Supporting Information

Mo^{6+}-Cation Enrichment of the Structure Chemistry of Iodates: Syntheses, Structures, and Calculations of $Ba(MoO_2)_2(IO_3)_4O$, $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$, and $Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$

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Table S1. Crystal data and structure refinement for $Ba(MoO_2)_2(IO_3)_4O$, $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$, and $Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$

Empirical formula	**$Ba(MoO_2)_2(IO_3)_4O$**	**$Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$**	**$Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$**
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Formula weight	1108.82	1487.56	1319.08
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group, Z	*P2(1)/c*，2	*C2/c*，4	*C2/c*，4
Unit cell dimensions	a=10.135(7)Å b=5.344(4)Å c=13.746(9)Å *β*=103.142(9)°	a=13.4573(19)Å b=7.9221(11)Å c=19.428(3)Å *β*=93.637(5)°	a=13.437(3)Å b=7.4041(15)Å c=20.198(4)Å *β*=108.658(4)°
Volume ($Å^3$)	725.0(8)	2067.0(5)	1903.8(7)
Calculated density (Mg/m^3)	5.079	4.78	4.602
Absorption coefficient (/mm)	12.998	12.893	9.974
F(000)	976	2624	2392
The range for data collection	2.06 to 27.45°	2.10 to 27.44°	2.13 to 27.44°
R(int)	0.03	0.0578	0.0179
Completeness	99.50%	99.90%	96.00%
Data / restraints / parameters	1642 / 0 / 113	2363 / 6 / 146	2086 / 0 / 155
Goodness-of-fit on F^2	1.079	1.066	1.137
Final R indices $[F_o^2 > 2\sigma(F_o^2)]^a$	R_1 = 0.0183 wR_2 = 0.0470	R_1 = 0.0374 wR_2 = 0.0862	R_1 = 0.0191 wR_2 = 0.0431
R indices (all data) ^{a}	R_1 = 0.0196 wR_2 = 0.0475	R_1 = 0.0453 wR_2 = 0.0903	R_1 = 0.0209 wR_2 = 0.0436
Largest diff. peak and hole (e·Å-3)	0.981 and -0.947	5.619 and -4.371	0.819 and -0.947

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Ba(MoO_2)_2(IO_3)_4O$, $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$, and $Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U_{eq}(Å^2)
		$Ba(MoO_2)_2(IO_3)_4O$		
Ba(1)	0	10000	5000	7(1)
Mo(1)	3455(1)	10958(1)	9026(1)	4(1)
I(1)	3879(1)	10428(1)	6565(1)	4(1)
I(2)	-1303(1)	10223(1)	7650(1)	4(1)
O(1)	5000	10000	10000	6(1)
O(2)	2563(2)	8115(5)	6186(2)	9(1)
O(3)	4482(3)	9492(5)	7888(2)	7(1)
O(4)	2597(2)	12881(5)	9676(2)	7(1)
O(5)	2528(2)	8279(5)	8946(2)	7(1)
O(6)	5284(3)	9199(5)	6118(2)	8(1)
O(7)	-2425(2)	7375(5)	7348(2)	7(1)
O(8)	-81(3)	9138(5)	6967(2)	6(1)
O(9)	-539(3)	9328(5)	8903(2)	8(1)
		$Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$		
Ba(1)	5000	8031(1)	2500	17(1)
Ba(2)	7390(1)	5128(1)	840(1)	11(1)
Mo(1)	8662(1)	7829(1)	2334(1)	10(1)
I(1)	4674(1)	6833(1)	603(1)	10(1)
I(2)	6805(1)	10158(1)	1004(1)	17(1)
O(1)	8478(4)	5287(7)	2186(3)	6(1)
O(2)	7340(4)	7717(7)	1836(3)	8(1)
O(3)	8249(5)	7847(8)	3151(3)	17(1)
O(4)	10000	7183(12)	2500	16(2)
O(5)	9065(5)	7275(8)	1202(3)	15(1)
O(6)	8827(5)	9912(8)	2176(4)	20(1)
O(7)	3999(5)	4925(8)	322(3)	17(1)
O(8)	5525(5)	5936(8)	1254(3)	14(1)
O(9)	3795(5)	7732(8)	1156(3)	17(1)
O(10)	6610(5)	11922(8)	389(3)	18(1)
O(11)	6829(5)	8497(8)	378(3)	18(1)
O(12)	5552(5)	9884(9)	1264(4)	21(1)
		$Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$		
Sr(1)	5000	-1690(1)	2500	5(1)
Mo(1)	4410(1)	5323(1)	4123(1)	3(1)
Mo(2)	3043(1)	1160(1)	3363(1)	4(1)
Mo(3)	3162(1)	-2571(1)	5898(1)	4(1)
I(1)	3802(1)	1210(1)	5033(1)	4(1)
O(1)	4640(2)	3487(4)	4998(1)	6(1)
O(2)	4712(2)	6941(4)	3605(1)	7(1)

O(3)	3234(2)	6042(3)	4210(1)	6(1)
O(4)	3045(2)	-1146(3)	5016(1)	6(1)
O(5)	3901(2)	3391(4)	3538(1)	7(1)
O(6)	3647(2)	338(4)	2802(1)	8(1)
O(7)	4305(2)	297(4)	4355(1)	6(1)
O(8)	5000	-5273(6)	2500	13(1)
O(9)	2666(2)	2118(4)	4350(1)	6(1)
O(10)	2600(2)	-3955(4)	6463(1)	6(1)
O(11)	3908(2)	-942(4)	6439(1)	8(1)
O(12)	4090(2)	-4082(4)	5803(1)	7(1)
O(13)	3101(2)	-2867(4)	2139(1)	9(1)

Table S3. Selected bond lengths (Å) and angles (deg.) for $Ba(MoO_2)_2(IO_3)_4O$, $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$, and $Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$.

