Electronic Supplementary Information

Synthesis, structure and characterizations of $M(IO_3)_2(HIO_3)$ (M = Ca, Sr), new anhydrous alkaline earth metal bis-iodate hydrogeniodate compounds

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Table S1 Crystallographic data and structure refinements for $M(IO_3)_2(HIO_3)$ (M = Ca, Sr).

Formula	**$Ca(IO_3)_2(HIO_3)$**	**$Sr(IO_3)_2(HIO_3)$**
F.W.	565.79	613.33
T (K)	293(2)	293(2)
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a (Å)	6.9647(14)	7.0697(14)
b (Å)	15.719(3)	15.986(3)
c (Å)	7.2042(14)	7.3802(15)
α (deg)	90.00	90.00
β (deg)	92.76(3)	93.13(3)
γ (deg)	90.00	90.00
V (Å^3)	787.8(3)	832.8(3)
Z	4	4
ρ_{cal} (g/cm^3)	4.770	4.891
μ (mm^{-1})	12.578	17.618
$F_{(000)}$	1008	1080
Crystal size (mm^3)	0.16 × 0.12 × 0.11	0.08 × 0.07 × 0.07
2θ range for data collection	5.856 to 59.996°	5.772 to 60.152°
	$-9 \le h \le 9$	$-9 \le h \le 9$
Index ranges	$-22 \le k \le 19$	$-22 \le k \le 22$
	$-10 \le l \le 8$	$-10 \le l \le 10$
Reflections collected	7098	7655
Independent reflections	2240	2373
R_{int}	0.0442	0.0501
R_{sigma}	0.0335	0.0458
Data/restraints/parameters	2240/0/118	2373/0/118
GOF on F^2	1.217	1.161
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0346, 0.0843	0.0438, 0.1003
R_1, wR_2 (all data)	0.0358, 0.0850	0.0471, 0.1024

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $M(IO_3)_2(HIO_3)$ (M = Ca, Sr). U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyck.	*x/a*	*y/b*	*z/c*	U_{eq}
			$Ca(IO_3)_2(HIO_3)$		
Ca1	4*e*	0.22814(19)	0.54636(8)	0.86712(18)	12.5(2)
I1	4*e*	0.85860(5)	0.22751(2)	0.97855(5)	8.59(10)
I2	4*e*	0.39268(5)	0.31679(2)	0.87569(5)	9.33(10)
I3	4*e*	0.26999(5)	0.47287(2)	1.36963(5)	9.63(10)
O1	4*e*	0.8756(8)	0.1802(3)	0.7468(6)	15.4(9)
O2	4*e*	0.8518(7)	0.3366(3)	0.8878(6)	13.6(9)
O3	4*e*	0.5979(7)	0.2168(3)	0.9969(7)	16.1(9)
O4	4*e*	0.4679(7)	0.3844(3)	1.0655(7)	19.0(10)
O5	4*e*	0.2277(7)	0.2464(3)	0.9848(8)	18.7(10)
O6	4*e*	0.1876(7)	0.3936(3)	0.7874(7)	13.5(9)
H6	4*e*	0.08851	0.374038	0.837204	16
O7	4*e*	0.1173(7)	0.4855(3)	1.1602(6)	13.3(9)
O8	4*e*	0.1742(7)	0.5532(3)	1.5184(6)	15.0(9)
O9	4*e*	0.4854(7)	0.5262(3)	1.2996(7)	16.2(9)
			$Sr(IO_3)_2(HIO_3)$		
Sr1	4*e*	0.24288(10)	0.54359(5)	0.87786(11)	11.46(17)
I1	4*e*	0.84717(7)	0.22889(3)	0.96634(7)	9.54(13)
I2	4*e*	0.37897(7)	0.31309(3)	0.86172(7)	11.09(13)
I3	4*e*	0.26450(7)	0.47368(3)	1.37467(7)	11.33(13)
O1	4*e*	0.8632(10)	0.1830(4)	0.7421(8)	18.4(13)
O2	4*e*	0.8475(8)	0.3364(3)	0.8815(8)	13.1(11)
O3	4*e*	0.5917(8)	0.2193(4)	0.9862(9)	18.6(13)
O4	4*e*	0.4441(9)	0.3834(4)	1.0446(9)	21.6(14)
O5	4*e*	0.2216(8)	0.2425(4)	0.9659(10)	21.5(14)
O6	4*e*	0.1790(8)	0.3865(4)	0.7662(9)	15.7(12)
H6	4*e*	0.065112	0.393719	0.794268	19
O7	4*e*	0.1112(8)	0.4852(4)	1.1725(8)	14.1(11)
O8	4*e*	0.1760(8)	0.5537(4)	1.5191(8)	14.7(12)
O9	4*e*	0.4764(8)	0.5236(4)	1.2986(9)	19.2(13)

