

Cu_{4.35}Cd_{1.65}As₁₆: the first polyarsenic compound in the Cu–Cd–As system

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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{As}–\text{As}) = 0.001$ Å; disorder in main residue; R factor = 0.036; wR factor = 0.072; data-to-parameter ratio = 22.6.

The first polyarsenic compound in the Cu–Cd–As system was obtained by solid-state reaction of the elements and has a refined composition of Cu_{4.35}(2)Cd_{1.65}(2)As₁₆ (tetracopper dicadmium hexadecaarsenide). It adopts the Cu₅InP₁₆ structure type. The asymmetric unit consists of one Cu site, a split Cu/Cd site and four As sites. The polyanionic structure can be described as being composed of As₆ rings in chair conformations which are connected in the 1-, 2-, 4- and 5-positions. The resulting layers evolve along the c axis perpendicular to the ab plane. One Cu atom exhibits site symmetry 2 and is tetrahedrally coordinated by four As atoms. The other Cu atom, representing the split site, and the corresponding Cd atom have different coordination spheres. While the Cu atom is tetrahedrally coordinated by four As atoms, the Cd atom has a [3 + 1] coordination with a considerably longer Cd–As distance.

Related literature

For Cu₅InP₁₆, see: Lange *et al.* (2008). For related polyphosphides, see: Pöttgen *et al.* (2006). For polyarsenides, see: Bauhofer *et al.* (1981); Jeitschko *et al.* (2000); Emmerling & Röhr (2002); Emmerling *et al.* (2004); Hönle *et al.* (2002). For binary Cu–Cd phases, see: Brandon *et al.* (1974); Kreiner & Schaeppers (1997); von Heidenstamm *et al.* (1968). For related structures, see: Mansmann (1965); Clark & Range (1976). For crystallographic background, see: Becker & Coppens (1974).

Experimental

Crystal data

 Cu_{4.35}Cd_{1.65}As₁₆
 $M_r = 1660.8$

 Monoclinic, $C2/c$
 $a = 11.8324$ (6) Å

 $b = 10.4423$ (4) Å

 $c = 8.0903$ (4) Å

 $\beta = 110.480$ (4)°

 $V = 936.44$ (8) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 34.73$ mm⁻¹
 $T = 293$ K

 $0.030 \times 0.020 \times 0.004$ mm

Data collection

 Stoe IPDS 2T diffractometer
 Absorption correction: numerical
 (*X-Area*; Stoe & Cie, 2011)

 $T_{\min} = 0.205$, $T_{\max} = 0.785$

 12811 measured reflections
 1268 independent reflections
 1113 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.053$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.072$
 $S = 1.83$

1268 reflections

56 parameters

 $\Delta\rho_{\max} = 1.50$ e Å⁻³
 $\Delta\rho_{\min} = -1.67$ e Å⁻³
Table 1

Selected bond lengths (Å).

Cu1–As1	2.4254 (9)	Cu2–As4 ⁱⁱ	2.524 (7)
Cu1–As3	2.3931 (9)	Cd2–As2	2.856 (5)
Cu2–As2	2.516 (5)	Cd2–As3	2.516 (5)
Cu2–As3	2.501 (5)	Cd2–As4 ⁱ	2.475 (5)
Cu2–As4 ⁱ	2.589 (6)	Cd2–As4 ⁱⁱ	2.569 (6)

 Symmetry codes: (i) $-x - \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$; (ii) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$.

Data collection: *X-Area* (Stoe & Cie, 2011); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *Superflip* (Palatinus & Chapuis, 2007) embedded in *JANA2006* (Petříček *et al.*, 2006); program(s) used to refine structure: *JANA2006*; molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2539).

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Cu_{4.35}Cd_{1.65}As₁₆: the first polyarsenic compound in the Cu-Cd-As system

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Comment

Besides the plethora of known polyphosphides (Pöttgen *et al.*, 2006) only few polyarsenides are known up to date (Bauhofer *et al.*, 1981; Jeitschko *et al.*, 2000; Emmerling & Röhr, 2002; Emmerling *et al.*, 2004; Hönle *et al.*, 2002).

