Hg$_2$(SeO$_3$)(SO$_4$): The First Sulfate Selenite with Large Birefringence Explored from d^{10} Transition Metal Compounds

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Supporting Information

Table S1. Calculated bond valences for the three compounds.

Compound	Bond	Bond lengths	Bond-valence	BVS
Hg₂(SeO₃)(SO₄)	Se(1)-O(1)	1.715(7)	1.296	3.788
	Se(1)-O(2)#1	1.749(7)	1.182	
	Se(1)-O(3)	1.711(8)	1.310	
	S(1)-O(4)	1.459(8)	1.526	6.107
	S(1)-O(5)	1.489(8)	1.440	
	S(1)-O(6)	1.475(7)	1.496	
	S(1)-O(7)#2	1.448(8)	1.609	
	Hg(1)-O(1)	2.176(7)	0.514	1.681
	Hg(1)-O(2)	2.249(7)	0.422	
	Hg(1)-O(3)#3	2.549(8)	0.188	
	Hg(1)-O(4)#4	2.560(8)	0.182	
	Hg(1)-O(4)	2.678(8)	0.132	
	Hg(1)-O(5)#5	2.453(8)	0.243	
	Hg(2)-O(1)#6	2.375(7)	0.300	1.817
	Hg(2)-O(2)#7	2.225(7)	0.451	
	Hg(2)-O(3)	2.194(7)	0.490	
	Hg(2)-O(6)	2.381(8)	0.296	
	Hg(2)-O(7)#7	2.401(8)	0.280	
La₂Hg₃(SeO₃)₄(SO₄)₂(H₂O)₂	Se(1)-O(1)	1.677(7)	1.436	4.002
	Se(1)-O(2)	1.708(7)	1.321	
	Se(1)-O(3)	1.730(7)	1.245	
	Se(2)-O(4)	1.729(7)	1.248	3.985
	Se(2)-O(5)	1.723(7)	1.269	
	Se(2)-O(6)	1.669(7)	1.468	
	Se(3)-O(7)	1.707(7)	1.325	4.125
	Se(3)-O(8)	1.688(8)	1.394	
	Se(3)-O(9)	1.685(7)	1.406	
	Se(4)-O(10)	1.730(7)	1.245	4.012
	Se(4)-O(11)	1.697(9)	1.361	
	Se(4)-O(12)	1.685(8)	1.406	
	Hg(1)-O(5)#1	2.370(7)	0.304	1.835
	Hg(1)-O(5)	2.505(7)	0.211	
	Hg(1)-O(6)	2.721(8)	0.118	
	Hg(1)-O(9)	2.152(7)	0.549	
	Hg(1)-O(10)	2.176(7)	0.514	
	Hg(1)-O(11)#2	2.660(9)	0.139	
	Hg(2)-O(3)#3	2.166(8)	0.528	1.749
	Hg(2)-O(3)#4	2.459(8)	0.239	

	Hg(2)-O(4)#1	2.294(7)	0.374	
	Hg(2)-O(5)#1	2.358(7)	0.315	
	Hg(2)-O(8)#4	2.568(8)	0.178	
	Hg(2)-O(10)#1	2.730(8)	0.115	
	Hg(3)-O(1)	2.427(8)	0.261	1.791
	Hg(3)-O(2)	2.346(7)	0.325	
	Hg(3)-O(8)	2.283(8)	0.385	
	Hg(3)-O(10)#2	2.527(8)	0.199	
	Hg(3)-O(11)	2.290(9)	0.378	
	Hg(3)-O(12)	2.453(9)	0.243	
	La(1)-O(2)	2.457(7)	0.463	3.283
	La(1)-O(4)#5	2.441(7)	0.483	
	La(1)-O(7)	2.549(7)	0.361	
	La(1)-O(13)#6	2.522(7)	0.388	
	La(1)-O(13)	2.572(7)	0.339	
	La(1)-O(14)	2.798(8)	0.184	
	La(1)-O(15)	2.589(8)	0.324	
	La(1)-O(16)	2.530(7)	0.380	
	La(1)-O(17)#6	2.549(7)	0.361	
	La(2)-O(6)	2.432(7)	0.495	3.145
	La(2)-O(7)	2.653(7)	0.273	
	La(2)-O(12)	2.477(7)	0.439	
	La(2)-O(14)	2.524(7)	0.386	
	La(2)-O(16)	2.880(8)	0.148	
	La(2)-O(18)#7	2.538(7)	0.372	
	La(2)-O(19)	2.469(8)	0.448	
	La(2)-O(22)#7	2.577(7)	0.335	
	La(2)-O(22)	2.687(7)	0.249	
	S(1)-O(13)	1.515(7)	1.343	5.991
	S(1)-O(14)	1.481(7)	1.472	
	S(1)-O(18)	1.462(7)	1.549	
	S(1)-O(21)	1.444(8)	1.627	
	S(2)-O(16)	1.497(7)	1.410	5.978
	S(2)-O(17)	1.466(7)	1.533	
	S(2)-O(20)	1.454(8)	1.583	
	S(2)-O(22)	1.486(7)	1.452	
$Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$	S(1)-O(1)	1.558(6)	1.192×0.7	6.073
	S(1)-O(2)	1.510(7)	1.357×0.7	
	S(1)-O(3)	1.517(7)	1.332×0.7	
	S(1)-O(4)	1.522(6)	1.321×0.7	
	Se(1)-O(1)	1.558(6)	1.857×0.3	
	Se(1)-O(2)	1.510(7)	2.114×0.3	
	Se(1)-O(3)	1.517(7)	2.075×0.3	

