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# Crystal structure of the 'missing' intermetallic compound $BaCu_5$

**Kiran Avinash and Justin Andrews***

Department of Chemistry, Purdue University, 560 Oval Dr., West Lafayette, IN 47907-2084, USA. *Correspondence e-mail: jlandrews@purdue.edu

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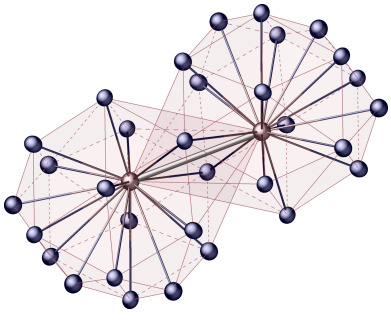



The copper-rich intermetallic compounds $CaCu_5$ and $SrCu_5$ are isostructural but the isomorphous compound $BaCu_5$ (barium pentacopper) has not been reported. The absence of any compound with the composition of $BaCu_5$ in the Ba–Cu phase diagram has previously been attributed to much larger radius of Ba. The structure of $BaCu_5$, which crystallizes in an orthorhombic cell (space group *Pnma*) with the rare $SrZn_5$ structure type is now reported The structure is characterized by a zigzag arrangement of infinite Ba chains ensconced in a Cu matrix. The Ba atom and three Cu atoms lie on special positions with *m* site symmetry and one Cu atom lies on a general crystallographic position.

## 1. Chemical context

Compounds with the stoichiometry (AE/RE)$(TM)_5$ (AE/RE = alkaline earth metal or rare earth; TM = transition metal) most often crystallize in the $CaCu_5$ structure type (space group *P6/mmm*). Materials that adopt this structure are important as permanent magnets and have been investigated as hydrogen storage alloys (Hou *et al.*, 2007; Xu *et al.*, 2022; Zhou *et al.*, 2023; Liang *et al.*, 2001). While the $CaCu_5$ structure type (*e.g.*, $SrCu_5$, $YCu_5$, Figure *1a*) is most common, some (AE/RE)$(TM)_5$ compounds adopt the $BaZn_5$ structure type (space group *Cmcm*) (Fig. 1*b*). Conversely, $UCu_5$ adopts the $AuBe_5$ structure type (space group $F\bar{4}3m$; Nakamura *et al.*, 1990) (Fig. 1*c*). Generally, the connectivity of the Cu metal–metal bonded cage is dictated by the size of the alkaline earth or

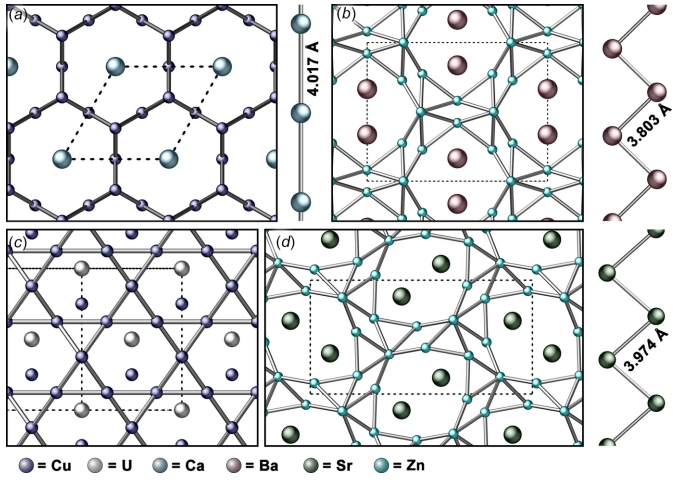


**Figure 1**
(*a*) Reported structure of $CaCu_5$. (*b*) Reported structure of $BaZn_5$. (*c*) Reported structure of $UCu_5$. (*d*) Reported structure of $SrZn_5$. The corresponding arrangement and bonding of alkaline-earth metals in each structure is shown, and relevant bond distances are highlighted. Note that in the case of the structure of $UCu_5$, there is no U—U bonding.

rare-earth metal. A less-common structure type is the $SrZn_5$ structure (space group *Pnma*) (Fig. 1*d*), for which only four members have been reported (Simura & Yamane, 2019; Schwickert & Pöttgen, 2014; Bruzzone & Merlo, 1983). The Cu cage arrangements for each structure are shown in Fig. 1*a–d*.

For the (AE)$Cu_5$ series of materials, the eponymous $CaCu_5$ and the larger $SrCu_5$ compounds are known to adopt the same structure (Bruzzone, 1971; Boeije *et al.*, 2017). However, a compound with the composition of $BaCu_5$ has never been reported. The original study that systematically explored the (Ca/Sr/Ba)—Cu phase diagram remarked on the conspicuous absence of a $BaCu_5$ compound and attributed its absence to the much larger size of Ba (Bruzzone, 1971).

Here we report on the structure of $BaCu_5$ and show that unlike $CaCu_5$, $SrCu_5$, and $BaZn_5$ (Bruzzone *et al.*, 1985) it adopts the very rare $SrZn_5$ structure type (Bruzzone & Merlo, 1983).

## 2. Structural commentary

$BaCu_5$ crystallizes in the orthorhombic *Pnma* space group and adopts the rare $SrZn_5$ structure type, rather than the more common $CaCu_5$ structure type adopted by the lighter alkaline-earth analogues $CaCu_5$ and $SrCu_5$. The asymmetric unit contains one crystallographically independent Ba atom and four crystallographically independent Cu atoms. The Ba atom and three Cu atoms occupy special positions with site symmetry *m*, whereas one Cu atom occupies a general position. The structure consists of a three-dimensional Cu framework that forms one-dimensional tunnels extending parallel to the crystallographic *a* axis, within which infinite zigzag chains of Ba atoms are accommodated (Fig. 2).

