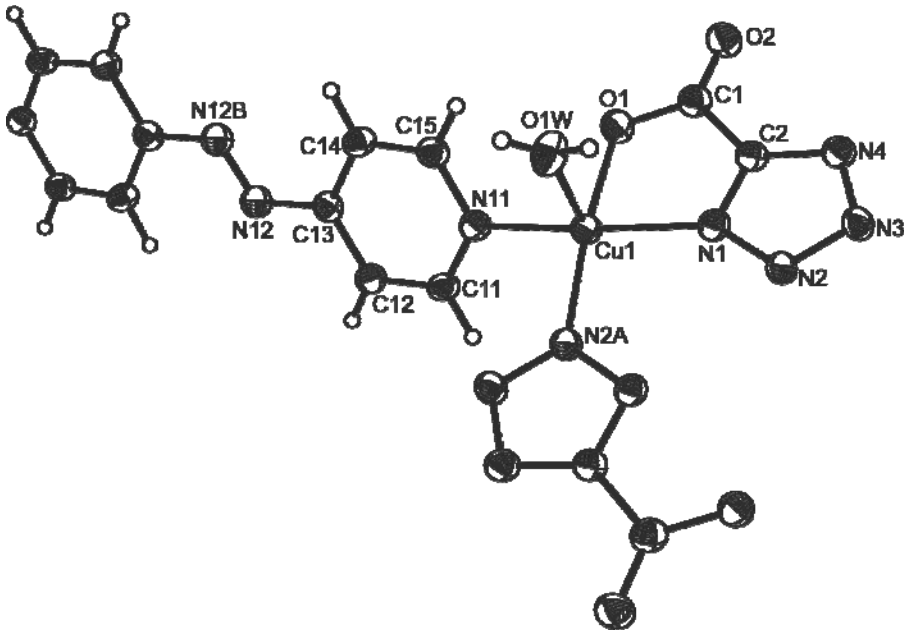

Fig. S11. Crystal structure of $[Cu(tzc)(azpy)_{0.5}(H_2O)]_n$ (**5**) with view of the coordination sphere of the copper(II) cation with displacement ellipsoids drawn at the 50% probability level. Selected atoms are labeled. Symmetry codes: A = -x, -y + 1, -z + 1; B = -x + 2, -y + 1, -z + 2.

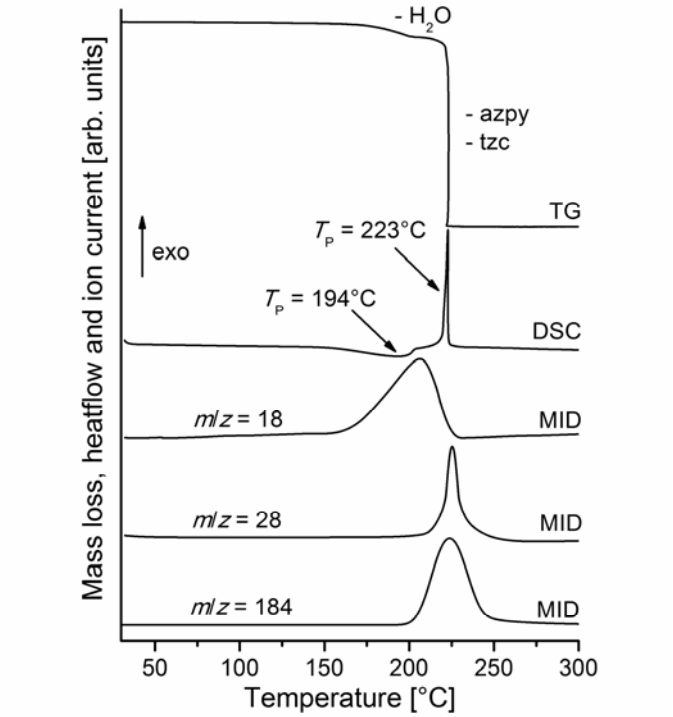

Fig. S12. TG, DSC and MS trend scan curves for compounds **5**. Heating rate = 3 °C·min^{-1}; *m*/*z* = 18 (water), 28 (N_2, decomposition product of tzc), 184 (azpy); given are the peak temperatures T_P [°C].