$Ba(MoO_2)_2(IO_3)_4O$

Ba(1)-O(9)$^{\#1}$	2.747(3)	O(9)$^{\#1}$-Ba(1)-O(4)$^{\#4}$	93.24(8)
Ba(1)-O(9)$^{\#2}$	2.747(3)	O(9)$^{\#2}$-Ba(1)-O(4)$^{\#4}$	108.00(8)
Ba(1)-O(8)$^{\#3}$	2.762(3)	O(8)$^{\#3}$-Ba(1)-O(4)$^{\#4}$	115.59(7)
Ba(1)-O(8)	2.762(3)	O(8)-Ba(1)-O(4)$^{\#4}$	64.41(7)
Ba(1)-O(2)$^{\#3}$	2.915(3)	O(2)$^{\#3}$-Ba(1)-O(4)$^{\#4}$	60.76(8)
Ba(1)-O(2)	2.915(3)	O(2)-Ba(1)-O(4)$^{\#4}$	119.25(8)
Ba(1)-O(4)$^{\#4}$	2.990(3)	O(9)$^{\#1}$-Ba(1)-O(4)$^{\#5}$	107.99(8)
Ba(1)-O(4)$^{\#5}$	2.990(3)	O(9)$^{\#2}$-Ba(1)-O(4)$^{\#5}$	72.00(8)
Mo(1)-O(5)	1.702(3)	O(8)$^{\#3}$-Ba(1)-O(4)$^{\#5}$	64.41(7)
Mo(1)-O(4)	1.722(3)	O(8)-Ba(1)-O(4)$^{\#5}$	115.59(7)
Mo(1)-O(1)	1.8854(9)	O(2)$^{\#3}$-Ba(1)-O(4)$^{\#5}$	119.24(8)
Mo(1)-O(7)$^{\#2}$	2.082(2)	O(2)-Ba(1)-O(4)$^{\#5}$	60.75(8)
Mo(1)-O(6)$^{\#6}$	2.188(3)	O(4)$^{\#4}$-Ba(1)-O(4)$^{\#5}$	180.00(9)
Mo(1)-O(3)	2.211(3)	O(5)-Mo(1)-O(4)	101.50(13)
I(1)-O(6)	1.798(3)	O(5)-Mo(1)-O(1)	100.06(9)
I(1)-O(2)	1.806(3)	O(4)-Mo(1)-O(1)	103.27(9)
I(1)-O(3)	1.851(3)	O(5)-Mo(1)-O(7)$^{\#2}$	95.27(11)
I(2)-O(9)	1.786(3)	O(4)-Mo(1)-O(7)$^{\#2}$	92.62(11)
I(2)-O(8)	1.811(3)	O(1)-Mo(1)-O(7)$^{\#2}$	155.13(7)
I(2)-O(7)	1.889(3)	O(5)-Mo(1)-O(6)$^{\#6}$	170.10(10)
O(9)$^{\#1}$-Ba(1)-O(9)$^{\#2}$	1.8855(9)	O(4)-Mo(1)-O(6)$^{\#6}$	87.06(12)
O(9)$^{\#1}$-Ba(1)-O(8)$^{\#3}$	2.990(3)	O(1)-Mo(1)-O(6)$^{\#6}$	82.57(8)
O(9)$^{\#2}$-Ba(1)-O(8)$^{\#3}$	2.188(3)	O(7)$^{\#2}$-Mo(1)-O(6)$^{\#6}$	79.22(10)
O(9)$^{\#1}$-Ba(1)-O(8)	2.082(2)	O(5)-Mo(1)-O(3)	89.88(11)
O(9)$^{\#2}$-Ba(1)-O(8)	2.747(3)	O(4)-Mo(1)-O(3)	162.49(10)
O(8)$^{\#3}$-Ba(1)-O(8)	180	O(1)-Mo(1)-O(3)	87.55(8)
O(9)$^{\#1}$-Ba(1)-O(2)$^{\#3}$	69.49(8)	O(7)$^{\#2}$-Mo(1)-O(3)	72.93(10)
O(9)$^{\#2}$-Ba(1)-O(2)$^{\#3}$	110.51(8)	O(6)$^{\#6}$-Mo(1)-O(3)	80.66(10)
O(8)$^{\#3}$-Ba(1)-O(2)$^{\#3}$	110.51(8)	O(6)-I(1)-O(2)	103.98(13)
O(8)-Ba(1)-O(2)$^{\#3}$	69.49(8)	O(6)-I(1)-O(3)	97.29(12)
O(9)$^{\#1}$-Ba(1)-O(2)	179.999(16)	O(2)-I(1)-O(3)	98.95(12)
O(9)$^{\#2}$-Ba(1)-O(2)	86.76(8)	O(9)-I(2)-O(8)	102.54(12)
O(8)$^{\#3}$-Ba(1)-O(2)	93.24(8)	O(9)-I(2)-O(7)	95.95(12)
O(8)-Ba(1)-O(2)	67.41(8)	O(8)-I(2)-O(7)	94.41(12)
O(2)$^{\#3}$-Ba(1)-O(2)	112.59(8)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z-1/2 #2 -x,y+1/2,-z+3/2 #3 -x,-y+2,-z+1 #4 -x,y-1/2,-z+3/2

