Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

An unprecedented μ_4-Sn_2Se_9 ligand: Solvothermal syntheses and Characterizations of novel lanthanum selenidostannates $[\{La(dien)_2\}_4(\mu_4\text{-}Sn_2Se_9)(\mu\text{-}Sn_2Se_6)]_\infty$ and $[La_2(en)_8(\mu\text{-}Se_2)]Sn_2Se_6$

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1. Synthesis of $[\{La(dien)_2\}_4(\mu_4\text{-}Sn_2Se_9)(\mu\text{-}Sn_2Se_6)]$ (**1**)

A mixture of La_2O_3 (82 mg, 0.25 mmol), Sn (59 mg, 0.50 mmol), and Se (158 mg, 2 mmol) and 3 mL dien was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 10 mL. The sealed autoclave was heated under autogenous pressure at 165 ºC for 4 days. Upon cooling to room temperature, red block crystals of **1** were obtained by filtering and washing with ethanol (68% yield based on Sn). The crystals are stable in dried air and ethanol. Elem anal. Calcd for $C_{32}H_{104}N_{24}Se_{15}La_4Sn_4$: C, 12.64; H, 3.45; N, 11.06. Found: C, 12.48; H, 3.52; N, 10.92. IR (KBr, cm^{-1}): 3927 (w), 3896 (w), 3868 (w), 3832 (w), 3739 (s), 3675 (w), 3617 (w), 3559 (w), 2359 (vs), 2339 (s), 1798 (w), 1740 (w), 1696 (w), 1650 (w), 1521 (s), 1457 (w), 1428 (w), 1003 (w), 937 (w), 799 (w), 667 (w), 539 (w), 439 (w), 440 (w).

2. Synthesis of $[La_2(en)_8(\mu\text{-}Se_2)]Sn_2Se_6$ (**2**)

A mixture of La_2O_3 (82 mg, 0.25 mmol), Sn (59 mg, 0.50 mmol), and Se (158 mg, 2 mmol) and 3 mL en was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 10 mL. The sealed autoclave was heated under autogenous pressure at 165 ºC for 4 days. Upon cooling to room temperature, yellow block crystals of **2** were obtained by filtering and washing with ethanol (61% yield based on Sn). The crystals are stable in dried air and ethanol. Elem anal. Calcd for

$C_{16}H_{64}N_{16}Se_8La_2Sn_2$: C, 11.81; H, 3.96; N, 13.77. Found: C, 11.67; H, 3.91; N, 13.61. IR (KBr, cm^{-1}): 3731 (w), 3486 (w), 3286 (w), 2945 (w), 2884 (w), 2360 (s), 2324 (s), 1650 (w), 1595 (s), 1508 (w), 1467 (s), 1330 (w), 1275 (w), 1160 (s), 1023 (vs), 667 (s), 519 (s), 424 (w).

3. X-ray structure determination

The intensity data were collected on a Rigaku Mercury CCD diffractometer at 293(2) K using graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å) with a ω-scan method to a maximum 2θ value of 50.00°. A red 0.30 × 0.18 × 0.10 mm^3 block crystal of **1** and a yellow 0.20 × 0.20 × 0.18 mm^3 block crystal of **2** were used for data collection. An absorption correction was applied for all the compounds using multi-scan method. The structures were solved with direct methods using the SHELXS-97 program [1] and refinement was performed against F^2 using the SHELXL-97 program.[2] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters using a riding model.

References
[1] G. M. Sheldrick, SHELXS-97, Program for structure solution, Universität of Göttingen, Germany, 1997.
[2] G. M. Sheldrick, SHELXL-97, Program for structure refinement, Universität of Göttingen, Germany, 1997.

