Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$CeCu_{5-x}In_{1+x}$ [x = 0.17 (1)] with the orthorhombic $CeCu_6$ structure

Svilen Bobev[a]* and Eric D. Bauer[b]

[a]Department of Chemistry and Biochemistry, 304A Drake Hall, University of Delaware, Newark, DE 19716, USA, and [b]MST-10 Mail Stop K764, Los Alamos National Laboratory, NM 87545, USA

Correspondence e-mail: sbobev@chem.udel.edu

Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(n–Cu) = 0.001 Å
Disorder in main residue
R factor = 0.020
wR factor = 0.050
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Large single crystals of the title compound, cerium copper indium, were synthesized from the elements using a eutectic Cu/In mixture as a solvent. $CeCu_{5-x}In_{1+x}$ [x = 0.17 (1)] is a new ternary derivative of the orthorhombic $CeCu_6$ structure type [space group *Pnma* (No. 62)]. This result differs from that of Kalychak, Baranyak, Belsky & Dmytrakh [*Dopl. Akad. Nauk Ukr. RSR Ser. B* (1988). **9**, 39–42], who found that $CeCu_{4.38}In_{1.62}$ belongs to a new structure type (space group *Pnnm*), derived from the parent $CeCu_6$ compound by doubling the *a* axis. In the present structure, all the atoms, except one of the Cu species, occupy special positions with mirror symmetry.

Received 13 April 2005
Accepted 19 April 2005
Online 27 April 2005

Comment

In this paper, we describe the title compound, $CeCu_{5-x}In_{1+x}$ [x = 0.17 (1)], (I) (Fig. 1), as part of our continuing synthetic and structural studies (Bobev & Bauer, 2005) of $CeCu_6$ (Cromer *et al.*, 1960) derivatives substituted with indium. While the existence of a large breadth of stoichiometry in $CeCu_{6-x}In_x$ has been known for almost a decade (Kasaya *et al.*, 1995), detailed structural studies in these systems are still lacking.

Here, as with our previous study of $PrCu_{5-x}In_{1+x}$ [x = 0.24 (1)] (Bobev & Bauer, 2005), we employed a flux growth

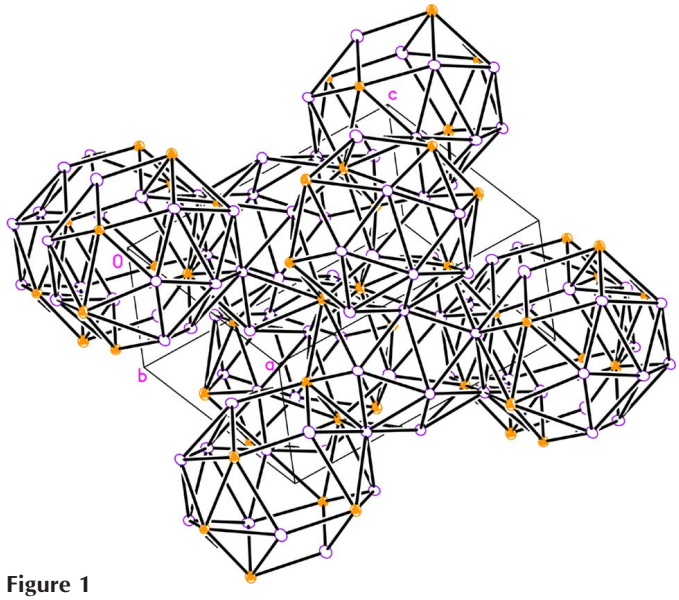

Figure 1
A view of the $CeCu_{5-x}In_{1+x}$ structure, oriented almost parallel to the direction of the body diagonal. The projection emphasizes the way the Ce-centered polyhedra made of In and Cu are packed. In1 and In2/Cu2 are shown as purple open circles; Cu3, Cu4 and Cu5 are drawn as shaded orange circles. Ce atoms have been omitted for clarity. The unit cell is outlined.

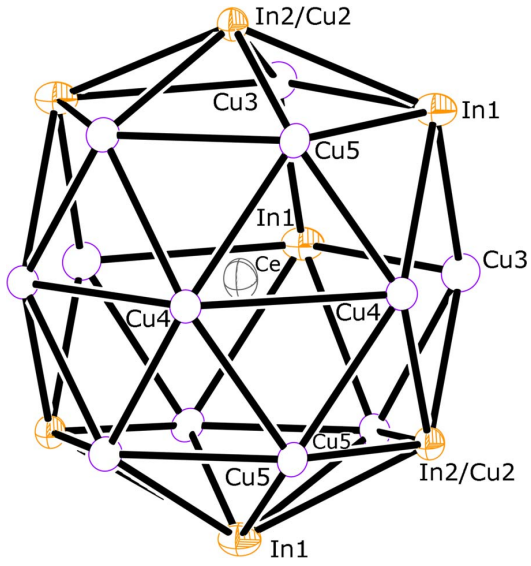

Figure 2
A view of the 19-vertex polyhedron around the Ce atom in (I). Displacement ellipsoids are drawn at the 98% probability level. Color key: In1 and In2/Cu2: orange; Cu3, Cu4 and Cu5: purple.

method (Canfield & Fisk, 1992) to circumvent the experimental difficulties associated with the more commonly used arc melting or induction furnace syntheses.

