Electronic Supplementary Information for Dalton Transactions

Supplementary Information

Nuclear and Magnetic Structures and Magnetic Properties of Synthetic Brochantite, $Cu_4(OH)_6SO_4$

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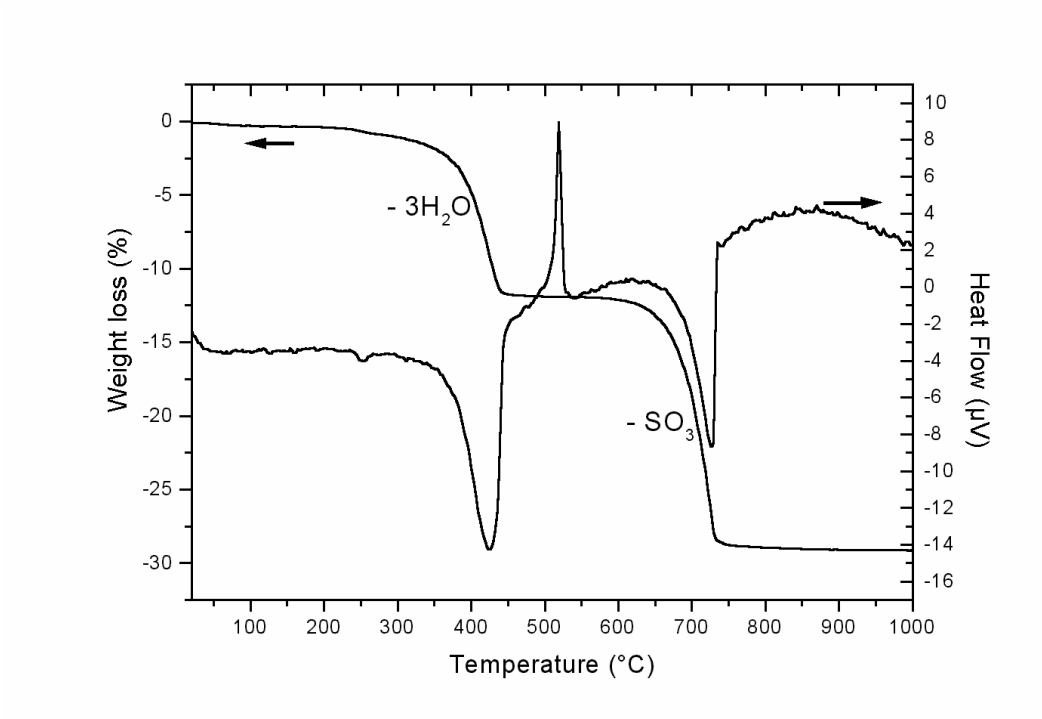

