Supporting Information:

# Solvothermal synthesis and characterization of two novel europium thioantimonates(III) containing [$Sb^{III}S_3$] unit as a unusual chelating ligand

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## General Remarks

All analytical grade chemicals were obtained commercially and used without further purification. Elemental analyses (C, H, and N) were performed using a PE2400 II elemental analyzer. Energy-dispersive X-ray analysis (EDXA) was taken by using a JEOL JSM-6700F field-emission scanning electron microscope. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the 4000-400 $cm^{-1}$ range.

## Crystal Structure Determination

Single-crystal X-ray diffraction data for **1** and **2** were recorded on a Rigaku Mercury CCD diffractometer using a $\omega$-scan method with graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) at 296(2) K to a maximum $2\theta$ value (50.20°). Absorption corrections were applied using multi-scan technique. The structures of **1** and **2** were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic temperature parameters. All H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Selected Bond Lengths (Å) and Angles (deg) for **1** are listed in Table S1.

Table S1 Selected bond lengths [Å] and angles [deg] for **1** and **2**.

| **1** | | | |
|---|---|---|---|
| Sb1-S3 | 2.377(2) | Eu1-N6 | 2.560(7) |
| Sb1-S1 | 2.412(2) | Eu1-N1 | 2.573(7) |
| Sb1-S2 | 2.429(2) | Eu1-N2 | 2.584(6) |
| Sb1-Eu1 | 3.7089(14) | Eu1-N5 | 2.606(5) |
| Eu1-N3 | 2.607(7) | Eu1-S1 | 2.7821(19) |
| Eu1-N4 | 2.608(7) | Eu1-S2 | 2.838(2) |
| S3-Sb1-S1 | 103.73(8) | N1-Eu1-N5 | 128.7(2) |
| S3-Sb1-S2 | 104.31(8) | N2-Eu1-N5 | 140.5(2) |
| S1-Sb1-S2 | 97.40(7) | N6-Eu1-N3 | 73.8(2) |
| N6-Eu1-N1 | 157.3(2) | N1-Eu1-N3 | 122.6(2) |
| N6-Eu1-N2 | 115.2(3) | N2-Eu1-N3 | 65.3(2) |
| N1-Eu1-N2 | 65.9(2) | N5-Eu1-N3 | 78.7(2) |
| N6-Eu1-N5 | 66.3(2) | N6-Eu1-N4 | 128.0(2) |
| N2-Eu1-N4 | 90.2(3) | N1-Eu1-N4 | 73.7(2) |
| N5-Eu1-N4 | 65.8(2) | N2-Eu1-S1 | 143.11(17) |

| | | | |
|---|---|---|---|
| N3-Eu1-N4 | 78.0(2) | N5-Eu1-S1 | 74.52(13) |
| N6-Eu1-S1 | 86.44(17) | N3-Eu1-S1 | 151.47(17) |
| N1-Eu1-S1 | 82.67(16) | N4-Eu1-S1 | 99.48(15) |
| N2-Eu1-S2 | 74.9(2) | N6-Eu1-S2 | 79.71(15) |
| N5-Eu1-S2 | 138.59(14) | N1-Eu1-S2 | 78.90(17) |
| N3-Eu1-S2 | 114.69(19) | S1-Eu1-S2 | 80.64(6) |
| N4-Eu1-S2 | 152.33(15) | | |
| | | **2** | |
| Eu1-N6 | 2.548(8) | Eu1-N4 | 2.589(8) |
| Eu1-N5 | 2.545(8) | Eu1-S2 | 2.785(3) |
| Eu1-N2 | 2.577(8) | Eu1-S1 | 2.859(3) |
| Eu1-N3 | 2.582(8) | Eu1-Sb1 | 3.6961(16) |
| Eu1-N1 | 2.578(8) | Sb1-S2 | 2.366(3) |
| Sb1-S3 | 2.467(3) | Sb1-S1 | 2.399(3) |
| N6-Eu1-N5 | 66.9(3) | N5-Eu1-N4 | 65.6(3) |
| N6-Eu1-N2 | 85.2(3) | N2-Eu1-N4 | 126.4(3) |
| N5-Eu1-N2 | 127.2(3) | N3-Eu1-N4 | 73.7(3) |
| N6-Eu1-N3 | 96.5(3) | N1-Eu1-N4 | 148.3(3) |
| N5-Eu1-N3 | 75.2(3) | N6-Eu1-S2 | 84.77(19) |
| N2-Eu1-N3 | 64.1(3) | N5-Eu1-S2 | 81.95(18) |
| N6-Eu1-N1 | 73.5(3) | N2-Eu1-S2 | 141.3(2) |
| N5-Eu1-N1 | 136.6(3) | N3-Eu1-S2 | 154.38(19) |
| N2-Eu1-N1 | 64.0(3) | N1-Eu1-S2 | 77.25(19) |
| N3-Eu1-N1 | 127.7(3) | N4-Eu1-S2 | 86.57(19) |
| N6-Eu1-N4 | 132.5(3) | N6-Eu1-S1 | 149.3(2) |
| N5-Eu1-S1 | 135.96(18) | N1-Eu1-S1 | 77.1(2) |
| N2-Eu1-S1 | 89.9(2) | N4-Eu1-S1 | 73.3(2) |
| N3-Eu1-S1 | 108.5(2) | S2-Eu1-S1 | 80.24(8) |

