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Supporting Information

Organic–inorganic hybrid Three-Dimensional Metal Sulfite-Oxalate with honeycomb-like structures

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The bond valence sum (BVS) calculated from the formula as given below

$S = \exp[(R_o-R)/B]$

$V = \Sigma S$

Where V is the oxidation state of cation and S is bond valence

For $[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$, **1**

Where B = 0.37, R_o for Mn-O = 1.790 Å and R is Mn-O bond length

S1= exp[(1.790-2.218)/0.37] = 0.3145

S2= exp[(1.790-2.1797)/0.37] = 0.3216

S3= exp[(1.790-2.1535)/0.37] = 0.3743

S4= exp[(1.790-2.2129)/0.37] = 0.3188

S4= exp[(1.790-2.2299)/0.37] = 0.3045

S4= exp[(1.790-2.2183)/0.37] = 0.3142

And $V = \Sigma S$

V = S1+S2+S3+S4+S5+S6 = 1.9479

For $[NaEu(C_2O_4)(SO_3)(H_2O)_3]$, **2**

Where B = 0.37, R_o for Eu-O = 2.074 Å and R is Eu-O bond length

S1= exp[(2.074-2.4269)/0.37] = 0.3852

S2= exp[(2.074-2.5210)/0.37] = 0.2987

S3= exp[(2.074-2.3655)/0.37] = 0.4548

S4= exp[(2.074-2.3559)/0.37] = 0.4667

S5= exp[(2.074-2.4361)/0.37] = 0.3758

S6= exp[(2.074-2.4662/0.37] = 0.3464

S7= exp[(2.074-2.4980)/0.37] = 0.3179

S8= exp[(2.074-2.4879)/0.37] = 0.3267

S9= exp[(2.074-2.6458/0.37] = 0.2132

And $V = \Sigma S$

V = S1+S2+S3+S4+S5+S6+S7+S8+S9 = 3.1854

(1) I. D. Brown and D. Altermatt, *Acta Crystallographica Section B*, 1985, **41**, 244-247.

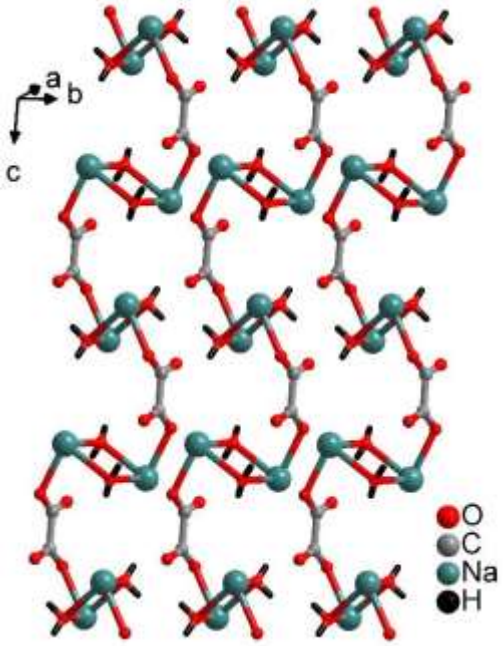

Fig. S1 Na oxalate chain along *c*-axis in $[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$, **1**

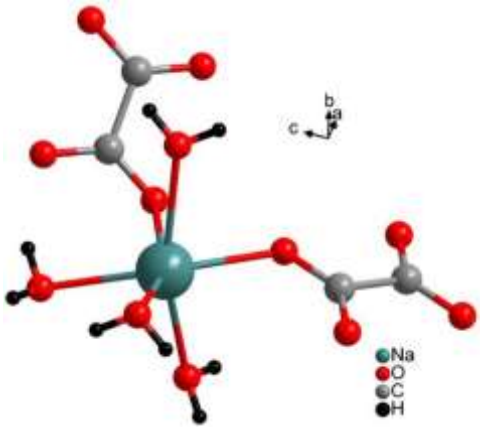

Fig. S2 Distorted octahedral geometry of Na atom in $[NaEu(C_2O_4)(SO_3)(H_2O)_3]$, **2**