Figure S1: TG-DTA traces recorded under air at a 3.5°C/mn heating rate

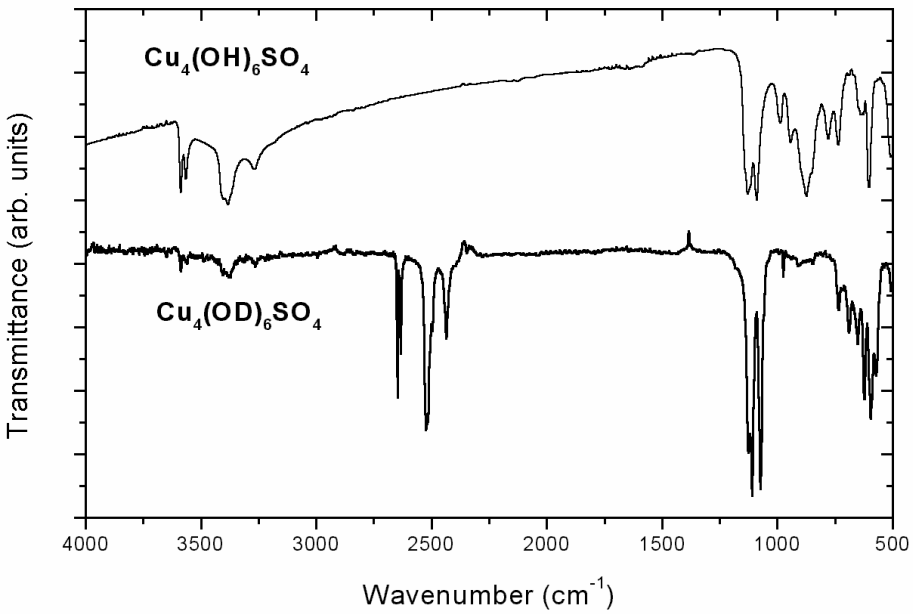

Figure S2: Infrared spectra of a) $Cu_4(OH)_6SO_4$ and b) $Cu_4(OD)_6SO_4$

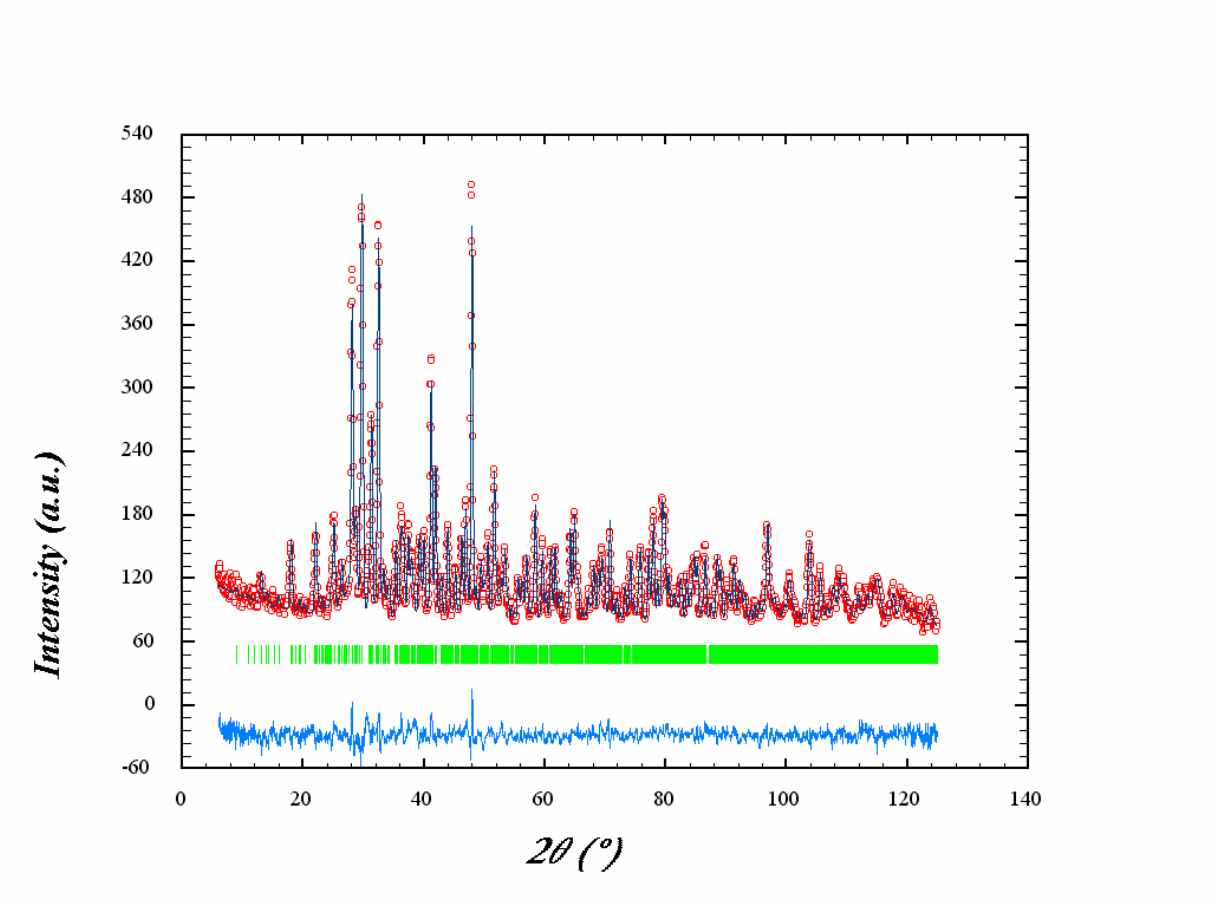

Figure S3. Observed (O) and calculated (—) profiles of the powder neutron pattern of $Cu_4(OH)_6SO_4$ obtained on the 3T2 diffractometer at 300 K with position of the Bragg reflections (short vertical lines) and difference between observed and calculated profiles.