Table S2. Hydrogen bonds for **1** [Å and °].

| D-H···A | d(D-H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| N1-H1C···S2#1 | 0.90 | 2.51 | 3.369(8) | 159.7 |
| N1-H1D···S3 | 0.90 | 2.54 | 3.437(7) | 177.2 |
| N2-H2C···S2 | 0.91 | 2.77 | 3.304(8) | 118.9 |
| N3-H3C···S3#2 | 0.90 | 2.65 | 3.511(9) | 159.4 |
| N4-H4C···S2#1 | 0.90 | 2.68 | 3.564(7) | 166.9 |
| N4-H4D···S3#3 | 0.90 | 2.62 | 3.479(7) | 160.2 |
| N5-H5C···S1#4 | 0.91 | 2.72 | 3.566(6) | 155.3 |
| N5-H5C···S1 | 0.91 | 2.76 | 3.265(5) | 116.0 |
| N6-H6C···S3#2 | 0.90 | 2.80 | 3.698(8) | 176.1 |

Symmetry transformations used to generate equivalent atoms: (#1) *x*, *-y*, *z*+1/2; (#2) *x*, *-y*, *z*-1/2; (#3) *x*, *y*+1, *z*; (#4) *-x*, *-y*, *z*.

Table S3. Hydrogen bonds for **2** [Å and °].

| D-H...A | d(D-H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| N1-H1B···Cl1#1 | 0.90 | 2.65 | 3.495(10) | 155.9 |
| N2-H2C···Cl1#2 | 0.91 | 2.83 | 3.722(11) | 167.9 |
| N3-H3A···Cl1 | 0.90 | 2.58 | 3.476(9) | 172.0 |
| N3-H3B···S1#3 | 0.90 | 2.75 | 3.553(10) | 149.0 |
| N4-H4A···S3 | 0.90 | 2.91 | 3.796(8) | 169.8 |
| N4-H4B···S1#3 | 0.90 | 2.76 | 3.635(9) | 164.4 |
| N5-H5C···Cl1 | 0.91 | 2.47 | 3.364(8) | 166.2 |
| N6-H6A···Cl1#2 | 0.90 | 2.53 | 3.382(8) | 159.1 |
| N6-H6B···Cl1#1 | 0.90 | 2.82 | 3.605(9) | 146.0 |

Symmetry transformations used to generate equivalent atoms: (#1) x, y-1, z;

(#2) -x-1/2, y-1/2, -z-1/2; (#3) -x, -y, -z.

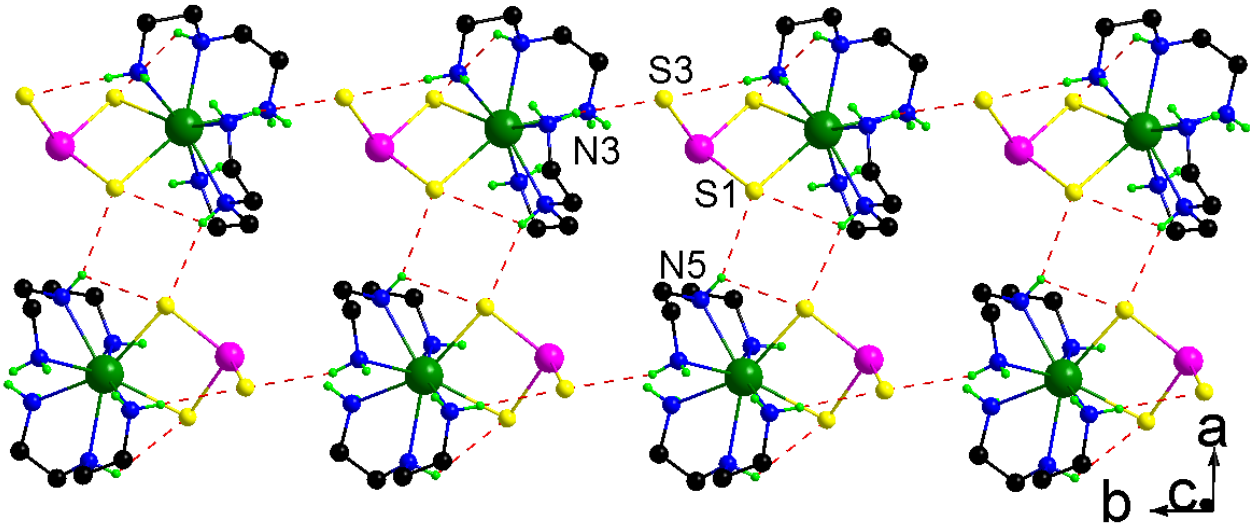


Figure S1 Part of the crystal structure of **1**, showing the formation of a 1-D chain constructed from N–H···S hydrogen bonds (H atoms bonded to C atoms omitted for clarity).

