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Cobaltaustinite, $CaCo(AsO_4)(OH)$

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(Co–O) = 0.005 Å
R factor = 0.045
wR 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.

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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 $CaCo(AsO_4)(OH)$, belongs to the adelite mineral group. The CoO_6 octahedra share edges to form chains extending parallel to the c axis, which are cross-linked by Ca^{2+} ions and by sharing vertices with isolated AsO_4 tetrahedra. The 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 = Cu, Zn, Co, Ni and Mg), with the average M—O distance decreasing from Cu—O in conichalcite, $CaCu(AsO_4)(OH)$ to Zn—O in austinite, $CaZn(AsO_4)(OH)$, Co—O in cobaltaustinite, Ni—O in nickelaustinite, $CaNi(AsO_4)(OH)$, and Mg—O in adelite, $CaMg(AsO_4)(OH)$. The donor–acceptor O—H···O distance [2.721 (7) Å] in cobaltaustinite is similar to those in austinite and nickelaustinite, but different from those in adelite and conichalcite.

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

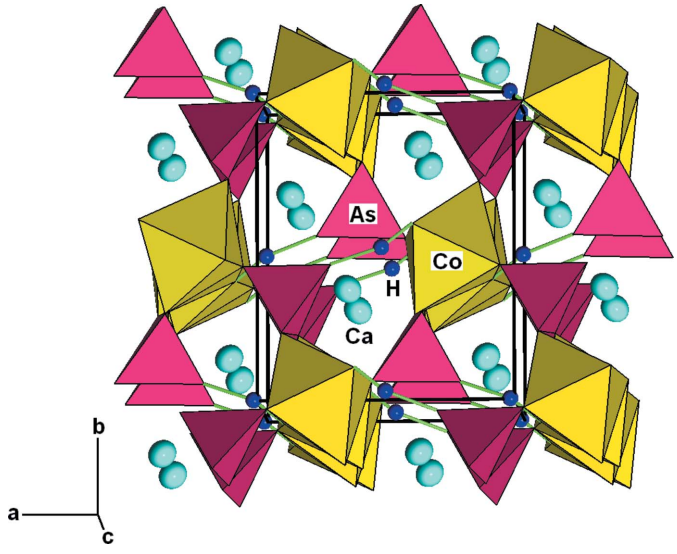

Figure 1
The crystal structure of cobaltaustinite. Ca^{2+} cations are drawn with anisotropic displacement ellipsoids at the 99% probability level and H atoms as spheres of arbitrary radii. Hydrogen bonding is indicated by green lines.

$A^{1+,2+}M^{2+,3+}(X^{4+,5+,6+}O_4)(OH)$, where A = Na, Ca or Pb, M = Al, Mg, Zn, Mn, Fe, Co, Cu or Ni, and X = Si, P, V or As. Among these minerals, seven are arsenates, namely adelite, $CaMg(AsO_4)(OH)$, austinite, $CaZn(AsO_4)(OH)$, conichalcite, $CaCu(AsO_4)(OH)$, duftite, $PbCu(AsO_4)(OH)$, gabrielsonite, $PbFe(AsO_4)(OH)$, nickelaustinite, $CaNi(AsO_4)(OH)$, and cobaltaustinite, $CaCo(AsO_4)(OH)$. 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 CoO_6 octahedra share edges to form chains running parallel to the c axis, which are cross-linked by Ca^{2+} ions and by sharing vertices with isolated 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—O bond lengths appear to decrease from Cu—O (2.115 Å) in conichalcite (Qurashi & Barnes, 1963) to Zn—O (2.106 Å) in austinite (Clark *et al.*, 1997), Co—O (2.092 Å) in cobaltaustinite (Table 1), Ni—O (2.085 Å) in nickelaustinite (Cesbron *et al.*, 1987), and Mg—O (2.075 Å) in adelite (Effenberger *et al.*, 2002). Of these MO_6 octahedra, the CuO_6 and 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 O5—H···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 O—H stretching mode at 3289 cm^{-1} for the title compound (deposition No. R050536; http//rruff.info), which is comparable with the value of 3284 cm^{-1} reported by Martens *et al.* (2003). Based on the correlation between O—H stretching frequences (ν_{OH}) and O—H···O distances (Libowitzky, 1999), an estimated ν_{OH} value of 3236 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 ν_{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, $Ca(Co_{0.95}Cu_{0.05})(AsO_4)(OH)$, was determined with a CAMECA SX50 electron microprobe (http//rruff.info).

Crystal data

$CaCo(AsO_4)(OH)$	$Z = 4$
$M_r = 255.17$	$D_x = 4.252$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.4919$ (9) Å	$\mu = 13.79$ mm^{-1}
$b = 8.9946$ (9) Å	$T = 273$ (2) K
$c = 5.9158$ (7) Å	Drusy coating, dark green
$V = 398.65$ (8) $Å^3$	0.05 × 0.05 × 0.04 mm

Data collection

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

Refinement

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

Table 1
Selected bond lengths (Å).

Ca—O5^{i}	2.302 (4)	Co—O1	2.107 (5)
Ca—O4	2.428 (5)	Co—O4	2.165 (5)
Ca—O2^{ii}	2.507 (5)	Co—O1^{v}	2.180 (5)
Ca—O1	2.514 (4)	Co—O3^{v}	2.190 (4)
Ca—O3^{iii}	2.550 (5)	As—O2^{ii}	1.682 (5)
Ca—O2	2.577 (5)	As—O3^{vi}	1.692 (5)
Ca—O4^{iii}	2.690 (6)	As—O4^{vii}	1.692 (5)
Co—O5^{iv}	1.953 (6)	As—O1	1.704 (4)
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—H···A	D—H	H···A	D···A	D—H···A
O5—H···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: *SAINT* (Bruker, 2005); data reduction: *SAINT*; 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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