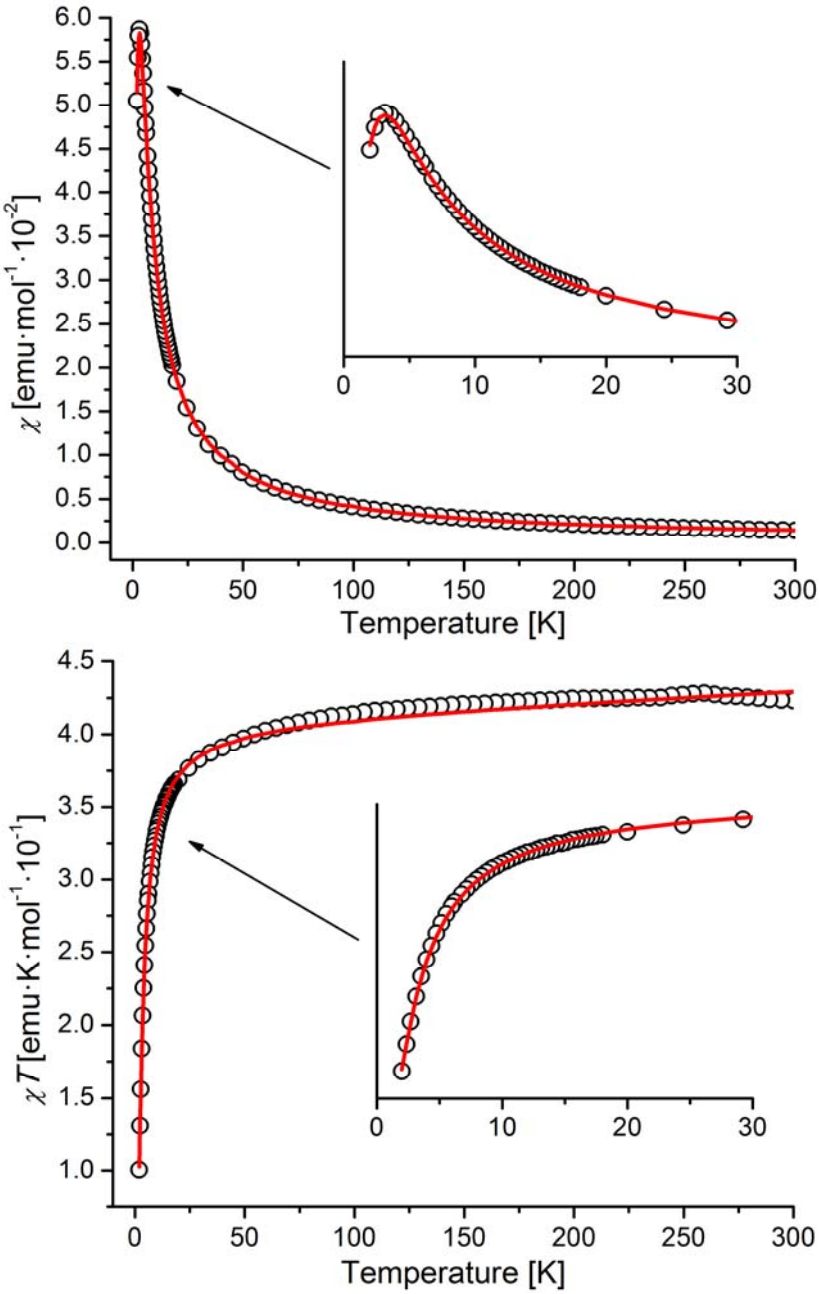

Fig. S13. Temperature dependence (from 300 to 1.8 K) of the magnetic susceptibility (top) and the product of the magnetic susceptibility and temperature (bottom) for compound **4**. The red lines correspond to the best fit of a magnetic dimer model.