The title compound Cu_{4.35}(2)Cd_{1.65}(2)As₁₆ is the first representative of a polyarsenide adopting the Cu₅InP₁₆ structure type (Lange *et al.*, 2008). In accordance to the situation in Cu₅InP₁₆ where Cu and In are occupying the same site, a similar behavior is observed for the title compound, but here with a Cu/Cd split position. Mixing of Cu and Cd on one site is a common feature in intermetallic compounds and has been observed for instance for Cd₃Cu₄ (Kreiner & Schaeppers, 1997) and Cd₈Cu₅ (von Heidenstamm *et al.*, 1968; Brandon *et al.*, 1974).

Cu—As distances in Cu_{4.35}(2)Cd_{1.65}(2)As₁₆ range from 2.3931 (9) Å to 2.589 (6) Å and are comparable with the distances of 2.404 (1) Å to 2.590 (1) Å in Cu₃As (Mansmann, 1965). The As—As distances in Cu_{4.35}(2)Cd_{1.65}(2)As₁₆ are between 2.4242 (8) Å and 2.4644 (10) Å, in good accordance with the As—As distances in NdFe₄As₁₂ (2.428 Å - 2.499 Å) (Jeitschko *et al.*, 2000). Cd—As distances are present between 2.475 (5) Å and 2.856 (5) Å which is consistent with values found for CdAs (2.473 (2) Å - 2.868 (2) Å) (Clark & Range, 1976).

Experimental

Cu_{4.35}(2)Cd_{1.65}(2)As₁₆ was prepared by a solid state reaction from the elements Cu (ChemPur, shot, 99.999%), Cd (ChemPur, granules, 99.9999%) and As (ChemPur, pieces, 99.9999%). Arsenic was purified by sublimation in evacuated silica ampoules using a temperature gradient of 573 K to room temperature to separate As₂O₃ from the bulk-As and at 873 K to 573 K to sublimate As directly. The purified As was stored under protection gas atmosphere prior to use. The starting materials were reacted in stoichiometric amounts according the reported composition at 753 K for 7 days followed by a homogenization step by grinding. The procedure was repeated two times to finalize the formation of the title compound. Single crystals of suitable size could be separated from the bulk phase.

Refinement

The highest peak is 0.99 Å away from As3 and the deepest hole is 0.81 Å away from As4. We have tested two different structure models to describe the Cu/Cd distribution in the title compound. In the first model, Cu and Cd were refined on one common position restricting the coordinates and displacement parameters while keeping an overall full occupancy. In the second model, the coordinates were not restricted, leading to a split position for Cu and Cd. Comparable to the first model the sum of occupancy factors of both split position were set to one. After an evaluation of the refinement results for both models we decided the second model for structure description due to better and more reliable displacement and statistical parameters.

Figures

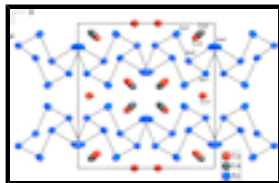


Fig. 1. Crystal structure of $\text{Cu}_{4.35}(2)\text{Cd}_{1.65}(2)\text{As}_{16}$, viewed along the c axis. Displacement ellipsoids are shown at the 90% probability level.

tetracopper dicadmium hexadecaarsenide

Crystal data

$\text{Cu}_{4.35}\text{Cd}_{1.65}\text{As}_{16}$

$M_r = 1660.8$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 11.8324(6)\ \text{\AA}$

$b = 10.4423(4)\ \text{\AA}$

$c = 8.0903(4)\ \text{\AA}$

$\beta = 110.480(4)^\circ$

$V = 936.44(8)\ \text{\AA}^3$

$Z = 2$

$F(000) = 1467$

$D_x = 5.888\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 12419 reflections

$\theta = 3.7\text{--}29.7^\circ$

$\mu = 34.73\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Plate, black

$0.03 \times 0.02 \times 0.004\ \text{mm}$

Data collection

Stoe IPDS 2T
diffractometer

Radiation source: X-ray tube
plane graphite

Detector resolution: $6.67\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: numerical
(*X-Area*; Stoe & Cie, 2011)

$T_{\min} = 0.205$, $T_{\max} = 0.785$

12811 measured reflections

1268 independent reflections

1113 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 29.3^\circ$, $\theta_{\min} = 3.7^\circ$

$h = -16 \rightarrow 16$

$k = -14 \rightarrow 14$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.072$

