Supporting Information

Stratified Sulfatometallates: Unlocking a New Dimension in Sulfatomolybdates

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Crystal Data and Structure Refinements

Table S1. *R*-factors of the structural refinements of $Na_2[MoO_2(SO_4)_2]$ distinguished between satellites and main reflections determined using single-crystal diffraction at T = 293 K

	$Na_2[MoO_2(SO_4)_2]$ Main reflections	$Na_2[MoO_2(SO_4)_2]$ Satellites
R_{int}	0.0508	0.1355
R_1 (all data)	0.0710	0.2413
wR_2	0.0997	0.2124

Table S2. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $Na_2[MoO_2(SO_4)_2]$at T = 293 K. Standard deviations are given in parentheses. For sodium cations Na6, Na7, Na8, Na10, Na11, Na12 and Na13, the isotropic displacement factor is given

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Mo1	4*e*		0.62710	0.09990	0.07070	0.02598(10)
Mo2	4*e*		0.37090	0.40190	0.07390	0.02589(10)
S1	4*e*		0.8706(1)	0.1494(1)	0.1428(1)	0.0259(3)
S2	4*e*		0.1271(1)	0.3510(1)	0.1380(1)	0.0259(3)
S3	4*e*		0.6231(1)	0.4135(1)	0.1043(1)	0.0279(3)
S4	4*e*		0.3751(1)	0.0851(1)	0.1019(1)	0.0279(3)
Na1	4*e*	0.557(11)	0.0022(6)	0.7505(5)	0.1291(8)	0.068(4)
Na2	4*e*	0.570(9)	0.2411(6)	0.7177(3)	0.1754(8)	0.052(3)
Na3	4*e*	0.729(9)	0.7570(2)	0.7842(2)	0.1800(3)	0.0421(11)
O41	4*e*		0.4734(2)	0.1006(2)	0.9967(4)	0.0312(9)
O11	4*e*		0.8578(3)	0.2274(2)	0.0668(4)	0.0448(11)
O21	4*e*		0.1419(3)	0.2740(2)	0.0583(4)	0.0416(11)
O31	4*e*		0.4759(2)	0.5997(2)	0.0025(4)	0.0333(9)
Na4	4*e*	0.421(10)	0.0589(10)	0.0161(9)	0.9932(18)	0.018(3)
O42	4*e*		0.3595(2)	0.9979(2)	0.1096(4)	0.0334(9)
Om21	4*e*		0.3885(3)	0.4670(2)	0.2355(4)	0.0391(10)
Om11	4*e*		0.6101(2)	0.0355(2)	0.2347(4)	0.0386(10)
O22	4*e*		0.2111(2)	0.4087(2)	0.0719(3)	0.0276(8)
O32	4*e*		0.6428(2)	0.4999(2)	0.1102(4)	0.0362(10)
Om12	4*e*		0.6241(2)	0.1902(2)	0.1677(4)	0.0366(10)
Om22	4*e*		0.3739(2)	0.3128(2)	0.1743(4)	0.0358(10)
O33	4*e*		0.7082(3)	0.3721(3)	0.0227(5)	0.0596(14)
O12	4*e*		0.7884(2)	0.0930(2)	0.0695(4)	0.0300(9)
O13	4*e*		0.6528(2)	0.6571(2)	0.1711(3)	0.0329(9)
O23	4*e*		0.3527(2)	0.8400(2)	0.1750(3)	0.0332(9)
O14	4*e*		0.9704(2)	0.1114(2)	0.1110(4)	0.0413(11)
O43	4*e*		0.2883(3)	0.1211(2)	0.0146(5)	0.0540(13)
O24	4*e*		0.0280(2)	0.3886(2)	0.1048(4)	0.0465(12)
O34	4*e*		0.6045(3)	0.3849(2)	0.2755(4)	0.0490(13)
Na5	4*e*	0.428(11)	0.9278(12)	0.4814(8)	0.9909(14)	0.027(4)
O44	4*e*		0.1076(3)	0.6147(2)	0.2259(5)	0.0539(13)