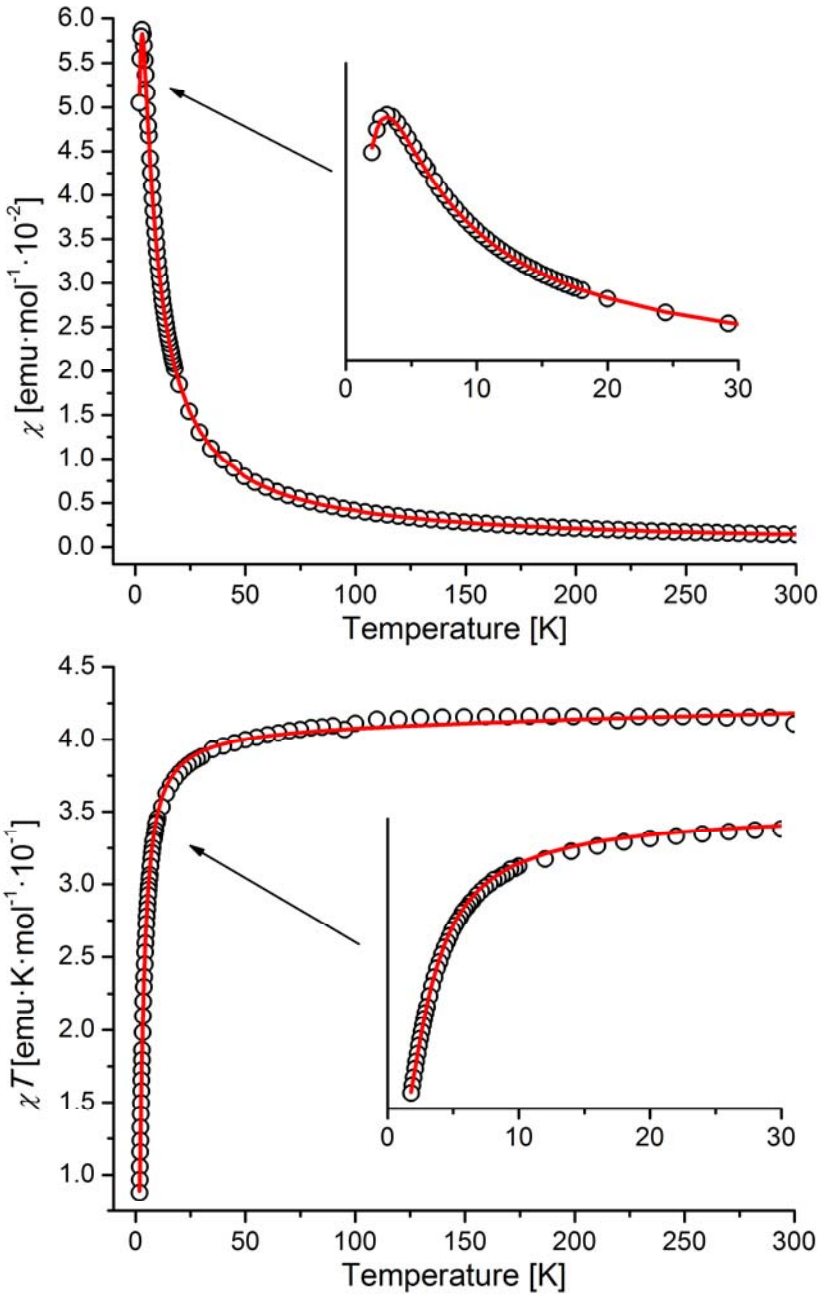

Fig. S14. Temperature dependence (from 300 to 1.8 K) of the magnetic susceptibility (top) and the product of the magnetic susceptibility and temperature (bottom) for compound **5**. The red lines correspond to the best fit of a magnetic dimer model.