The Ba atoms form planar zigzag chains with a nearest-neighbor Ba—Ba separation of 3.8366 (5) Å. The geometry of the chain is defined by a Ba—Ba—Ba angle ($\varphi$) of 81.70 (2)° and a Ba—Ba—Ba—Ba dihedral angle ($\omega$) of 180°, indicating that the chains are coplanar. The corresponding zigzag angle in the isostructural low-temperature $SrZn_5$ phase is slightly larger ($\varphi$ = 83.05°), while the overall chain topology is retained.

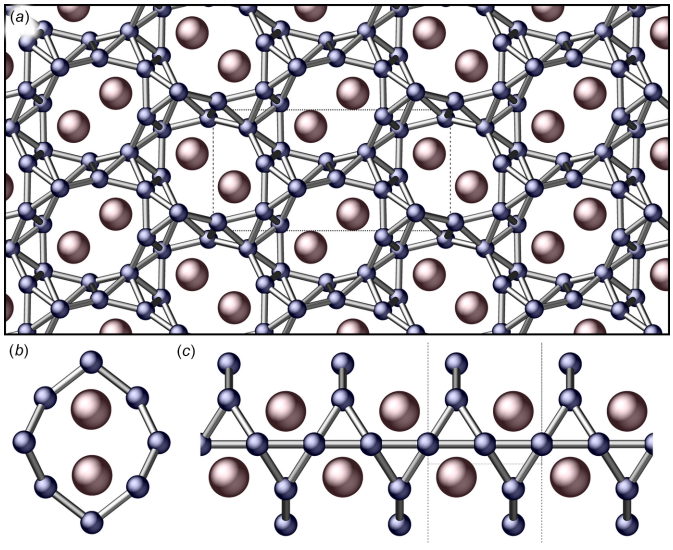


**Figure 2**
Structure of $BaCu_5$. (*a*) projection of the structure along the crystallographic *b*-axis direction. (*b*) Ba occupies one-dimensional tunnels in the Cu framework. (*c*) View of one zigzag chain of Ba atoms propagating along the crystallographic *a*-axis direction.

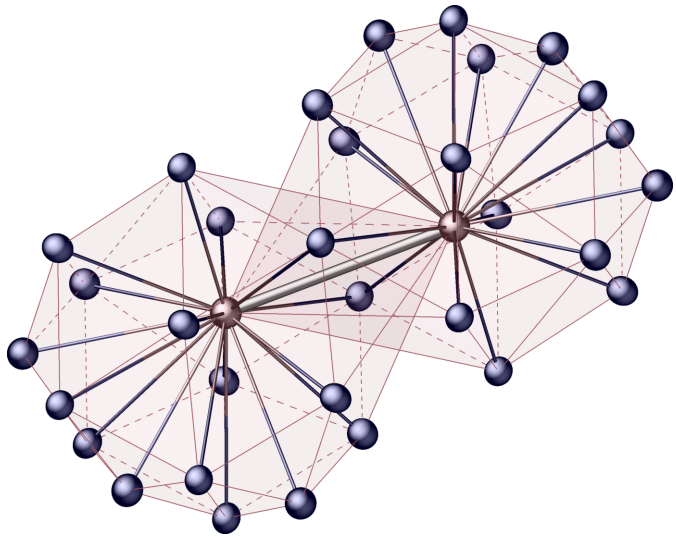

**Figure 3**
Local coordination around the Ba atoms in the structure. Each Ba atom is bonded to two neighboring Ba atoms and 17 Cu atoms with an average bond distance of 3.398 Å. The Ba—Ba distance is 3.8366 (5) Å, which is slightly longer than the Ba—Ba distance in $BaZn_5$ and slightly shorter than the Sr—Sr distance in $SrZn_5$.

Each Ba atom in $BaCu_5$ is coordinated by 17 Cu atoms with an average Ba—Cu distance of 3.3966 (6) Å (Fig. 3). The Ba—Ba distance is slightly longer than that reported for $BaZn_5$ (3.803 Å) and slightly shorter than the corresponding Sr—Sr distance (3.974 Å) in the isostructural $SrZn_5$ phase. The Cu framework in $BaCu_5$ is constructed from four crystallographically distinct Cu sites. The shortest Cu—Cu contacts are found around the general position Cu site, with distances ranging from 2.5012 (9) to 2.5404 (10) Å, whereas longer Cu—Ba contacts occur between 3.5163 (7) and 3.6461 (8) Å.

## 3. Database survey

A search of the PDF-5+ database (Kabekkodu *et al.*, 2024) for the $CaCu_5$ structure type returned 2080 entries: 434 of them contained Cu as the transition metal and 11 contained Ba as the alkaline earth metal but no entries contained both Ba and Cu. In contrast, a search for the $SrZn_5$ structure type returned just four hits, one of them being $SrZn_5$ itself, highlighting the exceptional rarity of this structure type

## 4. Synthesis and crystallization

The title compound was synthesized by modification of a previously reported synthesis (Wan *et al.*, 2024). Ba beads (Sigma Aldrich 99%) and Cu powder (Thermo Fisher 99%,

325 mesh) were pressed together in a 1:1 stoichiometric ratio in an argon filled glove box. The solids were sealed in a quartz ampoule under vacuum and heated at 873 K for 12 h. The reaction was then cooled down to room temperature over the course of 6 h. After the reaction, a mixture of several phases was present in the melt including single crystals of the layered electride BaCu and several previously unreported and highly disordered barium suboxides ($Ba_7O_3$) resulting from reaction between Ba and the quartz ampoule. Several unsuccessful attempts were made to synthesize phase-pure samples of $BaCu_5$ directly in quartz, steel, and niobium crucibles. Single crystals of $BaCu_5$ were picked out from the melt of the reaction. The broken pieces of the melts were submerged in polybutene oil inside an argon filled glovebox. The crystals were quickly transferred to the goniometer head.