Table S3 Anisotropic displacement parameters ($Å^2 \times 10^3$) for $M(IO_3)_2(HIO_3)$ (M = Ca, Sr).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			$Ca(IO_3)_2(HIO_3)$			
Ca1	11.5(5)	12.0(5)	13.9(5)	0.0(4)	0.6(4)	-1.6(4)
I1	8.56(19)	8.25(18)	9.01(17)	1.38(12)	0.85(12)	0.80(12)
I2	8.62(19)	8.59(18)	10.86(18)	-0.48(12)	1.23(12)	-0.25(13)
I3	10.03(19)	8.67(18)	10.11(17)	0.02(12)	-0.40(13)	-0.52(13)
O1	27(3)	11(2)	8.8(19)	-2.5(16)	3.1(17)	-1.4(19)
O2	18(2)	10(2)	13(2)	1.3(16)	2.1(17)	1.4(17)
O3	10(2)	18(2)	20(2)	7.2(19)	2.3(17)	2.2(18)
O4	17(2)	24(3)	16(2)	-10.7(19)	1.9(18)	-1(2)
O5	11(2)	13(2)	32(3)	8(2)	1.8(19)	-4.0(18)
O6	9(2)	10(2)	21(2)	1.5(17)	0.4(17)	1.5(16)
O7	12(2)	15(2)	12(2)	0.2(16)	-3.8(16)	0.3(17)
O8	17(2)	13(2)	16(2)	-5.4(17)	3.5(17)	-0.8(18)
O9	11(2)	19(2)	18(2)	0.0(18)	5.7(17)	-5.0(18)
			$Sr(IO_3)_2(HIO_3)$			
Sr1	9.7(3)	12.1(4)	12.6(4)	-0.6(3)	0.2(3)	-0.6(2)
I1	9.4(2)	10.2(2)	9.0(2)	0.88(17)	-0.31(17)	0.86(16)
I2	9.6(2)	10.4(2)	13.3(3)	-0.24(18)	0.54(17)	-0.09(16)
I3	10.9(2)	11.6(2)	11.3(3)	-0.23(18)	-1.33(17)	0.24(17)
O1	31(3)	17(3)	7(3)	0(2)	1(2)	-4(3)
O2	17(3)	4(2)	18(3)	4(2)	-1(2)	2(2)
O3	5(2)	25(3)	26(3)	8(3)	-1(2)	2(2)
O4	20(3)	20(3)	25(3)	-12(3)	1(3)	-3(3)
O5	9(3)	17(3)	38(4)	7(3)	2(3)	-3(2)
O6	9(2)	14(3)	25(3)	3(2)	-3(2)	6(2)
O7	13(3)	18(3)	11(3)	4(2)	-5(2)	3(2)
O8	18(3)	15(3)	11(3)	-6(2)	-1(2)	-2(2)
O9	13(3)	27(3)	19(3)	-8(3)	6(2)	-6(2)

Table S4 Selected interatomic distances and calculated bond valence values of the Ca and Sr atoms for $M(IO_3)_2(HIO_3)$ (M = Ca, Sr).

Atoms	Distance (Å)	Bond Valence	Atoms	Distance (Å)	Bond Valence
Ca1−O1[i]	2.359(5)	0.347	Sr1−O1[i]	2.498(6)	0.358
Ca1−O2[ii]	2.628(5)	0.168	Sr1−O2[ii]	2.715(6)	0.199
Ca1−O4[ii]	2.409(5)	0.303	Sr1−O4[ii]	2.540(6)	0.320
Ca1−O6	2.483(5)	0.267	Sr1−O6	2.674(6)	0.223
Ca1−O7	2.475(5)	0.248	Sr1−O7	2.586(6)	0.282
Ca1−O7[iii]	2.456(5)	0.253	Sr1−O7[iii]	2.553(6)	0.309
Ca1−O8[iv]	2.524(5)	0.222	Sr1−O8[iv]	2.669(6)	0.226
Ca1−O9[ii]	2.637(5)	0.164	Sr1−O9[ii]	2.659(6)	0.232
<Ca1−O>	2.496		<Sr1−O>	2.612	
BVS		2.15	BVS		1.97

[i] 1-*x*, 1/2+*y*, 3/2-*z*; [ii] 1-*x*, 1-*y*, 2-*z*; [iii] -*x*, 1-*y*, 2-*z*; [iv] *x*, *y*, -1+*z*.

