Journal Name

ARTICLE

Supporting Information for:

Kagome-type Isostructural 3D-Transition Metal Fluorosulfates with Spin 3/2 and 1: Synthesis, Structure and characterization

Subba R. Marri,[a] Jitendra Kumar,[a] Kitt Panyarat,[b] Satoshi Horike[c] and J. N. Behera[a]*

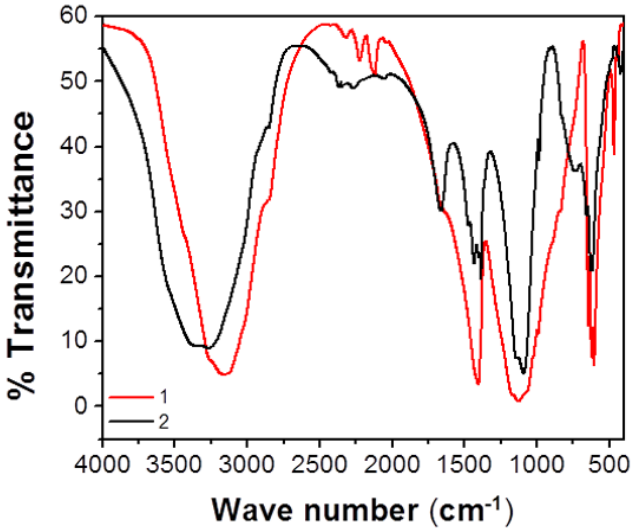


Fig. S1 FTIR spectra of $[H_3O][Co(SO_4)F]$, 1 and $[H_3O][Ni(SO_4)F]$, 2.

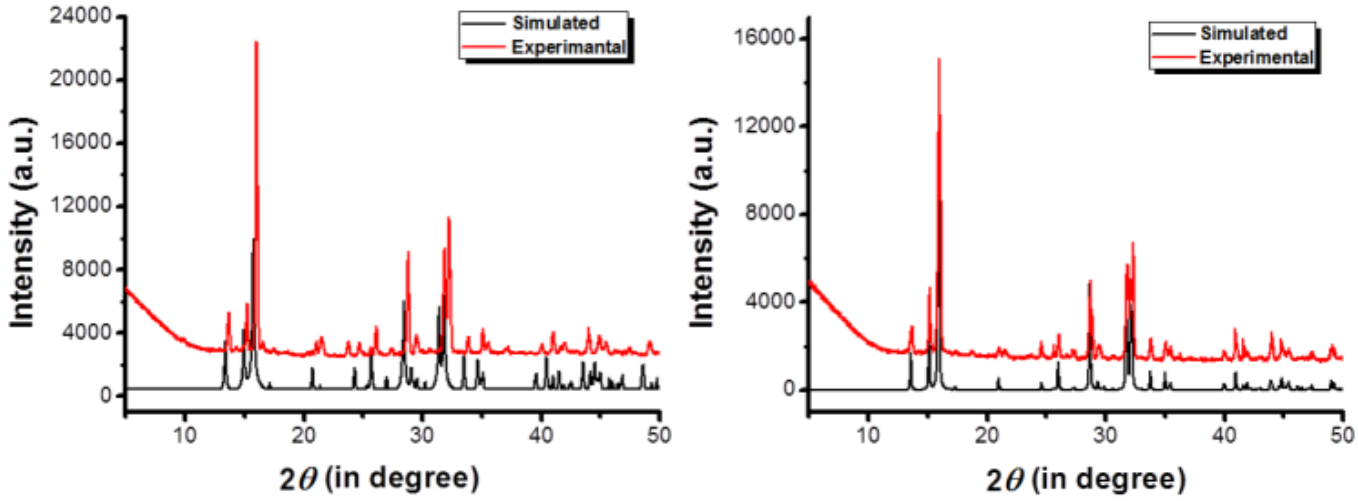
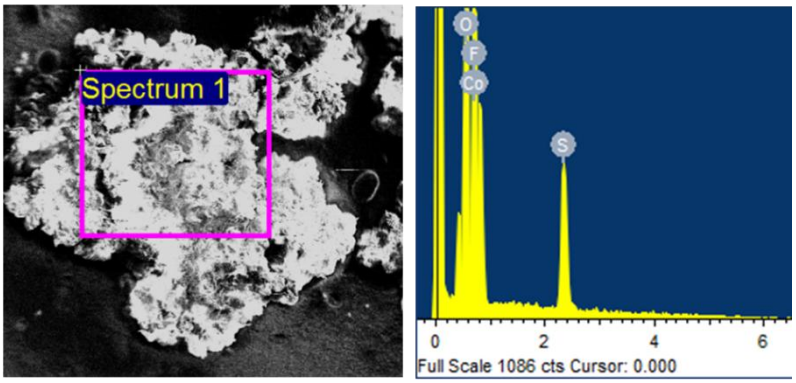