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

**Table 1**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $BaCu_5$ |
| $M_r$ | 455.04 |
| Crystal system, space group | Orthorhombic, *Pnma* |
| Temperature (K) | 150 |
| $a, b, c$ (Å) | 12.8420 (7), 5.0189 (3), 6.5445 (6) |
| $V$ (Å$^3$) | 421.81 (5) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 33.71 |
| Crystal size (mm) | 0.13 × 0.08 × 0.02 |
| | |
| Data collection | |
| Diffractometer | Bruker AXS D8 Quest |
| Absorption correction | Multi-scan (*SADABS*; Krause *et al.*, 2015) |
| $T_{min}$, $T_{max}$ | 0.135, 0.274 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 24524, 1112, 877 |
| $R_{int}$ | 0.080 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.834 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.030, 0.059, 1.09 |
| No. of reflections | 1112 |
| No. of parameters | 34 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.69, −1.76 |

Computer programs: *APEX5* and *SAINT* (Bruker, 2025), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2025/1* (Sheldrick, 2015*b*) and *ShelXle* (Hübschle *et al.*, 2011).

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## References

Boeije, M. F. J., Delczeg-Czirjak, E. K., van Dijk, N. H., Eriksson, O. & Brück, E. (2017). *J. Alloys Compd.* **722**, 549–554.
Bruker (2025). *APEX5* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruzzone, G. (1971). *J. Less-Common Met.* **25**, 361–366.
Bruzzone, G., Ferretti, M. & Merlo, F. (1985). *J. Less-Common Met.* **114**, 305–310.
Bruzzone, G. & Merlo, F. (1983). *J. Less-Common Met.* **92**, 75–79.
Hou, Y., Xu, Z., Peng, S., Rong, C., Liu, J. P. & Sun, S. (2007). *Adv. Mater.* **19**, 3349–3352.
Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* **44**, 1281–1284.
Kabekkodu, S. N., Dosen, A. & Blanton, T. N. (2024). *Powder Diffr.* **39**, 47–59.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Liang, G., Huot, J. & Schulz, R. (2001). *J. Alloys Compd.* **321**, 146–150.
Nakamura, H., Kitaoka, Y., Inoue, M., Asayama, K. & Ōnuki, Y. (1990). *J. Magn. Magn. Mater.* **90–91**, 459–460.
Schwickert, C. & Pöttgen, R. (2014). *Z. Naturforsch. B* **69**, 674–680.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Simura, R. & Yamane, H. (2019). *Acta Cryst.* E**75**, 1490–1493.
Wan, B., Yuan, Y., Zheng, L., Xu, Y., Zhao, S., Liu, K., Huang, D., Wu, L., Zhang, Z., Wang, G., Li, J., Zhang, S. & Gou, H. (2024). *J. Am. Chem. Soc.* **146**, 17508–17516.
Xu, J., Chen, X., Zhu, W., Zhang, W., Cui, H., Zhu, S., Liu, J., Liu, H., Yan, K. & Cheng, H. (2022). *Int. J. Hydrogen Energy* **47**, 22495–22509.
Zhou, P., Zhang, J., Bi, J., Xiao, X., Cao, Z., Zhan, L., Shen, H., Lu, M., Li, Z., Zhao, Y., Wang, L., Yan, M. & Chen, L. (2023). *J. Mater. Chem. A* **11**, 25963–25972.

# supporting information

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## Crystal structure of the 'missing' intermetallic compound $BaCu_5$

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### Computing details

### Barium pentacopper

*Crystal data*

$BaCu_5$
$M_r$ = 455.04
Orthorhombic, *Pnma*
*a* = 12.8420 (7) Å
*b* = 5.0189 (3) Å
*c* = 6.5445 (6) Å
*V* = 421.81 (5) Å$^3$
*Z* = 4
*F*(000) = 804
$D_x$ = 7.165 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6137 reflections
*θ* = 3.2–35.8°
*μ* = 33.71 mm$^{-1}$
*T* = 150 K
Block, black
0.13 × 0.08 × 0.02 mm

*Data collection*

Bruker AXS D8 Quest diffractometer
Radiation source: fine focus sealed tube X-ray source
Triumph curved graphite crystal monochromator
Detector resolution: 7.4074 pixels mm$^{-1}$
*ω* and phi scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min}$ = 0.135, $T_{max}$ = 0.274
24524 measured reflections
1112 independent reflections
877 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.080
$\theta_{max}$ = 36.4°, $\theta_{min}$ = 3.2°
*h* = −21→21
*k* = −8→8
*l* = −10→10

