Electronic Supplementary Material (ESI) for Dalton Transactions

3*d*-Metal derivatives of the $[Cu^{I}(SO_3)_4]^{7-}$ ion; Structure and Magnetism

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Electronic Supplementary Information

Table S1. Hydrogen Bond Distances and Angles for $Na_5[(Cu^{II}(H_2O)Cu^{I}(SO_3)_4]\cdot 6H_2O$

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
O(13) --H(1) ..O(8)(I)	0.83(5)	2.08(5)	2.901(5)	173(5)
O(13) --H(2) ..O(7)(II)	0.82(4)	1.98(3)	2.777(5)	166(5)
O(14) --H(3) ..O(11)(I)	0.83(5)	1.90(4)	2.727(5)	175(5)
O(14) --H(4) ..O(17)(V)	0.81(3)	2.59(5)	2.911(6)	105(5)
O(14) --H(4) ..O(8)(III)	0.81(3)	2.11(3)	2.916(5)	168(5)
O(15) --H(5) ..O(18)(IV)	0.83(5)	1.98(5)	2.808(6)	174(4)
O(15) --H(6) ..O(7)(IV)	0.82(4)	1.91(4)	2.716(6)	167(5)
O(16) --H(7) ..O(7)	0.81(4)	2.00(4)	2.793(5)	165(5)
O(16) --H(8) ..O(18)(IV)	0.83(3)	2.23(4)	3.020(5)	160(5)
O(17) --H(9) ..O(19)	0.82(5)	1.94(5)	2.737(6)	167(5)
O(17) --H(10) ..O(8) (IV)	0.82(4)	2.20(3)	2.958(6)	153(5)
O(18) --H(11) ..O(17) (V)	0.82(2)	1.95(3)	2.765(6)	175(8)
O(18) --H(12) ..O(10) (VI)	0.82(3)	1.94(3)	2.743(6)	167(5)
O(19) --H(13) ..O(8) (I)	0.82(3)	2.08(4)	2.829(5)	151(4)
O(19) --H(14) ..O(15)(IV)	0.83(5)	1.97(6)	2.769(6)	161(6)

I x,1/2-y,1/2+z; II x,1+y, z; III x,-1/2-y,1/2+z; IV -x,1/2+y,1/2-z; V -x,-y,1-z; VI -x,-1/2+y,1/2-z

Table S2. Hydrogen Bond Distances and Angles for

$\{[Cu^{II}(H_2O)(bipy)]_4[Cu^{I}(SO_3)_4]\}NO_3\cdot H_2O$

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
O(1) --H(1O) ..O(3) (I)	0.87(3)	1.86(3)	2.708(6)	166(4)
O(1) --H(2O) ..O(3) (II)	0.88(5)	1.85(5)	2.728(5)	177(10)

I 1-x, 3/2-y, z; II 5/4-y, 1/4+x, -3/4-z

Table S3. Hydrogen Bond Distances and Angles for $Na_{12}\{[Cu^{I}(SO_3)_4]_2(Mn^{II})\}.8H_2O$.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
O(14) --H(141) ..O(5)	0.89(6)	2.35(7)	2.995(6)	129(6)
O(14) --H(141) ..O(1) (I)	0.89(6)	2.59(7)	3.134(6)	121(6)
O(14) --H(142) ..O(22)(II)	0.89(5)	1.80(5)	2.676(6)	168(6)
O(19) --H(191) ..O(18)	0.89(5)	2.02(6)	2.842(6)	153(7)
O(19) --H(192) ..O(23)(III)	0.89(4)	2.20(6)	2.972(6)	145(7)
O(19) --H(192) ..O(6)(IV)	0.89(4)	2.32(7)	2.892(6)	122(6)
O(20) --H(201) ..O(5)(V)	0.89(4)	1.97(4)	2.808(6)	155(5)
O(20) --H(202) ..O(19)	0.90(2)	2.49(6)	2.998(6)	117(5)
O(20) --H(202) ..O(1)(VI)	0.90(2)	2.15(3)	2.980(6)	153(6)
O(23) --H(231) ..O(3)(V)	0.82(6)	2.12(6)	2.906(6)	161(5)
O(23) --H(232) ..O(1)	0.83(6)	2.00(6)	2.816(6)	168(6)