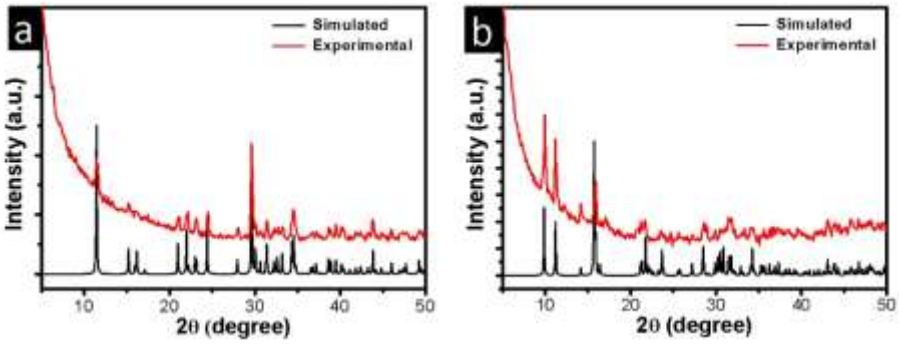

Fig. S3 PXRD pattern for (a) $[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$**, 1** and (b) $[NaEu(C_2O_4)(SO_3)(H_2O)_3]$, **2**

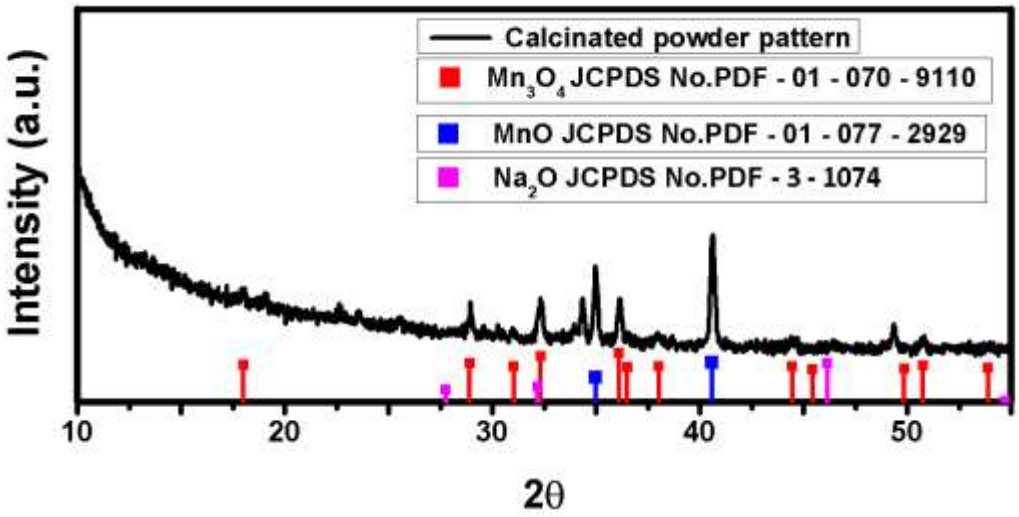

Fig. S4 Post-Calcinated PXRD pattern of $[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$**, 1**