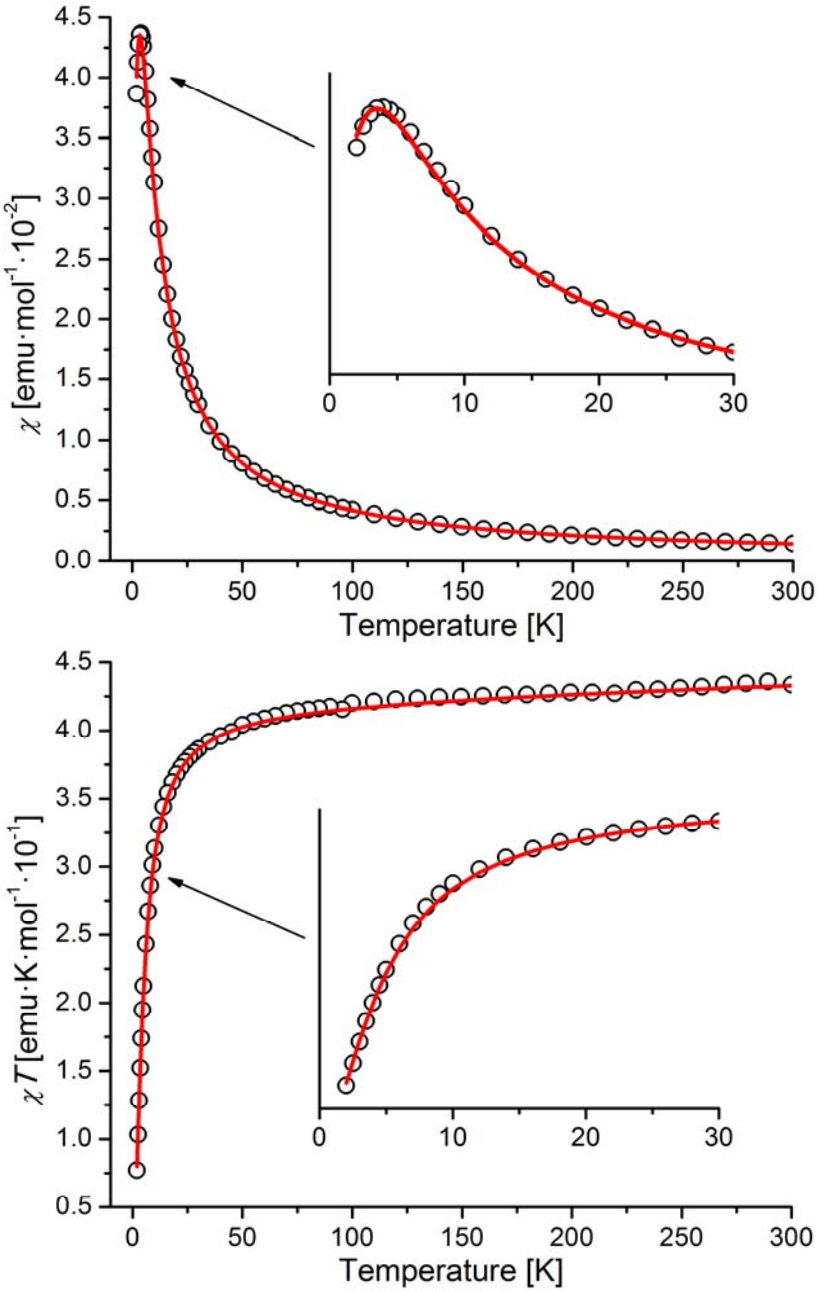

Fig. S15. Temperature dependence (from 300 to 1.8 K) of the magnetic susceptibility (top) and the product of the magnetic susceptibility and temperature (bottom) for compound **2**. The red lines correspond to the best fit of a magnetic chain model.