I -x, 1-y, 2-z; II 1-x, 1-y, 2-z; III -1/2-x, -1/2+y, 3/2-z; IV -1/2+x, 3/2-y, -1/2+z; V 1/2-x, 1/2+y, 3/2-z; VI 1/2+x, 3/2-y, -1/2+z

Table S4. Hydrogen Bond Distances and Angles for

$Na_3(H_2O)_6[Fe^{II}(H_2O)_6]_2\{[Cu^{I}(SO_3)_4]_2[Fe^{III}(H_2O)]_3(O)\}.H_2O$

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
O(4) --H(41) ..O(7) (I)	0.86(7)	1.96(8)	2.807(7)	173(12)
O(4) --H(42) ..O(3) (II)	0.86(7)	1.98(7)	2.792(9)	158(8)
O(7) --H(71) ..O(3) (III)	0.85(5)	1.85(5)	2.683(8)	167(6)
O(7) --H(72) ..O(3)	0.86(2)	1.87(3)	2.729(6)	177(12)
O(10) --H(101) ..O(6) (IV)	0.86(6)	2.18(12)	2.852(10)	135(9)
O(12) --H(121) ..O(1) (V)	0.86(7)	1.90(7)	2.729(9)	163(8)
O(12) --H(122) ..O(2) (I)	0.86(7)	2.57(9)	3.213(7)	132(8)
O(12) --H(122) ..O(6) (VI)	0.86(7)	2.11(10)	2.879(8)	150(10)

I 1-x,1-y,-z; II 1-y,x-y,z; III 2-x,1-y,-z; IV =-y,x-y,z; V 1+y,1-x+y,-z; VI x-y,x,-z