Se(1)-O(4)	1.522(6)	2.058×0.3	
Se(2)-O(5)	1.805(6)	1.016	
Se(2)-O(6)	1.665(6)	1.480	3.921
Se(2)-O(7)	1.680(7)	1.425	
Se(3)-O(5)	1.841(6)	0.922	
Se(3)-O(8)	1.663(6)	1.492	4.023
Se(3)-O(9)	1.636(7)	1.609	
Cd(1)-O(1)	2.402(5)	0.261	
Cd(1)-O(1)#1	2.299(6)	0.345	
Cd(1)-O(3)#2	2.231(7)	0.414	
Cd(1)-O(6)	2.302(6)	0.341	2.317
Cd(1)-O(7)#3	2.251(7)	0.391	
Cd(1)-O(8)#4	2.256(5)	0.385	
Ag(1)-O(4)#2	2.387(7)	0.208	
Ag(1)-O(6)#4	2.605(6)	0.115	
Ag(1)-O(8)	2.426(7)	0.186	
Ag(1)-O(8)#4	2.752(7)	0.077	0.755
Ag(1)-O(9)#5	2.759(7)	0.076	
Ag(1)-O(9)	2.683(7)	0.093	
Ag(2)-O(2)#3	2.398(8)	0.202	
Ag(2)-O(6)#1	2.347(7)	0.232	
Ag(2)-O(7)#3	2.484(5)	0.159	0.870
Ag(2)-O(7)#1	2.833(6)	0.062	
Ag(2)-O(9)#2	2.373(6)	0.215	

Symmetry transformations used to generate equivalent atoms:
For $Hg_2(SeO_3)(SO_4)$: #1 x+1,y,z; #2 x,-y+1/2,z+1/2; #3 x-1,y,z; #4 -x+1,y+1/2,-z+3/2; #5 -x+1,y-1/2,-z+3/2; #6 -x+2,y+1/2,-z+3/2; #7 x+1,-y+1/2,z+1/2

For $La_2Hg_3(SeO_3)_4(SO_4)_2(H_2O)_2$: #1 -x+1,-y+1,-z+1; #2 -x+2,-y+1,-z+1; #3 x-1,y,z; #4 -x+2,-y,-z+1; #5 x+1,y-1,z; #6 -x+3,-y,-z; #7 -x+2,-y+1,-z

For $Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$: #1 -x,-y+1,-z+1; #2 -x+1,-y+1,-z+1; #3 x,y+1,z; #4 -x+1,-y+1,-z+2; #5 -x+2,-y+1,-z+2

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Table S2. State energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of the three compounds.

Compound	k-point	L-CB	H-VB
Hg$_2$(SeO$_3$)(SO$_4$)	Z (0.000, 0.000, 0.500)	2.248452	-0.12755
	G (0.000, 0.000, 0.000)	1.831251	-0.00034
	Y (0.000, 0.500, 0.000)	2.281541	-0.1403
	A (-0.500, 0.500, 0.000)	2.94249	-0.01032
	B (-0.500, 0.000, 0.000)	2.774263	-0.01292
	D (-0.500, 0.000, 0.500)	3.022949	-0.1993
	E (-0.500, 0.500, 0.500)	3.165734	-0.07818
	C (0.000, 0.500, 0.500)	2.527822	-0.15376
La$_2$Hg$_3$(SeO$_3$)$_4$(SO$_4$)$_2$ (H$_2$O)$_2$	G (0.000, 0.000, 0.000)	2.998581	-0.03766
	F (0.000, 0.500, 0.000)	3.115381	0
	Q (0.000, 0.500, 0.500)	3.114743	-0.01074
	Z (0.000, 0.000, 0.500)	2.994337	-0.04353
	G (0.000, 0.000, 0.000)	2.998581	-0.03766
Ag$_2$Cd(Se$_2$O$_5$)(Se$_{0.3}$S$_{0.7}$O$_4$)	G (0.000, 0.000, 0.000)	2.992551	-0.1249
	F (0.000, 0.500, 0.000)	3.012731	-0.03566
	Q (0.000, 0.500, 0.500)	3.271196	0
	Z (0.000, 0.000, 0.500)	3.222415	-0.08449
	G (0.000, 0.000, 0.000)	2.992551	-0.1249

