Supporting Information for:

Lone-pair self-containment in pyritohedron-shaped closed cavities: Optimized hydrothermal synthesis, structure, magnetism and lattice thermal conductivity of 

$\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

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Figures

Figure S1. Calculated and observed powder X-ray diffraction patterns for $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

Figure S2. The corresponding EDXRD spectra (I) for $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

Figure S3. The corresponding EDXRD spectra (II) for $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

Figure S4. Infrared spectra of $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

Figure S5. UV/Vis/NIR absorption spectrum of $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

Figure S6. UV-vis diffuse reflectance spectra of $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

Figure S7. Co 2p doublet recorded for $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$. 
Figure S8. Co 2p doublet recorded for \(\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}\).

Figure S9. TGA diagram for \(\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}\).

Figure S10. View of Calculated Tellurium atoms lone pairs.

Figure S11. View down [001] of a slab of \(\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}\) showing the honeycomb layers, built up from Co and Te centered polyhedral.

Figure S12. Lattice thermal conductivity as a function of temperature for \(\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}\) samples.

Tables

Table S1. BVS of the atoms in \(\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}\)

![Graph showing calculated and observed powder X-ray diffraction patterns for \(\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}\).]
Figure S2. The corresponding EDXRD spectra (I) for Co$_{15}$F$_2$(TeO$_3$)$_{14}$.
Figure S3. The corresponding EDXRD spectra (II) for Co$_{13}$F$_2$(TeO$_3$)$_{14}$
Figure S4. Infrared spectra of $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$

Figure S5. UV/Vis/NIR absorption spectrum of $\text{Co}_{15}\text{F}_2(\text{TeO}_3)_{14}$
Figure S6. UV-vis diffuse reflectance spectra of Co$_{15}$F$_2$(TeO$_3$)$_{14}$.

Figure S7. Co 2p doublet recorded for Co$_{15}$F$_2$(TeO$_3$)$_{14}$. 
Figure S8. F 1s core level for Co$_{15}$F$_2$(TeO$_3$)$_{14}$.

Figure S9. TGA diagram for Co$_{15}$F$_2$(TeO$_3$)$_{14}$. 
Figure S10: View of Calculated Tellurium atoms lone pairs.

Figure S11: View down [001] of a slab of Co₁₅F₂(TeO₃)₁₄ showing the honeycomb layers, built up from Co and Te centered polyhedral. a-f:
a) The way the Co and Te centered polyhedral cap the top and bottom of each 12 ring of Co3 (turquoise) units and 6 rings of Te2 (lavender) groups (12-Co3+6-Te2 ring) result in closed pyritohedron-shaped cavities are shown sequentially: a) “empty” 12+6 ring hole (top right), 12-Co3+6-Te2 ring with capped hexads of Co2 (bright green) centered groups (6-Co2) on both sides (bottom left).

b) 12-Co3+6-Te2 ring+ 6-Co2 attached with trios of Te2 centered groups (3-Te2) (light blue) on both sides (top right), 12-Co3+6-Te2 ring + 6-Co2+3-Te2 attached with trios of Co1 (light orange)-centered groups (3-Co1) attached on both sides (bottom left).

c) 12-Co3+6-Te2 ring+6-Co2+3-Te2+3-Co1 attached with one of Te1 (gray) centered groups (1-Te1) on both sides (top right). Another trio of Co2-centered polyhedral capped the top of trios of Co1-centered octahedron (bottom left).

d) Another trio of Te3-centered polyhedral attached to the trios of Co1 and the abovementioned trios of Co2-centered groups (top right). Another Co3/Te2-centered polyhedral in the next Co3/Te2 layer attached the abovementioned trios of the Co2 layer (bottom left).

e) These honeycomb layers fused sequentially to form a continuous, three-dimensional structure, which encloses pyritohedron-shaped Te(IV) lone-pair self-contained cavities.

f) Note that rhombohedral crystal symmetry dictates that, with respect to the z direction, the adjacent basal Co3 sheets are laterally displaced from each other by $x = 1/3$ and $y = 2/3$. Thus, additional Co3 sheets capped afterwards face on the center of Co12 polyhedral units along the [001] direction in the next sheet, and there are no continuous channels of any significant size in this structure.
Figure S12. Lattice thermal conductivity as a function of temperature for Co$_{15}$F$_2$(TeO$_3$)$_{14}$ samples.

**Table S1.** BVS of the atoms in Co$_{15}$F$_2$O$_{42}$Te$_{14}$.

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* ($R$, $b$) parameters: Te$^{4+}$–O (1.977, 0.37), Co$^{2+}$–O (1.692, 0.37), Co$^{2+}$–F (1.640, 0.37)