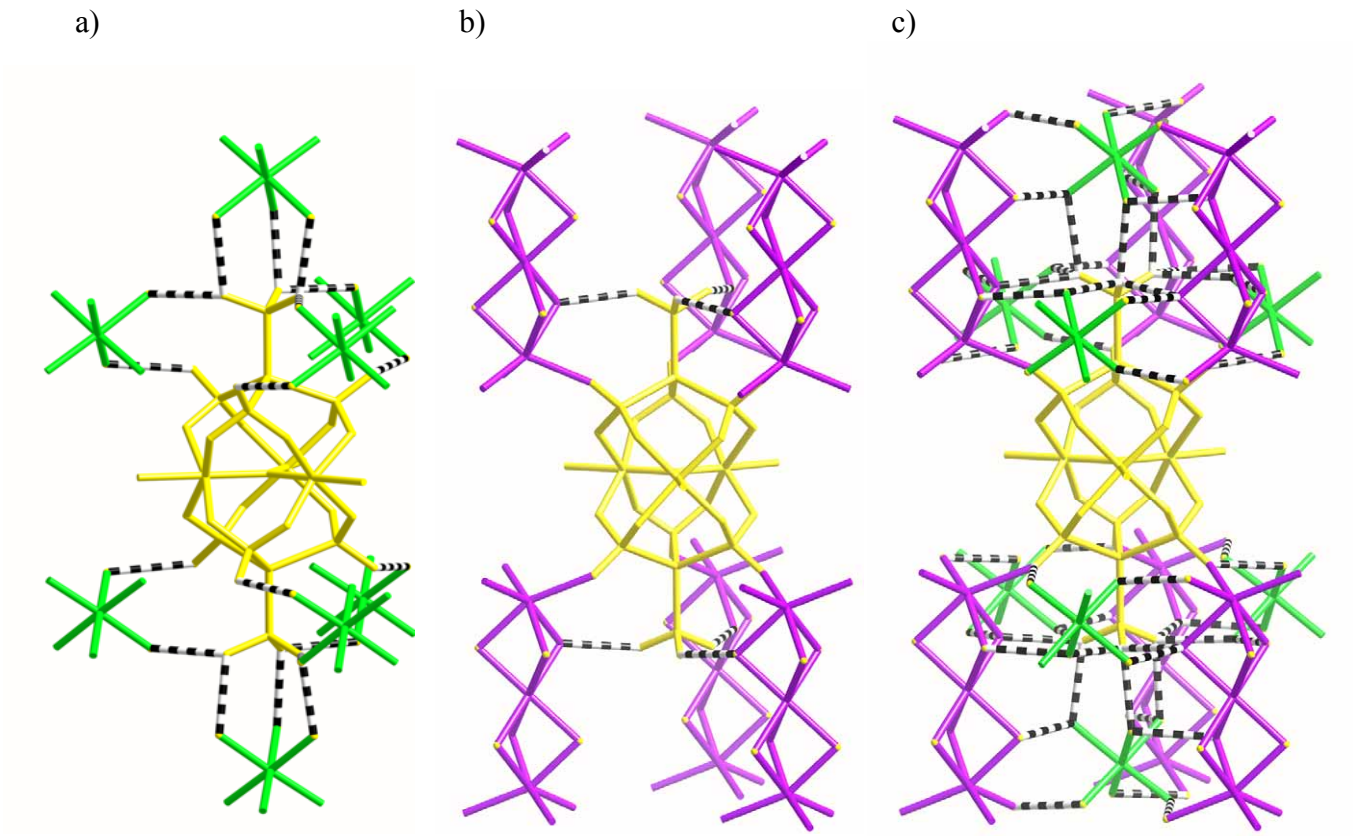

Figure S1. Stick representations of the cations surrounding the $\{[Cu^{I}(SO_3)_4]_2[Fe^{III}(H_2O)]_3(O)\}^{7-}$ complex anion in $Na_3(H_2O)_6[Fe^{II}(H_2O)_6]_2\{[Cu^{I}(SO_3)_4]_2[Fe^{III}(H_2O)]_3(O)\}.H_2O$. The complex anion is represented by yellow connections; the links from Na^+ ions to water molecules and sulfite oxygen atoms are indicated by pink connections; the green connections represent the octahedral $Fe(H_2O)_6^{2+}$ ions. Striped connections represent hydrogen bonds.

a) the complex anion and the $Fe(H_2O)_6^{2+}$ cations b) the complex anion and the $Na_3(H_2O)_6^{3+}$ cations (including connections to the sulfite oxygen atoms from Na^+ ions) c) the complex anion with both types of cation.

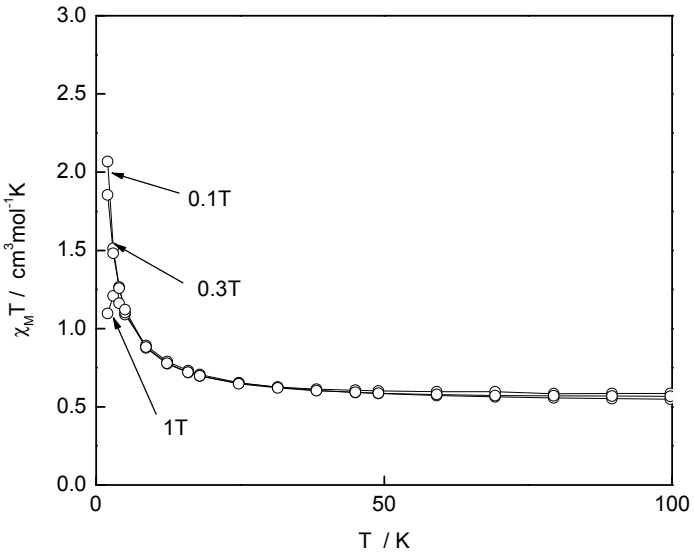

Figure S2 Plots of $\chi_M T$ vs temperature (2 – 100 K) for $Na_5[(Cu^{II}(H_2O)Cu^{I}(SO_3)_4]\cdot 6H_2O$ in DC fields of 1 T, 0.3 T and 0.1 T. The solid lines just join the points.