Computational Method

Single-crystal structural data of compounds $Hg_2(SeO_3)(SO_4)$, $La_2Hg_3(SeO_3)_4(SO_4)_2(H_2O)_2$ and $Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$ were used for the theoretical calculations. The electronic structures were performed using a plane-wave basis set and pseudo-potentials within density functional theory (DFT) implemented in the total-energy code CASTEP [1]. For the exchange and correlation functional, we chose Perdew–Burke–Ernzerhof (PBE) in the generalized gradient approximation (GGA) [2]. The interactions between the ionic cores and the electrons were described by the ultrasoft pseudopotential [3]. The following valence-electron configurations were considered in the computation: $La\text{-}5d^16s^2$, $Ag\text{-}4d^{10}4p^65s^1$, $Cd\text{-}4d^{10}4p^25s^2$, $Hg\text{-}5d^{10}5p^26s^2$, $Se\text{-}4s^24p^4$, $O\text{-}2s^22p^4$, $S\text{-}3s^23p^4$ and $H\text{-}1s^1$. The numbers of plane waves included in the basis sets were determined by cutoff energy of 750 eV, 750 eV and 765 eV for $Hg_2(SeO_3)(SO_4)$, $La_2Hg_3(SeO_3)_4(SO_4)_2(H_2O)_2$ and $Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$ respectively. The numerical integration of the Brillouin zone was performed using Monkhorst-Pack k-point sampling of $4 \times 4 \times 2$, $3 \times 3 \times 2$ and $4 \times 4 \times 3$ for $Hg_2(SeO_3)(SO_4)$, $La_2Hg_3(SeO_3)_4(SO_4)_2(H_2O)_2$ and $Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$ respectively. The other parameters and convergent criteria were the default values of CASTEP code.

The calculations of linear optical properties in terms of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ were made. The imaginary part of the dielectric function ε_2 was given in the following equation:

$$\varepsilon^{ij}_2(\omega) = \frac{8\pi^2h^2e^2}{(m^2V)}\sum_k\sum_{cv}(f_c - f_v)\frac{p^i_{cv}(k)p^j_{cv}(k)}{E^2_{vc}}\delta[E_c(k) - E_v(k)\text{-}h\omega]$$

The f_c and f_v represent the Fermi distribution functions of the conduction and valence band. The term $p^i_{cv}(k)$ denotes the momentum matrix element transition from the energy level c of the conduction band to the level v of the valence band at the kth point in the Brillouin zone (BZ), and V is the volume of the unit cell.
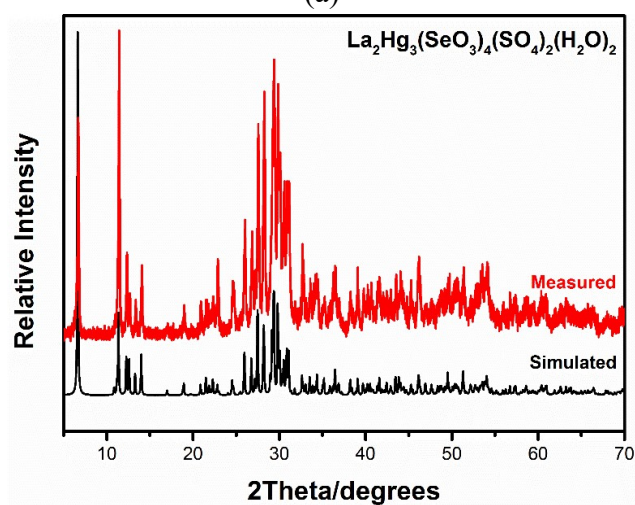
The real part $\varepsilon_1(\omega)$ of the dielectric function $\varepsilon(\omega)$ follows from the Kramer–Kronig relationship. All the other optical constants may be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. For