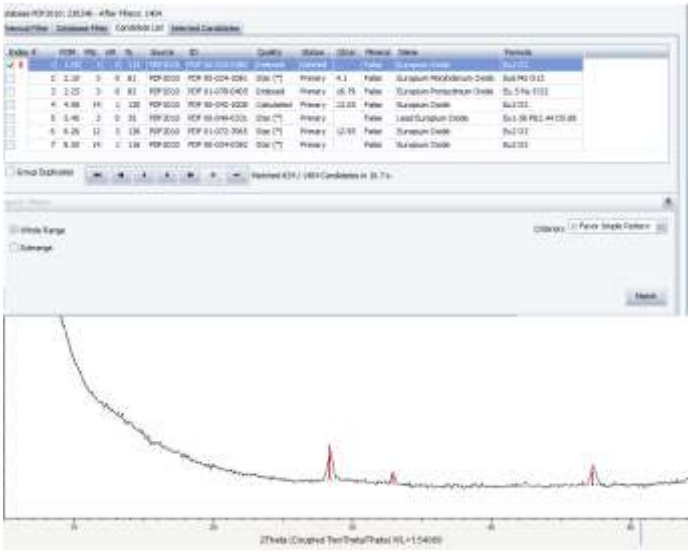

Fig. S5 Post-Calcinated PXRD pattern of [$NaEu(C_2O_4)(SO_3)(H_2O)_3$], **2**

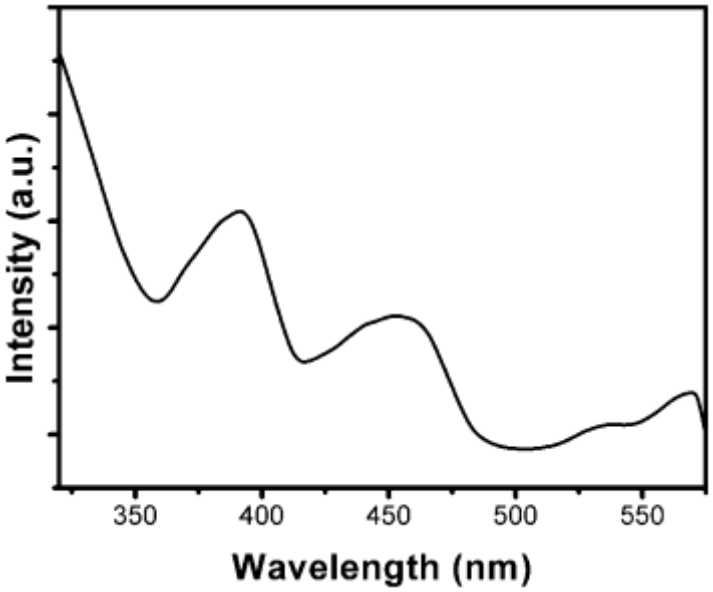

Fig. S6 Excitation spectrum of [$NaEu(C_2O_4)(SO_3)(H_2O)_3$], **2**

Table S1. Hydrogen bonding table for complexes **1**-**2**.[#]

D–H···A	Symmetry of A	D–H	H···A	D–A	∠D–H···A
$[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$ (1)					
O1W–H1W1···O3	-x,y,1/2-z	0.82(4)	2.02(4)	2.829(2)	168(3)
O1W–H2W1···O2	-x,2-y,-z	0.81(2)	2.15(3)	2.856(2)	146(3)
$[NaEu(C_2O_4)(SO_3)(H_2O)_3]$ (2)					
O1W–H1W1···O7	1-x,1-y,1-z	0.81(3)	1.96(3)	2.738(2)	162(3)
O2W–H1W2···O1		0.81(3)	2.07(3)	2.813(2)	153(3)
O3W–H1W3···O1W	1-x,1-y,-z	0.82(3)	2.01(3)	2.795(2)	158(3)
O1W–H2W1···O3		0.82(4)	2.07(4)	2.856(3)	159(3)
O2W–H2W2···O5	x,1+y,z	0.82(2)	1.980(18)	2.741(2)	155(3)
O3W–H2W3···O1	-1+x,y,z	0.81(3)	2.30(3)	3.107(3)	170(4)

[#]Where 'D' is donor and 'A' is acceptor, the bond lengths are in (Å) and angles are in (°).

Table S2. Complete list of bond lengths [Å] and bond angles [◦] for complex **1-2**[#]

$[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$ (1)