Table S1. Selected bond lengths /Å and angles /° for **1**

Sn(1)–Se(1)	2.4892(17)	Sn(1)–Se(2)	2.4450(18)
Sn(1)–Se(3)	2.5571(17)	Sn(1)–Se(3)#1	2.6127(19)
Sn(2)–Se(4)	2.4828(18)	Sn(2)–Se(5)	2.4825(17)
Sn(2)–Se(6)	2.5173(17)	Sn(2)–Se(7)#2	2.5606(17)
La(1)–Se(1)	3.4016(17)	La(1)–Se(4)	3.2126(17)
La(1)–Se(5)	3.2884(17)	La(2)–Se(6)	3.1166(16)
La(2)–Se(7)	3.2214(16)	La(2)–Se(8)	2.9955(9)
Se(7)–Se(8)#2	2.6860(16)		
La(1)–N(1)	2.670(12)	La(1)–N(2)	2.696(12)
La(1)–N(3)	2.669(12)	La(1)–N(4)	2.690(11)
La (1)–N(5)	2.667(11)	La(1)–N(6)	2.672(11)
La(2)–N(7)	2.703(11)	La(2)–N(8)	2.725(11)
La(2)–N(9)	2.727(12)	La(2)–N(10)	2.754(13)
La(2)–N(11)	2.716(11)	La(2)–N(12)	2.623(11)
Se(1)–Sn(1)–Se(2)	116.62(6)	Se(3)–Sn(1)–Se(3)[a]	93.70(6)
Se(1)–Sn(1)–Se(3)	112.10(6)	Se(2)–Sn(1)–Se(3)	112.42(7)
Se(2)–Sn(1)–Se(3)#1	109.23(7)	Se(1)–Sn(1)–Se(3)#1	110.39(7)
Se(4)–Sn(2)–Se(5)	106.02(6)	Se(4)–Sn(2)–Se(6)	111.32(6)
Se(4)–Sn(2)–Se(7)#2	104.99(6)	Se(5)–Sn(2)–Se(6)	108.46(6)