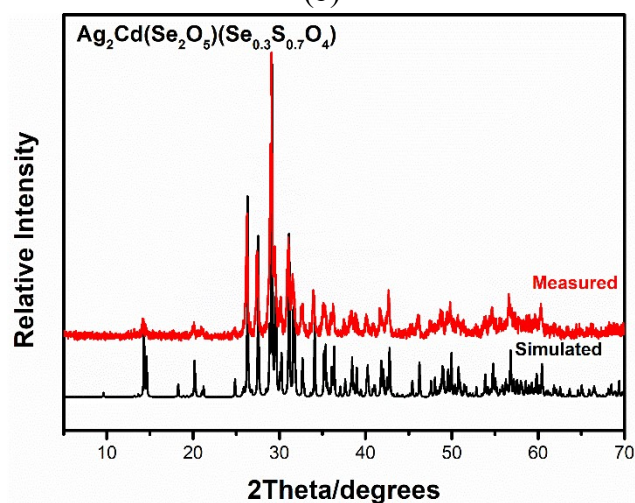example, the refractive index n(ω) can be calculated using the following expression[4]:

$$n(\omega)=(\frac{1}{\sqrt{2}})[\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)}+\varepsilon_1(\omega)]^{1/2}$$
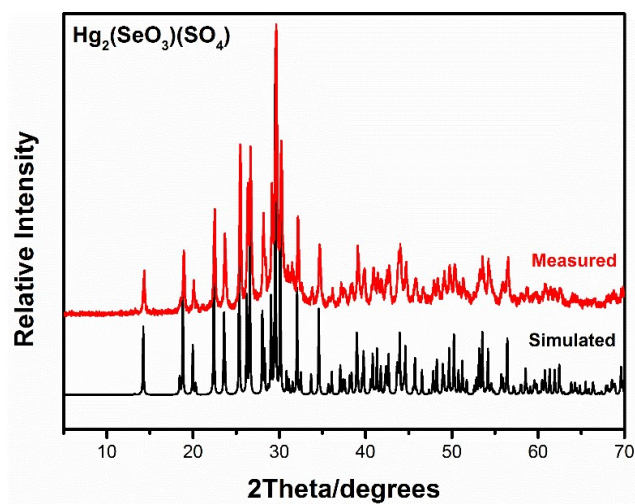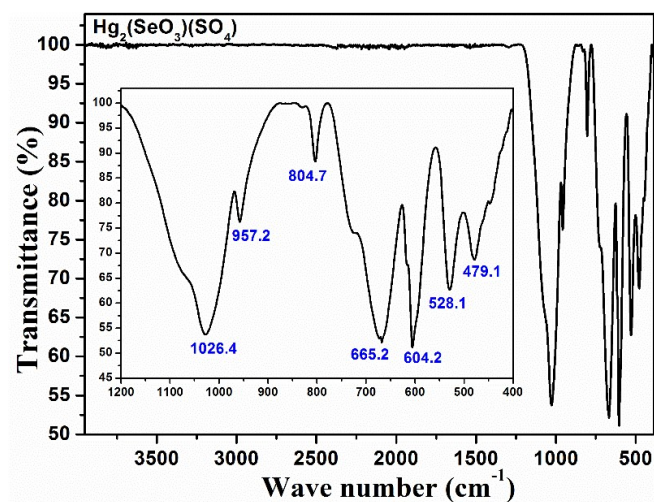
(a)

(b)

(c)