The stoichiometry breadth displayed by (I) is not unusual for intermetallic compounds with this structure type, as evidenced by studies on the properties of the non-stoichiometric $CeCu_{5-x}In_{1+x}$ [$0 < x < \frac{3}{4}$] and $CeCu_{5+x}In_{1-x}$ [$0 < x < 1$] (Kasaya *et al.*, 1995). However, in this study, we find no evidence for the existence of a superstructure with a doubled *a* axis, as reported for $CeCu_{4.38}In_{1.62}$ (Kalychak *et al.*, 1988). This phase is said to belong to a new structure type with space group *Pnnm*, and can be derived from the archetype $CeCu_6$, which crystallizes in space group *Pnma* (Cromer *et al.*, 1960), by doubling the *a* axis of the unit cell. The ordering in $CeCu_{4.38}In_{1.62}$ could arise from the different synthetic approaches – arc-melting and subsequent annealing (Kalychak *et al.*, 1988) as opposed to flux growth in Cu–In flux (this study). Further systematic investigations of the phase width and its dependence on the synthetic conditions are currently under way.

The Ce atoms in (I) have a high coordination number of 19, as shown in Fig. 2. All the interatomic distances in (I) are within the expected ranges for such intermetallic compounds. The physical properties of (I) will be reported later.

Experimental

All starting materials were used as received [Ce (Ames Laboratory, ingots, 99.99% metal basis), Cu (Alfa, granules, 99.999%) and In (Alfa, rods, 99.999%)]. Mixtures of the elements in a Ce/Cu/In ratio of 1:2:5 were loaded in an alumina crucible, which was subsequently enclosed in an evacuated fused-silica jacket by flame-sealing. The reaction was carried out at a temperature of 1373 K for 4 h, followed by slow cooling (3 K h^{-1}) to 1073 K. At this point, the molten flux (Cu/In eutectic) was removed by centrifugation. The recovered product consisted of relatively large and well defined crystals with a silver metallic luster, which were later identified as the title compound, (I). The unit-cell parameters determined here compare well with those previously reported for the non-stoichiometric $CeCu_{5-x}In_{1+x}$ ($0 < x < 0.75$; Kasaya *et al.*, 1995), The crystals of (I) are stable in air and moisture over extended periods of time (greater than *ca* three months), and decompose slowly in solutions of mineral acids.

Crystal data

$CeCu_{4.82}In_{1.17}$
M_r = 581.61
Orthorhombic, *Pnma*
a = 8.4056 (7) Å
b = 5.0939 (4) Å
c = 10.7380 (8) Å
V = 459.77 (6) Å^3
Z = 4
D_x = 8.402 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1436 reflections
θ = 3.1–26.4°
μ = 37.16 mm^{-1}
T = 93 (2) K
Plate, metallic grey
0.08 × 0.08 × 0.04 mm

Data collection

Bruker APEX 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.08, T_{max} = 0.226
1436 measured reflections
501 independent reflections
448 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 26.4°
h = −8 → 10
k = −5 → 5
l = −13 → 4

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.050
S = 1.23
501 reflections
42 parameters
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.11 e Å^{-3}
$\Delta\rho_{min}$ = −1.11 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0058 (3)

Starting from the structure of $CeCu_6$ (Cromer *et al.*, 1960), the structural model for (I) was developed by a step-by-step approach similar to that used for $PrCu_{5-x}In_{1+x}$ [*x* = 0.24 (1)] (Bobev & Bauer, 2005). The highest peak is located 1.43 Å from atom Cu5 and the deepest hole is 1.15 Å from Cu4.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was funded in part by a University of Delaware start-up grant. Work at LANL is carried out under the auspices of the DOE.

References

Bobev, S. & Bauer, E. D. (2005). *Acta Cryst.* E**61**, i79–i81.
Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Canfield, P. C. & Fisk, Z. (1992). *Philos. Mag. B*, **65**, 1117–1123.
Cromer, D. T., Larson, A. C. & Roff, R. B. Jr (1960). *Acta Cryst.* **13**, 913–918.
Kalychak, Y. M., Baranyak, V. M., Belsky, V. M. & Dmytrakh, O. V. (1988). *Dop. Akad. Nauk Ukr. RSR Ser. B*, **9**, 39–42.
Kasaya, M., Satoh, N., Miyazaki, T. & Kumazaki, H. (1995). *Physica B*, **206–207**, 314–316.
Sheldrick, G. M. (2001). *SHELXTL*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.