Na6	4*e*	0.402	0.3561(9)	0.6495(8)	0.3063(19)	0.0433(14)
Na7	4*e*	0.155	0.6353(19)	0.8436(16)	0.321(5)	0.079(7)
Na8	4*e*	0.237	0.8737(6)	0.4548(5)	1.0159(10)	0.0149(17)
Na9	4*e*	0.135	0.1168(16)	0.0334(13)	0.980(3)	-0.001(5)
Na10	2*c*	0.076	1	1/2	1	0.020(8)
Na11	4*e*	0.095	0.635(4)	0.794(3)	0.211(5)	0.052(7)
Na12	4*e*	0.111	0.1263(17)	0.080(2)	1.032(3)	0.007(4)
Na13	4*e*	0.134	0.6295(16)	0.8792(16)	0.370(4)	0.031(4)

Table S3. Anisotropic displacement parameters U_{ij} / Å^2 in $Na_2[MoO_2(SO_4)_2]$ at T = 293 K. Standard deviations are given in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	0.02613(18)	0.0324(2)	0.01940(16)	-0.00387(13)	0.00189(12)	-0.00070(13)
Mo2	0.02584(18)	0.0323(2)	0.01953(17)	-0.00411(13)	-0.00167(12)	0.00031(12)
S1	0.0234(4)	0.0329(5)	0.0215(4)	-0.0006(4)	0.0007(3)	0.0033(4)
S2	0.0248(5)	0.0320(5)	0.0208(4)	-0.0014(4)	0.0005(3)	-0.0033(4)
S3	0.0206(4)	0.0310(5)	0.0320(5)	0.0027(4)	-0.0013(4)	0.0039(4)
S4	0.0217(4)	0.0306(5)	0.0314(5)	0.0031(4)	0.0007(4)	-0.0021(4)
Na1	0.075(6)	0.097(8)	0.032(4)	-0.057(5)	0.002(3)	-0.003(4)
Na2	0.083(6)	0.028(3)	0.046(4)	-0.013(3)	0.018(3)	-0.005(2)
Na3	0.057(2)	0.0297(16)	0.0392(18)	-0.0107(12)	-0.0054(13)	0.0018(11)
O41	0.0222(13)	0.0427(18)	0.0289(15)	-0.0065(12)	-0.0005(11)	0.0014(12)
O11	0.060(2)	0.0405(19)	0.0342(17)	-0.0107(16)	-0.0016(15)	0.0172(14)
O21	0.052(2)	0.0350(17)	0.0381(17)	-0.0099(15)	0.0042(15)	-0.0147(14)
O31	0.0273(15)	0.0460(19)	0.0266(14)	-0.0061(12)	0.0017(11)	-0.0022(12)
Na4	0.007(5)	0.019(4)	0.029(4)	-0.008(3)	-0.002(4)	0.001(3)
O42	0.0436(18)	0.0279(15)	0.0288(15)	-0.0033(13)	0.0041(12)	0.0064(12)
Om21	0.0414(17)	0.051(2)	0.0248(15)	-0.0106(15)	0.0011(12)	-0.0067(14)
Om11	0.0390(17)	0.052(2)	0.0251(15)	-0.0072(14)	-0.0013(12)	0.0055(14)
O22	0.0241(13)	0.0331(15)	0.0257(14)	0.0013(11)	-0.0016(11)	0.0011(11)
O32	0.0477(19)	0.0280(16)	0.0328(16)	-0.0124(13)	-0.0071(13)	-0.0006(12)
Om12	0.0323(16)	0.0440(18)	0.0334(16)	-0.0017(13)	0.0032(12)	-0.0079(13)
Om22	0.0298(15)	0.0433(19)	0.0345(16)	-0.0023(13)	-0.0002(12)	0.0095(13)
O33	0.039(2)	0.064(3)	0.076(3)	0.0200(18)	0.0010(18)	-0.020(2)
O12	0.0233(13)	0.0364(16)	0.0303(15)	0.0016(11)	0.0000(11)	-0.0073(12)
O13	0.0381(16)	0.0352(16)	0.0254(14)	-0.0035(13)	-0.0002(12)	-0.0001(12)
O23	0.0427(17)	0.0318(16)	0.0250(14)	-0.0026(13)	0.0000(12)	0.0030(12)
O14	0.0222(14)	0.060(2)	0.0417(18)	0.0058(14)	0.0031(13)	-0.0016(15)
O43	0.0332(18)	0.064(3)	0.064(2)	0.0058(17)	-0.0032(16)	0.020(2)
O24	0.0265(16)	0.081(3)	0.0326(17)	0.0084(16)	-0.0049(13)	-0.0009(16)
O34	0.048(2)	0.058(2)	0.041(2)	-0.0070(18)	-0.0090(16)	0.0167(17)
Na5	0.018(11)	0.034(5)	0.028(4)	-0.003(6)	-0.014(5)	-0.004(3)
O44	0.053(2)	0.074(3)	0.0350(18)	0.0039(19)	0.0102(16)	0.0157(17)
Na9	-0.009(7)	-0.026(9)	0.031(12)	-0.031(6)	-0.012(7)	0.010(8)