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.059
*S* = 1.09
1112 reflections
34 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0111P)^2 + 7.083P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.69 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.76 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ba1 | 0.58888 (3) | 0.750000 | 0.13690 (6) | 0.00983 (8) |
| Cu1 | 0.48045 (6) | 0.750000 | 0.57102 (13) | 0.00970 (14) |
| Cu2 | 0.35376 (4) | 0.49998 (11) | 0.35225 (9) | 0.00888 (10) |
| Cu3 | 0.28152 (7) | 0.750000 | 0.05359 (12) | 0.00979 (15) |
| Cu4 | 0.21455 (6) | 0.250000 | 0.16200 (12) | 0.00922 (14) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ba1 | 0.01055 (14) | 0.01004 (15) | 0.00890 (14) | 0.000 | 0.00060 (13) | 0.000 |
| Cu1 | 0.0087 (3) | 0.0103 (3) | 0.0101 (3) | 0.000 | −0.0008 (3) | 0.000 |
| Cu2 | 0.0100 (2) | 0.0077 (2) | 0.0089 (2) | −0.00029 (18) | −0.00062 (19) | 0.00011 (19) |
| Cu3 | 0.0115 (3) | 0.0099 (3) | 0.0080 (3) | 0.000 | −0.0009 (3) | 0.000 |
| Cu4 | 0.0098 (3) | 0.0099 (3) | 0.0080 (3) | 0.000 | −0.0012 (3) | 0.000 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ba1—Cu1 | 3.1640 (10) | Cu1—Cu2$^{ix}$ | 2.5217 (9) |
| Ba1—Cu4$^{i}$ | 3.1935 (9) | Cu1—Cu2$^{vi}$ | 2.5217 (9) |
| Ba1—Cu3$^{ii}$ | 3.1974 (9) | Cu1—Cu4$^{x}$ | 2.5740 (11) |
| Ba1—Cu3$^{iii}$ | 3.2590 (6) | Cu1—Cu1$^{vi}$ | 2.7228 (7) |
| Ba1—Cu3$^{i}$ | 3.2590 (6) | Cu1—Cu1$^{v}$ | 2.7228 (7) |
| Ba1—Cu4$^{iv}$ | 3.2610 (6) | Cu2—Cu3 | 2.5012 (9) |
| Ba1—Cu4$^{ii}$ | 3.2610 (6) | Cu2—Cu2$^{xi}$ | 2.5092 (11) |
| Ba1—Cu1$^{v}$ | 3.2778 (6) | Cu2—Cu2$^{viii}$ | 2.5097 (11) |
| Ba1—Cu1$^{vi}$ | 3.2778 (6) | Cu2—Cu4 | 2.5140 (9) |
| Ba1—Cu2$^{i}$ | 3.5163 (7) | Cu2—Cu3$^{x}$ | 2.5157 (9) |
| Ba1—Cu2$^{vii}$ | 3.5163 (7) | Cu2—Cu4$^{x}$ | 2.5404 (9) |
| Ba1—Cu2 | 3.5606 (7) | Cu3—Cu4$^{xii}$ | 2.5633 (11) |
| Cu1—Cu2 | 2.5043 (9) | Cu3—Cu4$^{xiii}$ | 2.7460 (5) |
| Cu1—Cu2$^{viii}$ | 2.5043 (9) | Cu3—Cu4 | 2.7460 (5) |
| | | | |
| Cu1—Ba1—Cu4$^{i}$ | 153.88 (2) | Cu3—Cu2—Ba1$^{i}$ | 62.95 (2) |
| Cu1—Ba1—Cu3$^{ii}$ | 76.80 (2) | Cu1—Cu2—Ba1$^{i}$ | 124.28 (3) |
| Cu4$^{i}$—Ba1—Cu3$^{ii}$ | 77.08 (2) | Cu2$^{xi}$—Cu2—Ba1$^{i}$ | 69.096 (9) |
| Cu1—Ba1—Cu3$^{iii}$ | 124.627 (16) | Cu2$^{viii}$—Cu2—Ba1$^{i}$ | 110.903 (9) |
| Cu4$^{i}$—Ba1—Cu3$^{iii}$ | 50.361 (13) | Cu4—Cu2—Ba1$^{i}$ | 61.31 (2) |
| Cu3$^{ii}$—Ba1—Cu3$^{iii}$ | 81.212 (10) | Cu3$^{x}$—Cu2—Ba1$^{i}$ | 116.33 (2) |
| Cu1—Ba1—Cu3$^{i}$ | 124.627 (16) | Cu1$^{vi}$—Cu2—Ba1$^{i}$ | 80.03 (2) |
| Cu4$^{i}$—Ba1—Cu3$^{i}$ | 50.361 (13) | Cu4$^{x}$—Cu2—Ba1$^{i}$ | 167.17 (3) |
| Cu3$^{ii}$—Ba1—Cu3$^{i}$ | 81.212 (10) | Cu3—Cu2—Ba1 | 80.12 (2) |
| Cu3$^{iii}$—Ba1—Cu3$^{i}$ | 100.71 (3) | Cu1—Cu2—Ba1 | 59.92 (2) |
| Cu1—Ba1—Cu4$^{iv}$ | 81.686 (19) | Cu2$^{xi}$—Cu2—Ba1 | 110.636 (9) |
| Cu4$^{i}$—Ba1—Cu4$^{iv}$ | 81.722 (10) | Cu2$^{viii}$—Cu2—Ba1 | 69.365 (9) |
| Cu3$^{ii}$—Ba1—Cu4$^{iv}$ | 50.312 (12) | Cu4—Cu2—Ba1 | 125.65 (3) |