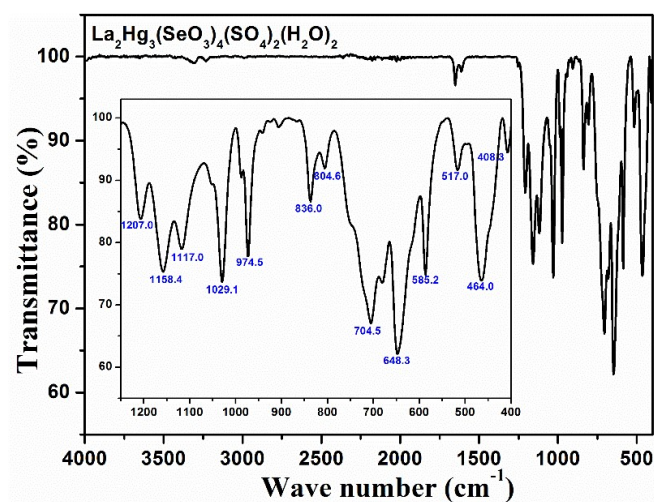**Figure S1.** Simulated and experimental powder X-ray diffractometer patterns of $Hg_2(SeO_3)(SO_4)$ (a), $La_2Hg_3(SeO_3)_4(SO_4)_2(H_2O)_2$ (b) and $Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$ (c).
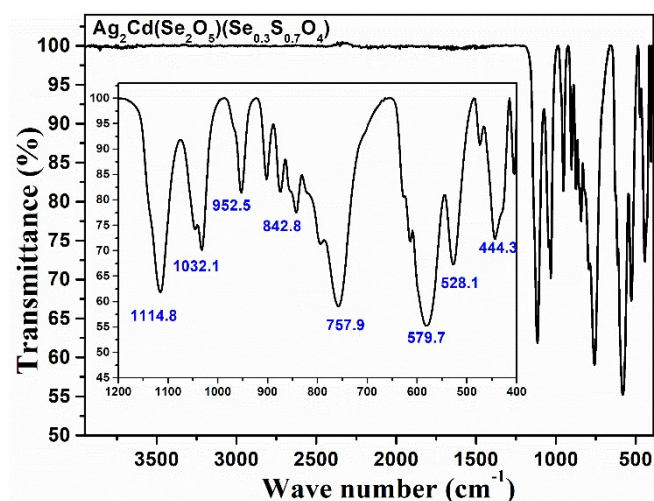
Figure S2. IR spectra of $Hg_2(SeO_3)(SO_4)$ (a), $La_2Hg_3(SeO_3)_4(SO_4)_2(H_2O)_2$ (b) and $Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$ (c).
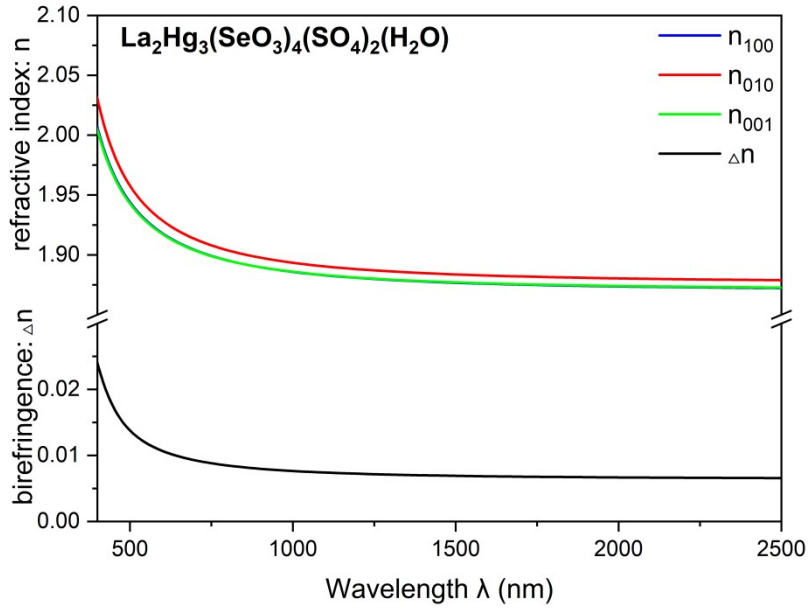
(a)
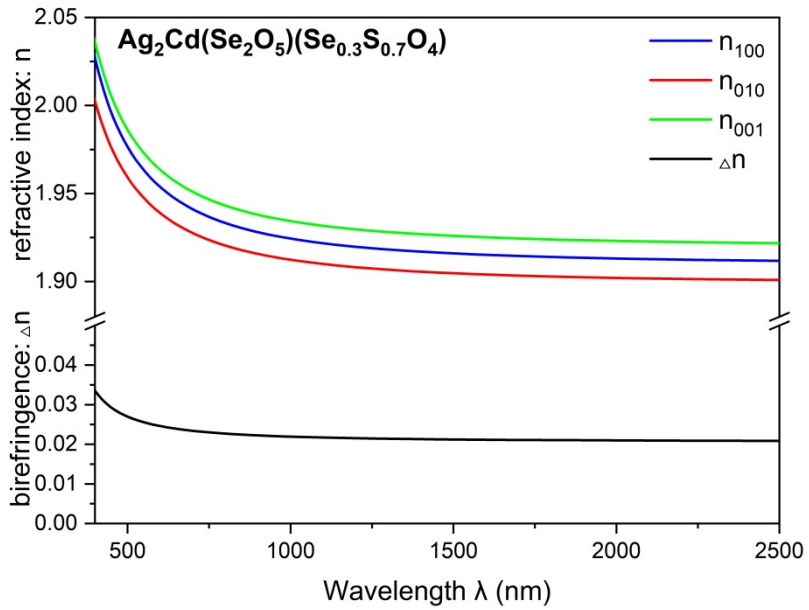
(b)

