Supporting Information for

Uncommon structural and bonding properties in Ag$_{16}$B$_4$O$_{10}$

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Figure S1. Temperature dependent powder X-ray diffraction indicating Ag$_{16}$B$_4$O$_{10}$ start to decompose into elemental Ag at about 623 K.
| Table S1. Crystal data, data collection and refinement details for Ag$_{16}$B$_4$O$_{10}$ at 298 K. |
|---|
| **Empirical formula** | Ag$_{16}$B$_4$O$_{10}$ |
| **Formula weight** | 1929.16 |
| **Space group (no.), Z** | I4$_1$/a (88), 4 |
| **Lattice parameters /Å,** |  
| $a$ | 13.3481(5) |
| $c$ | 8.6228(4) |
| $V$/Å$^3$ | 1536.3(1) |
| $\rho_{\text{xray}}$/g×cm$^{-3}$ | 8.340 |
| **Crystal size /mm$^3$** | 0.12 × 0.08 × 0.06 |
| **Diffractometer** | SMART APEX I, Bruker AXS |
| **X-ray radiation, $\lambda$/Å** | MoK$_\alpha$, 0.71073 |
| **Absorption correction** | Multi-scan, SADABS |
| **2$\theta$ range /°** | 5.62 $\leq 2\theta \leq$ 103.92 |
| **Index ranges** | $-29 \leq h \leq 29, -27 \leq k \leq 29, -19 \leq l \leq 17$ |
| **Reflections collected** | 31920 |
| **Data, $R_{\text{int}}$** | 4280, 0.032 |
| **No. of parameters** | 170 |
| **Transmission: $t_{\text{min}}$, $t_{\text{max}}$** | 0.198, 0.381 |
| **Final R indices [I > 2$\sigma$(I)]** | R1 = 0.033, wR2 = 0.080 |
| **R indices (all data)** | R1 = 0.037, wR2 = 0.082 |
| **Deposition no.** | CSD- 1951872 |
Table S2. Atomic coordinates and displacement parameters $U_{eq}/10^{-4}$ Å$^2$.

| Atom | Site | $x$       | $y$       | $z$       | $U_{eq}$   |
|------|------|-----------|-----------|-----------|------------|
| Ag1  | 16f  | 0.16299(2)| 0.54868(2)| 0.02757(2)| 135.8(3)   |
| Ag2  | 16f  | 0.25826(2)| 0.73949(2)| 0.01031(2)| 136.7(3)   |
| Ag3  | 16f  | 0.35583(2)| 0.45035(2)| 0.00220(2)| 140.7(3)   |
| Ag4  | 16f  | 0.10879(2)| 0.69713(2)| 0.25948(2)| 148(3)     |
| O1   | 8e   | 0         | ¾         | 0.0738(2) | 102(2)     |
| O2   | 16f  | 0.1208(1) | 0.7899(1) | –0.1258(2)| 103(2)     |
| O3   | 16f  | 0.3371(1) | 0.3329(1) | 0.1788(2) | 123(2)     |
| B    | 16f  | 0.4160(2) | 0.2933(2) | 0.2730(3) | 108(3)     |

Table S3. Selected interatomic distances /Å and angles /°.

| Atomic contact | Distance /Å | Atomic contact | Angle /° |
|----------------|-------------|----------------|----------|
| Ag1 — O2       | 2.350(2)    | O1 — B — O2    | 106.4(2) |
| — O3           | 2.264(2)    |                | 107.6(2) |
| Ag2 — O2       | 2.280(1)    | O1 — B — O3    | 111.9(2) |
| — O3           | 2.307(2)    | O2 — B — O2    | 107.4(2) |
| Ag3 — O3       | 2.200(2)    | O2 — B — O3    | 111.3(2) |
| Ag4 — O1       | 2.274(1)    |                | 111.9(2) |
| B — O1         | 1.512(3)    |                |          |
| — O2           | 1.485(3)    |                |          |
| — O2           | 1.496(3)    |                |          |
| — O3           | 1.431(3)    |                |          |

Table S4. Refined atomic parameters against PXRD in space group $I 4_1/a$:2. The refined lattice parameters are $a = 13.3614(4)$ Å and $c = 8.6288(3)$ Å.