#5 x,-y+5/2,z-1/2 #6 -x+1,y+1/2,-z+3/2 #7 -x+1,-y+2,-z+2 #8 -x+1,y-1/2,-z+3/2

$Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$

Ba(1)-O(1)$^{\#1}$	2.757(5)	O(8)$^{\#3}$-Ba(1)-O(4)$^{\#1}$	122.90(12)

Ba(1)-O(1)$^{\#2}$	2.757(5)	O(9)$^{\#6}$-Ba(2)-O(8)	136.71(19)
Ba(1)-O(12)$^{\#3}$	2.949(7)	O(9)$^{\#6}$-Ba(2)-O(2)	113.45(17)
Ba(1)-O(6)$^{\#4}$	2.978(7)	O(8)-Ba(2)-O(2)	64.55(17)
Ba(1)-O(6)$^{\#5}$	2.978(7)	O(9)$^{\#6}$-Ba(2)-O(7)$^{\#7}$	125.60(19)
Ba(1)-O(9)$^{\#3}$	2.994(6)	O(8)-Ba(2)-O(7)$^{\#7}$	70.72(19)
Ba(1)-O(9)	2.994(6)	O(2)-Ba(2)-O(7)$^{\#7}$	120.87(17)
Ba(1)-O(8)	3.055(6)	O(9)$^{\#6}$-Ba(2)-O(3)$^{\#4}$	68.7(2)
Ba(1)-O(8)$^{\#3}$	3.055(6)	O(8)-Ba(2)-O(3)$^{\#4}$	68.02(19)
Ba(1)-O(4)$^{\#1}$	3.290(9)	O(2)-Ba(2)-O(3)$^{\#4}$	88.14(18)
Ba(2)-O(9)$^{\#6}$	2.722(6)	O(7)$^{\#7}$-Ba(2)-O(3)$^{\#4}$	109.07(19)
Ba(2)-O(8)	2.759(6)	O(9)$^{\#6}$-Ba(2)-O(11)$^{\#8}$	99.5(2)
Ba(2)-O(2)	2.824(6)	O(8)-Ba(2)-O(11)$^{\#8}$	122.74(19)
Ba(2)-O(7)$^{\#7}$	2.837(6)	O(2)-Ba(2)-O(11)$^{\#8}$	108.41(18)
Ba(2)-O(3)$^{\#4}$	2.839(6)	O(7)$^{\#7}$-Ba(2)-O(11)$^{\#8}$	66.84(19)
Ba(2)-O(11)$^{\#8}$	2.864(7)	O(3)$^{\#4}$-Ba(2)-O(11)$^{\#8}$	162.82(19)
Ba(2)-O(10)$^{\#9}$	2.864(6)	O(9)$^{\#6}$-Ba(2)-O(10)$^{\#9}$	71.73(19)
Ba(2)-O(5)	2.875(6)	O(8)-Ba(2)-O(10)$^{\#9}$	88.4(2)
Ba(2)-O(11)	2.901(7)	O(2)-Ba(2)-O(10)$^{\#9}$	146.07(19)
Ba(2)-O(1)	2.918(5)	O(7)$^{\#7}$-Ba(2)-O(10)$^{\#9}$	62.18(17)
Ba(2)-O(10)$^{\#8}$	3.249(7)	O(3)$^{\#4}$-Ba(2)-O(10)$^{\#9}$	61.70(19)
Mo(1)-O(6)	1.696(7)	O(11)$^{\#8}$-Ba(2)-O(10)$^{\#9}$	103.36(19)
Mo(1)-O(3)	1.716(6)	O(9)$^{\#6}$-Ba(2)-O(5)	80.49(19)
Mo(1)-O(4)	1.881(3)	O(8)-Ba(2)-O(5)	120.31(18)
Mo(1)-O(2)	1.971(5)	O(2)-Ba(2)-O(5)	56.95(17)
Mo(1)-O(1)	2.047(5)	O(7)$^{\#7}$-Ba(2)-O(5)	132.07(18)
Mo(1)-O(5)	2.338(6)	O(3)$^{\#4}$-Ba(2)-O(5)	118.31(18)
I(1)-O(9)	1.795(7)	O(11)$^{\#8}$-Ba(2)-O(5)	69.76(18)
I(1)-O(8)	1.798(6)	O(10)$^{\#9}$-Ba(2)-O(5)	149.98(19)
I(1)-O(7)	1.828(6)	O(9)$^{\#6}$-Ba(2)-O(11)	151.0(2)
I(2)-O(11)	1.794(6)	O(8)-Ba(2)-O(11)	69.69(19)
I(2)-O(12)	1.803(7)	O(2)-Ba(2)-O(11)	61.78(17)
I(2)-O(10)	1.847(6)	O(7)$^{\#7}$-Ba(2)-O(11)	67.80(18)
O(1)$^{\#1}$-Ba(1)-O(1)$^{\#2}$	99.2(2)	O(3)$^{\#4}$-Ba(2)-O(11)	135.66(19)
O(1)$^{\#1}$-Ba(1)-O(12)$^{\#3}$	68.63(17)	O(11)$^{\#8}$-Ba(2)-O(11)	59.8(2)
O(1)$^{\#2}$-Ba(1)-O(12)$^{\#3}$	73.69(18)	O(10)$^{\#9}$-Ba(2)-O(11)	129.64(18)
O(1)$^{\#1}$-Ba(1)-O(6)$^{\#4}$	163.95(18)	O(5)-Ba(2)-O(11)	73.51(18)
O(1)$^{\#2}$-Ba(1)-O(6)$^{\#4}$	96.58(18)	O(9)$^{\#6}$-Ba(2)-O(1)	61.68(17)
O(12)$^{\#3}$-Ba(1)-O(6)$^{\#4}$	113.47(19)	O(8)-Ba(2)-O(1)	98.23(17)
O(1)$^{\#1}$-Ba(1)-O(6)$^{\#5}$	96.58(18)	O(2)-Ba(2)-O(1)	52.17(15)
O(1)$^{\#2}$-Ba(1)-O(6)$^{\#5}$	163.95(18)	O(7)$^{\#7}$-Ba(2)-O(1)	168.90(19)
O(12)$^{\#3}$-Ba(1)-O(6)$^{\#5}$	115.3(2)	O(3)$^{\#4}$-Ba(2)-O(1)	64.24(17)
O(6)$^{\#4}$-Ba(1)-O(6)$^{\#5}$	67.9(3)	O(11)$^{\#8}$-Ba(2)-O(1)	122.27(17)
O(1)$^{\#1}$-Ba(1)-O(9)$^{\#3}$	126.72(17)	O(10)$^{\#9}$-Ba(2)-O(1)	117.77(16)
O(1)$^{\#2}$-Ba(1)-O(9)$^{\#3}$	60.31(17)	O(5)-Ba(2)-O(1)	54.12(17)