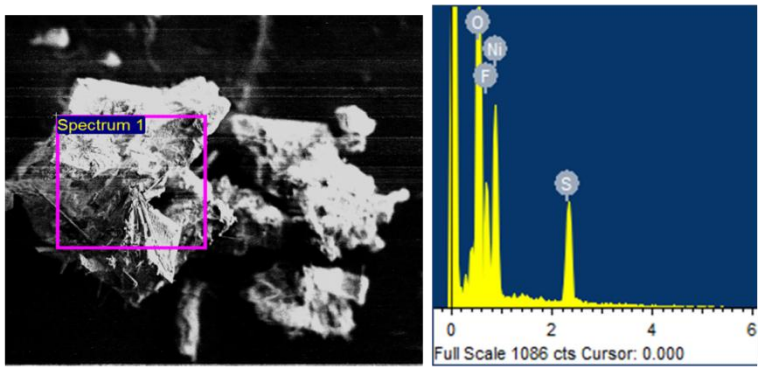
Fig.S2 PXRD pattern of $[H_3O][Co(SO_4)F]$, 1 and $[H_3O][Ni(SO_4)F]$, 2 showing the phase purity of as synthesized materials.

(a)



Element	Weight (%)	Atomic (%)
O K	36.97	37.08
F K	24.31	28.48
S K	18.40	16.77
Co L	20.32	17.67
Total	100.00	

(b)



Element	Weight (%)	Atomic (%)
O K	46.48	54.57
F K	16.60	24.15
S K	17.53	10.16
Ni L	18.89	11.12
Total	100.00	

Fig. S3. EDAX analysis of (a) of $[H_3O][Co(SO_4)F]$, 1, (b) $[H_3O][Ni(SO_4)F]$, 2