Mn1-O1	2.2181(13)	Na1-O2^{e}	2.3589(15)	S1-O1	1.5471(12)
Mn1-O1^{b}	2.1797(12)	Na1-O3^{e}	2.5146(15)	S1-O2	1.5225(12)
Mn1-O2^{a}	2.1535(12)	Na1-O4	2.3410(16)	S1-O3	1.5315(13)
Mn1-O3^{c}	2.2129(12)	Na1-O5^{g}	2.9900(19)	O4-C1	1.2500(2)
Mn1-O4	2.2299(13)	Na1-O1W	2.3171(18)	O5-C1	1.2560(2)
Mn1-O5^{d}	2.2183(14)	Na1-O1W^{f}	2.507(2)	C1-C1^{d}	1.5440(3)
O1^{b}-Mn1-O1	74.93(5)	O2^{e}-Na1-O5^{g}	111.24(5)	O2-S1-Na1^{h}	48.83(5)
O2^{a}-Mn1-O1	104.82(5)	O1W^{f}-Na1-O5^{g}	158.62(6)	O3-S1-Na1^{h}	54.80(5)
O2^{a}-Mn1-O1^{b}	94.19(5)	O3^{e}-Na1-O5^{g}	65.26(4)	O1-S1-Na1^{h}	110.90(5)
O3^{c}-Mn1-O1	93.78(5)	O1W-Na1-S1^{e}	129.22(5)	S1-O1-Mn1^{b}	134.29(7)
O2^{a}-Mn1-O3^{c}	84.48(5)	O4-Na1-S1^{e}	131.41(5)	S1-O1-Mn1	117.27(7)
O1^{b}-Mn1-O3^{c}	167.95(5)	O2^{e}-Na1-S1^{e}	29.07(3)	Mn1^{b}-O1-Mn1	105.07(5)
O2^{a}-Mn1-O5^{d}	94.14(5)	O1W^{f}-Na1-S1^{e}	112.17(5)	S1-O2-Mn1^{i}	124.38(7)
O1^{b}-Mn1-O5^{d}	107.00(5)	O3^{e}-Na1-S1^{e}	29.85(3)	S1-O2-Na1^{h}	102.10(7)
O3^{c}-Mn1-O5^{d}	85.05(5)	O5^{g}-Na1-S1^{e}	89.12(4)	Mn1^{i}-O2-Na1^{h}	112.36(6)
O1-Mn1-O5^{d}	160.82(5)	O1W-Na1-C1	78.07(6)	S1-O3-Mn1^{c}	114.89(7)
O2^{a}-Mn1-O4	167.36(5)	O4-Na1-C1	20.70(4)	S1-O3-Na1^{h}	95.36(6)
O1^{b}-Mn1-O4	93.45(5)	O2^{e}-Na1-C1	132.11(6)	Mn1^{c}-O3-Na1^{h}	107.46(5)
O3^{c}-Mn1-O4	90.10(5)	O1W^{f}-Na1-C1	75.37(5)	C1-O4-Mn1	115.67(11)
O1-Mn1-O4	86.89(5)	O3^{e}-Na1-C1	148.95(6)	C1-O4-Na1	117.87(11)
O5^{d}-Mn1-O4	73.97(5)	O5^{g}-Na1-C1	84.87(5)	Mn1-O4-Na1	120.93(6)
O1W-Na1-O4	98.46(6)	S1^{e}-Na1-C1	152.10(5)	C1-O5-Mn1^{d}	116.05(11)
O1W-Na1-O2^{e}	142.78(7)	O1W-Na1-Na1^{f}	41.02(5)	C1-O5-Na1^{g}	103.98(12)
O4-Na1-O2^{e}	114.38(6)	O4-Na1-Na1^{f}	90.46(5)	Mn1^{d}-O5-Na1^{g}	93.02(5)
O1W-Na1-O1W^{f}	78.37(7)	O2^{e}-Na1-Na1^{f}	118.34(6)	Na1-O1W-Na1^{f}	101.63(6)
O4-Na1-O1W^{f}	82.87(6)	O1W^{f}-Na1-Na1^{f}	37.35(4)	O4-C1-O5	126.26(16)
O2^{e}-Na1-O1W^{f}	88.41(6)	O3^{e}-Na1-Na1^{f}	132.42(5)	O4-C1-C1^{d}	117.01(19)
O1W-Na1-O3^{e}	108.62(6)	O5^{g}-Na1-Na1^{f}	128.44(5)	O5-C1-C1^{d}	116.72(19)
O4-Na1-O3^{e}	136.07(6)	S1^{e}-Na1-Na1^{f}	130.13(4)	O4-C1-Na1	41.44(8)
O2^{e}-Na1-O3^{e}	58.88(4)	C1-Na1-Na1^{f}	72.71(4)	O5-C1-Na1	89.38(10)
O1W^{f}-Na1-O3^{e}	135.36(6)	O2-S1-O3	103.55(7)	C1^{d}-C1-Na1	146.99(12)
O1W-Na1-O5^{g}	89.79(6)	O2-S1-O1	104.77(7)		
O4-Na1-O5^{g}	81.34(5)	O3-S1-O1	103.62(7)		

$[NaEu(C_2O_4)(SO_3)(H_2O)_3]$ (2)