O(12)$^{\#3}$-Ba(1)-O(9)$^{\#3}$	58.67(19)	O(11)-Ba(2)-O(1)	110.12(16)
O(6)$^{\#4}$-Ba(1)-O(9)$^{\#3}$	59.96(18)	O(9)$^{\#6}$-Ba(2)-O(10)$^{\#8}$	60.19(17)
O(6)$^{\#5}$-Ba(1)-O(9)$^{\#3}$	111.68(18)	O(8)-Ba(2)-O(10)$^{\#8}$	139.21(17)
O(1)$^{\#1}$-Ba(1)-O(9)	60.31(17)	O(2)-Ba(2)-O(10)$^{\#8}$	153.59(17)
O(1)$^{\#2}$-Ba(1)-O(9)	126.72(17)	O(7)$^{\#7}$-Ba(2)-O(10)$^{\#8}$	71.99(18)
O(12)$^{\#3}$-Ba(1)-O(9)	126.78(18)	O(3)$^{\#4}$-Ba(2)-O(10)$^{\#8}$	110.29(17)
O(6)$^{\#4}$-Ba(1)-O(9)	111.67(18)	O(11)$^{\#8}$-Ba(2)-O(10)$^{\#8}$	52.59(17)
O(6)$^{\#5}$-Ba(1)-O(9)	59.95(18)	O(10)$^{\#9}$-Ba(2)-O(10)$^{\#8}$	59.5(2)
O(9)$^{\#3}$-Ba(1)-O(9)	170.9(3)	O(5)-Ba(2)-O(10)$^{\#8}$	96.94(17)
O(1)$^{\#1}$-Ba(1)-O(8)	112.49(15)	O(11)-Ba(2)-O(10)$^{\#8}$	110.14(17)
O(1)$^{\#2}$-Ba(1)-O(8)	108.77(17)	O(1)-Ba(2)-O(10)$^{\#8}$	118.17(16)
O(12)$^{\#3}$-Ba(1)-O(8)	176.84(18)	O(6)-Mo(1)-O(3)	102.3(3)
O(6)$^{\#4}$-Ba(1)-O(8)	64.58(17)	O(6)-Mo(1)-O(4)	99.3(4)
O(6)$^{\#5}$-Ba(1)-O(8)	61.82(19)	O(3)-Mo(1)-O(4)	101.9(2)
O(9)$^{\#3}$-Ba(1)-O(8)	120.56(17)	O(6)-Mo(1)-O(2)	94.6(3)
O(9)-Ba(1)-O(8)	53.53(16)	O(3)-Mo(1)-O(2)	96.8(3)
O(1)$^{\#1}$-Ba(1)-O(8)$^{\#3}$	108.77(17)	O(4)-Mo(1)-O(2)	153.7(2)
O(1)$^{\#2}$-Ba(1)-O(8)$^{\#3}$	112.49(15)	O(6)-Mo(1)-O(1)	161.5(3)
O(12)$^{\#3}$-Ba(1)-O(8)$^{\#3}$	62.75(18)	O(3)-Mo(1)-O(1)	95.4(3)
O(6)$^{\#4}$-Ba(1)-O(8)$^{\#3}$	61.83(19)	O(4)-Mo(1)-O(1)	82.1(3)
O(6)$^{\#5}$-Ba(1)-O(8)$^{\#3}$	64.59(17)	O(2)-Mo(1)-O(1)	77.9(2)
O(9)$^{\#3}$-Ba(1)-O(8)$^{\#3}$	53.53(16)	O(6)-Mo(1)-O(5)	88.4(3)
O(9)-Ba(1)-O(8)$^{\#3}$	120.56(17)	O(3)-Mo(1)-O(5)	168.4(3)
O(8)-Ba(1)-O(8)$^{\#3}$	114.2(2)	O(4)-Mo(1)-O(5)	80.43(16)
O(1)$^{\#1}$-Ba(1)-O(4)$^{\#1}$	49.60(11)	O(2)-Mo(1)-O(5)	77.7(2)
O(1)$^{\#2}$-Ba(1)-O(4)$^{\#1}$	49.59(11)	O(1)-Mo(1)-O(5)	73.5(2)
O(12)$^{\#3}$-Ba(1)-O(4)$^{\#1}$	60.16(13)	O(9)-I(1)-O(8)	98.6(3)
O(6)$^{\#4}$-Ba(1)-O(4)$^{\#1}$	146.07(13)	O(9)-I(1)-O(7)	100.0(3)
O(6)$^{\#5}$-Ba(1)-O(4)$^{\#1}$	146.07(13)	O(8)-I(1)-O(7)	99.6(3)
O(9)$^{\#3}$-Ba(1)-O(4)$^{\#1}$	94.54(13)	O(11)-I(2)-O(12)	99.2(3)
O(9)-Ba(1)-O(4)$^{\#1}$	94.54(13)	O(11)-I(2)-O(10)	97.1(3)
O(8)-Ba(1)-O(4)$^{\#1}$	122.90(12)	O(12)-I(2)-O(10)	100.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,y+1/2,z	#2 -x+3/2,y+1/2,-z+1/2	#3 -x+1,y,-z+1/2	#4 -x+3/2,y-1/2,-z+1/2
#5 x-1/2,y-1/2,z	#6 x+1/2,y-1/2,z	#7 -x+1,-y+1,-z	#8 -x+3/2,-y+3/2,-z
#9 x,y-1,z	#10 -x+2,y,-z+1/2	#11 x+1/2,y+1/2,z	#12 x,y+1,z

$Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$

Sr(1)-O(13)	2.571(3)	O(13)-Sr(1)-O(11)$^{\#5}$	130.88(8)
Sr(1)-O(13)$^{\#1}$	2.571(3)	O(13)$^{\#1}$-Sr(1)-O(11)$^{\#5}$	78.34(8)
Sr(1)-O(6)	2.577(3)	O(6)-Sr(1)-O(11)$^{\#5}$	70.40(8)
Sr(1)-O(6)$^{\#1}$	2.577(3)	O(6)$^{\#1}$-Sr(1)-O(11)$^{\#5}$	63.79(8)
Sr(1)-O(2)$^{\#2}$	2.590(2)	O(2)$^{\#2}$-Sr(1)-O(11)$^{\#5}$	135.64(8)
Sr(1)-O(2)$^{\#3}$	2.590(2)	O(2)$^{\#3}$-Sr(1)-O(11)$^{\#5}$	78.89(8)

Sr(1)-O(8)	2.653(4)	O(8)-Sr(1)-O(11)$^{\#5}$	131.84(6)
Sr(1)-O(11)$^{\#4}$	2.921(3)	O(11)$^{\#4}$-Sr(1)-O(11)$^{\#5}$	96.32(11)
Sr(1)-O(11)$^{\#5}$	2.921(3)	O(2)-Mo(1)-O(3)	104.36(12)
Mo(1)-O(2)	1.723(3)	O(2)-Mo(1)-O(5)	105.13(12)
Mo(1)-O(3)	1.729(3)	O(3)-Mo(1)-O(5)	98.04(12)
Mo(1)-O(5)	1.842(3)	O(2)-Mo(1)-O(1)$^{\#6}$	91.45(12)
Mo(1)-O(1)$^{\#6}$	2.026(3)	O(3)-Mo(1)-O(1)$^{\#6}$	96.75(11)
Mo(1)-O(1)	2.172(3)	O(5)-Mo(1)-O(1)$^{\#6}$	154.20(11)
Mo(1)-O(12)$^{\#5}$	2.176(3)	O(2)-Mo(1)-O(1)	158.42(12)
Mo(2)-O(6)	1.704(2)	O(3)-Mo(1)-O(1)	90.42(11)
Mo(2)-O(13)$^{\#7}$	1.707(3)	O(5)-Mo(1)-O(1)	87.87(11)
Mo(2)-O(10)$^{\#8}$	1.931(3)	O(1)$^{\#6}$-Mo(1)-O(1)	70.97(12)
Mo(2)-O(5)	1.981(3)	O(2)-Mo(1)-O(12)$^{\#5}$	86.67(11)
Mo(2)-O(7)	2.263(3)	O(3)-Mo(1)-O(12)$^{\#5}$	168.44(11)
Mo(2)-O(9)	2.318(2)	O(5)-Mo(1)-O(12)$^{\#5}$	82.05(11)
Mo(3)-O(11)	1.717(3)	O(1)$^{\#6}$-Mo(1)-O(12)$^{\#5}$	79.28(10)
Mo(3)-O(12)	1.732(3)	O(1)-Mo(1)-O(12)$^{\#5}$	78.02(9)
Mo(3)-O(10)	1.862(2)	O(6)-Mo(2)-O(13)$^{\#7}$	106.61(13)
Mo(3)-O(4)	2.033(3)	O(6)-Mo(2)-O(10)$^{\#8}$	98.92(12)
Mo(3)-O(3)$^{\#9}$	2.141(3)	O(13)$^{\#7}$-Mo(2)-O(10)$^{\#8}$	95.42(12)
Mo(3)-O(4)$^{\#8}$	2.242(3)	O(6)-Mo(2)-O(5)	92.44(12)
I(1)-O(9)	1.827(3)	O(13)$^{\#7}$-Mo(2)-O(5)	96.67(12)
I(1)-O(7)	1.838(2)	O(10)$^{\#8}$-Mo(2)-O(5)	160.31(11)
I(1)-O(4)	2.014(3)	O(6)-Mo(2)-O(7)	96.11(11)
I(1)-O(1)	2.041(3)	O(13)$^{\#7}$-Mo(2)-O(7)	157.27(11)
O(13)-Sr(1)-O(13)$^{\#1}$	140.35(12)	O(10)$^{\#8}$-Mo(2)-O(7)	81.52(11)
O(13)-Sr(1)-O(6)	63.49(9)	O(5)-Mo(2)-O(7)	81.33(10)