| | | | |
|---|---|---|---|
| Cu3$^{iii}$—Ba1—Cu4$^{iv}$ | 46.300 (19) | Cu3$^{x}$—Cu2—Ba1 | 165.63 (3) |
| Cu3$^{i}$—Ba1—Cu4$^{iv}$ | 119.62 (2) | Cu1$^{vi}$—Cu2—Ba1 | 62.497 (19) |
| Cu1—Ba1—Cu4$^{ii}$ | 81.686 (19) | Cu4$^{x}$—Cu2—Ba1 | 115.76 (2) |
| Cu4$^{i}$—Ba1—Cu4$^{ii}$ | 81.722 (10) | Ba1$^{i}$—Cu2—Ba1 | 65.654 (13) |
| Cu3$^{ii}$—Ba1—Cu4$^{ii}$ | 50.312 (13) | Cu3—Cu2—Ba1$^{xiv}$ | 59.59 (2) |
| Cu3$^{iii}$—Ba1—Cu4$^{ii}$ | 119.62 (2) | Cu1—Cu2—Ba1$^{xiv}$ | 115.14 (2) |
| Cu3$^{i}$—Ba1—Cu4$^{ii}$ | 46.300 (19) | Cu2$^{xi}$—Cu2—Ba1$^{xiv}$ | 110.245 (9) |
| Cu4$^{iv}$—Ba1—Cu4$^{ii}$ | 100.62 (3) | Cu2$^{viii}$—Cu2—Ba1$^{xiv}$ | 69.755 (9) |
| Cu1—Ba1—Cu1$^{v}$ | 49.969 (13) | Cu4—Cu2—Ba1$^{xiv}$ | 61.011 (18) |
| Cu4$^{i}$—Ba1—Cu1$^{v}$ | 124.885 (15) | Cu3$^{x}$—Cu2—Ba1$^{xiv}$ | 60.956 (19) |
| Cu3$^{ii}$—Ba1—Cu1$^{v}$ | 80.84 (2) | Cu1$^{vi}$—Cu2—Ba1$^{xiv}$ | 163.78 (3) |
| Cu3$^{iii}$—Ba1—Cu1$^{v}$ | 76.838 (17) | Cu4$^{x}$—Cu2—Ba1$^{xiv}$ | 59.30 (2) |
| Cu3$^{i}$—Ba1—Cu1$^{v}$ | 162.05 (3) | Ba1$^{i}$—Cu2—Ba1$^{xiv}$ | 109.741 (17) |
| Cu4$^{iv}$—Ba1—Cu1$^{v}$ | 46.364 (19) | Ba1—Cu2—Ba1$^{xiv}$ | 132.941 (16) |
| Cu4$^{ii}$—Ba1—Cu1$^{v}$ | 119.22 (2) | Cu3—Cu2—Ba1$^{vi}$ | 164.61 (3) |
| Cu1—Ba1—Cu1$^{vi}$ | 49.969 (13) | Cu1—Cu2—Ba1$^{vi}$ | 61.115 (19) |
| Cu4$^{i}$—Ba1—Cu1$^{vi}$ | 124.885 (15) | Cu2$^{xi}$—Cu2—Ba1$^{vi}$ | 69.874 (9) |
| Cu3$^{ii}$—Ba1—Cu1$^{vi}$ | 80.84 (2) | Cu2$^{viii}$—Cu2—Ba1$^{vi}$ | 110.127 (9) |
| Cu3$^{iii}$—Ba1—Cu1$^{vi}$ | 162.05 (3) | Cu4—Cu2—Ba1$^{vi}$ | 115.22 (2) |
| Cu3$^{i}$—Ba1—Cu1$^{vi}$ | 76.838 (17) | Cu3$^{x}$—Cu2—Ba1$^{vi}$ | 59.18 (2) |
| Cu4$^{iv}$—Ba1—Cu1$^{vi}$ | 119.22 (2) | Cu1$^{vi}$—Cu2—Ba1$^{vi}$ | 58.38 (2) |
| Cu4$^{ii}$—Ba1—Cu1$^{vi}$ | 46.364 (19) | Cu4$^{x}$—Cu2—Ba1$^{vi}$ | 60.531 (19) |
| Cu1$^{v}$—Ba1—Cu1$^{vi}$ | 99.92 (3) | Ba1$^{i}$—Cu2—Ba1$^{vi}$ | 132.043 (17) |
| Cu1—Ba1—Cu2$^{i}$ | 155.461 (14) | Ba1—Cu2—Ba1$^{vi}$ | 108.234 (16) |