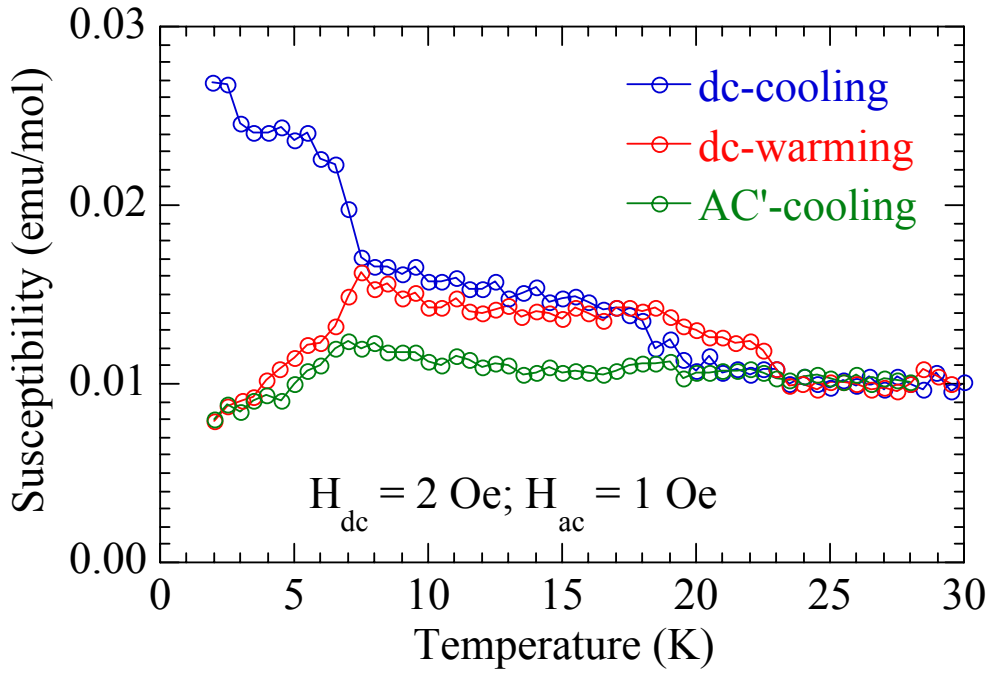

Figure S4. ac- and dc-susceptibilities measured in low applied fields (H_{ac} = 1 Oe (17 Hz), H_{dc} = 2 Oe).