Eu1-O1	2.4269(16)	Eu1-O7^{m}	2.4879(16)	S1-O2	1.5549(16)
Eu1-O2	2.5210(15)	Na1-O2W	2.395(2)	S1-O3	1.5176(17)
Eu1-O2^{k}	2.3655(15)	Na1-O2W^{n}	2.323(2)	O4-C1	1.257(3)
Eu1-O3^{j}	2.3559(16)	Na1-O3W	2.478(2)	O5-C1	1.251(3)
Eu1-O4	2.4361(16)	Na1-O3W^{o}	2.3743(19)	O6-C2	1.251(3)
Eu1-O5^{l}	2.4662(17)	Na1-O4	2.3933(17)	O7-C2	1.259(3)
Eu1-O6	2.4980(15)	Na1-O6	2.3065(18)	C1-C1^{l}	1.538(4)
Eu1-O1W	2.6458(16)	S1-O1	1.5349(16)	C2-C2^{m}	1.541(4)
O3^{j}-Eu1-O2^{k}	81.26(5)	O5^{l}-Eu1-C1	46.44(5)	O3W-Na1-Na1^{n}	148.86(7)
O3^{j}-Eu1-O1	147.93(5)	O7^{m}-Eu1-C1	148.70(5)	C1-Na1-Na1^{n}	89.53(5)
O2^{k}-Eu1-O1	122.36(5)	O6-Eu1-C1	84.26(5)	O6-Na1-Na1^{o}	106.08(6)
O3^{j}-Eu1-O4	102.07(6)	O2-Eu1-C1	131.19(5)	O2W^{n}-Na1-Na1^{o}	96.16(6)
O2^{k}-Eu1-O4	139.44(5)	O1W-Eu1-C1	67.98(5)	O3W^{o}-Na1-Na1^{o}	45.74(5)
O1-Eu1-O4	74.69(5)	S1-Eu1-C1	111.88(4)	O4-Na1-Na1^{o}	121.62(6)
O3^{j}-Eu1-O5^{l}	69.19(6)	O3^{j}-Eu1-Na1	86.79(4)	O2W-Na1-Na1^{o}	149.63(7)
O2^{k}-Eu1-O5^{l}	78.47(5)	O2^{k}-Eu1-Na1	165.71(4)	O3W-Na1-Na1^{o}	43.33(4)
O1-Eu1-O5^{l}	132.21(6)	O1-Eu1-Na1	71.73(4)	C1-Na1-Na1^{o}	103.06(6)
O4-Eu1-O5^{l}	65.74(5)	O4-Eu1-Na1	36.44(4)	Na1^{n}-Na1-Na1^{o}	133.23(6)
O3^{j}-Eu1-O7^{m}	78.95(6)	O5^{l}-Eu1-Na1	90.00(4)	O6-Na1-Eu1	38.14(4)
O2^{k}-Eu1-O7^{m}	87.10(5)	O7^{m}-Eu1-Na1	98.32(4)	O2W^{n}-Na1-Eu1	119.21(5)
O1-Eu1-O7^{m}	80.89(6)	O6-Eu1-Na1	34.76(4)	O3W^{o}-Na1-Eu1	157.27(6)