Table S5 Selected bond lengths, interatomic distances, calculated bond valence values and bond angles of the iodine atoms for $Sr(IO_3)_2(HIO_3)$

Atoms	Distance (Å)	Bond Valence	Atoms	Angle (°)
I1−O1	1.820(6)	1.640	O1−I1−O2	93.8(3)
I1−O2	1.829(5)	1.600	O1−I1−O3	98.6(3)
I1−O3	1.827(6)	1.609	O2−I1−O3	97.2(3)
<I1−O>	1.825		<O−I1−O>	96.3
I1···O1[i]	2.473(6)	0.281		
I1···O5[ii]	2.656(6)	0.171		
I1···O8[iii]	2.808(6)	0.114		
BVS (I1)		5.42		
I2−O4	1.797(6)	1.745	O4−I2−O5	102.2(3)
I2−O5	1.788(6)	1.788	O4−I2−O6	92.7(3)
I2−O6	1.940(6)	1.186	O5−I2−O6	94.6(3)
<I2−O>	1.842		<O−I2−O>	95.9
I2···O3	2.281(6)	0.473		
I2···O9[iv]	3.065(6)	0.057		
BVS (I2)		5.25		
I3−O7	1.805(6)	1.708	O7−I3−O8	101.8(3)
I3−O8	1.799(6)	1.736	O7−I3−O9	99.7(3)
I3−O9	1.813(6)	1.671	O8−I3−O9	101.0(3)
<I3−O>	1.806		<O−I3−O>	100.8
I3···O9[v]	2.948(3)	0.078		
BVS (I3)		5.19		

[i] *x*, 0.5-*y*, 0.5+*z*; [ii] 1+*x*, *y*, *z*; [iii] 1-*x*, -0.5+*y*, 2.5-*z*; [iv] 1-*x*, 1-*y*, 2-*z*; [v] 1-*x*, 1-*y*, 3-*z*.

Table S6 Calculated bond valence sum (BVS) of the O atoms for $M(IO_3)_2(HIO_3)$ (M = Ca, Sr)*.

$Ca(IO_3)_2(HIO_3)$						
Bond Valence	Ca1	I1	I2	I3	H6	BVS
O1	0.347	1.566 0.328				2.24
O2	0.168	1.575			0.344	2.09
O3		1.575	0.485			2.06
O4	0.303		1.778	0.070		2.15
O5		0.206	1.717			1.92
O6	0.248		1.145		0.850	2.24
O7	0.267 0.253			1.667		2.19
O8	0.222	0.133		1.708		2.06
O9	0.164		0.085	1.680 0.098		2.03
$Sr(IO_3)_2(HIO_3)$						
Bond Valence	Sr1	I1	I2	I3	H6	BVS
O1	0.358	1.640 0.281				2.28
O2	0.199	1.600			0.244	2.04
O3		1.609	0.473			2.08
O4	0.320		1.745			2.07
O5		0.171	1.788			1.96
O6	0.223		1.186		0.850	2.26
O7	0.309 0.282			1.708		2.30
O8	0.226	0.114		1.736		2.08
O9	0.232		0.057	1.671 0.078		2.04

* The bond valence parameters R_0 of Ca−O, Sr−O and I−O bonds in the calculations were 1.967, 2.118 and 2.003, respectively.[1] For O−H···O hydrogen bond, the value of R_0 was 0.790 for O−H bond, and 1.409 for O···H bond.[2] The bond valence parameters B of all bonds were 0.37.