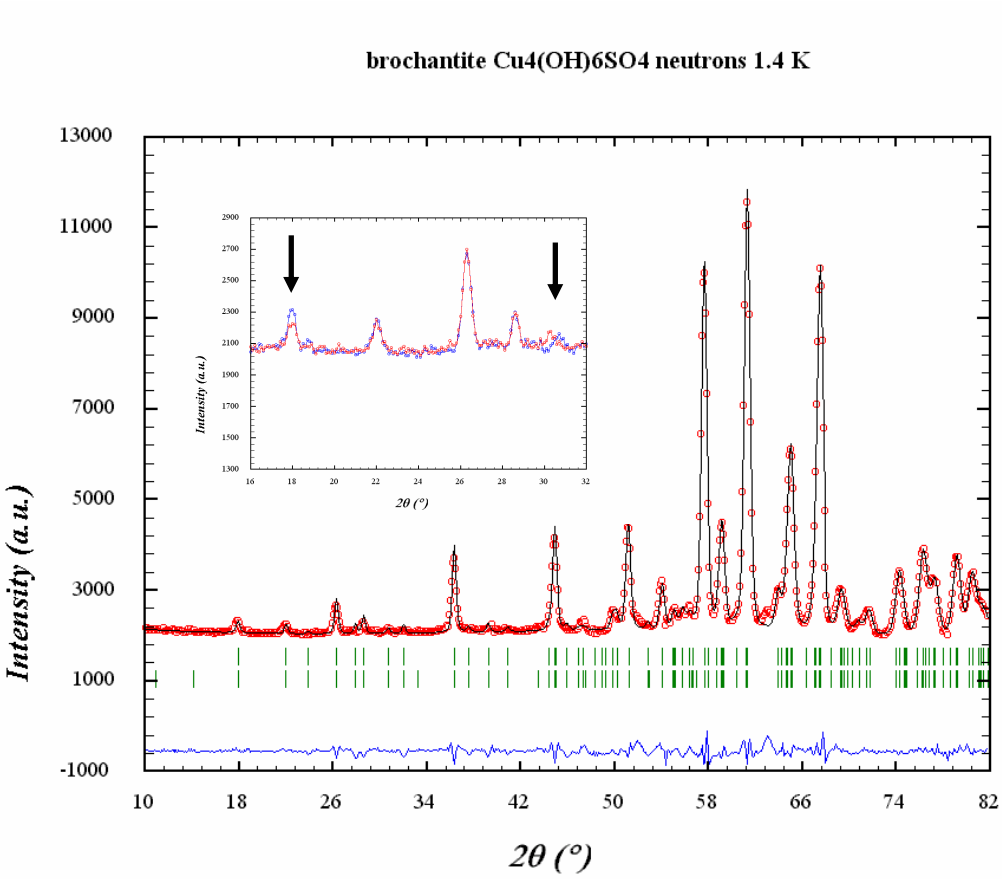

Figure S5. Observed (O) and calculated (——) profiles of the neutron pattern of $Cu_4(OH)_6SO_4$ obtained on the G4.1 diffractometer at 1.4 K with position of the Bragg reflections (short vertical lines, nuclear, magnetic) and difference between observed and calculated profiles. Inset : Zoom in the 16 to 32° region for the 1.4 K (blue) and 12 K (red) data, the arrows evidencing the magnetic contributions at 18 and 30.7°.

Table S1. Fractional atomic positions and isothermal temperature factors from neutron powder diffraction data at 300 K for deuterated brochantite.

Atom	x/a	y/b	z/c	B (Å^2)	Occupancy
Cu1	0.2942(7)	0.4889(8)	0.5297(17)	0.84(13)	4.0
Cu2	0.2940(8)	0.4938(10)	1.0210(21)	0.82(15)	4.0
Cu3	0.1168(6)	0.2558(10)	0.1788(17)	0.91(13)	4.0
Cu4	0.1192(7)	0.2579(10)	0.6867(20)	0.83(13)	4.0
S	0.3936(12)	0.1824(13)	0.3330(44)	0.90(24)	4.0
OH1	0.0970(10)	0.1333(12)	0.4297(26)	0.86(20)	4.0
OH2	0.0867(9)	0.1299(12)	0.9189(25)	0.99(18)	4.0
OH3	0.1582(11)	0.3826(13)	0.4571(27)	1.14(23)	4.0
OH4	0.1590(9)	0.3871(11)	0.9385(21)	1.23(20)	4.0
OH5	0.2488(8)	0.5940(10)	0.2538(31)	1.52(16)	4.0
OH6	0.3625(7)	0.3932(10)	0.8139(28)	1.33(15)	4.0
O1	0.2870(11)	0.1459(11)	0.2700(41)	2.87(22)	4.0
O2	0.3809(8)	0.3433(9)	0.3158(31)	2.08(17)	4.0
O3	0.4446(13)	0.1452(17)	0.0807(33)	3.11(30)	4.0
O4	0.4441(11)	0.1549(14)	0.5431(19)	2.43(17)	4.0
D1	0.0226(12)	0.1056(15)	0.3840(34)	2.51(24)	4.0
D2	0.0137(9)	0.1096(12)	0.8902(23)	1.24(18)	4.0
H3	0.1060(11)	0.4581(12)	0.4277(29)	1.39(21)	0.17(8)
D3	0.1060(11)	0.4581(12)	0.4277(29)	1.39(21)	3.83(8)
H4	0.1066(14)	0.4468(14)	0.9118(31)	2.11(27)	0.26(8)
D4	0.1066(14)	0.4468(14)	0.9118(31)	2.11(27)	3.74(8).
D5	0.1714(8)	0.5995(10)	0.2232(30)	2.25(16)	4.0
H6	0.3443(9)	0.3068(11)	0.8081(31)	1.57(19)	0.46(5)
D6	0.3443(9)	0.3068(11)	0.8081(31)	1.57(19)	3.54(5)