$S = 1.83$

1268 reflections

56 parameters

6 constraints

Weighting scheme based on measured s.u.'s $w = 1/$

$[\sigma^2(I) + 0.0004I^2]$

$(\Delta/\sigma)_{\max} = 0.007$

$\Delta\rho_{\max} = 1.50\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -1.67\ \text{e \AA}^{-3}$

Extinction correction: B-C type 1 Gaussian isotropic
(Becker & Coppens, 1974)

0 restraints

Extinction coefficient: 0.021 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0	0.41450 (10)	0.25	0.0156 (3)	
Cu2	-0.0942 (5)	0.1309 (5)	-0.0886 (9)	0.0198 (9)	0.587 (6)
Cd2	-0.0713 (4)	0.1064 (5)	-0.0867 (7)	0.0198 (9)	0.413 (6)
As1	-0.15337 (5)	0.56586 (5)	0.08461 (8)	0.01309 (19)	
As2	-0.23875 (5)	0.30964 (6)	-0.22826 (8)	0.01406 (19)	
As3	0.07426 (6)	0.27955 (6)	0.07165 (9)	0.0171 (2)	
As4	-0.33882 (6)	0.48506 (7)	-0.13511 (9)	0.0232 (2)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0132 (5)	0.0182 (5)	0.0157 (5)	0	0.0055 (4)	0
Cu2	0.0171 (16)	0.0237 (16)	0.0194 (4)	-0.0067 (9)	0.0076 (10)	-0.0062 (10)
Cd2	0.0171 (16)	0.0237 (16)	0.0194 (4)	-0.0067 (9)	0.0076 (10)	-0.0062 (10)
As1	0.0115 (3)	0.0139 (3)	0.0130 (3)	-0.0003 (2)	0.0033 (2)	0.0001 (2)
As2	0.0126 (3)	0.0143 (3)	0.0143 (3)	0.0015 (2)	0.0034 (2)	0.0016 (2)
As3	0.0153 (3)	0.0172 (3)	0.0198 (3)	0.0025 (2)	0.0074 (2)	0.0046 (2)
As4	0.0128 (3)	0.0296 (3)	0.0265 (4)	-0.0031 (3)	0.0061 (3)	-0.0155 (3)

Geometric parameters (\AA , $^\circ$)

Cu1—As1	2.4254 (9)	Cd2—As2	2.856 (5)
Cu1—As1 ⁱ	2.4254 (9)	Cd2—As3	2.516 (5)
Cu1—As3	2.3931 (9)	Cd2—As4 ⁱⁱ	2.475 (5)
Cu1—As3 ⁱ	2.3931 (9)	Cd2—As4 ⁱⁱⁱ	2.569 (6)
Cu2—Cd2	0.370 (8)	As1—As2 ^v	2.4644 (10)
Cu2—As2	2.516 (5)	As1—As3 ^{vi}	2.4307 (10)
Cu2—As3	2.501 (5)	As1—As4	2.4408 (8)
Cu2—As4 ⁱⁱ	2.589 (6)	As2—As3 ^{vii}	2.4242 (8)
Cu2—As4 ⁱⁱⁱ	2.524 (7)	As2—As4	2.4392 (10)
Cd2—Cd2 ^{iv}	2.845 (7)		
As1—Cu1—As1 ⁱ	98.67 (4)	As3 ^{vi} —As1—As4	105.22 (3)
As1—Cu1—As3	114.38 (2)	Cu2—As2—Cd2	3.1 (2)
As1—Cu1—As3 ⁱ	110.77 (2)	Cu2—As2—As1 ^{viii}	107.87 (17)
As1 ⁱ —Cu1—As3	110.77 (2)	Cu2—As2—As3 ^{vii}	109.44 (12)
As1 ⁱ —Cu1—As3 ⁱ	114.38 (2)	Cu2—As2—As4	138.19 (17)
As3—Cu1—As3 ⁱ	107.85 (4)	Cd2—As2—As1 ^{viii}	105.21 (13)
Cd2—Cu2—As2	155.1 (16)	Cd2—As2—As3 ^{vii}	108.99 (10)
Cd2—Cu2—As3	88.1 (11)	Cd2—As2—As4	141.07 (12)
Cd2—Cu2—As4 ⁱⁱ	68.2 (12)	As1 ^{viii} —As2—As3 ^{vii}	105.49 (3)