| Cu4$^{i}$—Ba1—Cu2$^{i}$ | 43.679 (16) | Ba1$^{xiv}$—Cu2—Ba1$^{vi}$ | 106.895 (17) |
| Cu3$^{ii}$—Ba1—Cu2$^{i}$ | 114.50 (2) | Cu2$^{viii}$—Cu3—Cu2 | 60.23 (3) |
| Cu3$^{iii}$—Ba1—Cu2$^{i}$ | 79.602 (18) | Cu2$^{viii}$—Cu3—Cu2$^{xii}$ | 156.30 (4) |
| Cu3$^{i}$—Ba1—Cu2$^{i}$ | 43.118 (17) | Cu2—Cu3—Cu2$^{xii}$ | 114.536 (16) |
| Cu4$^{iv}$—Ba1—Cu2$^{i}$ | 122.57 (2) | Cu2$^{viii}$—Cu3—Cu2$^{xv}$ | 114.536 (16) |
| Cu4$^{ii}$—Ba1—Cu2$^{i}$ | 89.381 (18) | Cu2—Cu3—Cu2$^{xv}$ | 156.30 (4) |
| Cu1$^{v}$—Ba1—Cu2$^{i}$ | 149.426 (17) | Cu2$^{xii}$—Cu3—Cu2$^{xv}$ | 59.83 (3) |
| Cu1$^{vi}$—Ba1—Cu2$^{i}$ | 108.340 (16) | Cu2$^{viii}$—Cu3—Cu4$^{xii}$ | 140.72 (3) |
| Cu1—Ba1—Cu2$^{vii}$ | 155.461 (14) | Cu2—Cu3—Cu4$^{xii}$ | 140.72 (3) |
| Cu4$^{i}$—Ba1—Cu2$^{vii}$ | 43.679 (16) | Cu2$^{xii}$—Cu3—Cu4$^{xii}$ | 59.33 (3) |
| Cu3$^{ii}$—Ba1—Cu2$^{vii}$ | 114.50 (2) | Cu2$^{xv}$—Cu3—Cu4$^{xii}$ | 59.33 (3) |
| Cu3$^{iii}$—Ba1—Cu2$^{vii}$ | 43.118 (17) | Cu2$^{viii}$—Cu3—Cu4$^{xiii}$ | 57.03 (2) |
| Cu3$^{i}$—Ba1—Cu2$^{vii}$ | 79.602 (18) | Cu2—Cu3—Cu4$^{xiii}$ | 111.88 (3) |
| Cu4$^{iv}$—Ba1—Cu2$^{vii}$ | 89.381 (18) | Cu2$^{xii}$—Cu3—Cu4$^{xiii}$ | 112.01 (3) |
| Cu4$^{ii}$—Ba1—Cu2$^{vii}$ | 122.57 (2) | Cu2$^{xv}$—Cu3—Cu4$^{xiii}$ | 57.54 (2) |
| Cu1$^{v}$—Ba1—Cu2$^{vii}$ | 108.340 (16) | Cu4$^{xii}$—Cu3—Cu4$^{xiii}$ | 105.34 (2) |
| Cu1$^{vi}$—Ba1—Cu2$^{vii}$ | 149.426 (17) | Cu2$^{viii}$—Cu3—Cu4 | 111.88 (3) |
| Cu2$^{i}$—Ba1—Cu2$^{vii}$ | 41.807 (19) | Cu2—Cu3—Cu4 | 57.03 (2) |
| Cu1—Ba1—Cu2 | 43.227 (16) | Cu2$^{xii}$—Cu3—Cu4 | 57.54 (2) |
| Cu4$^{i}$—Ba1—Cu2 | 155.890 (14) | Cu2$^{xv}$—Cu3—Cu4 | 112.01 (3) |
| Cu3$^{ii}$—Ba1—Cu2 | 113.91 (2) | Cu4$^{xii}$—Cu3—Cu4 | 105.34 (2) |
| Cu3$^{iii}$—Ba1—Cu2 | 148.851 (17) | Cu4$^{xiii}$—Cu3—Cu4 | 132.09 (4) |
| Cu3$^{i}$—Ba1—Cu2 | 108.245 (15) | Cu2$^{viii}$—Cu3—Ba1$^{xiv}$ | 77.99 (3) |
| Cu4$^{iv}$—Ba1—Cu2 | 122.08 (2) | Cu2—Cu3—Ba1$^{xiv}$ | 77.99 (3) |