Se(5)–Sn(2)–Se(7)#2	117.91(6)	Se(6)–Sn(2)–Se(7)#2	108.10(6)
Sn(1)–Se(1)–La(1)	111.56(5)	Sn(1)–Se(3)–Sn(1)#1	86.30(6)
Sn(2)–Se(4)–La(1)	87.24(5)	Sn(2)–Se(5)–La(1)	85.57(5)
Sn(2)–Se(6)–La(2)	106.23(5)	Sn(2)#2–Se(7)–La(2)	121.60(6)
Se(7)#2–Se(8)–La(2)#2	68.83(3)	Se(7)#2–Se(8)–La(2)	111.17(3)
La(8)–Se(8)–La(2)#2	180.00(4)	Se(1)–La(1)–Se(4)	136.61(4)
Se(1)–La(1)–Se(5)	143.19(5)	Se(4)–La(1)–Se(5)	75.18(4)
Se(1)–La(1)–N(1)	72.4(3)	Se(1)–La(1)–N(2)	75.1(3)
Se(1)–La(1)–N(3)	128.4(3)	Se(1)–La(1)–N(4)	71.3(3)
Se(1)–La(1)–N(5)	68.0(2)	Se(1)–La(1)–N(6)	86.9(2)
Se(4)–La(1)–N(1)	64.7(3)	Se(4)–La(1)–N(2)	91.9(3)
Se(4)–La(1)–N(3)	77.1(3)	Se(4)–La(1)–N(4)	148.1(3)
Se(4)–La(1)–N(5)	132.8(2)	Se(4)–La(1)–N(6)	77.0(2)
Se(5)–La(1)–N(1)	137.7(3)	Se(5)–La(1)–N(2)	131.0(3)
Se(5)–La(1)–N(3)	66.8(3)	Se(5)–La(1)–N(4)	86.8(3)
Se(5)–La(1)–N(5)	76.0(2)	Se(5)–La(1)–N(6)	83.6(2)
N(1)–La(1)–N(2)	65.5(4)	N(1)–La(1)–N(3)	113.9(4)
N(1)–La(1)–N(4)	135.0(4)	N(1)–La(1)–N(5)	122.8(4)
N(1)–La(1)–N(6)	75.3(4)	N(2)–La(1)–N(3)	64.2(4)
N(2)–La(1)–N(4)	80.2(4)	N(2)–La(1)–N(5)	134.9(4)
N(2)–La(1)–N(6)	140.1(4)	N(3)–La(1)–N(4)	71.7(4)
N(3)–La(1)–N(5)	122.9(4)	N(3)–La(1)–N(6)	144.6(4)
N(4)–La(1)–N(5)	64.3(4)	N(4)–La(1)–N(6)	127.4(4)
N(5)–La(1)–N(6)	63.2(3)	Se(6)–La(2)–Se(7)	130.79(5)
Se(7)–La(2)–Se(8)	51.04(3)	Se(6)–La(2)–Se(8)	87.40(4)
Se(6)–La(2)–N(7)	77.4(3)	Se(6)–La(2)–N(8)	75.7(3)
Se(6)–La(2)–N(9)	78.6(3)	Se(6)–La(2)–N(10)	147.9(3)
Se(6)–La(2)–N(11)	132.6(3)	Se(6)–La(2)–N(12)	70.3(2)
Se(7)–La(2)–N(7)	67.7(2)	Se(7)–La(2)–N(8)	114.8(3)
Se(7)–La(2)–N(9)	150.5(3)	Se(7)–La(2)–N(10)	73.6(3)
Se(7)–La(2)–N(11)	79.6(2)	Se(7)–La(2)–N(12)	112.2(2)
Se(8)–La(2)–N(7)	74.4(3)	Se(8)–La(2)–N(8)	136.9(3)
Se(8)–La(2)–N(9)	150.7(3)	Se(8)–La(2)–N(10)	122.9(3)
Se(8)–La(2)–N(11)	90.6(2)	Se(8)–La(2)–N(12)	73.4(2)
N(7)–La(2)–N(8)	63.4(4)	N(7)–La(2)–N(9)	126.0(4)
N(7)–La(2)–N(10)	99.1(4)	N(7)–La(2)–N(11)	146.6(3)
N(7)–La(2)–N(12)	134.8(4)	N(8)–La(2)–N(9)	64.0(4)
N(8)–La(2)–N(10)	74.4(4)	N(8)–La(2)–N(11)	129.8(4)
N(8)–La(2)–N(12)	132.8(3)	N(9)–La(2)–N(10)	78.1(4)
N(9)–La(2)–N(11)	80.6(3)	N(9)–La(2)–N(12)	77.7(4)
N(10)–La(2)–N(11)	63.9(4)	N(10)–La(2)–N(12)	124.9(4)
N(11)–La(2)–N(12)	63.8(3)		

Symmetry transformations used to generate equivalent atoms: #1) –x, –y+1, –z+1, #2) –x+2, –y,

−z.