Table S4. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $Na_2[MoO_2(SO_4)_2]$ at T = 373 K. Standard deviations are given in parentheses. For sodium cations Na3, Na4, Na7, Na8 and Na9, the isotropic displacement factor is given

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Na1	8*d*	0.648(9)	0.7571(4)	0.3241(5)	0.7161(2)	0.648(9)
Na2	8*d*	0.294(7)	0.010(3)	0.3736(9)	0.7651(13)	0.294(7)
Na3	8*d*	0.171(12)	-0.0211(17)	0.4935(19)	0.5039(10)	0.171(12)
Na4	8*d*	0.063(13)	-0.069(7)	0.481(4)	0.519(2)	0.063(13)
Na5	8*d*	0.411(15)	-0.1216(8)	0.5041(9)	0.5405(5)	0.411(15)
Na6	8*d*	0.16(4)	0.649(2)	0.245(6)	0.671(4)	0.16(4)
Na7	8*d*	0.10(4)	0.6426(19)	0.222(5)	0.641(4)	0.10(4)
Na8	8*d*	0.073(16)	0.642(2)	0.145(8)	0.629(2)	0.073(16)
Na9	4*a*	0.01(2)	4	4	-4	0.01(2)
Mo1	8*d*		0.37180(3)	0.57341(4)	0.59877(2)	0.03086(16)
O1	8*d*		0.3892(3)	0.7345(4)	0.5339(2)	0.0476(9)
O2	8*d*		0.3757(2)	0.6724(5)	0.6875(2)	0.0456(8)
S1	8*d*		0.12908(8)	0.64180(13)	0.64971(7)	0.0334(3)
O11	8*d*		0.1494(2)	0.8276(4)	0.6586(2)	0.0383(7)
O12	8*d*		0.2121(2)	0.5714(4)	0.59247(19)	0.0360(7)
O13	8*d*		0.1432(3)	0.5643(5)	0.7268(2)	0.0524(10)
O14	8*d*		0.0292(3)	0.6074(5)	0.6129(3)	0.0595(11)
S2	8*d*		0.62351(8)	0.60358(16)	0.58538(7)	0.0366(3)
O21	8*d*		0.5255(2)	0.4977(4)	0.5999(2)	0.0403(7)
O22	8*d*		0.6420(3)	0.6090(4)	0.4991(2)	0.0423(8)
O23	8*d*		0.6071(3)	0.7742(6)	0.6149(3)	0.0712(13)
O24	8*d*		0.7089(3)	0.5197(7)	0.6246(3)	0.0757(14)