D/(H+D) = 0.96

Table S2. Interatomic distances (Å) and angles (°) for deuteriated brochantite from neutron data at 300 K.

Cu1-OH1	1.99(2)	OH1-Cu1-OH3	165(6)	OH3-Cu1-O2	94.5(10)
Cu1-OH3	2.03(2)	OH1-Cu1-OH5	78.0(10)	OH5-Cu1-OH6	171(10)
Cu1-OH5	1.93(2)	OH1-Cu1-OH6	93.8(10)	OH5-Cu1-O1	90.2(13)
Cu1-OH6	1.98(2)	OH1-Cu1-O1	82.2(9)	OH5-Cu1-O2	87.0(8)
Cu1-O1	2.36(2)	OH1-Cu1-O2	94.5(9)	OH6-Cu1-O1	92.1(10)
Cu1-O2	2.39(2)	OH3-Cu1-OH5	90.6(11)	OH6-Cu1-O2	90.3(11)
<Cu1-O>	2.11	OH3-Cu1-OH6	98.0(12)	O1-Cu1-O2	176(10)
		OH3-Cu1-O1	88.3(10)		
Cu2-OH2	2.03(2)	OH2-Cu2-OH4	170(9)	OH4-Cu2-O2	95.7(10)
Cu2-OH4	2.02(2)	OH2-Cu2-OH5	83.5(9)	OH5-Cu2-OH6	171(10)
Cu2-OH5	1.92(2)	OH2-Cu2-OH6	90.0(10)	OH5-Cu2-O1	93.2(14)
Cu2-OH6	1.97(2)	OH2-Cu2-O1	84.8(11)	OH5-Cu2-O2	87.2(9)
Cu2-O1	2.36(2)	OH2-Cu2-O2	93.6(9)	OH6-Cu2-O1	92.4(10)
Cu2-O2	2.39(2)	OH4-Cu2-OH5	92.6(11)	OH6-Cu2-O2	87.1(11)
<Cu2-O>	2.12	OH4-Cu2-OH6	94.8(10)	O1-Cu2-O2	178(10)
		OH4-Cu2-O1	86.0(10)		
Cu3-OH1	2.00(2)	OH1-Cu3-OH2	100.6(13)	OH2-Cu3-O3	93.2(11)
Cu3-OH2	1.97(2)	OH1-Cu3-OH3	78.9(7)	OH3-Cu3-OH4	97.2(11)
Cu3-OH3	2.06(2)	OH1-Cu3-OH4	172(10)	OH3-Cu3-O1	91.8(10)
Cu3-OH4	2.11(2)	OH1-Cu3-O1	80.4(9)	OH3-Cu3-O3	90.5(11)
Cu3-O1	2.43(2)	OH1-Cu3-O3	98.7(12)	OH4-Cu3-O1	93.2(10)
Cu3-O3	2.41(2)	OH2-Cu3-OH3	176(10)	OH4-Cu3-O3	87.9(10)
<Cu3-O>	2.16	OH2-Cu3-OH4	82.9(8)	O1-Cu3-O3	177(10)
		OH2-Cu3-O1	84.4(10)		
Cu4-OH1	1.95(2)	OH1-Cu4-OH2	98.2(12)	OH2-Cu4-O4	97.8(10)
Cu4-OH2	2.00(2)	OH1-Cu4-OH3	81.5(9)	OH3-Cu4-OH4	94.1(11)
Cu4-OH3	2.00(2)	OH1-Cu4-OH4	173(10)	OH3-Cu4-OH5	103.4(11)
Cu4-OH4	1.96(2)	OH1-Cu4-OH5	69.8(8)	OH3-Cu4-O4	84.7(10)
Cu4-OH5	2.33(1)	OH1-Cu4-O4	89.1(10)	OH4-Cu4-OH5	106.0(11)
Cu4-O4	2.42(2)	OH2-Cu4-OH3	177(10)	OH4-Cu4-O4	96.1(10)
<Cu4-O>	2.11	OH2-Cu4-OH4	85.9(9)	OH5-Cu4-O4	156(3)
		OH2-Cu4-OH5	74.2(7)		
Cu1-Cu2	2.96(2)	Cu3-Cu4	2.97(2)	Cu1-Cu2-Cu1	178(10)
Cu1-Cu2	3.07(2)	Cu3-Cu4	3.06(2)	Cu3-Cu4-Cu3	179(10)