| Atom | Site | $x$       | $y$       | $z$       |
|------|------|-----------|-----------|-----------|
| Ag1  | 16f  | 0.1633(3) | 0.5497(2) | 0.0265(3) |
| Ag2  | 16f  | 0.2578(3) | 0.7394(2) | 0.0139(4) |
| Ag3  | 16f  | 0.3550(2) | 0.4506(3) | 0.0005(3) |
| Ag4  | 16f  | 0.1087(2) | 0.6966(3) | 0.2607(5) |
| O1   | 8e   | 0         | ¾         | 0.0738    |
| O2   | 16f  | 0.1208    | 0.7899    | –0.1258   |
| O3   | 16f  | 0.3371    | 0.3329    | 0.1788    |
| B    | 16f  | 0.4160    | 0.2933    | 0.2730    |
## Computational details

### Pseudopotentials (scalar relativistic) and basis sets

|                | Ag                                      | B                                          | O                                          |
|----------------|-----------------------------------------|--------------------------------------------|--------------------------------------------|
| Pseudopotential| [Ar]3d^{10}4s^{2}4p^{6}4d^{10}5s^{1}    | [He] 2s^{2}2p                           | [He] 2s^{2}2p^{4}                         |
| core ref.      | [S1]                                    | [S2]                                       | [S2]                                       |
|                | exponent coefficient                    | exponent coefficient                        | exponent coefficient                        |
| s-shell        | 9.088442 -1.9648132 7.540731 2.794005   | 1.690560 0.983666 0.256979                 | 47.105518 -0.272208 5.911346 0.577763     |
|                | 1.480158 0.653851 0.35                  | 1.690560 0.983666 0.256979                 | 47.105518 -0.272208 5.911346 0.577763     |
|                | -6.083378 6.4168543 0.7539735 0.2730597 | 5.399913 1.271217 0.361909                 | 16.692219 3.900702 1.078253 0.284189     |
|                | 0.36704 1.0                              | 5.399913 1.271217 0.361909                 | 16.692219 3.900702 1.078253 0.284189     |
| sp-shell       | 0.18 1.0 1.0                            | 0.12 1.0 1.0                              | 0.12 1.0 1.0                              |
| d-shell        | 7.99473 -0.0163876 2.784773 1.209744    | 0.5 1.0                                    | 1.2 1.0                                    |
|                | 0.505393 0.198851                       | 0.5 1.0                                    | 1.2 1.0                                    |
|                | 0.2730597 0.361909                      | 0.361909                                   | 0.284189                                   |
|                | 0.2814107 0.284189                      | 0.284189                                   | 0.284189                                   |
|                | 0.4863264 0.361909                      | 0.361909                                   | 0.361909                                   |
|                | 0.3867258 1.0                           | 0.3867258 1.0                             | 0.3867258 1.0                             |
|                | 0.12                                       | 0.12                                       | 0.12                                       |
|                | 1.0                                       | 1.0                                       | 1.0                                       |

**Tolerance parameters used in the CRYSTAL17 input:**

- TOLINTEG 12 12 12 12 24
- TOLPSEUD 12
- TOLDEE 8
- BIPOLAR 128 128
### Structural parameters used in the calculation

| Lattice |          |
|---------|----------|
| a / Å   | 13.3481  |
| c / Å   | 8.6228   |

| Site parameter |          |
|----------------|----------|
| Ag1            | 0.16199  |
|                | 0.54868  |
|                | 0.02757  |
| Ag2            | 0.25826  |
|                | 0.73949  |
|                | 0.01031  |
| Ag3            | 0.35583  |
|                | 0.45035  |
|                | 0.00220  |
| Ag4            | 0.10879  |
|                | 0.69713  |
|                | 0.25948  |
| O1             | 0.00000  |
|                | 0.75000  |
|                | 0.07380  |
| O2             | 0.12081  |
|                | 0.78993  |
|                | -0.12579 |
| O3             | 0.33712  |
|                | 0.33285  |
|                | 0.17879  |
| B              | 0.41600  |
|                | 0.29325  |
|                | 0.2730   |

[S1] Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Energy-adjusted *ab initio* pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta*, 1990, 77, 123-141.

[S2] Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Ab initio* energy-adjusted pseudopotentials for elements of groups 13–17, *Mol. Phys*. 1993, 80, 1431-1441.