O(13)$^{\#1}$-Sr(1)-O(6)	147.30(8)	O(6)-Mo(2)-O(9)	164.29(12)
O(13)-Sr(1)-O(6)$^{\#1}$	147.30(8)	O(13)$^{\#7}$-Mo(2)-O(9)	88.76(11)
O(13)$^{\#1}$-Sr(1)-O(6)$^{\#1}$	63.49(9)	O(10)$^{\#8}$-Mo(2)-O(9)	82.47(10)
O(6)-Sr(1)-O(6)$^{\#1}$	108.74(12)	O(5)-Mo(2)-O(9)	82.32(10)
O(13)-Sr(1)-O(2)$^{\#2}$	91.76(8)	O(7)-Mo(2)-O(9)	68.51(9)
O(13)$^{\#1}$-Sr(1)-O(2)$^{\#2}$	72.77(8)	O(11)-Mo(3)-O(12)	103.26(13)
O(6)-Sr(1)-O(2)$^{\#2}$	137.99(9)	O(11)-Mo(3)-O(10)	105.44(12)
O(6)$^{\#1}$-Sr(1)-O(2)$^{\#2}$	73.33(8)	O(12)-Mo(3)-O(10)	99.17(12)
O(13)-Sr(1)-O(2)$^{\#3}$	72.77(8)	O(11)-Mo(3)-O(4)	93.35(12)
O(13)$^{\#1}$-Sr(1)-O(2)$^{\#3}$	91.76(8)	O(12)-Mo(3)-O(4)	95.39(11)
O(6)-Sr(1)-O(2)$^{\#3}$	73.33(8)	O(10)-Mo(3)-O(4)	152.75(11)

O(6)$^{\#1}$-Sr(1)-O(2)$^{\#3}$	137.99(9)	O(11)-Mo(3)-O(3)$^{\#9}$	90.47(12)
O(2)$^{\#2}$-Sr(1)-O(2)$^{\#3}$	133.91(12)	O(12)-Mo(3)-O(3)$^{\#9}$	165.66(12)
O(13)-Sr(1)-O(8)	70.17(6)	O(10)-Mo(3)-O(3)$^{\#9}$	80.80(11)
O(13)$^{\#1}$-Sr(1)-O(8)	70.17(6)	O(4)-Mo(3)-O(3)$^{\#9}$	79.46(10)
O(6)-Sr(1)-O(8)	125.63(6)	O(11)-Mo(3)-O(4)$^{\#8}$	160.42(12)
O(6)$^{\#1}$-Sr(1)-O(8)	125.63(6)	O(12)-Mo(3)-O(4)$^{\#8}$	89.52(11)
O(2)$^{\#2}$-Sr(1)-O(8)	66.95(6)	O(10)-Mo(3)-O(4)$^{\#8}$	86.72(10)
O(2)$^{\#3}$-Sr(1)-O(8)	66.95(6)	O(4)-Mo(3)-O(4)$^{\#8}$	70.43(11)
O(13)-Sr(1)-O(11)$^{\#4}$	78.34(8)	O(3)$^{\#9}$-Mo(3)-O(4)$^{\#8}$	76.15(10)
O(13)$^{\#1}$-Sr(1)-O(11)$^{\#4}$	130.88(8)	O(9)-I(1)-O(7)	89.47(11)
O(6)-Sr(1)-O(11)$^{\#4}$	63.78(8)	O(9)-I(1)-O(4)	90.64(11)
O(6)$^{\#1}$-Sr(1)-O(11)$^{\#4}$	70.40(8)	O(7)-I(1)-O(4)	88.47(11)
O(2)$^{\#2}$-Sr(1)-O(11)$^{\#4}$	78.89(8)	O(9)-I(1)-O(1)	90.41(11)
O(2)$^{\#3}$-Sr(1)-O(11)$^{\#4}$	135.64(8)	O(7)-I(1)-O(1)	86.56(11)
O(8)-Sr(1)-O(11)$^{\#4}$	131.84(6)	O(4)-I(1)-O(1)	174.91(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2	#2 -x+1,y-1,-z+1/2	#3 x,y-1,z	#4 x,-y,z-1/2
#5 -x+1,-y,-z+1	#6 -x+1,-y+1,-z+1	#7 -x+1/2,y+1/2,-z+1/2	#8 -x+1/2,-y-1/2,-z+1
#9 -x+1/2,-y+1/2,-z+1	#10 x,y+1,z	#11 -x+1/2,y-1/2,-z+1/2	