Table S5. Anisotropic displacement parameters U_{ij} / Å^2 in $Na_2[MoO_2(SO_4)_2]$ at *T* = 373 K. Standard deviations are given in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.104(3)	0.051(2)	0.043(2)	0.019(2)	0.0092(19)	0.0006(15)
Na2	0.093(12)	0.038(4)	0.083(18)	0.022(7)	0.067(13)	0.011(5)
Na5	0.040(5)	0.055(4)	0.048(4)	-0.017(3)	-0.015(3)	0.015(3)
Na6	0.085(14)	0.102(17)	0.04(2)	0.002(11)	0.011(10)	0.011(16)
Mo1	0.0288(2)	0.0221(2)	0.0417(3)	-0.00194(13)	0.00471(14)	-0.00079(14)
O1	0.0471(19)	0.0320(17)	0.064(2)	-0.0009(14)	0.0125(16)	0.0087(16)
O2	0.0391(18)	0.0406(19)	0.057(2)	-0.0020(14)	0.0020(15)	-0.0120(16)
S1	0.0262(5)	0.0261(5)	0.0478(6)	-0.0010(4)	0.0025(4)	0.0043(4)
O11	0.0427(17)	0.0251(15)	0.0471(19)	0.0012(13)	-0.0040(14)	0.0043(14)
O12	0.0313(15)	0.0324(17)	0.0444(18)	-0.0004(12)	-0.0012(12)	-0.0048(13)
O13	0.065(2)	0.043(2)	0.049(2)	0.0003(17)	0.0140(18)	0.0179(16)
O14	0.0269(16)	0.046(2)	0.106(3)	-0.0063(15)	-0.0116(19)	0.003(2)
S2	0.0251(5)	0.0413(6)	0.0435(6)	-0.0016(4)	-0.0021(4)	-0.0077(5)
O21	0.0315(15)	0.0321(16)	0.057(2)	0.0014(13)	0.0080(14)	0.0016(14)
O22	0.053(2)	0.0331(17)	0.0406(18)	-0.0096(14)	0.0053(14)	0.0015(14)
O23	0.065(3)	0.053(3)	0.095(3)	-0.015(2)	0.015(2)	-0.035(2)

O24	0.047(2)	0.104(4)	0.076(3)	0.004(2)	-0.024(2)	0.019(3)

Table S6. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in β-$K_2[MoO_2(SO_4)_2]$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
K1	4*e*	1.06036(7)	0.14163(5)	0.38368(8)	0.03123(13)
K2	4*e*	0.36525(7)	0.85228(6)	0.57500(8)	0.03653(14)
Mo1	4*e*	0.73860(2)	0.55604(2)	0.50925(2)	0.01827(6)
O1	4*e*	0.5926(2)	0.52038(18)	0.3763(3)	0.0329(4)
O2	4*e*	0.7600(3)	0.44778(16)	0.6435(3)	0.0378(5)
S1	4*e*	0.64663(6)	0.69180(5)	0.82676(7)	0.01721(11))
O11	4*e*	0.75672(18)	0.78185(14)	0.8699(2)	0.0215(3)
O12	4*e*	0.50561(19)	0.73298(17)	0.8321(2)	0.0297(4)
O13	4*e*	0.6843(2)	0.59260(17)	0.9255(2)	0.0323(4)
O14	4*e*	0.65244(19)	0.66503(15)	0.6466(2)	0.0233(3)
S2	4*e*	0.91252(6)	0.39121(5)	0.29178(7)	0.01854(11))
O21	4*e*	1.0611(2)	0.36618(16)	0.3635(3)	0.0321(4)
O22	4*e*	0.87750(19)	0.50452(14)	0.3632(2)	0.0227(3)
O23	4*e*	0.8211(2)	0.30468(17)	0.3347(3)	0.0437(6)
O24	4*e*	0.9015(3)	0.40821(18)	0.1171(2)	0.0398(5)

