# Supporting Information

# Investigation of the $GeO_2$-1,6-diaminohexane-water-pyridine-HF Phase Diagram Leading to the Discovery of Two Novel Layered Germanates with Extra-Large Rings

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**Table S1.** Crystallographic Data and Structure Refinement Parameters for SU-63 and SU-64

| Identification code | SU-63 | | SU-64 | |
|---|---|---|---|---|
| Empirical formula (*) | $\|1.5H_2DAH\|[Ge_7O_{14}(OH)_3]\cdot 2H_2O$ | | $\|11H_2DAH\|[Ge_9O_{18}X_4][Ge_7O_{14}(OH)_3]_6\cdot 16H_2O$ | |
| Formula weight | 996.5 g $mol^{-1}$ (*) | | 7296.8 g $mol^{-1}$ (*) | |
| Temperature | 100 K | | 150 K | |
| Wavelength | 0.90800 Å | | 0.6889 Å | |
| Crystal system | Hexagonal | | Triclinic | |
| Space group | *P6₃cm* | | *P-1* | |
| Unit cell dimensions | *a* = 28.794(2) Å | α = 90° | *a* = 12.101(4) Å | α = 87.86(1)° |
| | b = 28.794(2) Å | β = 90° | b = 18.113(6) Å | β = 89.50(2)° |
| | c = 20.603(4) Å | γ = 120° | c = 22.444(8) Å | γ = 83.17(1)° |
| Volume | 14793(3) $Å^3$ | | 4881(3) $Å^3$ | |
| *Z* | 18 | | 1 | |
| Density (calculated) | 1.576 g/$cm^3$ | | 2.238 g/$cm^3$ | |
| Absorption coefficient | 6.353 $mm^{-1}$ | | 7.817 $mm^{-1}$ | |
| *F*(000) | 6480 | | 3070 | |
| Crystal size | 150 × 80 × 20 μm | | 30 × 8 × 2 μm | |
| Theta range for data collection | 2.58°<θ<27.23° | | 1.38°<θ<25.50° | |
| Index ranges | $-33 \le h \le 35$, $-35 \le k \le 35$, $-18 \le l \le 24$ | | $-14 \le h \le 14$, $-22 \le k \le 22$, $-26 \le l \le 25$ | |
| Reflections collected | 51182 | | 42228 | |
| Independent reflections | 8692 [*R*(int) = 0.0954] | | 15210 [*R*(int) = 0.1435] | |
| Completeness to $\theta = 33.84°$ | 0.982 | | 0.762 | |
| Absorption correction | multi-scan | | empirical | |
| Max. and min. transmission | 0.4491 and 0.8835 | | 0.566 and 1.0 | |
| Refinement method | Full-matrix least-squares on $F^2$ | | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8692 / 3 / 339 | | 15210 / 11 / 617 | |
| Goodness-of-fit on $F^2$ | 1.030 | | 1.049 | |
| Final R indices [$I>2\sigma(I)$] | R1 = 0.0851, wR2 = 0.2163 | | R1 = 0.1296, wR2 = 0.3363 | |
| *R* indices (all data) | R1 = 0.1112, wR2 = 0.2422 | | R1 = 0.1922, wR2 = 0.3799 | |
| Largest diff. peak and hole | -1.024 and 1.607e.$Å^{-3}$ | | -2.321 and 2.042e.$Å^{-3}$ | |

*The formula here includes $H_2DAH^{2+}$ cations and water, were determined by CHN analysis and TG.

**Table S2.** Selected hydrogen-bond lengths in SU-64

| Atom label | Is bonded to | Distance in Å |
|---|---|---|
| NA1 | O16 | 2.86(2) |
| | O33 | 3.10(1) |
| | O39 | 3.01(1) |
| | O55 | 2.94(2) |
| NA2 | O6 | 3.00(2) |
| | O6 | 2.74(1) |
| | O52 | 2.72(1) |
| NB1 | O9 | 2.86(2) |
| | O12 | 2.68(2) |
| | O27 | 2.85(2) |
| | O60 | 2.90(2) |
| NB2 | O12 | 2.94(1) |
| | O25 | 2.67(2) |
| | O48 | 2.86(2) |
| | O61 | 2.88(2) |
| NC1 | O5 | 2.88(2) |
| | O23 | 2.83(2) |
| | O29 | 2.99(1) |
| | O46 | 2.86(2) |
| NC2 | O2 | 3.05(2) |
| | O14 | 2.96(1) |
| | O32 | 2.75(2) |
| | O51 | 2.80(2) |
| ND1 | O1 | 3.05(2) |
| | O26 | 2.89(2) |
| | O31 | 3.05(1) |
| | O43 | 3.02(1) |
| | O44 | 2.97(1) |
| | O50 | 2.85(3) |