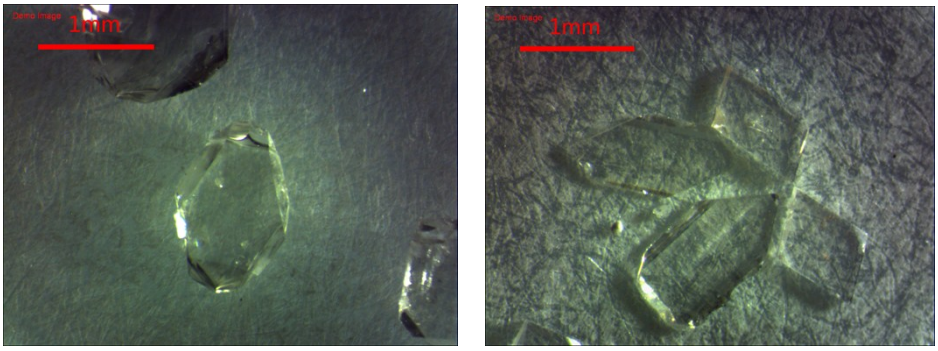
Ref:

[1] I. D. Brown and D. Altermatt, *Acta Cryst.*, 1985, B41, 244–247.

[2] D. Yu, D. Xue and H. Ratajczak, *Phys. B*, 2006, 371, 170–176.

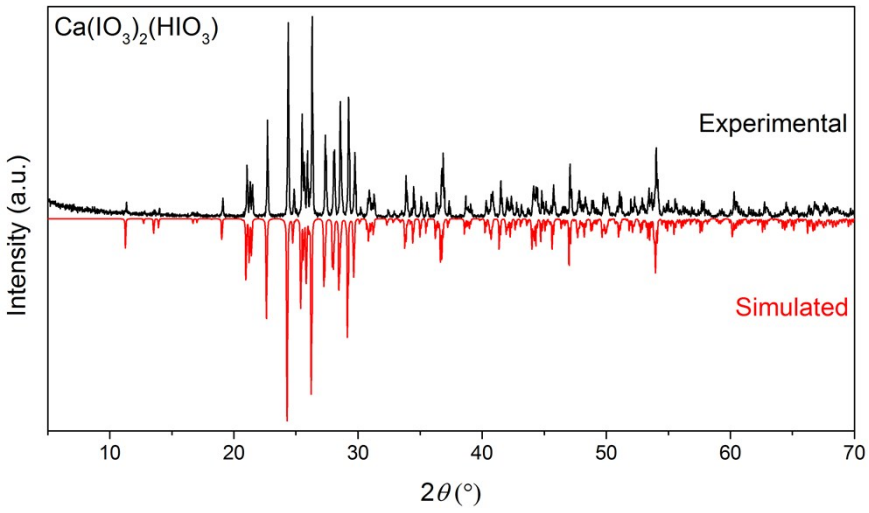
Table S7 The state energies (eV) of the lowest conduction band (LCB) and the highest valence band (HVB) for $M(IO_3)_2(HIO_3)$ (M = Ca, Sr).

Compound	*k*-point	HVB	LCB
$Ca(IO_3)_2(HIO_3)$	Z (0.000, 0.000, 0.500)	-0.539	3.539
	G (0.000, 0.000, 0.000)	-0.391	3.227
	Y (0.000, 0.500, 0.000)	-0.415	3.285
	A (-0.500, 0.500, 0.000)	-0.350	3.004
	B (-0.500, 0.000, 0.000)	-0.329	2.967
	D (-0.500, 0.000, 0.500)	-0.455	3.068
	E (-0.500, 0.500, 0.500)	-0.465	3.049
	C (0.000, 0.500, 0.500)	-0.540	3.543
$Sr(IO_3)_2(HIO_3)$	Z (0.000, 0.000, 0.500)	-0.581	3.566
	G (0.000, 0.000, 0.000)	-0.393	3.251
	Y (0.000, 0.500, 0.000)	-0.407	3.341
	A (-0.500, 0.500, 0.000)	-0.318	3.005
	B (-0.500, 0.000, 0.000)	-0.301	2.983
	D (-0.500, 0.000, 0.500)	-0.504	3.086
	E (-0.500, 0.500, 0.500)	-0.508	3.066
	C (0.000, 0.500, 0.500)	-0.581	3.569