Table S4. Bond valence sum, and global instability index (GII) of $Ba(MoO_2)_2(IO_3)_4O$, $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$, and $Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$.

	bond valence sum				
compound	Ba^{2+}/Sr^{2+}	Mo^{6+}	I^{5+}	O^{2-}	GII
$Ba(MoO_2)_2(IO_3)_4O$	1.79	5.99	4.84-4.95	1.74-2.20	0.14
$Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$	1.81-2.33	6.36	5.01-5.10	1.81-2.21	0.18
$Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$	2.19	5.92-6.15	5.04	1.79-2.18	0.11

Table S5. Bond valence sum (H is not calculated) for the O atoms of $Ba(MoO_2)_2(IO_3)_4O$, $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$, and $Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$.

compound	O^{2-} bond valence sum (H is not calculated)						
$Ba(MoO_2)_2(IO_3)_4O$	**O(1)**	**O(2)**	**O(3)**	**O(4)**	**O(5)**	**O(6)**	**O(7)**
	2.12	1.89	1.95	1.80	1.74	2.20	1.98
	O(8)	**O(9)**					
	1.96	2.08					
$Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$	**O(1)**	**O(2)**	**O(3)**	**O(4)**	**O(5)**	**O(6)**	**O(7)**
	1.14	1.07	1.90	2.21	0.51	1.93	1.83
	O(8)	**O(9)**	**O(10)**	**O(11)**	**O(12)**		
	2.14	2.21	1.81	2.16	1.88		
$Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$	**O(1)**	**O(2)**	**O(3)**	**O(4)**	**O(5)**	**O(6)**	**O(7)**
	2.12	1.92	2.15	2.09	2.01	2.02	1.94
	O(8)	**O(9)**	**O(10)**	**O(11)**	**O(12)**	**O(13)**	
	0.24	1.94	2.06	1.79	2.09	2.02	

Table S6. The basic information of the existing metal iodates in the Mo(VI)-I(V)-O system.

No.	Chemical formula	I/ Mo	A/(Mo+I)	Anionic groups
1	$Ba((MoO_2)_6(IO_4)_2O_4)(H_2O)$[1]	0.33	0.125	$[(MoO_2)_3(IO_4)O_2]^-$ layer
2	$Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$	0.33	0.125	$[(MoO_2)_3(IO_4)O_2]^-$ layer
3	α-$KMoO_3(IO_3)$[2]	1	0.5	$[MoO_3(IO_3)]^-$ layer
4	β-$KMoO_3(IO_3)$[3]	1	0.5	$[MoO_3(IO_3)]^-$ layer
5	$Li(MoO_3)(IO_3)$[4]	1	0.5	$[MoO_3(IO_3)]^-$ layer
6	$Rb(MoO_3(IO_3)$[2]	1	0.5	$[MoO_3(IO_3)]^-$ layer
7	$Cs(MoO_3(IO_3)$[2]	1	0.5	$[MoO_3(IO_3)]^-$ layer
8	$Ba[(MoO_2)_2(IO_3)_4O]$	2	0.17	$[(MoO_2)_2(IO_3)_4O]^{2-}$ layer
9	$Ba_3(MoO_2)_2(IO_3)_4O(OH)_4\cdot 2H_2O$	2	0.5	$[Mo_2O_{11}]^{10-}$ dimer and IO_3^- pyramid
10	$K_2MoO_2(IO_3)_4$[5]	4	0.4	$[MoO_2(IO_3)_4]^{2-}$ cluster
11	$Ag_2(MoO_2)(IO_3)_4$[6]	4	0.4	$[MoO_2(IO_3)_4]^{2-}$ cluster
12	$BaMoO_2(IO_3)_4(H_2O)$[5]	4	0.2	$[MoO_2(IO_3)_4]^{2-}$ cluster
13	$Ln((MoO_2)(IO_3)_4(OH))$ (Ln = La, Eu, Sm, Nd)[7,8]	4	0.2	$[(MoO_2)(IO_3)_4]^{3-}$ cluster

Table S7. The basic information of the existing metal iodates in the V(V)-I(V)-O system.