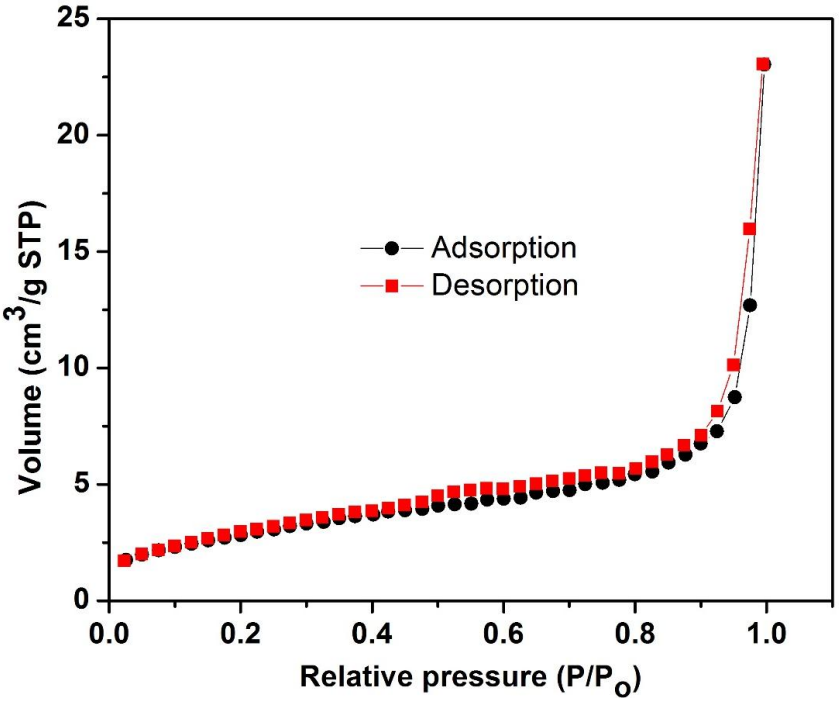


Fig. S5 N2 adsorption isotherm for Compound $[H_3O][Ni(SO_4)F]$, 2

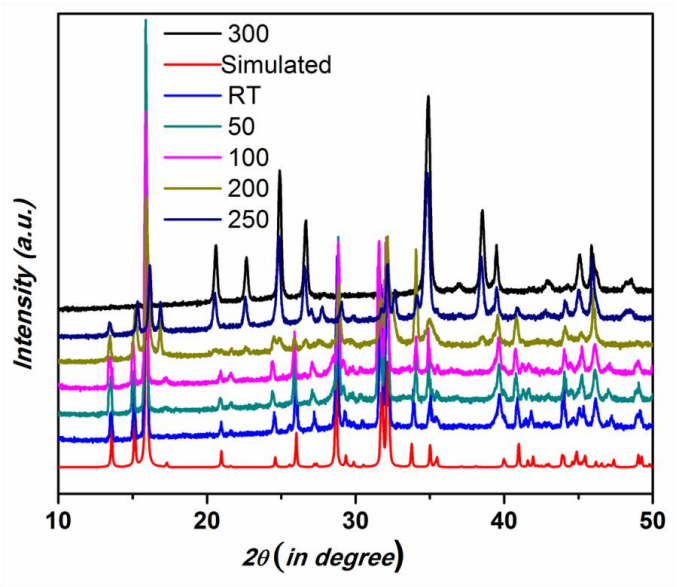


Fig. S6 Temperature dependent PXRD patterns $[H_3O][Ni(SO_4)F]$, 2

Table S1. Complete list of bond lengths [Å] and bond angles [º] for 1-2

$[H_3O][Co(SO_4)F]$, **1**					
Co1-F1	1.991(4)	Co2-F1	1.999(4)	S1-O1	1.472(4)
Co1-O1	2.056(4)	Co2-O4	2.073(4)	S1-O2	1.468(4)
Co1-O3	2.154(4)	Co2-O2	2.171(4)	S2-O3	1.467(4)
				S2-O4	1.479(4)
F1-Co1-F1i	180.0(2)	F1-Co2-F1ii	88.0(2)	O1-S1-O1iii	106.1(4)
F1-Co1-O1	91.06(17)	F1-Co2-O2	92.94(17)	O1-S1-O2	110.9(2)
F1-Co1-O1i	88.94(17)	F1-Co2-O2ii	91.23(18)	O1-S1-O2iii	110.3(3)
F1-Co1-O3	92.82(15)	F1-Co2-O4	89.21(17)	O2-S1-O2iii	108.4(4)
F1-Co1-O3i	87.18(15)	F1-Co2-O4ii	177.05(17)	O3-S2-O3iv	109.4(4)
O1-Co1-O1i	180.00(17)	O2-Co2-O2ii	174.2(2)	O3-S2-O4	111.1(2)
O1-Co1-O3	88.77(17)	O2-Co2-O4	88.13(17)	O3-S2-O4iv	109.0(3)
O1-Co1-O3i	91.23(17)	O2-Co2-O4ii	87.91(17)	O4-S2-O4iv	107.2(4)
O3-Co1-O3i	180.00(4)	O4-Co2-O4ii	93.6(3)	Co1-F1-Co2	126.2(2)
S1-O1-Co1	135.6(3)	S1-O2-Co2	136.3(3)	S2-O3-Co1	134.3(3)
S2-O4-Co2	136.4(3)				
$[H_3O][Ni(SO_4)F]$, **2**					
Ni1-F1	1.966(3)	Ni2-F1	1.968(4)	S1-O1	1.474(4)
Ni1-O3	2.051(4)	Ni2-O2	2.033(4)	S1-O2vi	1.470(4)
Ni1-O1	2.138(4)	Ni2-O4	2.110(4)	S2-O4	1.470(4)
				S2-O3vi	1.479(4)
F1-Ni1-F1v	89.3(2)	F1-Ni2-F1vi	180.0(2)	O1-S1-O1vii	108.4(3)
F1-Ni1-O1	92.88(16)	F1-Ni2-O2	89.01(16)	O1-S1-O2vi	111.1(2)
F1-Ni1-O1v	91.16(17)	F1-Ni2-O2vi	90.99(16)	O1-S1-O2viii	110.2(2)
F1-Ni1-O3	88.93(16)	F1-Ni2-O4	87.41(15)	O2vi-S1-O2viii	105.9(4)
F1-Ni1-O3v	178.07(16)	F1-Ni2-O4vi	92.59(15)	O4-S2-O4ix	108.9(3)
O1-Ni1-O1v	174.3(2)	O2-Ni2-O2vi	180.00(15)	O4-S2-O3vi	111.0(2)
O1-Ni1-O3	88.24(17)	O2-Ni2-O4	88.98(16)	O4-S2-O3x	109.1(2)
O1-Ni1-O3v	87.84(16)	O2-Ni2-O4vi	91.02(16)	O3vi-S2-O3x	107.7(4)
O3-Ni1-O3v	92.9(2)	O4-Ni2-O4vi	180.0(2)	Ni1-F1-Ni2	127.27(19)
S1-O1-Ni1	136.1(3)	S1vi-O2-Ni2	134.8(3)	S2vi-O3-Ni1	136.0(3)
S2-O4-Ni2	133.8(3)				