Table S2. Selected bond lengths /Å and angles /° for **2**

Sn(1)–Se(2)	2.452(2)	Sn(1)–Se(3)	2.463(2)
Sn(1)–Se(4)	2.594(2)	Sn(1)–Se(4)#1	2.590(2)
La(1)–Se(1)	3.143(2)	La(1)–Se(1)#2	3.140(2)
Se(1)–Se(1)#2	2.385(4)		
La(1)–N(1)	2.732(16)	La(1)–N(2)	2.749(16)
La(1)–N(3)	2.735(15)	La(1)–N(4)	2.707(17)
La (1)–N(5)	2.702(17)	La(1)–N(6)	2.866(18)
La(1)–N(7)	2.737(15)	La(1)–N(8)	2.759(16)
Se(2)–Sn(1)–Se(3)	112.53(9)	Se(4)–Sn(1)–Se(4)[a]	92.71(7)
Se(2)–Sn(1)–Se(4)	115.23(9)	Se(3)–Sn(1)–Se(4)	109.51(9)
Se(3)–Sn(1)–Se(4)#1	112.75(9)	Se(2)–Sn(1)–Se(4)#1	112.65(9)
Sn(1)–Se(4)–Sn(1) #1	87.29(7)	La(1)–Se(1)–La(1)#2	67.76(9)
Se(1)#2–Se(1)–La(1)#2	67.62(9)	Se(1)#2–Se(1)–La(1)	135.39(7)
Se(1)–La(1)–Se(1)#2	44.61(7)	Se(1)–La(1)–N(1)	76.9(4)
Se(1)–La(1)–N(2)	73.3(3)	Se(1)–La(1)–N(3)	141.4(3)
Se(1)–La(1)–N(4)	144.0(4)	Se(1)–La(1)–N(5)	123.7(5)
Se(1)–La(1)–N(6)	108.1(4)	Se(1)–La(1)–N(7)	71.6(4)
Se(1)–La(1)–N(8)	81.0(4)	Se(1)#2–La(1)–N(1)	75.5(4)
Se(1)#2–La(1)–N(2)	111.5(3)	Se(1)#2–La(1)–N(3)	148.1(4)
Se(1)#2–La(1)–N(4)	136.9(4)	Se(1)#2–La(1)–N(5)	84.6(4)
Se(1)#2–La(1)–N(6)	69.9(4)	Se(1)#2–La(1)–N(7)	74.2(3)
Se(1)#2–La(1)–N(8)	118.5(4)	N(1)–La(1)–N(2)	63.1(5)
N(1)–La(1)–N(3)	77.3(6)	N(1)–La(1)–N(4)	137.5(6)
N(1)–La(1)–N(5)	66.2(6)	N(1)–La(1)–N(6)	117.3(5)
N(1)–La(1)–N(7)	146.5(6)	N(1)–La(1)–N(8)	125.1(5)
N(2)–La(1)–N(3)	69.6(5)	N(2)–La(1)–N(4)	109.3(5)
N(2)–La(1)–N(5)	119.5(5)	N(2)–La(1)–N(6)	178.6(5)
N(2)–La(1)–N(7)	116.3(5)	N(2)–La(1)–N(8)	62.6(5)
N(3)–La(1)–N(4)	61.9(5)	N(3)–La(1)–N(5)	69.1(6)
N(3)–La(1)–N(6)	109.1(5)	N(3)–La(1)–N(7)	135.6(5)
N(3)–La(1)–N(8)	91.0(5)	N(4)–La(1)–N(5)	87.3(6)
N(4)–La(1)–N(6)	69.4(5)	N(4)–La(1)–N(7)	75.8(5)
N(4)–La(1)–N(8)	70.0(5)	N(5)–La(1)–N(6)	60.1(5)
N(5)–La(1)–N(7)	124.2(5)	N(5)–La(1)–N(8)	155.3(6)
N(6)–La(1)–N(7)	64.2(5)	N(6)–La(1)–N(8)	117.2(5)
N(7)–La(1)–N(8)	60.7(5)		

Symmetry transformations used to generate equivalent atoms: #1) –x, –y+1, –z+2; #2) –x, –y+1, –z+1.

