

Acta Crystallographica Section E

**Structure Reports**

**Online**

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

## **Cobaltaustinite, $\text{CaCo}(\text{AsO}_4)(\text{OH})$**

**Hexiong Yang, Gelu Costin, John Keogh, Ren Lu and Robert T. Downs**

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Cobaltaustinite,  $\text{CaCo}(\text{AsO}_4)(\text{OH})$ 

Hexiong Yang,\* Gelu Costin,  
John Keogh, Ren Lu and  
Robert T. Downs

University of Arizona, Department of  
Geosciences, 1040 East 4th Street, Tucson,  
AZ 85721-0077, USA

Correspondence e-mail: [hyang@u.arizona.edu](mailto:hyang@u.arizona.edu)

## Key indicators

Single-crystal X-ray study

$T = 273 \text{ K}$

Mean  $\sigma(\text{Co}-\text{O}) = 0.005 \text{ \AA}$

$R$  factor = 0.045

w $R$  factor = 0.078

Data-to-parameter ratio = 16.8

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

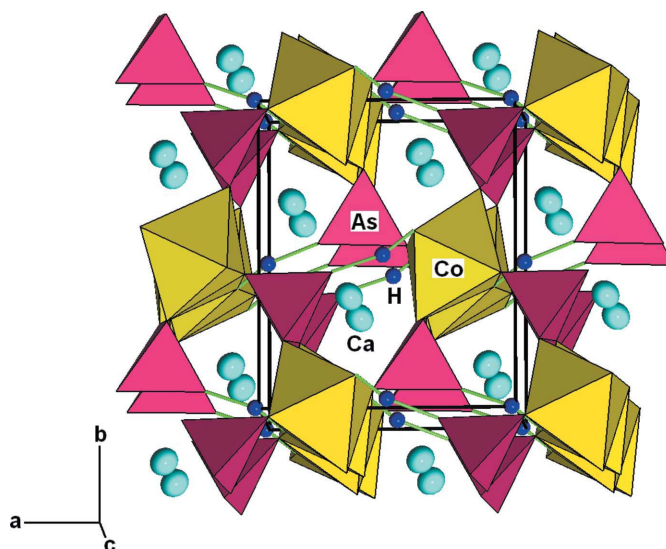
This study presents the first structural report of a natural cobaltaustinite sample (calcium cobalt arsenate hydroxide) based on single-crystal X-ray diffraction data. Cobaltaustinite, with the ideal formula  $\text{CaCo}(\text{AsO}_4)(\text{OH})$ , belongs to the adelite mineral group. The  $\text{CoO}_6$  octahedra share edges to form chains extending parallel to the  $c$  axis, which are cross-linked by  $\text{Ca}^{2+}$  ions and by sharing vertices with isolated  $\text{AsO}_4$  tetrahedra. The  $\text{Ca}^{2+}$  ions are situated in square antiprisms formed by eight O atoms. The major structural difference between the five calcium arsenates in the adelite group is shown in the bonding environments around the octahedrally coordinated  $M^{2+}$  cations ( $M = \text{Cu}, \text{Zn}, \text{Co}, \text{Ni}$  and  $\text{Mg}$ ), with the average  $M-\text{O}$  distance decreasing from  $\text{Cu}-\text{O}$  in conichalcite,  $\text{CaCu}(\text{AsO}_4)(\text{OH})$  to  $\text{Zn}-\text{O}$  in austinite,  $\text{CaZn}(\text{AsO}_4)(\text{OH})$ ,  $\text{Co}-\text{O}$  in cobaltaustinite,  $\text{Ni}-\text{O}$  in nickelaustinite,  $\text{CaNi}(\text{AsO}_4)(\text{OH})$ , and  $\text{Mg}-\text{O}$  in adelite,  $\text{CaMg}(\text{AsO}_4)(\text{OH})$ . The donor-acceptor  $\text{O}-\text{H}\cdots\text{O}$  distance [ $2.721(7) \text{ \AA}$ ] in cobaltaustinite is similar to those in austinite and nickelaustinite, but different from those in adelite and conichalcite.

Received 30 December 2006

Accepted 19 January 2007

## Comment

More than a dozen minerals belong to the adelite group, which crystallize in the orthorhombic space group  $P2_12_12_1$  (Qurashi & Barnes, 1963, 1964) and have the general formula



**Figure 1**

The crystal structure of cobaltaustinite.  $\text{Ca}^{2+}$  cations are drawn with anisotropic displacement ellipsoids at the 99% probability level and H atoms as spheres of arbitrary radii. Hydrogen bonding is indicated by green lines.