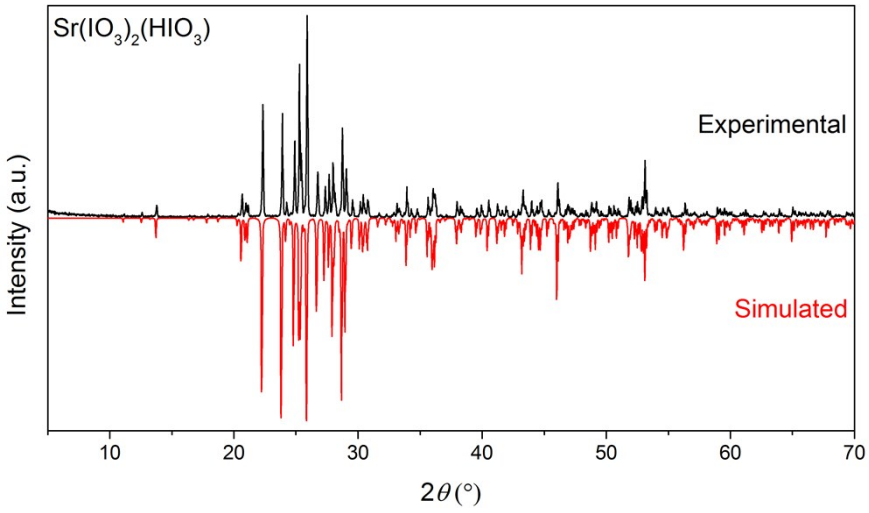


(a) **(b)**

Fig. S1 Photos of $Ca(IO_3)_2(HIO_3)$ (a) and $Sr(IO_3)_2(HIO_3)$ (b) single crystals by the hydrothermal method.



(a)



(b)

Fig. S2 Experimental powder XRD patterns of $Ca(IO_3)_2(HIO_3)$ (a) and $Sr(IO_3)_2(HIO_3)$ (b) and the simulated patterns.

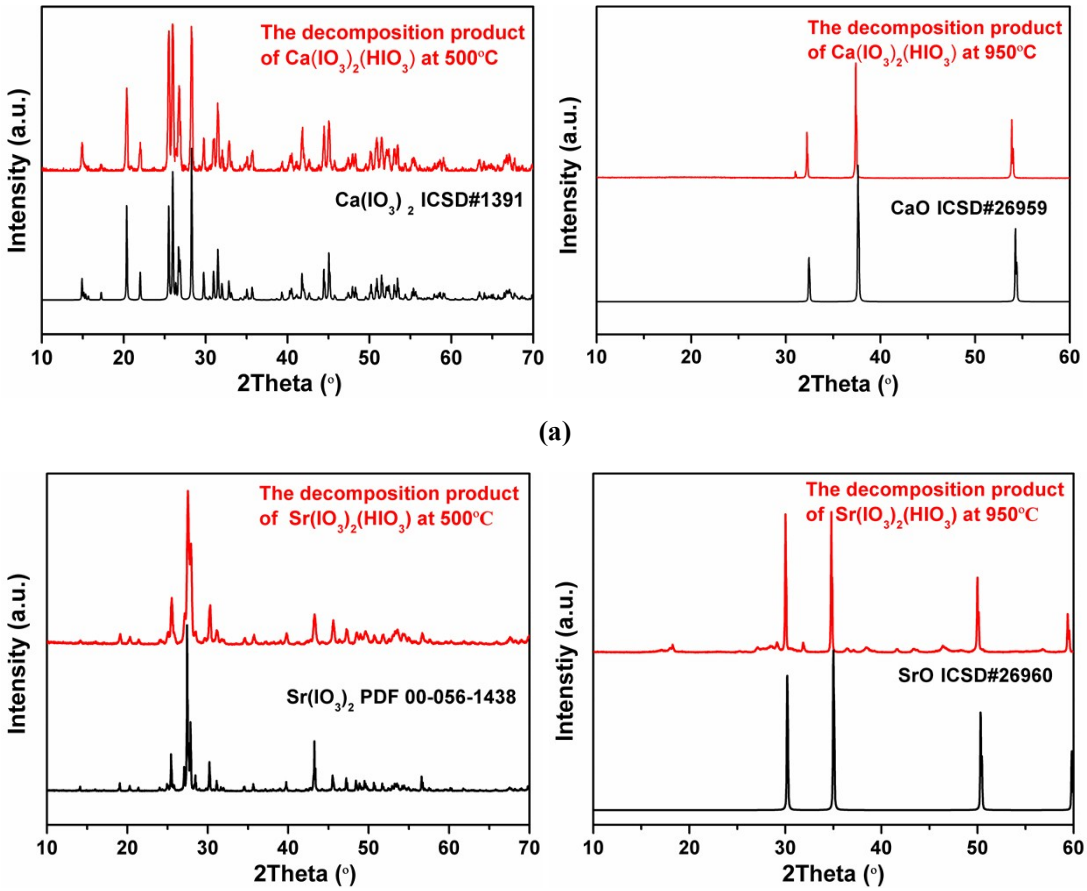
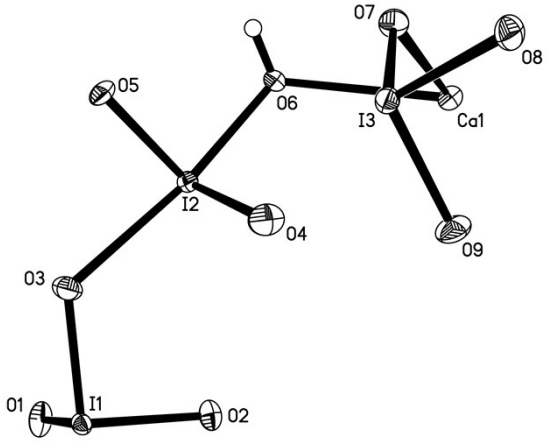
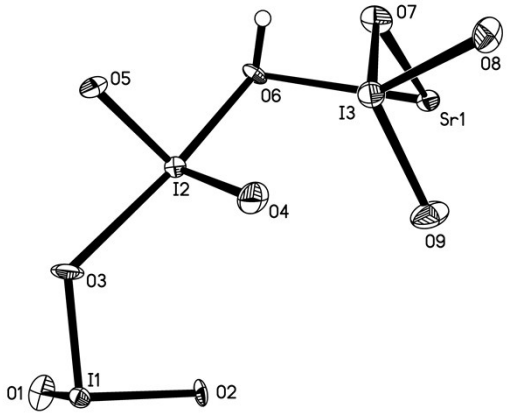