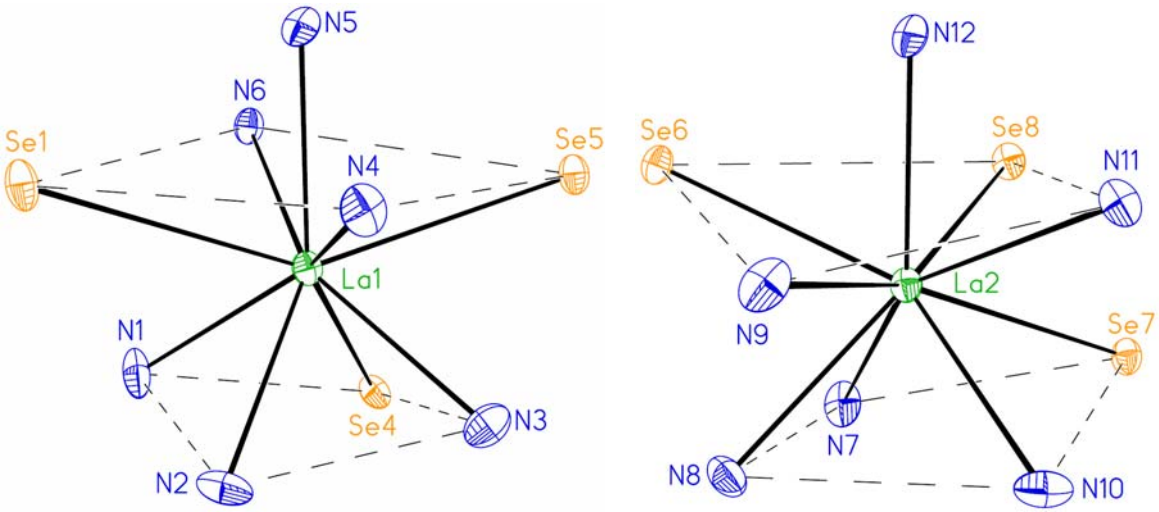

Figure S1. Crystal structures of La(1)N_6Se_3 and La(2)N_6Se_3 polyhedra in **1**.

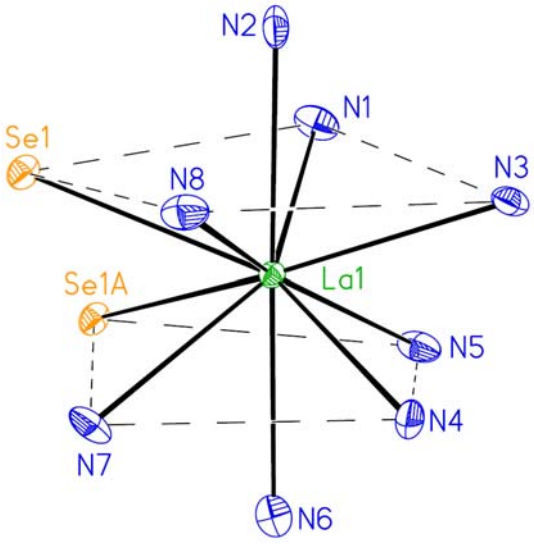

Figure S2. Crystal structures of LaN_8Se_2 polyhedron in **2**.

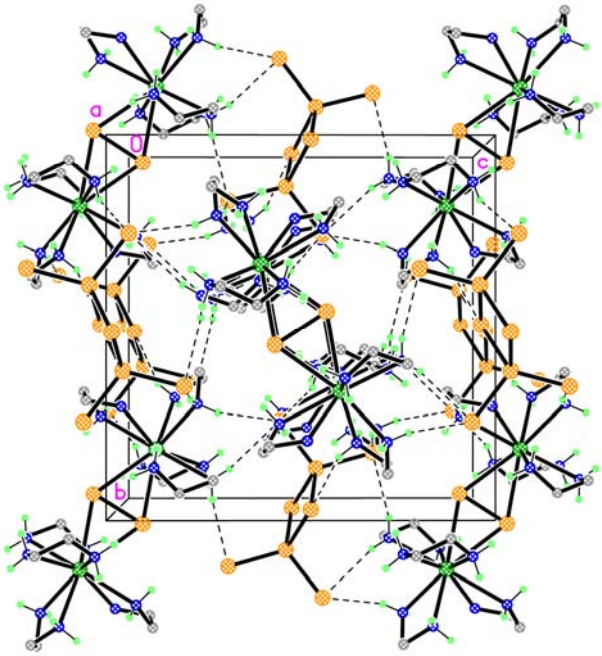

Figure S3. Crystal packing of **2**, showing intermolecular N–H···Se interactions. Hydrogen atoms of CH_2 are omitted for clarity.