Table S7. Anisotropic displacement parameters U_{ij} / Å^2 in β-$K_2[MoO_2(SO_4)_2]$. Standard deviations are given in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K1	0.0391(3)	0.0195(2)	0.0349(3)	0.0025(2)	0.0056(2)	-0.0007(2)
K2	0.0354(3)	0.0378(3)	0.0386(3)	0.0058(3)	0.0125(3)	0.0065(3)
Mo1	0.02039(10)	0.01622(9)	0.01895(10)	-0.00174(7)	0.00540(7)	-0.00156(7)
O1	0.0254(9)	0.0365(10)	0.0372(11)	-0.0096(8)	0.0060(8)	-0.0134(9)
O2	0.0557(14)	0.0254(10)	0.0366(11)	0.0045(9)	0.0196(10)	0.0074(8)
S1	0.0193(2)	0.0205(3)	0.0153(2)	-0.00275(19)	0.00410(19)	-0.00082(19)
O11	0.0201(8)	0.0215(8)	0.0238(8)	-0.0031(6)	0.0060(6)	-0.0047(6)
O12	0.0192(8)	0.0426(11)	0.0283(9)	-0.0023(8)	0.0075(7)	-0.0076(8)
O13	0.0427(11)	0.0274(9)	0.0244(9)	-0.0069(8)	-0.0014(8)	0.0078(7)
O14	0.0299(9)	0.0247(8)	0.0156(7)	0.0023(7)	0.0051(6)	-0.0025(6)
S2	0.0187(2)	0.0162(2)	0.0199(2)	0.00061(19)	0.00083(19)	-0.00247(19)
O21	0.0224(9)	0.0246(9)	0.0446(11)	0.0058(7)	-0.0084(8)	-0.0102(8)
O22	0.0257(8)	0.0173(8)	0.0270(9)	0.0028(6)	0.0098(7)	-0.0029(6)
O23	0.0376(12)	0.0228(10)	0.0754(17)	-0.0092(8)	0.0234(11)	-0.0055(10)
O24	0.0669(16)	0.032(1)	0.0179(9)	0.0141(10)	-0.0005(9)	-0.0054(8)

Satellite Reflections in $Na_2[MoO_2(SO_4)_2]$ in the Reciprocal Space

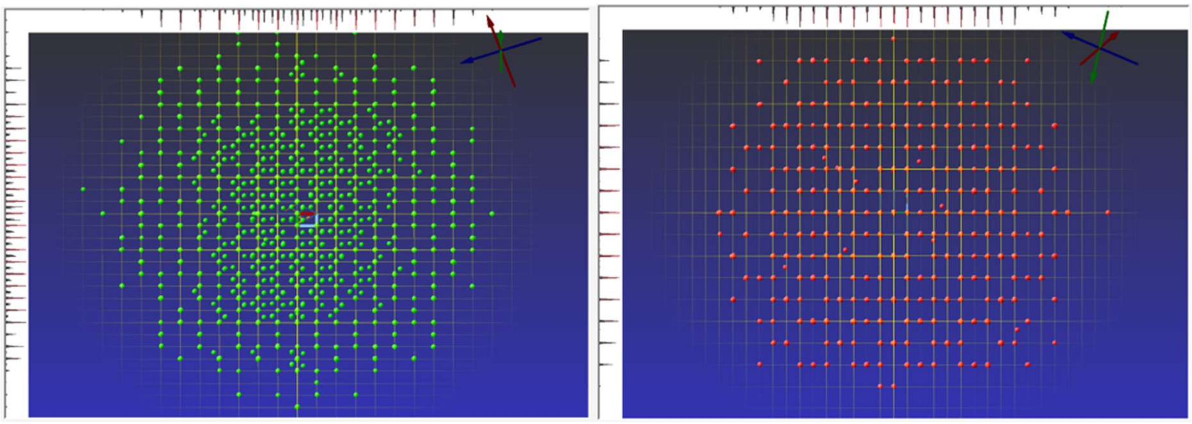

Figure S1. Reciprocal Space at 293 K (left, green) and 373 K (right, red) depicted in the software package APEX.[1]