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Cd2—Cu2—As4 ⁱⁱⁱ	92.7 (15)	As1 ^{viii} —As2—As4	98.12 (3)
As2—Cu2—As3	93.76 (19)	As3 ^{vii} —As2—As4	93.81 (3)
As2—Cu2—As4 ⁱⁱ	95.40 (19)	Cu1—As3—Cu2	106.49 (17)
As2—Cu2—As4 ⁱⁱⁱ	110.1 (3)	Cu1—As3—Cd2	113.57 (14)
As3—Cu2—As4 ⁱⁱ	139.5 (3)	Cu1—As3—As1 ^{vi}	102.24 (3)
As3—Cu2—As4 ⁱⁱⁱ	108.6 (2)	Cu1—As3—As2 ^{ix}	105.39 (3)
As4 ⁱⁱ —Cu2—As4 ⁱⁱⁱ	105.0 (2)	Cu2—As3—Cd2	8.44 (18)
Cu2—Cd2—Cd2 ^{iv}	149.6 (16)	Cu2—As3—As1 ^{vi}	121.65 (17)
Cu2—Cd2—As2	21.8 (14)	Cu2—As3—As2 ^{ix}	118.91 (13)
Cu2—Cd2—As3	83.5 (11)	Cd2—As3—As1 ^{vi}	122.14 (14)
Cu2—Cd2—As4 ⁱⁱ	103.9 (12)	Cd2—As3—As2 ^{ix}	111.47 (11)
Cu2—Cd2—As4 ⁱⁱⁱ	79.0 (15)	As1 ^{vi} —As3—As2 ^{ix}	100.07 (3)
Cd2 ^{iv} —Cd2—As2	170.7 (3)	Cu2 ^x —As4—Cu2 ⁱⁱⁱ	145.40 (19)
Cd2 ^{iv} —Cd2—As3	97.37 (17)	Cu2 ^x —As4—Cd2 ^x	7.97 (17)
Cd2 ^{iv} —Cd2—As4 ⁱⁱ	92.32 (19)	Cu2 ^x —As4—Cd2 ⁱⁱⁱ	138.18 (18)
Cd2 ^{iv} —Cd2—As4 ⁱⁱⁱ	71.60 (19)	Cu2 ^x —As4—As1	110.54 (12)
As2—Cd2—As3	85.72 (15)	Cu2 ^x —As4—As2	102.12 (16)
As2—Cd2—As4 ⁱⁱ	89.91 (14)	Cu2 ⁱⁱⁱ —As4—Cd2 ^x	138.99 (18)
As2—Cd2—As4 ⁱⁱⁱ	99.07 (19)	Cu2 ⁱⁱⁱ —As4—Cd2 ⁱⁱⁱ	8.26 (17)
As3—Cd2—As4 ⁱⁱ	146.1 (3)	Cu2 ⁱⁱⁱ —As4—As1	94.09 (12)
As3—Cd2—As4 ⁱⁱⁱ	106.8 (2)	Cu2 ⁱⁱⁱ —As4—As2	99.75 (14)
As4 ⁱⁱ —Cd2—As4 ⁱⁱⁱ	107.07 (19)	Cd2 ^x —As4—Cd2 ⁱⁱⁱ	132.39 (17)
Cu1—As1—As2 ^v	113.16 (3)	Cd2 ^x —As4—As1	118.43 (12)
Cu1—As1—As3 ^{vi}	111.70 (3)	Cd2 ^x —As4—As2	101.77 (14)
Cu1—As1—As4	119.01 (3)	Cd2 ⁱⁱⁱ —As4—As1	96.10 (10)
As2 ^v —As1—As3 ^{vi}	106.52 (3)	Cd2 ⁱⁱⁱ —As4—As2	107.52 (12)
As2 ^v —As1—As4	99.93 (3)	As1—As4—As2	94.29 (3)

Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $-x-1/2, y-1/2, -z-1/2$; (iii) $-x-1/2, -y+1/2, -z$; (iv) $-x, -y, -z$; (v) $x, -y+1, z+1/2$; (vi) $-x, -y+1, -z$; (vii) $x-1/2, -y+1/2, z-1/2$; (viii) $x, -y+1, z-1/2$; (ix) $x+1/2, -y+1/2, z+1/2$; (x) $-x-1/2, y+1/2, -z-1/2$.

Fig. 1