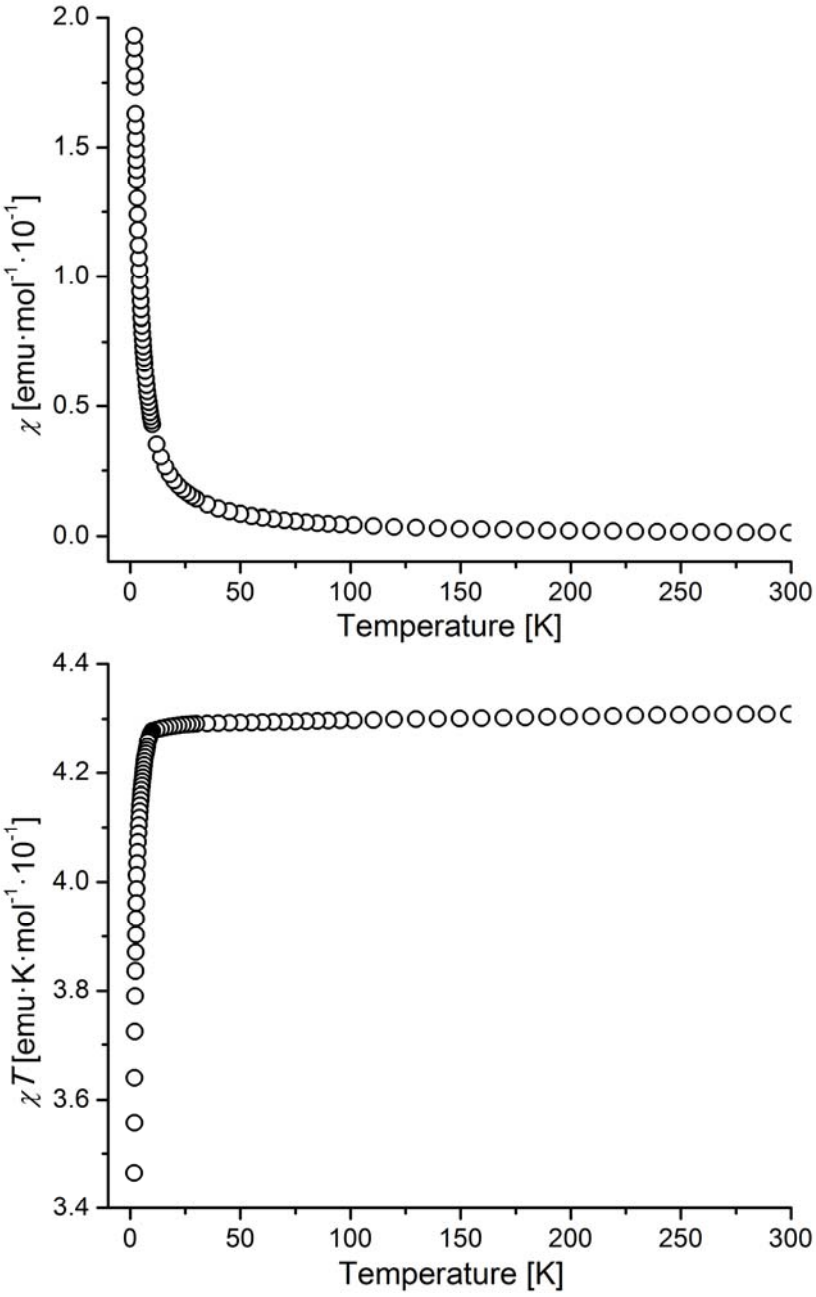

Fig. S16. Temperature dependence (from 300 to 1.8 K) of the magnetic susceptibility (top) and the product of the magnetic susceptibility and temperature (bottom) for compound **3**.

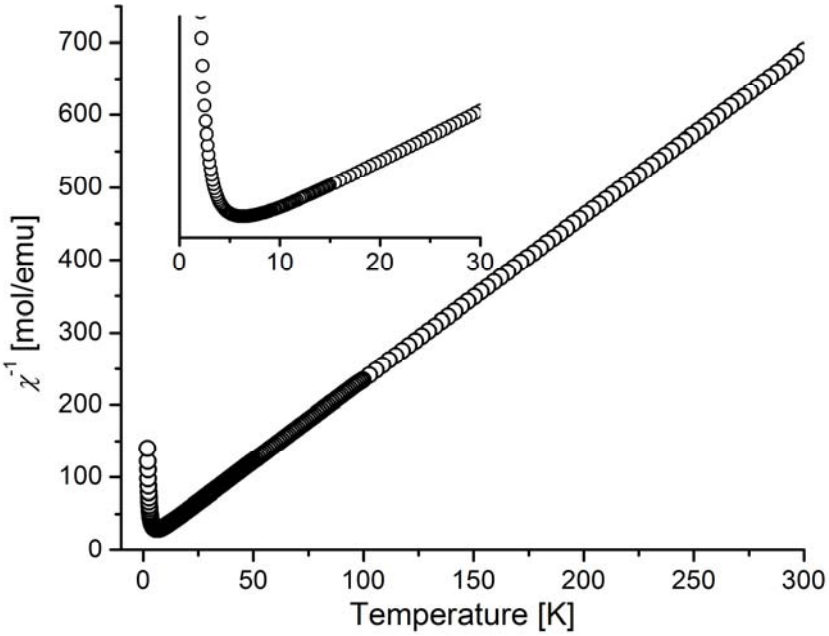

Fig. S17. Temperature dependence (from 300 to 1.8 K) of the reciprocal magnetic susceptibility for compound **1**.

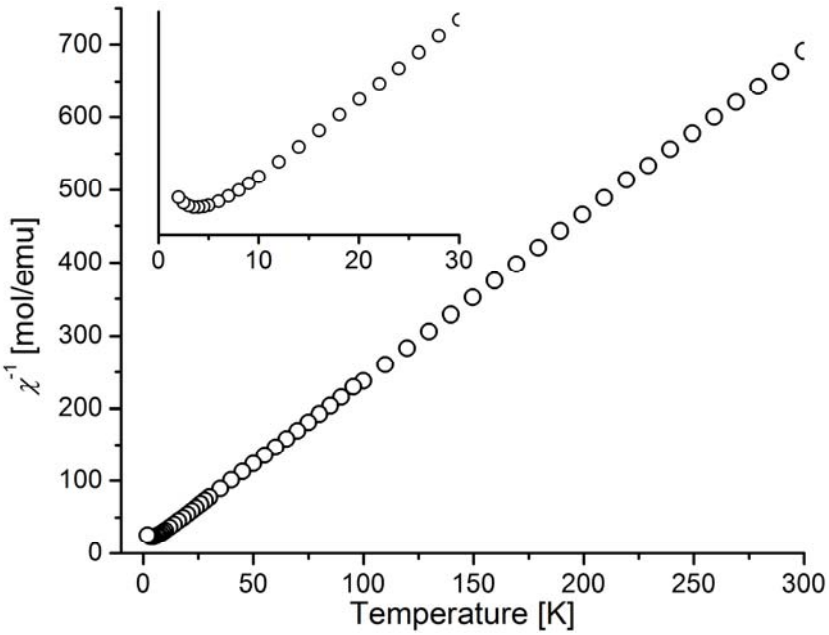

Fig. S18. Temperature dependence (from 300 to 1.8 K) of the reciprocal magnetic susceptibility for compound **2**.