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| Cu4$^{ii}$—Ba1—Cu2 | 89.354 (17) | Cu2$^{xii}$—Cu3—Ba1$^{xiv}$ | 78.32 (3) |
| Cu1$^{v}$—Ba1—Cu2 | 78.967 (18) | Cu2$^{xv}$—Cu3—Ba1$^{xiv}$ | 78.32 (3) |
| Cu1$^{vi}$—Ba1—Cu2 | 43.030 (17) | Cu4$^{xii}$—Cu3—Ba1$^{xiv}$ | 130.44 (4) |
| Cu2$^{i}$—Ba1—Cu2 | 114.346 (13) | Cu4$^{xiii}$—Cu3—Ba1$^{xiv}$ | 66.05 (2) |
| Cu2$^{vii}$—Ba1—Cu2 | 131.585 (13) | Cu4—Cu3—Ba1$^{xiv}$ | 66.05 (2) |
| Cu2—Cu1—Cu2$^{viii}$ | 60.14 (3) | Cu2$^{viii}$—Cu3—Ba1$^{iii}$ | 73.931 (19) |
| Cu2—Cu1—Cu2$^{ix}$ | 155.73 (4) | Cu2—Cu3—Ba1$^{iii}$ | 119.72 (3) |
| Cu2$^{viii}$—Cu1—Cu2$^{ix}$ | 114.397 (19) | Cu2$^{xii}$—Cu3—Ba1$^{iii}$ | 122.43 (3) |
| Cu2—Cu1—Cu2$^{vi}$ | 114.397 (19) | Cu2$^{xv}$—Cu3—Ba1$^{iii}$ | 76.602 (19) |
| Cu2$^{viii}$—Cu1—Cu2$^{vi}$ | 155.73 (4) | Cu4$^{xii}$—Cu3—Ba1$^{iii}$ | 66.89 (2) |
| Cu2$^{ix}$—Cu1—Cu2$^{vi}$ | 59.67 (3) | Cu4$^{xiii}$—Cu3—Ba1$^{iii}$ | 63.582 (17) |
| Cu2—Cu1—Cu4$^{x}$ | 60.01 (3) | Cu4—Cu3—Ba1$^{iii}$ | 164.25 (3) |
| Cu2$^{viii}$—Cu1—Cu4$^{x}$ | 60.01 (3) | Ba1$^{xiv}$—Cu3—Ba1$^{iii}$ | 129.602 (13) |
| Cu2$^{ix}$—Cu1—Cu4$^{x}$ | 140.84 (3) | Cu2$^{viii}$—Cu3—Ba1$^{i}$ | 119.72 (3) |
| Cu2$^{vi}$—Cu1—Cu4$^{x}$ | 140.84 (3) | Cu2—Cu3—Ba1$^{i}$ | 73.931 (19) |
| Cu2—Cu1—Cu1$^{vi}$ | 57.51 (3) | Cu2$^{xii}$—Cu3—Ba1$^{i}$ | 76.602 (19) |
| Cu2$^{viii}$—Cu1—Cu1$^{vi}$ | 112.73 (5) | Cu2$^{xv}$—Cu3—Ba1$^{i}$ | 122.43 (3) |
| Cu2$^{ix}$—Cu1—Cu1$^{vi}$ | 111.77 (5) | Cu4$^{xii}$—Cu3—Ba1$^{i}$ | 66.89 (2) |
| Cu2$^{vi}$—Cu1—Cu1$^{vi}$ | 56.89 (3) | Cu4$^{xiii}$—Cu3—Ba1$^{i}$ | 164.25 (3) |
| Cu4$^{x}$—Cu1—Cu1$^{vi}$ | 104.97 (3) | Cu4—Cu3—Ba1$^{i}$ | 63.583 (17) |
| Cu2—Cu1—Cu1$^{v}$ | 112.73 (5) | Ba1$^{xiv}$—Cu3—Ba1$^{i}$ | 129.602 (13) |
| Cu2$^{viii}$—Cu1—Cu1$^{v}$ | 57.51 (3) | Ba1$^{iii}$—Cu3—Ba1$^{i}$ | 100.71 (3) |
| Cu2$^{ix}$—Cu1—Cu1$^{v}$ | 56.89 (3) | Cu2$^{xi}$—Cu4—Cu2 | 59.87 (3) |
| Cu2$^{vi}$—Cu1—Cu1$^{v}$ | 111.77 (5) | Cu2$^{xi}$—Cu4—Cu2$^{xvi}$ | 113.220 (18) |
| Cu4$^{x}$—Cu1—Cu1$^{v}$ | 104.97 (3) | Cu2—Cu4—Cu2$^{xvi}$ | 152.53 (4) |
| Cu1$^{vi}$—Cu1—Cu1$^{v}$ | 134.34 (7) | Cu2$^{xi}$—Cu4—Cu2$^{xii}$ | 152.53 (4) |
| Cu2—Cu1—Ba1 | 76.85 (3) | Cu2—Cu4—Cu2$^{xii}$ | 113.220 (18) |
| Cu2$^{viii}$—Cu1—Ba1 | 76.85 (3) | Cu2$^{xvi}$—Cu4—Cu2$^{xii}$ | 59.20 (3) |
| Cu2$^{ix}$—Cu1—Ba1 | 78.89 (3) | Cu2$^{xi}$—Cu4—Cu3$^{x}$ | 59.39 (3) |
| Cu2$^{vi}$—Cu1—Ba1 | 78.89 (3) | Cu2—Cu4—Cu3$^{x}$ | 59.39 (3) |
| Cu4$^{x}$—Cu1—Ba1 | 129.48 (4) | Cu2$^{xvi}$—Cu4—Cu3$^{x}$ | 143.57 (3) |
| Cu1$^{vi}$—Cu1—Ba1 | 67.19 (3) | Cu2$^{xii}$—Cu4—Cu3$^{x}$ | 143.57 (3) |
| Cu1$^{v}$—Cu1—Ba1 | 67.19 (3) | Cu2$^{xi}$—Cu4—Cu1$^{xii}$ | 143.74 (3) |
| Cu2—Cu1—Ba1$^{v}$ | 122.72 (3) | Cu2—Cu4—Cu1$^{xii}$ | 143.74 (3) |
| Cu2$^{viii}$—Cu1—Ba1$^{v}$ | 76.898 (19) | Cu2$^{xvi}$—Cu4—Cu1$^{xii}$ | 58.63 (3) |
| Cu2$^{ix}$—Cu1—Ba1$^{v}$ | 74.474 (19) | Cu2$^{xii}$—Cu4—Cu1$^{xii}$ | 58.63 (3) |
| Cu2$^{vi}$—Cu1—Ba1$^{v}$ | 119.61 (3) | Cu3$^{x}$—Cu4—Cu1$^{xii}$ | 104.50 (4) |
| Cu4$^{x}$—Cu1—Ba1$^{v}$ | 66.475 (19) | Cu2$^{xi}$—Cu4—Cu3 | 111.18 (3) |
| Cu1$^{vi}$—Cu1—Ba1$^{v}$ | 162.71 (5) | Cu2—Cu4—Cu3 | 56.58 (2) |
| Cu1$^{v}$—Cu1—Ba1$^{v}$ | 62.84 (2) | Cu2$^{xvi}$—Cu4—Cu3 | 110.69 (3) |
| Ba1—Cu1—Ba1$^{v}$ | 130.031 (13) | Cu2$^{xii}$—Cu4—Cu3 | 56.67 (2) |
| Cu2—Cu1—Ba1$^{vi}$ | 76.898 (19) | Cu3$^{x}$—Cu4—Cu3 | 104.61 (2) |
| Cu2$^{viii}$—Cu1—Ba1$^{vi}$ | 122.72 (3) | Cu1$^{xii}$—Cu4—Cu3 | 104.18 (2) |
| Cu2$^{ix}$—Cu1—Ba1$^{vi}$ | 119.61 (3) | Cu2$^{xi}$—Cu4—Cu3$^{xvii}$ | 56.58 (2) |
| Cu2$^{vi}$—Cu1—Ba1$^{vi}$ | 74.474 (19) | Cu2—Cu4—Cu3$^{xvii}$ | 111.18 (3) |
| Cu4$^{x}$—Cu1—Ba1$^{vi}$ | 66.475 (19) | Cu2$^{xvi}$—Cu4—Cu3$^{xvii}$ | 56.67 (2) |
| Cu1$^{vi}$—Cu1—Ba1$^{vi}$ | 62.84 (2) | Cu2$^{xii}$—Cu4—Cu3$^{xvii}$ | 110.70 (3) |
| Cu1$^{v}$—Cu1—Ba1$^{vi}$ | 162.71 (5) | Cu3$^{x}$—Cu4—Cu3$^{xvii}$ | 104.61 (2) |