Figure S3. Calculated refractive indices and birefringence of La$_2$Hg$_3$(SeO$_3$)$_4$(SO$_4$)$_2$(H$_2$O)$_2$ (a) and Ag$_2$Cd(Se$_2$O$_5$)(Se$_{0.3}$S$_{0.7}$O$_4$) (b).
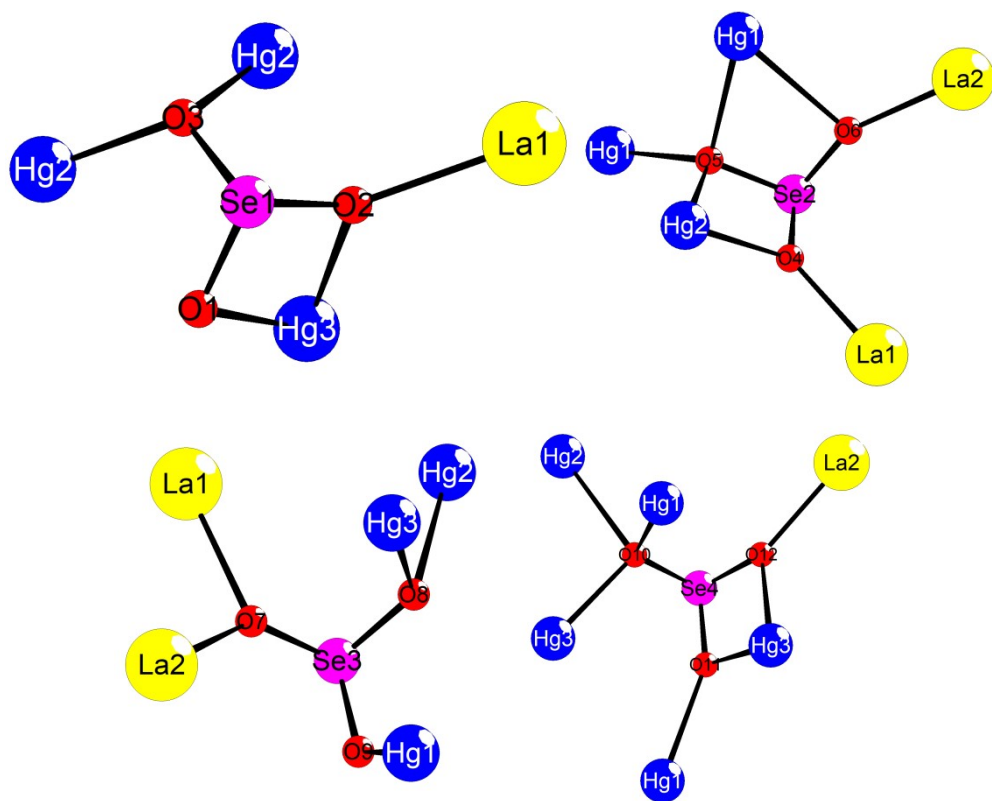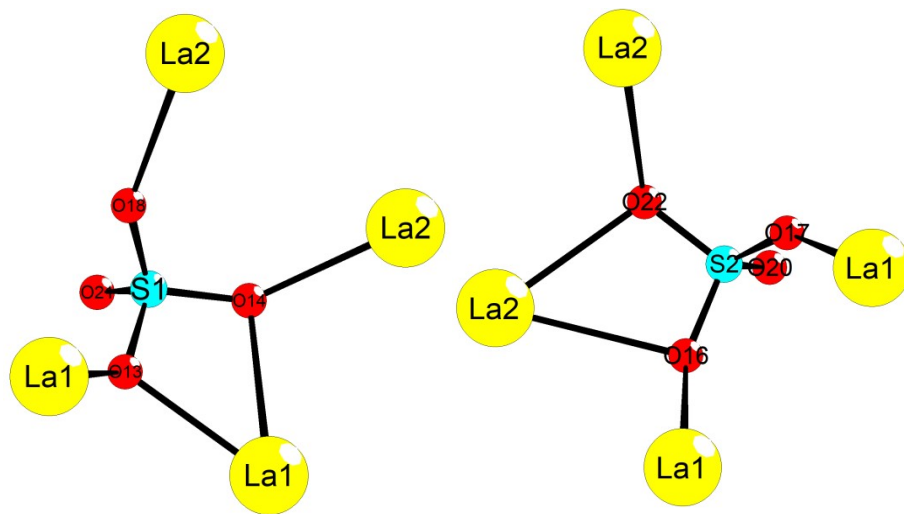
(a)