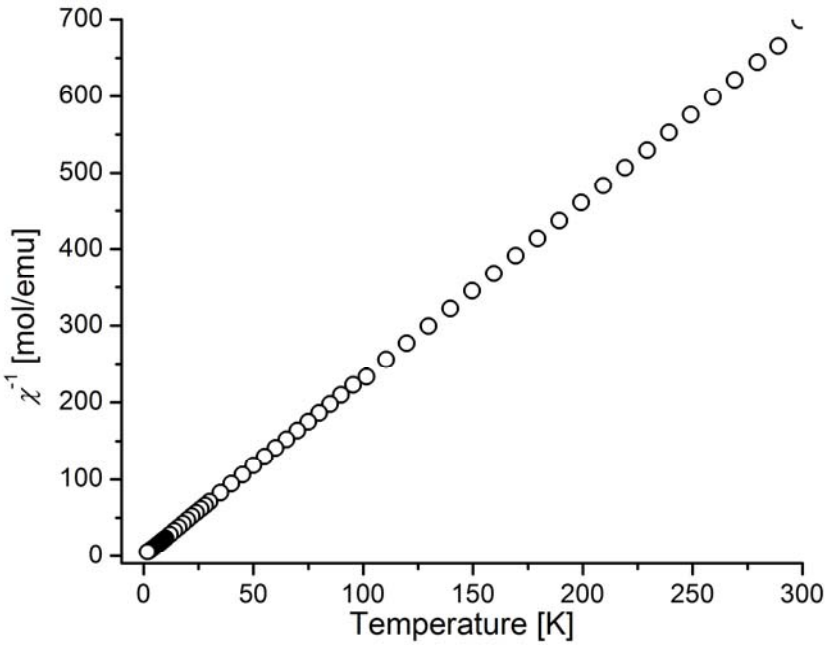

Fig. S19. Temperature dependence (from 300 to 1.8 K) of the reciprocal magnetic susceptibility for compound **3**.

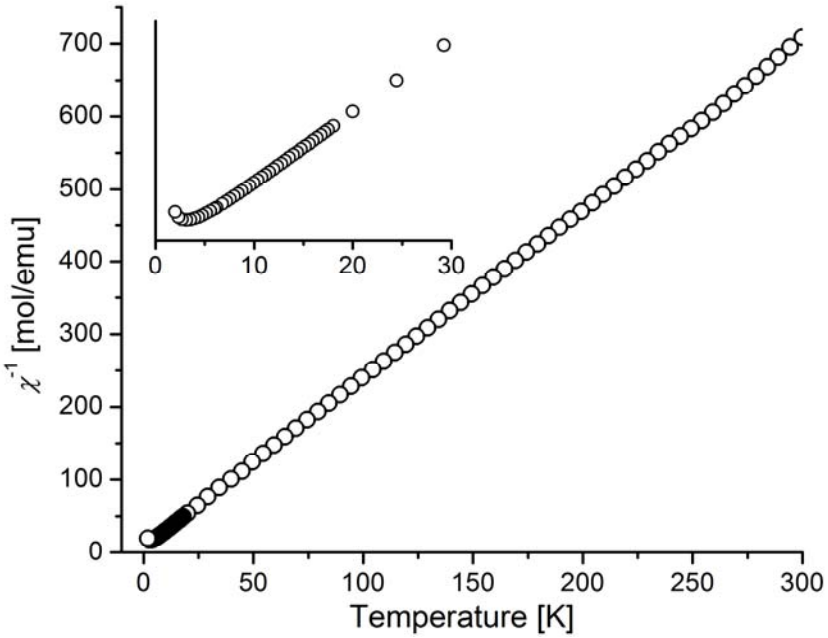

Fig. S20. Temperature dependence (from 300 to 1.8 K) of the reciprocal magnetic susceptibility for compound **4**.