Symmetry elements (i) -x+1, -y, -z; (ii) x, -y+1/2, -z+1/2; (iii) x, -y+1/2, -z-1/2; (iv) -x+3/2, -y, z; (v) x, -y+1/2, -z+1/2; (vi) -x+1, -y, -z; (vii) x, -y+1/2, -z-1/2; (viii) -x+1, y+1/2, z-1/2; (ix) -x+1/2, -y, z; (x) x-1/2, y, -z.

Table S2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2 x 103) for 1-2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)		x	y	z	U(eq)
$[H_3O][Co(SO_4)F]$, **1**									
Co1	5000	0	0	11(1)	O1	5030(3)	1430(4)	-2081(7)	17(1)
Co2	6269(1)	2500	2500	10(1)	O2	6352(3)	2770(4)	-752(7)	17(1)
S1	5701(1)	2500	-2500	12(1)	O4	7345(3)	1097(4)	2202(7)	19(1)
S2	7500	0	874(3)	11(1)	O3	6610(3)	-221(4)	-409(6)	15(1)
F1	5178(3)	1209(4)	2266(7)	23(1)	O1Wa	3552(11)	1836(13)	4420(20)	41(4)
					O1Wb	3680(10)	716(14)	4650(20)	45(4)
$[H_3O][Ni(SO_4)F]$, **2**									
Ni1	6267(1)	2500	2500	9(1)	O1	6348(3)	2778(4)	-730(6)	15(1)
Ni2	5000	0	0	10(1)	O2	4994(3)	-1425(4)	2077(6)	14(1)
S1	5686(1)	2500	-2500	10(1)	O3	7353(3)	1112(4)	2197(6)	17(1)
S2	2500	0	-865(3)	9(1)	O4	3403(3)	207(4)	441(6)	14(1)
F1	5192(3)	1207(3)	2253(6)	19(1)	O1Wa	3535(8)	1879(9)	4378(18)	37(4)
					O1Wb	3663(8)	693(10)	4654(17)	40(4)

Table S3. Anisotropic displacement parameters (Å2 x 103) for 1-2.The anisotropic displacement factor exponent takes the form: -2 π2[h2 a*2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12		U11	U22	U33	U23	U13	U12
$[H_3O][Co(SO_4)F]$, **1**													
Co1	12(1)	9(1)	13(1)	1(1)	-1(1)	-2(1)	O1	20(2)	17(2)	14(2)	7(2)	-4(2)	-7(2)
Co2	9(1)	10(1)	11(1)	-1(1)	0	0	O2	18(2)	21(2)	12(2)	0(2)	-2(2)	-4(2)
S1	13(1)	11(1)	11(1)	1(1)	0	0	O4	21(2)	17(2)	19(2)	-7(2)	-4(2)	9(2)
S2	9(1)	11(1)	11(1)	0	0	2(1)	O3	9(2)	21(2)	17(2)	-4(2)	-3(1)	0(2)
F1	19(2)	20(2)	29(2)	-8(2)	6(2)	-9(1)	O1Wa	39(7)	43(8)	42(8)	-2(6)	9(6)	-16(6)
							O1Wb	37(7)	60(10)	38(7)	-6(6)	9(6)	-7(6)
$[H_3O][Ni(SO_4)F]$, **2**													
Ni1	9(1)	9(1)	10(1)	-1(1)	0	0	O1	16(2)	17(2)	10(2)	0(2)	-1(2)	-4(2)
Ni2	10(1)	7(1)	12(1)	1(1)	-1(1)	-1(1)	O2	18(2)	14(2)	11(2)	7(2)	-4(2)	-7(2)
S1	10(1)	9(1)	10(1)	1(1)	0	0	O3	17(2)	17(2)	16(2)	-7(2)	-2(2)	7(2)
S2	9(1)	10(1)	9(1)	0	0	2(1)	O4	10(2)	17(2)	14(2)	-2(2)	-3(1)	-1(2)
F1	17(2)	15(2)	23(2)	-4(1)	4(2)	-6(1)	O1Wa	37(7)	31(6)	42(7)	3(5)	7(5)	-8(5)
							O1Wb	36(7)	54(8)	32(7)	-3(5)	9(5)	-11(6)