No.	Chemical formula	I/V	A/(V+I)	Anionic groups
1	$Ln(VO_3)_2(IO_3)$ (Ln = Sm, Pr, Nd, La, Eu, Ce)[9]	0.5	0.33	$[VO_3]^-$ chains and isolated $[IO_3]^-$ pyramid
2	$Zn_2(VO_4)(IO_3)$[10]	1	1	Isolated $[VO_4]^{3-}$ polyhedron and $[IO_3]^-$ pyramid
3	$Li[(VO)_2(IO_3)_2]$[11]	1	0.25	$[(VO)_2(IO_3)_2]^-$ layer
4	$Rb(VO)_2(IO_3)_3O_2$[12]	1.5	0.2	$[(VO)_2(IO_3)_3O_2]^-$ chain
5	$Cs(VO)_2(IO_3)_3O_2$[12]	1.5	0.2	$[(VO)_2(IO_3)_3O_2]^-$ chain
6	$Na(VO_2)(IO_3)_2\cdot H_2O$[13]	2	0.33	$[(VO_2)(IO_3)_2]^-$ chain
7	$Rb[VO_2(IO_3)_2]$[12]	2	0.33	$[VO_2(IO_3)_2]^-$ chain
8	$Ag_2(V_2O_4)(IO_3)_4$[6]	2	0.33	$[(V_2O_4)(IO_3)_4]^{2-}$ chain
9	$Ag_2(VO_2)(IO_3)_3$[6]	3	0.5	$[(VO_2)(IO_3)_3]^{2-}$ chain
10	$LaVO_2(IO_3)_4\cdot H_2O$[14]	4	0.2	$[VO_2(IO_3)_4]^{3-}$ cluster
11	$Ba_2VO_2(IO_3)_4(IO_3)$[5]	5	0.33	$[VO_2(IO_3)_4]^{3-}$ cluster and isolated $[IO_3]^-$ pyramid

Figure S1. Asymmetric units of (a) $Ba(MoO_2)_2(IO_3)_4O$, (b) $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$, and (c) $Sr[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$, respectively.

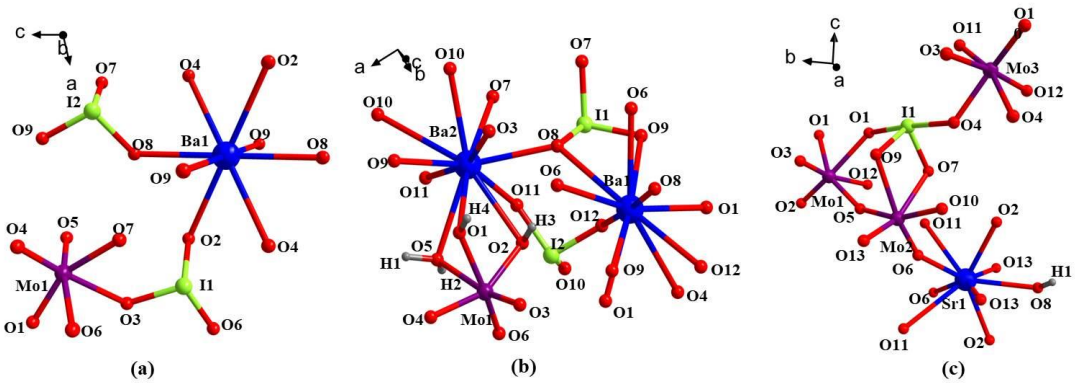


Figure S2. The UV-Vis-NIR diffuse reflectance spectra of $Ba(MoO_2)_2(IO_3)_4O$ and $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$.

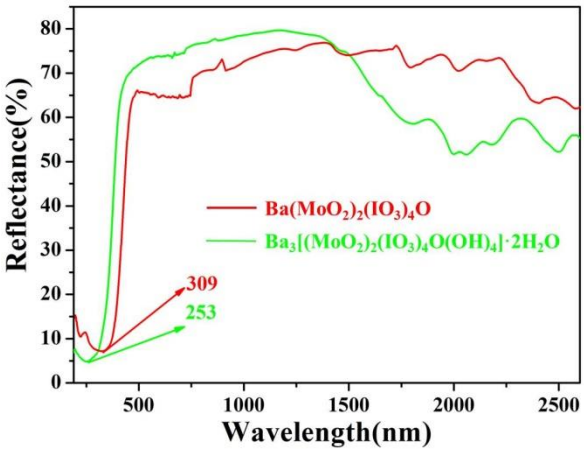
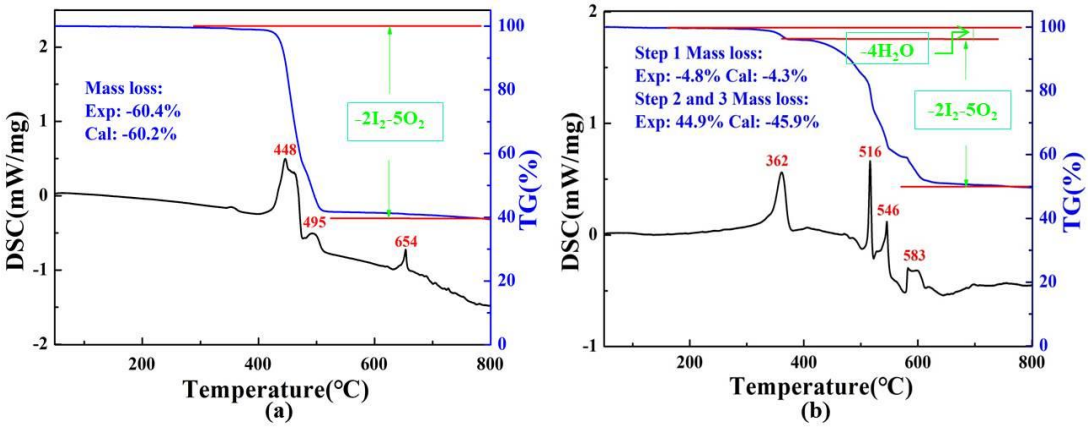


Figure S3. The TG-DSC curves of (a) $Ba(MoO_2)_2(IO_3)_4O$ and (b) $Ba_3[(MoO_2)_2(IO_3)_4O(OH)_4]\cdot 2H_2O$.



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