De Wolff Section

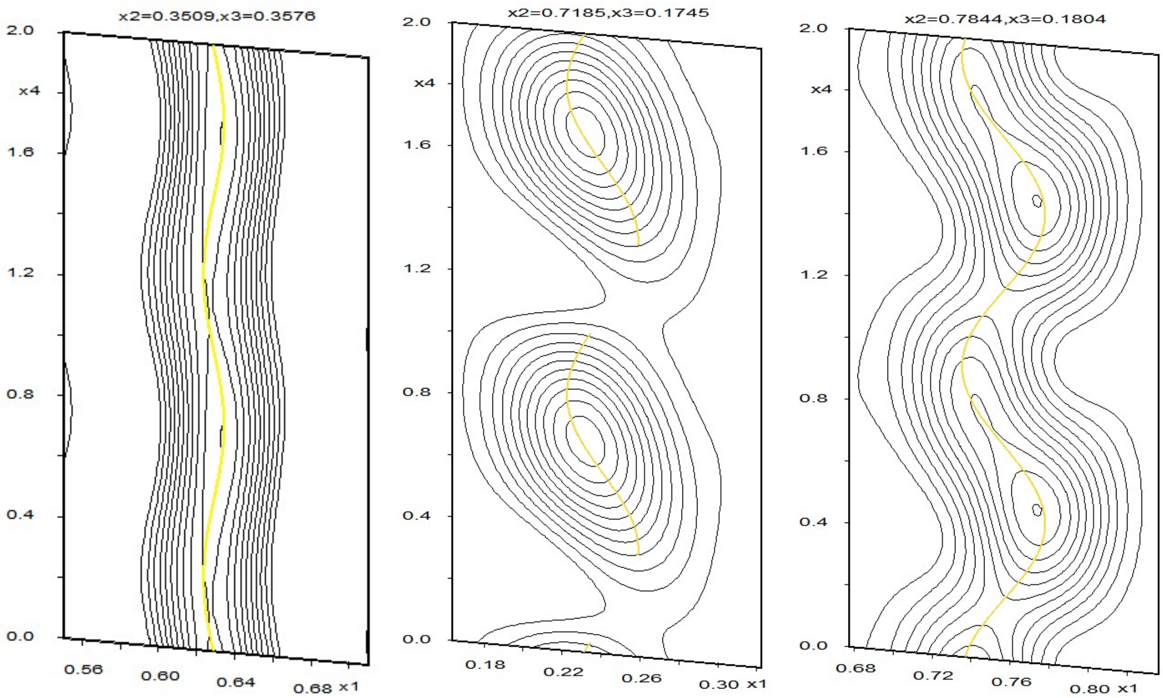

Figure S2. Representative de Wolff plots of S, Na2-x1-x4, Na3-x1-x4.

Centroid Shift of Molybdenum

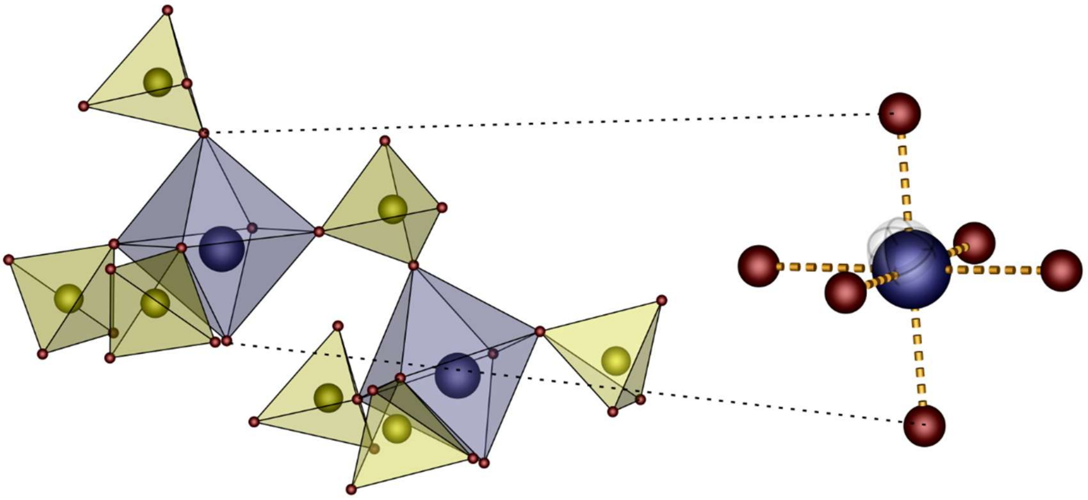

Figure S3. Centroid shift in the molybdate octahedra due to the number of coordinating sulfate tetrahedra in $Na_2[MoO_2(SO_4)_2]$.