Table S4. Performance indicators for water-mediated proton-conductor

Compound	Proton conductivity (S Cm^{-1})	Activation energy (eV)	Temperature (^{o}C) and Relative humidity (%)	Reference
$[Mo_5P_2O_{23}][Cu(phen)(H_2O)]_3 \cdot 5\ H_2O$ phen= phenanthroline	2.2×10^{-5}	0.23	28 °C, 98 % RH	1
$(NH_4)_2(adp)[Zn_2(ox)_3] \cdot 3\ H_2O$ adp=adipate	8×10^{-3}	0.63	25 °C, 98 % RH	2
$V[Cr(CN)_6]_{2/3}\ nH_2O$	2.6×10^{-3}	0.1	50 °C, 100 % RH	3
$[Eu_L(H_2O)_3] \cdot 2H_2O$ (L = N-phenyl-N′-phenyl bicyclo [2,2,2]-oct-7- ene-2,3,5,6-tetracarboxdiimide tetracarboxylic acid)	1.6×10^{-5}	0.91	75 °C, 97% RH	4
$Eu_2(CO_3)(ox)_2(H2O)_2] \cdot 4H_2O$ (ox = oxalate)	2.08×10^{-3}	0.47 (25−90 °C) 0.26 (100−150 °C)	150 °C	5
$K_2(H_2adp)[Zn_2(ox)_3] \cdot 3H_2O$	1.2×10^{-4}	0.45	98% RH	6
$Cu_3[Co(CN)_6]2 \cdot nH_2O$	2.57×10^{-5}	1.21	27 °C ,100 % RH	7
UiO−66	6.93×10^{-3}	0.22	65 °C ,95 % RH	8
$[Zn(l\text{-}L_{cl})(Cl)] \cdot H2O$ L_{Cl}=3-methyl-2-(pyridin-4-ylmethylamino)- butanoic acid	4.45×10^{-5}	0.35	30 °C, 98 % RH	9
HKUST-1-H_2O	1.5×10^{-5}	n/a	RT, methanol vapor	10
CMOF-3	3.5×10−5	0.17	RT, 98 % RH	11

References:

[1] C. Dey, T. Kundu and R. Banerjee, *Chem. Commun*., 2012, **48**, 266.
[2] M. Sadakiyo, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc*., 2009, **131**, 9906.
[3] S.-i. Ohkoshi, K. Nakagawa, K. Tomono, K. Imoto, Y. Tsunobuchi and H. Tokoro, *J. Am. Chem. Soc*., 2010, **132**, 6620.
[4] M. Zhu, Z.-M. Hao, X.-Z. Song, X. Meng, S.-N. Zhao, S.-Y. Song and H.-J. Zhang, *Chem. Commun*., 2014, **50**, 1912.
[5] Q. Tang, Y. Liu, S. Liu, D. He, J. Miao, X. Wang, G. Yang, Z. Shi and Z. Zheng, *J. Am. Chem. Soc*., 2014, **136**, 12444.
[6] M. Sadakiyo, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc*., 2014, **136**, 13166.
[7] C. Xiao, Z. Chu, X.-M. Ren, T.-Y. Chen and W. Jin, *Chem. Commun*., 2015, **51**, 7947.
[8] J. M. Taylor, S. Dekura, R. Ikeda and H. Kitagawa, *Chem. Mater*., 2015, **27**, 2286.
[9] S. C. Sahoo, T. Kundu and R. Banerjee, *J. Am. Chem. Soc*., 2011, **133**, 17950.
[10] N. C. Jeong, B. Samanta, C. Y. Lee, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc*., 2011, **134**, 51.
[11] J. M. Taylor, R. K. Mah, I. L. Moudrakovski, C. I. Ratcliffe, R. Vaidhyanathan and G. K. Shimizu, *J. Am. Chem. Soc.*, 2010, **132**, 14055.