O4-Eu1-O7^{m}	133.42(5)	O2-Eu1-Na1	128.35(4)	O4-Na1-Eu1	37.20(4)
O5^{l}-Eu1-O7^{m}	146.55(5)	O1W-Eu1-Na1	106.81(4)	O2W-Na1-Eu1	82.35(5)
O3^{j}-Eu1-O6	73.66(5)	S1-Eu1-Na1	99.751(17)	O3W-Na1-Eu1	79.49(5)
O2^{k}-Eu1-O6	144.84(5)	C1-Eu1-Na1	50.76(4)	C1-Na1-Eu1	54.52(4)
O1-Eu1-O6	75.21(5)	O3-S1-O1	104.37(9)	Na1^{n}-Na1-Eu1	103.95(4)
O4-Eu1-O6	71.20(5)	O3-S1-O2	103.73(9)	Na1^{o}-Na1-Eu1	120.16(4)
O5^{l}-Eu1-O6	113.66(5)	O1-S1-O2	100.00(9)	S1-O1-Eu1	103.69(8)
O7^{m}-Eu1-O6	64.44(5)	O3-S1-Eu1	109.76(7)	S1-O2-Eu1^{k}	144.96(9)
O3^{j}-Eu1-O2	134.17(5)	O1-S1-Eu1	48.19(6)	S1-O2-Eu1	99.07(7)
O2^{k}-Eu1-O2	65.95(6)	O2-S1-Eu1	51.90(6)	Eu1^{k}-O2-Eu1	114.05(6)
O1-Eu1-O2	57.12(5)	O6-Na1-O2W^{n}	154.74(7)	S1-O3-Eu1^{p}	135.10(10)
O4-Eu1-O2	123.71(5)	O6-Na1-O3W^{o}	121.52(7)	C1-O4-Na1	112.73(13)
O5^{l}-Eu1-O2	128.85(5)	O2W^{n}-Na1-O3W^{o}	82.69(7)	C1-O4-Eu1	120.80(14)
O7^{m}-Eu1-O2	68.72(5)	O6-Na1-O4	75.33(6)	Na1-O4-Eu1	106.37(6)
O6-Eu1-O2	116.65(5)	O2W^{n}-Na1-O4	82.94(6)	C1-O5-Eu1^{l}	120.18(14)
O3^{j}-Eu1-O1W	136.11(6)	O3W^{o}-Na1-O4	159.26(8)	C2-O6-Na1	128.22(14)
O2^{k}-Eu1-O1W	77.18(5)	O6-Na1-O2W	78.44(6)	C2-O6-Eu1	120.80(13)
O1-Eu1-O1W	74.40(5)	O2W^{n}-Na1-O2W	88.48(7)	Na1-O6-Eu1	107.10(6)
O4-Eu1-O1W	72.90(5)	O3W^{o}-Na1-O2W	105.75(7)	C2-O7-Eu1^{m}	121.32(14)
O5^{l}-Eu1-O1W	69.30(5)	O4-Na1-O2W	88.71(6)	Na1^{n}-O2W-Na1	91.52(7)
O7^{m}-Eu1-O1W	136.56(5)	O6-Na1-O3W	83.44(7)	Na1^{o}-O3W-Na1	90.93(7)
O6-Eu1-O1W	137.71(5)	O2W^{n}-Na1-O3W	105.77(7)	O5-C1-O4	126.8(2)
O2-Eu1-O1W	67.88(5)	O3W^{o}-Na1-O3W	89.07(7)	O5-C1-C1^{l}	116.4(2)
O3^{j}-Eu1-S1	152.73(4)	O4-Na1-O3W	80.56(6)	O4-C1-C1^{l}	116.8(2)
O2^{k}-Eu1-S1	94.45(4)	O2W-Na1-O3W	160.81(7)	O5-C1-Na1	95.21(13)
O1-Eu1-S1	28.12(4)	O6-Na1-C1	91.23(6)	O4-C1-Na1	45.33(10)
O4-Eu1-S1	98.59(4)	O2W^{n}-Na1-C1	71.85(6)	C1^{l}-C1-Na1	132.60(19)
O5^{l}-Eu1-S1	136.61(4)	O3W^{o}-Na1-C1	137.54(7)	O5-C1-Eu1	166.60(16)
O7^{m}-Eu1-S1	73.93(4)	O4-Na1-C1	21.94(6)	O4-C1-Eu1	39.88(10)
O6-Eu1-S1	96.73(4)	O2W-Na1-C1	106.89(6)	C1^{l}-C1-Eu1	76.93(16)
O2-Eu1-S1	29.04(4)	O3W-Na1-C1	66.96(6)	Na1-C1-Eu1	74.72(5)
O1W-Eu1-S1	67.39(4)	O6-Na1-Na1^{n}	118.65(6)	O6-C2-O7	127.2(2)
O3^{j}-Eu1-C1	92.83(6)	O2W^{n}-Na1-Na1^{n}	45.09(5)	O6-C2-C2^{m}	116.8(2)
O2^{k}-Eu1-C1	121.77(5)	O3W^{o}-Na1-Na1^{n}	96.02(6)	O7-C2-C2^{m}	116.0(2)
O1-Eu1-C1	91.58(5)	O4-Na1-Na1^{n}	84.24(5)		
O4-Eu1-C1	19.33(5)	O2W-Na1-Na1^{n}	43.39(5)		

#Symmetry transformations used to generate equivalent atoms: (a) x,-y,z-1/2; (b) -x+1/2,-y+1/2,-z+1; (c) -x+1/2,-y-1/2,-z+1; (d) -x,y,-z+1/2; (e) -x+1/2,y+1/2,-z+3/2; (f) -x,-y+1,-z+1; (g) -x,-y,-z+1; (h) -x+1/2,y-1/2,-z+3/2; (i) x,-y,z+1/2; (j) x-1,y,z; (k) -x+1,-y+1,-z+1; (l) -x+1,-y+1,-z; (m) -x,-y+2,-z+1; (n) -x+1,-y+2,-z; (o)-x,-y+2,-z; (p) x+1,y,z