$A^{1+,2+}M^{2+,3+}(X^{4+,5+,6+}O_4)(OH)$ , where  $A = \text{Na, Ca or Pb}$ ,  $M = \text{Al, Mg, Zn, Mn, Fe, Co, Cu or Ni}$ , and  $X = \text{Si, P, V or As}$ . Among these minerals, seven are arsenates, namely adelite,  $\text{CaMg}(\text{AsO}_4)(\text{OH})$ , austinite,  $\text{CaZn}(\text{AsO}_4)(\text{OH})$ , conichalcite,  $\text{CaCu}(\text{AsO}_4)(\text{OH})$ , duftite,  $\text{PbCu}(\text{AsO}_4)(\text{OH})$ , gabrielsonite,  $\text{PbFe}(\text{AsO}_4)(\text{OH})$ , nickelaustinite,  $\text{CaNi}(\text{AsO}_4)(\text{OH})$ , and cobaltaustinite,  $\text{CaCo}(\text{AsO}_4)(\text{OH})$ . Cation substitutions in these arsenate minerals are common and complete solid solutions have been found, for example between austinite and conichalcite, Zn–Cu (Taggart & Foord, 1980; Jambor *et al.*, 1980), and between duftite and conichalcite, Pb–Ca (Jambor *et al.*, 1980). Because of the biological and geochemical importance of arsenic, especially its role in water and waste management, the crystal chemistry of As-bearing minerals has been investigated extensively (see review by O'Day, 2006). Of the seven arsenate minerals in the adelite group, the crystal structures of adelite (Effenberger *et al.*, 2002), austinite (Giuseppetti & Tadini, 1988; Clark *et al.*, 1997), conichalcite (Qurashi & Barnes, 1963), nickelaustinite (Cesbron *et al.*, 1987) and duftite (Kharisun *et al.*, 1998) have already been determined. Effenberger *et al.* (2002) presented structure refinements for adelite and cobaltaustinite at the 2002 EMPG (European Mineralogical, Petrological and Geochemical) meeting, but did not publish the cobaltaustinite structure. This study presents the first reported structure of cobaltaustinite based on single-crystal X-ray diffraction data.

Cobaltaustinite is isostructural with the other arsenate minerals in the adelite group. The  $\text{CoO}_6$  octahedra share edges to form chains running parallel to the  $c$  axis, which are cross-linked by  $\text{Ca}^{2+}$  ions and by sharing vertices with isolated  $\text{AsO}_4$  tetrahedra (Fig. 1). The principal difference between the five calcium arsenates in the group is shown in the bonding environments around the octahedrally coordinated  $M$  cations. The average  $M\text{—O}$  bond lengths appear to decrease from  $\text{Cu—O}$  (2.115 Å) in conichalcite (Qurashi & Barnes, 1963) to  $\text{Zn—O}$  (2.106 Å) in austinite (Clark *et al.*, 1997),  $\text{Co—O}$  (2.092 Å) in cobaltaustinite (Table 1),  $\text{Ni—O}$  (2.085 Å) in nickelaustinite (Cesbron *et al.*, 1987), and  $\text{Mg—O}$  (2.075 Å) in adelite (Effenberger *et al.*, 2002). Of these  $\text{MO}_6$  octahedra, the  $\text{CuO}_6$  and  $\text{ZnO}_6$  octahedra are the most distorted in terms of the polyhedral quadratic elongation and angle variance (Robinson *et al.*, 1971), with values of 1.015 Å and 21.53°, respectively.