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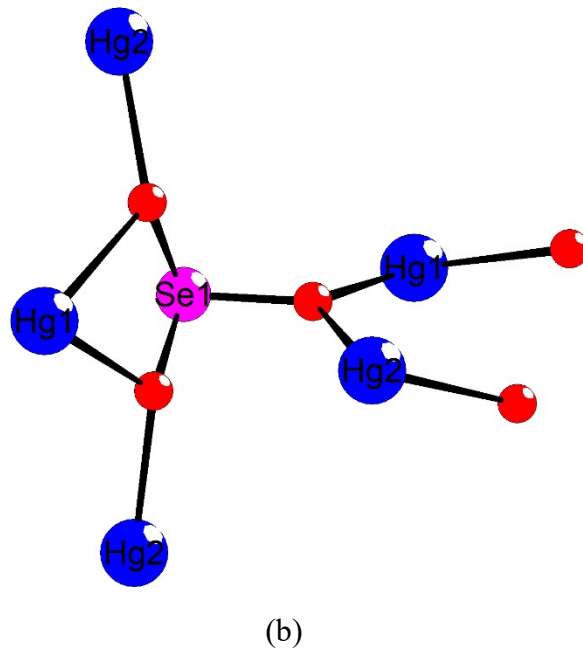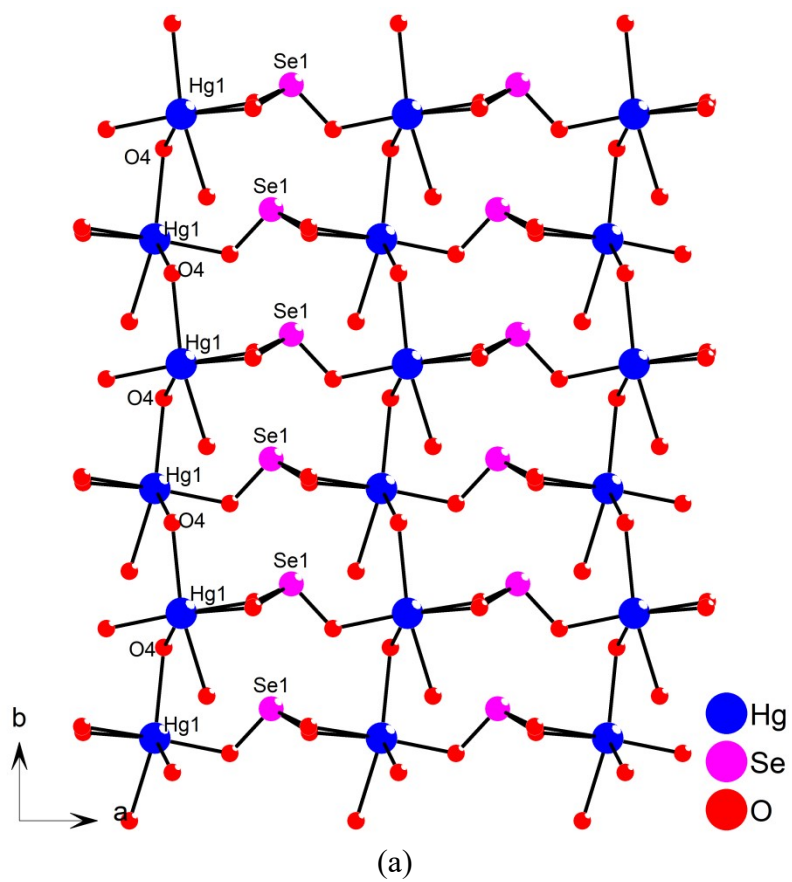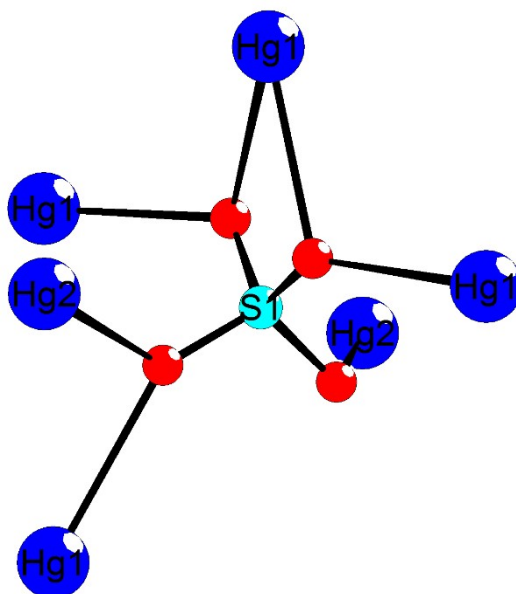
(c)