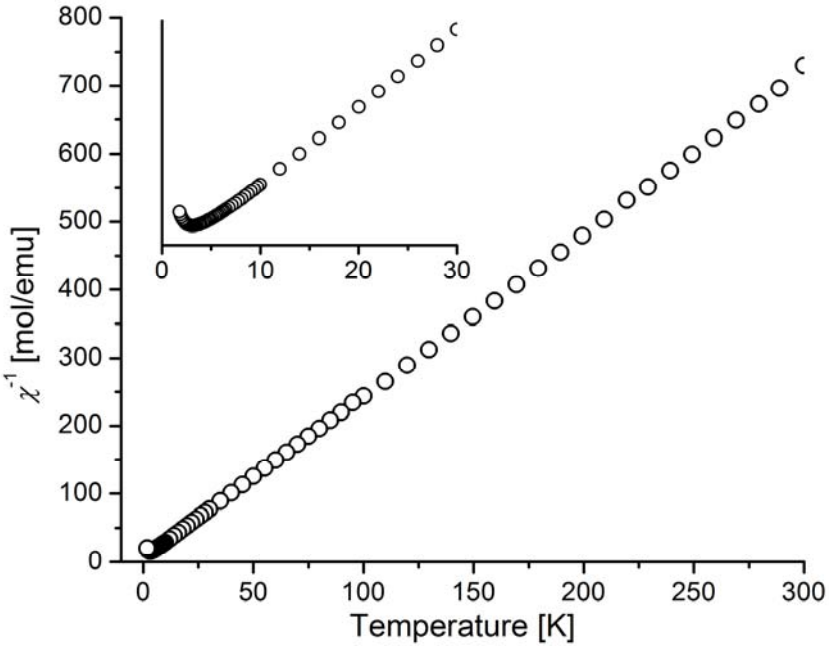

Fig. S21. Temperature dependence (from 300 to 1.8 K) of the reciprocal magnetic susceptibility for compound **5**.

Table S1. Selected bond lengths [Å] and angles [°] for compound **1**.

Cu(1)-O(2A)	1.980(2)
Cu(1)-N(2)	1.994(2)
Cu(1)-N(1A)	2.025(2)
Cu(1)-N(11)	2.032(2)
Cu(1)-O(2W)	2.387(2)
Cu(1)-O(1W)	2.421(2)
O(2A)-Cu(1)-N(2)	174.52(7)
O(2A)-Cu(1)-N(1A)	81.39(7)
N(2)-Cu(1)-N(1A)	93.33(7)
O(2A)-Cu(1)-N(11)	86.37(7)
N(2)-Cu(1)-N(11)	98.99(8)
N(1A)-Cu(1)-N(11)	167.40(7)
O(2A)-Cu(1)-O(2W)	89.00(6)
N(2)-Cu(1)-O(2W)	89.87(7)
N(1A)-Cu(1)-O(2W)	93.45(7)
N(11)-Cu(1)-O(2W)	89.27(7)
O(2A)-Cu(1)-O(1W)	91.71(6)
N(2)-Cu(1)-O(1W)	89.80(7)
N(1A)-Cu(1)-O(1W)	90.78(7)
N(11)-Cu(1)-O(1W)	86.61(7)
O(2W)-Cu(1)-O(1W)	175.77(5)

Symmetry codes: A = -x + 1, -y + 1, -z + 1; B = -x + 2, -y + 2, -z.

Table S2. Hydrogen bonding in compound **1**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1W-H1A	0.840	1.921	173.04	2.757	O2 [x, y, z - 1]
O1W-H1B	0.840	1.987	164.20	2.804	O3W [-x + 1, -y + 1, -z + 1]
O1W-H1C	0.840	2.004	171.11	2.837	O1W [-x + 1, -y + 2, -z]
O2W-H2A	0.840	1.915	163.50	2.731	O2 [x + 1, y, z - 1]
O2W-H2B	0.840	1.950	170.00	2.781	O2W [-x + 2, -y + 1, -z + 1]
O2W-H2C	0.840	1.972	150.63	2.735	O3W
O3W-H3A	0.840	2.157	152.90	2.930	N3 [x, y - 1, z]
O3W-H3A	0.840	2.581	122.07	3.110	N4 [x, y - 1, z]
O3W-H3B	0.840	2.041	150.84	2.804	O1W [-x + 1, -y + 1, -z + 1]
O3W-H3C	0.840	2.015	143.34	2.735	O2W

Table S3. Selected bond lengths [Å] and angles [°] for compound **2**.