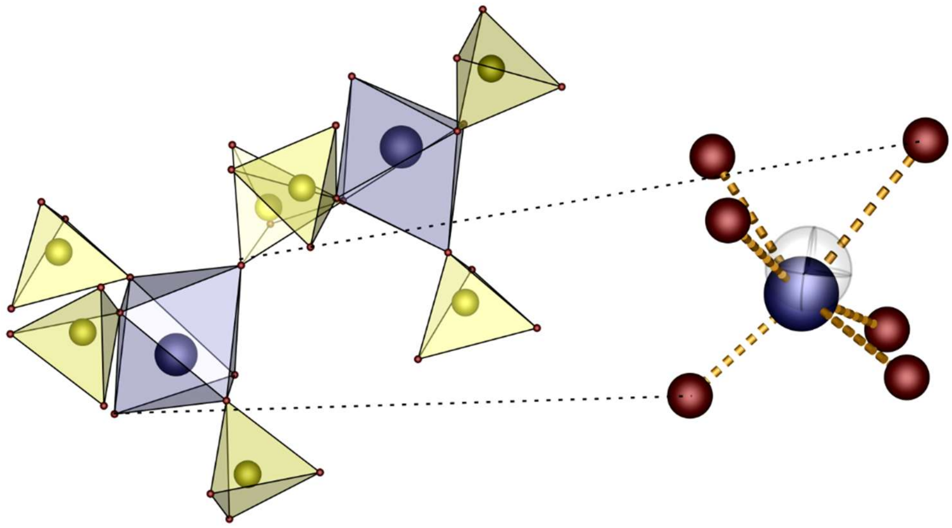

Figure S4. Centroid shift in the molybdate due to the number of coordinating sulfate tetrahedra in $K_2[MoO_2(SO_4)_2]$.

Coordination of Sodium Cations

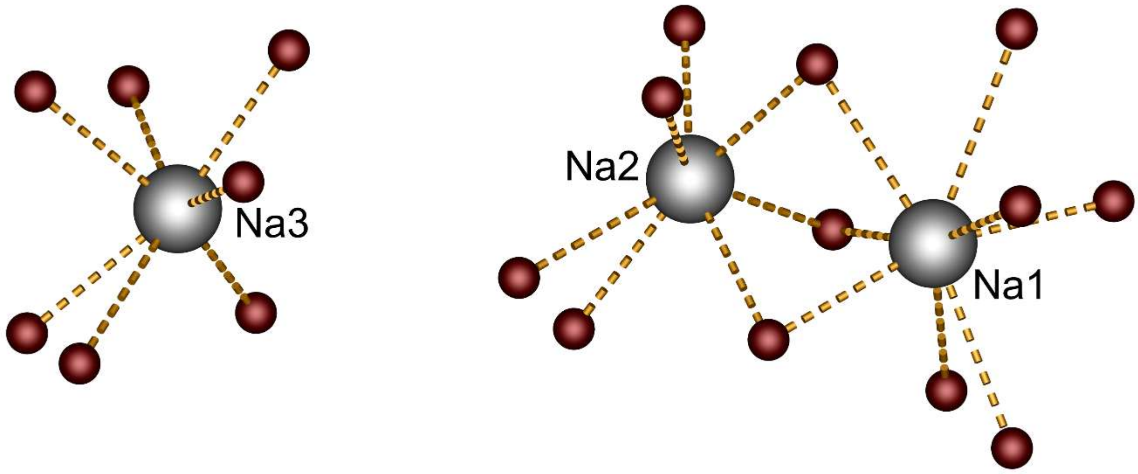

Figure S5. Coordination environment of chosen sodium cations in $Na_2[MoO_2(SO_4)_2]$.