Table S3. Atomic positions from neutron powder data at 1.4 K for deuteriated brochantite.

Atom	x/a	y/b	z/c	Mx (μ_B)	Occupancy
Cu1	0.289(1)	0.488(2)	0.522(4)	0.22(11)	4.0
Cu2	0.303(1)	0.495(1)	1.037(3)	0.22(11)	4.0
Cu3	0.126(1)	0.264(1)	0.186(4)	0.74(7)	4.0
Cu4	0.118(1)	0.253(2)	0.661(3)	0.74(7)	4.0
S	0.386(4)	0.184(4)	0.313(13)		4.0
OH1	0.099(2)	0.123(3)	0.409(5)		4.0
OH2	0.090(2)	0.119(3)	0.898(5)		4.0
OH3	0.178(2)	0.399(3)	0.471(5)		4.0
OH4	0.177(2)	0.383(3)	0.991(5)		4.0
OH5	0.246(2)	0.602(2)	0.234(4)		4.0
OH6	0.384(1)	0.396(2)	0.804(5)		4.0
O1	0.279(2)	0.134(2)	0.261(5)		4.0
O2	0.371(1)	0.343(2)	0.304(5)		4.0
O3	0.460(2)	0.146(2)	0.166(3)		4.0
O4	0.440(2)	0.153(2)	0.573(5)		4.0
H1	0.007(2)	0.095(2)	0.386(5)		0.05(8)
D1	0.007(2)	0.095(2)	0.386(5)		3.95(8)
D2	0.006(2)	0.136(2)	0.895(4)		4.0
D3	0.097(2)	0.454(3)	0.463(5)		4.0
H4	0.111(1)	0.442(3)	0.923(6)		0.17(8)
D4	0.111(1)	0.442(3)	0.923(6)		3.83(8).
D5	0.132(1)	0.603(1)	0.178(5)		4.0
H6	0.325(1)	0.296(2)	0.754(5)		0.30(6)
D6	0.325(1)	0.296(2)	0.754(7)		3.70(6)

Table S4. Atomic positions and magnetic moment of the copper atoms within the cell at 1.4K.

Atom	x/a	y/b	z/c	M_x (μ_B)
Cu11	0.289(1)	0.488(2)	0.522(4)	0.22(11)
Cu12	0.711	0.512	0.478	-0.22(11)
Cu13	0.211	0.988	0.478	0.22(11)
Cu14	0.789	0.012	0.522	-0.22(11)
Cu21	0.303(1)	0.495(1)	1.037(3)	0.22(11)
Cu22	0.697	0.505	-0.037	-0.22(11)
Cu23	0.197	0.995	-0.037	0.22(11)
Cu24	0.803	0.005	1.037	-0.22(11)
Cu31	0.126(1)	0.264(1)	0.186(4)	-0.74(7)
Cu32	0.874	0.736	0.814	0.74(7)
Cu33	0.374	0.764	0.814	-0.74(7)
Cu34	0.626	0.236	0.186	0.74(7)
Cu41	0.118(1)	0.253(2)	0.661(3)	-0.74(7)
Cu42	0.882	0.747	0.339	0.74(7)
Cu43	0.382	0.753	0.339	-0.74(7)
Cu44	0.618	0.247	0.661	0.74(7)