Cu(1)-N(4A)	1.977(4)
Cu(1)-O(1)	1.983(4)
Cu(1)-O(2A)	2.485(3)
Cu(1)-N(11)	2.034(3)
Cu(1)-N(1)	2.364(4)
N(4A)-Cu(1)-O(1)	173.68(15)
N(4A)-Cu(1)-N(11)	90.59(8)
O(1)-Cu(1)-N(11)	89.28(8)
N(11)-Cu(1)-N(11B)	177.38(17)
N(4A)-Cu(1)-N(1)	104.59(16)
O(1)-Cu(1)-N(1)	81.73(15)
N(11)-Cu(1)-N(1)	90.98(8)

Symmetry codes: A = x + 1, y, z; B = x, -y + 1/2, z; C = x, -y + 3/2, z.

Table S4. Selected bond lengths [Å] and angles [°] for compound **3**.

Cu(1)-O(1)	2.004(2)
Cu(1)-N(2A)	2.006(2)
Cu(1)-N(1)	2.022(2)
Cu(1)-N(12B)	2.035(2)
Cu(1)-N(11)	2.377(2)
Cu(1)-O(1W)	2.408(2)
O(1)-Cu(1)-N(2A)	175.14(6)
O(1)-Cu(1)-N(1)	81.70(6)
N(2A)-Cu(1)-N(1)	93.46(7)
O(1)-Cu(1)-N(12B)	87.32(6)
N(2A)-Cu(1)-N(12B)	97.47(7)
N(1)-Cu(1)-N(12B)	168.19(6)
O(1)-Cu(1)-N(11)	87.00(6)
N(2A)-Cu(1)-N(11)	93.76(6)
N(1)-Cu(1)-N(11)	92.90(6)
N(12B)-Cu(1)-N(11)	90.84(6)

O(1)-Cu(1)-O(1W)	88.73(5)
N(2A)-Cu(1)-O(1W)	90.24(5)
N(1)-Cu(1)-O(1W)	83.39(5)
N(12B)-Cu(1)-O(1W)	92.07(5)
N(11)-Cu(1)-O(1W)	174.71(5)

Symmetry codes: A = -x + 1, -y + 1, -z + 1; B = -x + 1/2, y - 1/2, -z + ½.

Table S5. Hydrogen bonding in compound **3**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1W-H1W	0.840	1.983	171.98	2.817	O2 [-x + 3/2, y - 1/2, -z + 1/2]
O1W-H2W	0.840	1.977	169.71	2.808	O2 [x, y - 1, z]

Table S6. Selected bond lengths [Å] and angles [°] for compound **4** and **5**.

	Compound **4**	Compound **5**
Cu(1)-N(11)	1.979(2)	1.996(3)
Cu(1)-O(1)	1.980(2)	1.985(2)
Cu(1)-N(2A)	1.983(2)	1.992(3)
Cu(1)-N(1)	2.000(2)	2.003(3)
Cu(1)-O(1W)	2.218(2)	2.202(3)
N(11)-Cu(1)-O(1)	87.50(6)	87.87(10)
N(11)-Cu(1)-N(2A)	96.04(7)	95.89(11)
O(1)-Cu(1)-N(2A)	172.63(7)	172.81(11)
N(11)-Cu(1)-N(1)	165.50(7)	165.70(11)
O(1)-Cu(1)-N(1)	81.31(6)	81.54(10)
N(2A)-Cu(1)-N(1)	94.09(7)	93.68(11)
N(11)-Cu(1)-O(1W)	100.61(6)	98.72(11)
O(1)-Cu(1)-O(1W)	92.57(6)	93.73(11)
N(2A)-Cu(1)-O(1W)	93.13(7)	91.75(12)
N(1)-Cu(1)-O(1W)	89.15(6)	91.58(11)

Symmetry codes: A = -x, -y + 1, -z + 1; B = -x + 2, -y + 1, -z + 2.

Table S7. Hydrogen bonding in compound **4**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1W-H1W	0.840	2.134	152.45	2.905	N3 [x + 1, y, z]
O1W-H2W	0.840	1.981	163.06	2.795	O2 [x, -y + 3/2, z - 1/2]
O1W-H2W	0.840	2.592	138.18	3.267	O1 [x, -y + 3/2, z -1/2]

Table S8. Hydrogen bonding in compound **5**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1W-H1W	0.840	2.099	154.18	2.879	N3 [x + 1, y, z]
O1W-H2W	0.840	1.932	163.54	2.748	O2 [x, -y + 3/2, z - 1/2]
O1W-H2W	0.840	2.570	137.47	3.239	O1 [x, -y + 3/2, z -1/2]