Figure S4. 2D mercuric selenite layer (a), coordination environment of Se(1)O$_3$ group (b) and coordination environment of SO$_4$ (c) in Hg$_2$(SeO$_3$)(SO$_4$).
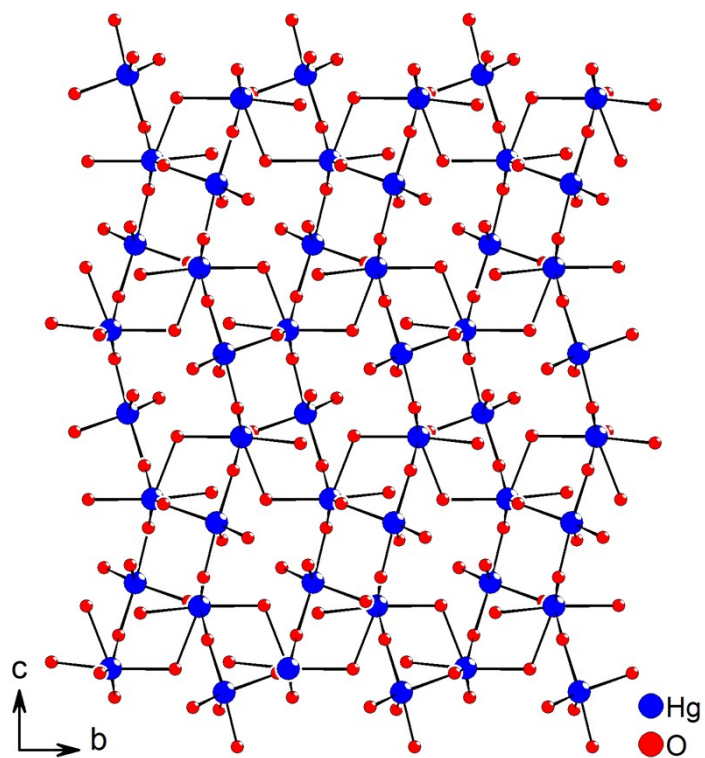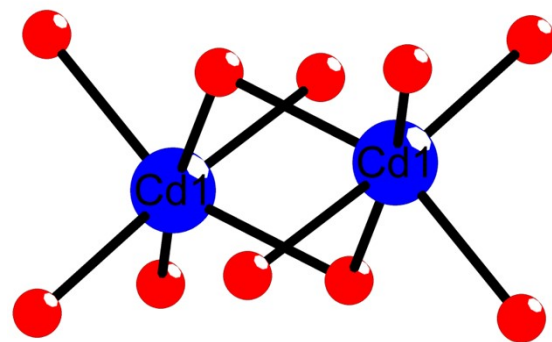

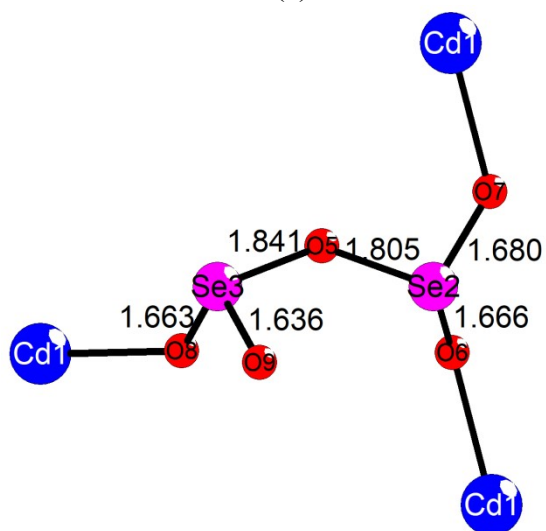**Figure S5.** 2D mercury oxide layer of Hg$_2$(SeO$_3$)(SO$_4$).
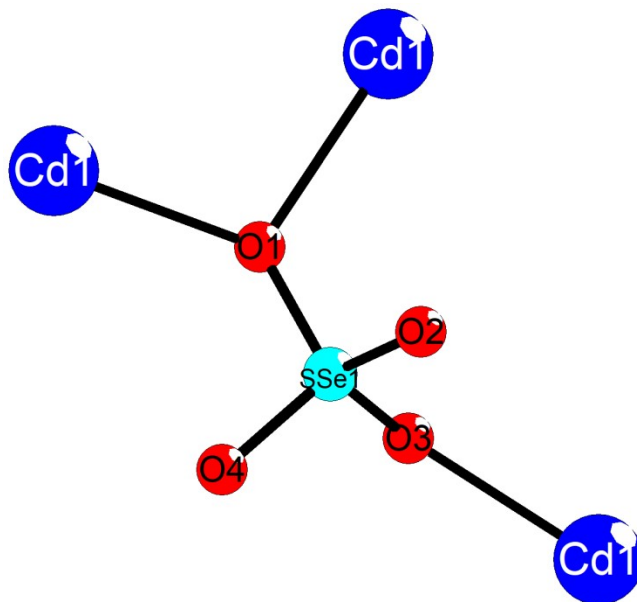
(a)

(b)

Figure S6. The coordination environment of SeO$_3$ group (a) and SO$_4$ tetrahedrons (b) in La$_2$Hg$_3$(SeO$_3$)$_4$(SO$_4$)$_2$(H$_2$O)$_2$.

(a)

(b)

(c)

Figure S7. The [Cd_2O_{10}] dimers (a), coordination environment of Se_2O_5 group (b) and coordination environment of $SSeO_4$ (c) in $Ag_2Cd(Se_2O_5)(Se_{0.3}S_{0.7}O_4)$.

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