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| Ba1—Cu1—Ba1$^{vi}$ | 130.031 (13) | Cu1$^{xii}$—Cu4—Cu3$^{xvii}$ | 104.18 (2) |
| Ba1$^{v}$—Cu1—Ba1$^{vi}$ | 99.92 (3) | Cu3—Cu4—Cu3$^{xvii}$ | 132.09 (4) |
| Cu3—Cu2—Cu1 | 115.87 (3) | Cu2$^{xi}$—Cu4—Ba1$^{i}$ | 75.01 (2) |
| Cu3—Cu2—Cu2$^{xi}$ | 120.112 (16) | Cu2—Cu4—Ba1$^{i}$ | 75.01 (2) |
| Cu1—Cu2—Cu2$^{xi}$ | 120.072 (16) | Cu2$^{xvi}$—Cu4—Ba1$^{i}$ | 77.54 (3) |
| Cu3—Cu2—Cu2$^{viii}$ | 59.887 (16) | Cu2$^{xii}$—Cu4—Ba1$^{i}$ | 77.54 (3) |
| Cu1—Cu2—Cu2$^{viii}$ | 59.929 (16) | Cu3$^{x}$—Cu4—Ba1$^{i}$ | 126.65 (4) |
| Cu2$^{xi}$—Cu2—Cu2$^{viii}$ | 180.0 | Cu1$^{xii}$—Cu4—Ba1$^{i}$ | 128.85 (4) |
| Cu3—Cu2—Cu4 | 66.39 (2) | Cu3—Cu4—Ba1$^{i}$ | 66.06 (2) |
| Cu1—Cu2—Cu4 | 174.38 (4) | Cu3$^{xvii}$—Cu4—Ba1$^{i}$ | 66.06 (2) |
| Cu2$^{xi}$—Cu2—Cu4 | 60.062 (15) | Cu2$^{xi}$—Cu4—Ba1$^{xviii}$ | 76.585 (18) |
| Cu2$^{viii}$—Cu2—Cu4 | 119.936 (15) | Cu2—Cu4—Ba1$^{xviii}$ | 122.42 (3) |
| Cu3—Cu2—Cu3$^{x}$ | 113.79 (2) | Cu2$^{xvi}$—Cu4—Ba1$^{xviii}$ | 76.763 (18) |
| Cu1—Cu2—Cu3$^{x}$ | 113.52 (3) | Cu2$^{xii}$—Cu4—Ba1$^{xviii}$ | 122.09 (3) |
| Cu2$^{xi}$—Cu2—Cu3$^{x}$ | 60.085 (16) | Cu3$^{x}$—Cu4—Ba1$^{xviii}$ | 66.81 (2) |
| Cu2$^{viii}$—Cu2—Cu3$^{x}$ | 119.915 (16) | Cu1$^{xii}$—Cu4—Ba1$^{xviii}$ | 67.162 (19) |
| Cu4—Cu2—Cu3$^{x}$ | 61.28 (3) | Cu3—Cu4—Ba1$^{xviii}$ | 164.27 (3) |
| Cu3—Cu2—Cu1$^{vi}$ | 135.92 (4) | Cu3$^{xvii}$—Cu4—Ba1$^{xviii}$ | 63.642 (17) |
| Cu1—Cu2—Cu1$^{vi}$ | 65.604 (19) | Ba1$^{i}$—Cu4—Ba1$^{xviii}$ | 129.673 (13) |
| Cu2$^{xi}$—Cu2—Cu1$^{vi}$ | 60.164 (15) | Cu2$^{xi}$—Cu4—Ba1$^{xiv}$ | 122.42 (3) |
| Cu2$^{viii}$—Cu2—Cu1$^{vi}$ | 119.837 (15) | Cu2—Cu4—Ba1$^{xiv}$ | 76.585 (18) |
| Cu4—Cu2—Cu1$^{vi}$ | 116.79 (3) | Cu2$^{xvi}$—Cu4—Ba1$^{xiv}$ | 122.09 (3) |
| Cu3$^{x}$—Cu2—Cu1$^{vi}$ | 103.34 (3) | Cu2$^{xii}$—Cu4—Ba1$^{xiv}$ | 76.763 (19) |
| Cu3—Cu2—Cu4$^{x}$ | 104.34 (3) | Cu3$^{x}$—Cu4—Ba1$^{xiv}$ | 66.81 (2) |
| Cu1—Cu2—Cu4$^{x}$ | 61.36 (3) | Cu1$^{xii}$—Cu4—Ba1$^{xiv}$ | 67.162 (19) |
| Cu2$^{xi}$—Cu2—Cu4$^{x}$ | 119.601 (15) | Cu3—Cu4—Ba1$^{xiv}$ | 63.642 (17) |
| Cu2$^{viii}$—Cu2—Cu4$^{x}$ | 60.399 (15) | Cu3$^{xvii}$—Cu4—Ba1$^{xiv}$ | 164.27 (3) |
| Cu4—Cu2—Cu4$^{x}$ | 113.34 (2) | Ba1$^{i}$—Cu4—Ba1$^{xiv}$ | 129.673 (13) |
| Cu3$^{x}$—Cu2—Cu4$^{x}$ | 65.79 (2) | Ba1$^{xviii}$—Cu4—Ba1$^{xiv}$ | 100.62 (3) |
| Cu1$^{vi}$—Cu2—Cu4$^{x}$ | 112.24 (3) | | |

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*+1/2, *y*, −*z*+1/2; (iii) −*x*+1, −*y*+2, −*z*; (iv) *x*+1/2, *y*+1, −*z*+1/2; (v) −*x*+1, −*y*+2, −*z*+1; (vi) −*x*+1, −*y*+1, −*z*+1; (vii) −*x*+1, *y*+1/2, −*z*; (viii) *x*, −*y*+3/2, *z*; (ix) −*x*+1, *y*+1/2, −*z*+1; (x) −*x*+1/2, −*y*+1, *z*+1/2; (xi) *x*, −*y*+1/2, *z*; (xii) −*x*+1/2, −*y*+1, *z*−1/2; (xiii) *x*, *y*+1, *z*; (xiv) *x*−1/2, *y*, −*z*+1/2; (xv) −*x*+1/2, *y*+1/2, *z*−1/2; (xvi) −*x*+1/2, *y*−1/2, *z*−1/2; (xvii) *x*, *y*−1, *z*; (xviii) *x*−1/2, *y*−1, −*z*+1/2.