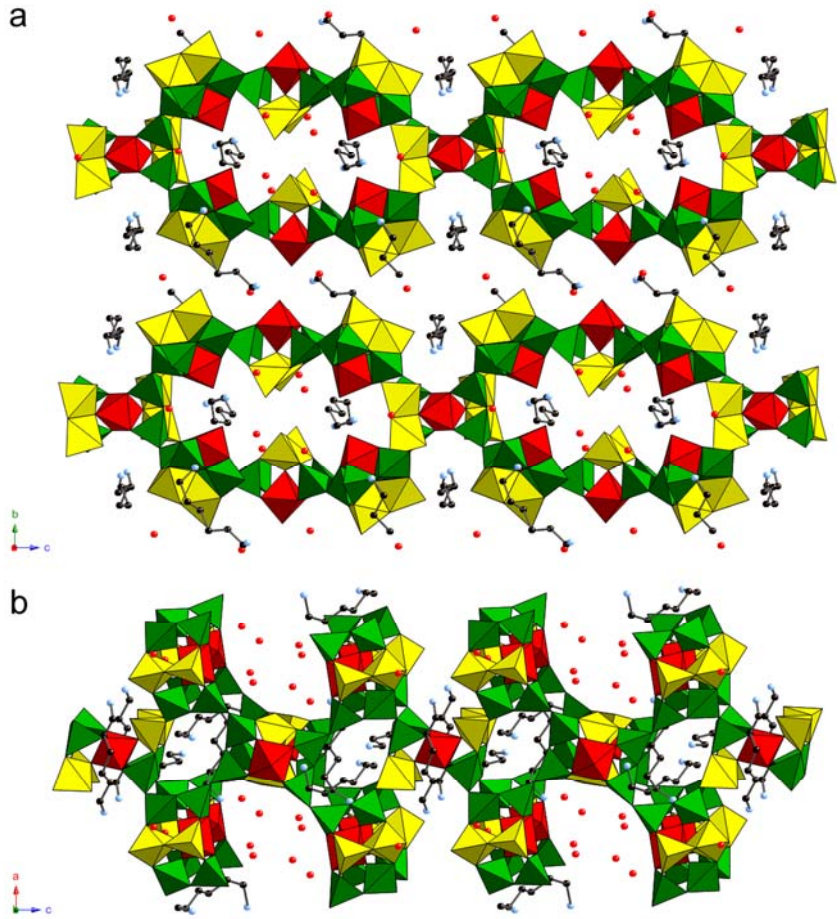


**Figure S1.** Polyhedral representation of SU-64 viewed along (a) [100] and (b) [010], with three complete asymmetric $H_2DAH^{2+}$ counterions.

**The topology embedding Systre file of SU-64 in CGD format:**

```
# DATA computed from Systre
CRYSTAL
  NAME SU-44 topology
  GROUP Pmmm
  CELL 1.25954 2.20814 2.54176 90.0000 90.0000 90.0000
  NODE 3 4  0.00000 0.27264 0.50000
  NODE 1 8  0.00000 0.00000 0.00000
  NODE 2 6  0.50000 0.27252 0.19506
  EDGE  0.00000 0.27264 0.50000   0.50000 0.27252 0.19506
  EDGE  0.50000 0.27252 0.19506   0.50000 0.72748 0.19506
  EDGE  0.00000 0.00000 0.00000   0.50000 0.27252 0.19506
  EDGE  0.50000 0.27252 0.19506   0.50000 0.27252 -0.19506
# EDGE_CENTER  0.25000 0.27258 0.34753
# EDGE_CENTER  0.50000 0.50000 0.19506
# EDGE_CENTER  0.25000 0.13626 0.09753
# EDGE_CENTER  0.50000 0.27252 0.00000
END

Coordination sequences:
Node 1:    8 22 42 76 128 176 238 322 370 492
Node 2:    6 20 45 82 119 175 242 306 397 489
Node 3:    4 16 43 79 124 165 233 322 387 481

# Data computed from TOPOS
4,6,8-c net with stoichiometry (4-c)2(6-c)4(8-c)

Node 1
Point symbol {3^4.4^12.5^4.6^8}

Node 2
Point {3^2.4^5.5^4.6^4}

Node 3
Point symbol {4^4.6^2}

Total point symbol for the net
{3^2.4^5.5^4.6^4}4{3^4.4^12.5^4.6^8}{4^4.6^2}2
```