The donor–acceptor  $\text{O5—H}\cdots\text{O2}$  distance in cobaltaustinite is 2.721 (7) Å, very similar to the values in austinite [2.723 (2) Å; Clark *et al.*, 1997] and nickelaustinite [2.73 (1) Å; Cesbron *et al.*, 1987], but different from those in adelite [2.766 (2) Å; Effenberger *et al.*, 2002] and conichalcite (2.61 Å; Qurashi & Barnes, 1963). Using Raman spectroscopy, we obtained an  $\text{O—H}$  stretching mode at  $3289\text{ cm}^{-1}$  for the title compound (deposition No. R050536; <http://rruff.info>), which is comparable with the value of  $3284\text{ cm}^{-1}$  reported by Martens *et al.* (2003). Based on the correlation between  $\text{O—H}$  stretching frequencies ( $\nu_{\text{OH}}$ ) and  $\text{O—H}\cdots\text{O}$  distances (Libowitzky, 1999), an estimated  $\nu_{\text{OH}}$  value of  $3236\text{ cm}^{-1}$  is predicted for cobaltaustinite, which agrees reasonably well with the experimental values, considering the accuracy of the

empirical equation (Libowitzky, 1999) and the effects of chemical substitution on the  $\nu_{\text{OH}}$  band positions for the adelite group of minerals (Martens *et al.*, 2003).

## Experimental

The cobaltaustinite crystal used in this study is from Dome Rock, Mingary, South Australia, Australia, and is a sample from the RRUFF project (deposition No. R050536; <http://rruff.info>), donated by the University of Arizona Mineral Museum (No. 16265) and described by Nickel & Birsch (1988). The chemical composition,  $\text{Ca}(\text{Co}_{0.95}\text{Cu}_{0.05})\text{—}(\text{AsO}_4)(\text{OH})$ , was determined with a CAMECA SX50 electron microprobe (<http://rruff.info>).

### Crystal data

$\text{CaCo}(\text{AsO}_4)(\text{OH})$	$Z = 4$
$M_r = 255.17$	$D_x = 4.252\text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.4919$ (9) Å	$\mu = 13.79\text{ mm}^{-1}$
$b = 8.9946$ (9) Å	$T = 273$ (2) K
$c = 5.9158$ (7) Å	Drusy coating, dark green
$V = 398.65$ (8) Å <sup>3</sup>	$0.05 \times 0.05 \times 0.04\text{ mm}$

### Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	5752 measured reflections
$\varphi$ and $\omega$ scans	1344 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2005)	870 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.507$ , $T_{\max} = 0.576$	$R_{\text{int}} = 0.062$
	$\theta_{\text{max}} = 32.5^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2)]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$wR(F^2) = 0.078$	$\Delta\rho_{\text{max}} = 1.00\text{ e \AA}^{-3}$
$S = 0.98$	$\Delta\rho_{\text{min}} = -0.82\text{ e \AA}^{-3}$
1344 reflections	Absolute structure: Flack (1983),
80 parameters	with 488 Friedel pairs
All H-atom parameters refined	Flack parameter: $-0.01$ (3)

**Table 1**  
Selected bond lengths (Å).

$\text{Ca—O5}^i$	2.302 (4)	$\text{Co—O1}$	2.107 (5)
$\text{Ca—O4}$	2.428 (5)	$\text{Co—O4}$	2.165 (5)
$\text{Ca—O2}^{ii}$	2.507 (5)	$\text{Co—O1}^v$	2.180 (5)
$\text{Ca—O1}$	2.514 (4)	$\text{Co—O3}^v$	2.190 (4)
$\text{Ca—O3}^{iii}$	2.550 (5)	$\text{As—O2}^{ii}$	1.682 (5)
$\text{Ca—O2}$	2.577 (5)	$\text{As—O3}^{vi}$	1.692 (5)
$\text{Ca—O4}^{iii}$	2.690 (6)	$\text{As—O4}^{vii}$	1.692 (5)
$\text{Co—O5}^{iv}$	1.953 (6)	$\text{As—O1}$	1.704 (4)
$\text{Co—O5}^v$	1.961 (5)		

Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (iv)  $x, y, z - 1$ ; (v)  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$ ; (vi)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (vii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ .

**Table 2**  
Hydrogen-bond geometry (Å, °).

$D\text{—H}\cdots A$	$D\text{—H}$	$H\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
$\text{O5—H}\cdots\text{O2}$	1.02 (9)	1.74 (9)	2.721 (7)	159 (8)

Electron microprobe analysis revealed that the cobaltaustinite sample studied here contains a small amount of Cu. However, the structure refinements with and without 5% Cu substituted for Co in the octahedral site did not produce any significant differences in terms of *R* factors, bond distances or bond angles. Hence, the final refinement assumed a full occupancy of the octahedral site by Co only. The H atom was located in a difference Fourier map and its position and isotropic displacement parameter were refined freely.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XTALDRAW* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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