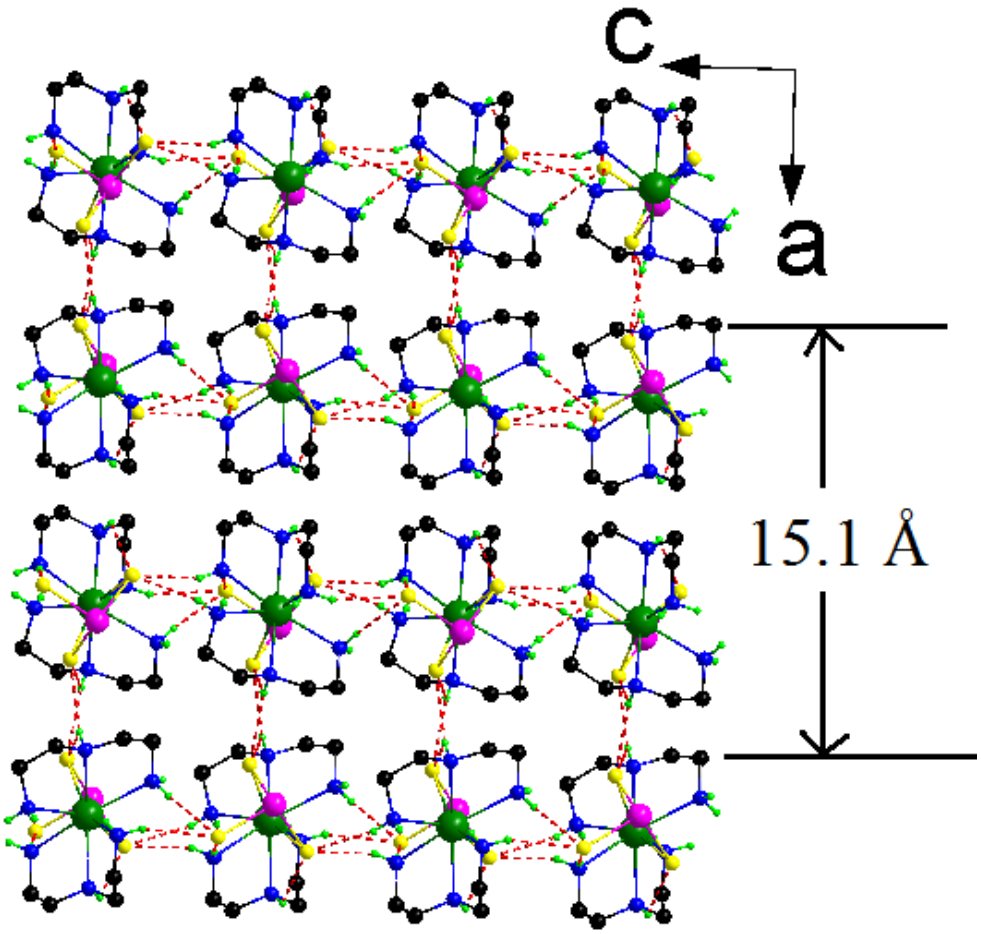


Figure S2 The stacking sequence of the layers of **1** described as type –AAA- (H atoms bonded to C atoms omitted for clarity).

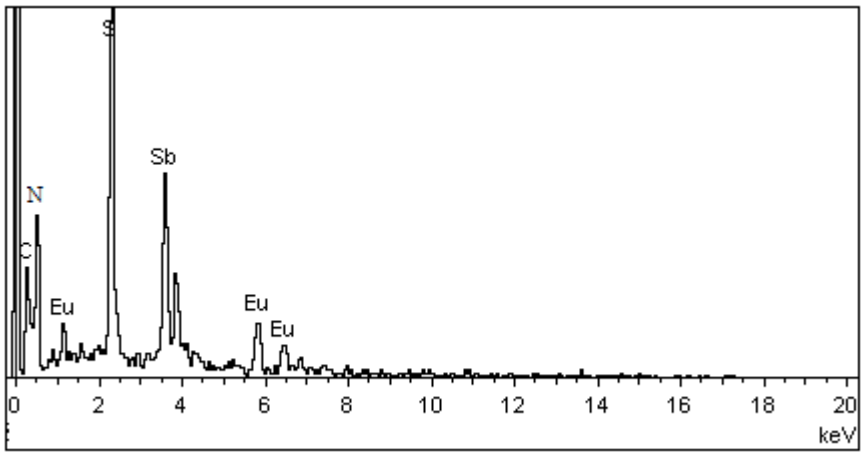


Figure S3 EDS spectrum of **1**.