Fig. S3 Powder XRD patterns of the decomposition productions at 500°C and 950°C for $Ca(IO_3)_2(HIO_3)$ (a) and $Sr(IO_3)_2(HIO_3)$ (b).

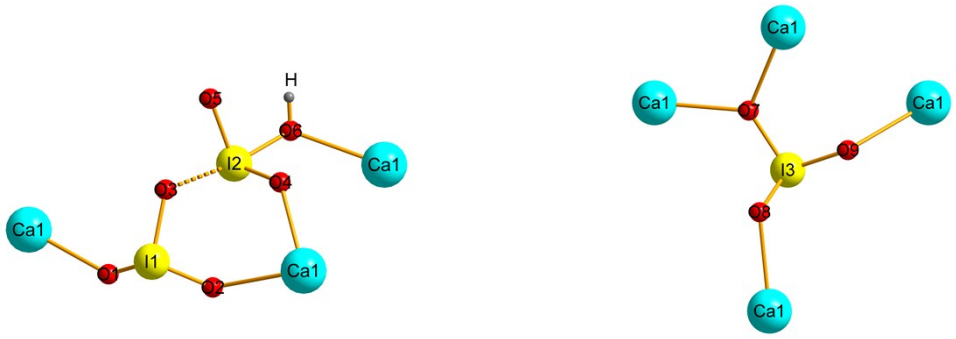


(a)



(b)

Fig. S4 Views of the asymmetric units of $Ca(IO_3)_2(HIO_3)$ (a) and $Sr(IO_3)_2(HIO_3)$ (b) with 50% probability displacement.



(a) **(b)**

Fig. S5 Coordination environments of the $[HIO_3]\cdot[IO_3]^-$ complex (a) and $[I(3)O_3]^-$ (b) on Ca^{2+} in the structure of $Ca(IO_3)_2(HIO_3)$.

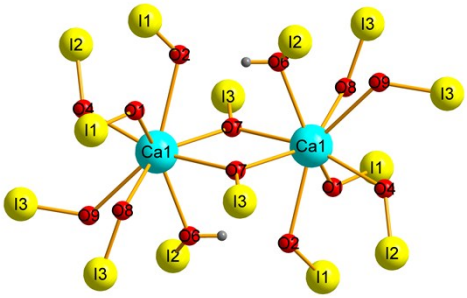


Fig. S6 Ca_2O_{14} dimer in the structure of $Ca(IO_3)_2(HIO_3)$.