Table S3. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å×10^3) for **1-2** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	y	Z	U(eq)		x	Y	Z	U(eq)
$[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$ (1)									
Mn1	1862(1)	1035(1)	3633(1)	12(1)	O3	3368(1)	-2580(2)	6635(1)	16(1)
Na1	875(1)	3110(2)	5984(1)	31(1)	O4	739(1)	1351(2)	4115(1)	19(1)
S1	2567(1)	-1256(1)	6413(1)	11(1)	O5	-705(1)	1322(3)	3233(1)	24(1)
O1	2679(1)	759(2)	5733(1)	16(1)	O1W	-577(1)	3681(3)	5426(2)	26(1)
O2	2733(1)	-519(2)	7760(1)	15(1)	C1	11(1)	1327(3)	3178(2)	15(1)
$[NaEu(C_2O_4)(SO_3)(H_2O)_3]$ (2)									
Eu1	3687(1)	6287(1)	3406(1)	5(1)	O6	1111(3)	9213(2)	3127(2)	8(1)
S1	7304(1)	7326(1)	4541(1)	7(1)	O7	-1231(3)	11846(2)	4228(2)	9(1)
Na1	2415(2)	9638(1)	650(1)	11(1)	O1W	8196(3)	4194(2)	2222(2)	10(1)
O1	6115(3)	7978(2)	3338(2)	10(1)	O2W	4737(3)	10719(2)	1676(2)	13(1)
O2	6107(3)	6032(2)	5155(2)	8(1)	O3W	-94(3)	8054(2)	365(2)	14(1)
O3	9869(3)	6218(2)	3672(2)	11(1)	C1	5304(4)	5787(3)	-228(2)	7(1)
O4	5001(3)	6831(2)	811(2)	9(1)	C2	-30(4)	10302(3)	4231(2)	7(1)
O5	6023(3)	5902(2)	-1596(2)	9(1)					

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for complex **1-2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12		U11	U22	U33	U23	U13	U12
$[Na_2Mn_2(C_2O_4)(SO_3)_2(H_2O)_2]$(1)													
Mn1	13(1)	12(1)	11(1)	-1(1)	5(1)	0(1)	O3	20(1)	12(1)	19(1)	1(1)	12(1)	3(1)
Na1	22(1)	50(1)	19(1)	-7(1)	6(1)	-2(1)	O4	14(1)	28(1)	13(1)	-3(1)	4(1)	0(1)
S1	14(1)	10(1)	10(1)	0(1)	5(1)	-1(1)	O5	14(1)	44(1)	16(1)	-6(1)	8(1)	-3(1)
O1	23(1)	11(1)	11(1)	2(1)	6(1)	-2(1)	O1W	24(1)	33(1)	27(1)	-7(1)	15(1)	-8(1)
O2	20(1)	16(1)	12(1)	-1(1)	10(1)	0(1)	C1	15(1)	16(1)	13(1)	-2(1)	7(1)	0(1)
$[NaEu(C_2O_4)(SO_3)(H_2O)_3]$(2)													
Eu1	5(1)	5(1)	3(1)	0(1)	-1(1)	-2(1)	O6	10(1)	9(1)	5(1)	0(1)	-1(1)	-3(1)
S1	7(1)	7(1)	6(1)	1(1)	-2(1)	-3(1)	O7	10(1)	8(1)	7(1)	1(1)	-2(1)	-1(1)
Na1	13(1)	12(1)	7(1)	2(1)	-2(1)	-4(1)	O1W	12(1)	9(1)	9(1)	1(1)	-3(1)	-4(1)
O1	10(1)	10(1)	11(1)	4(1)	-5(1)	-4(1)	O2W	19(1)	10(1)	9(1)	2(1)	-2(1)	-6(1)
O2	8(1)	10(1)	8(1)	4(1)	-3(1)	-6(1)	O3W	16(1)	14(1)	10(1)	0(1)	-3(1)	-5(1)
O3	7(1)	11(1)	12(1)	0(1)	-1(1)	-3(1)	C1	5(1)	7(1)	7(1)	1(1)	-1(1)	-1(1)
O4	11(1)	8(1)	6(1)	0(1)	-2(1)	-3(1)	C2	6(1)	7(1)	8(1)	0(1)	-1(1)	-3(1)
O5	14(1)	10(1)	4(1)	-1(1)	-1(1)	-6(1)							