Selected Ionic Radii after Shannon

Table S8. Ionic radii / pm after Shannon[2] with respect to their coordination number

Ion	Charge	Coordination	Ionic radius
K	1	IX	155
Na	1	VII	112
Na	1	VIII	124
Mo	6	VI	59
S	6	IV	12
O	-2	III	136
O	-2	IV	138

FT-IR Spectroscopy

Table S9. Assignments of vibrations in the FT-IR spectra

Wavenumber / cm^{-1}	Vibration
1400—950	ν_{sym}(S—O)[3-6]
	ν_{asym}(S—O)[3-6]
650—400	δ(S—O)[3-6]
990—600	ν_{sym}(Mo—O)[7]
	ν_{asym}(Mo—O)[7]
< 400 (not detectable)	δ(Mo—O)[7]
3700—3500	ν(O—H)[8]
1630—1600	δ(O—H)[8]

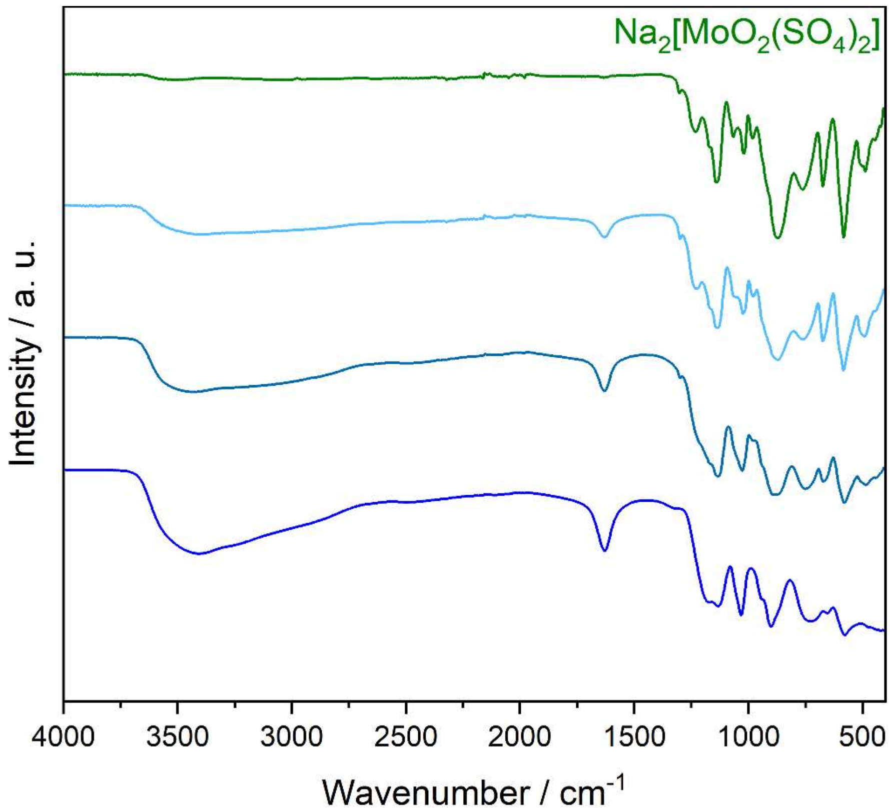

Figure S6. FT-IR spectra of $Na_2[MoO_2(SO_4)_2]$ after contact to ambient air. Dark green directly after opening the ampoule; light blue after exposing to air, middle blue after 30 min; dark blue after one night.

MAPLE Calculations

Table S10. Calculated MAPLE values of the binary and tertiary compounds

Compound	MAPLE Value in kJ mol^{-1}
K_2SO_4[9]	33098
Na_2O[10]	2907
MoO_3[11]	25353
SO_3[12]	29930

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