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Crystal structure study of a cobaltoan dolomite from Kolwezi, Democratic Republic of Congo

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A structural study has been undertaken on a cobaltoan dolomite, with chemical formula $\text{CaMg}_{0.83}\text{Co}_{0.17}(\text{CO}_3)_2$ (calcium magnesium cobalt dicarbonate), from Kolwezi, Democratic Republic of Congo. Pale-pink euhedral cobaltoan dolomite was associated with kolwezite $[(\text{Cu}_{1.33}\text{Co}_{0.67})\text{-(CO}_3\text{)(OH)}_2]$ and cobaltoan malachite $[(\text{Cu},\text{Co})_2(\text{CO}_3)\text{-(OH)}_2]$. A crystal with a Co:Mg ratio of 1:5.6 (SEM/EDAX measurement), twinned on $(11\bar{2}0)$ was used for crystal structural refinement. The refinement of the structural model of Reeder & Wenk [*Am. Mineral.* (1983), **68**, 769–776; Ca at site $3a$ with site symmetry $\bar{3}$; Mg site at site $3b$ with site symmetry $\bar{3}$; C at site $6c$ with site symmetry 3 ; O at site $18f$ with site symmetry 1] showed that Co is totally incorporated in the Mg site, with refined occupancy $\text{Mg}_{0.83}\text{Co}_{0.17}$, which compares with $\text{Mg}_{0.85}\text{Co}_{0.15}$ from chemical data. The Co substitution reflects in the expansion of the cell volume, with a pronounced increasing of the c cell parameter.

Keywords: crystal structure; dolomite; cobaltoan; Kolwezi.

CCDC reference: 1049359

1. Related literature

For general background, see: Barton *et al.* (2015); Pertlik (1986). For isotypic structures, see: Reeder & Wenk (1983). For kolwezite, see: Deliens & Piret (1980).

2. Experimental

2.1. Crystal data

$\text{CaMg}_{0.83}\text{Co}_{0.17}(\text{CO}_3)_2$

$M_r = 190.38$

Trigonal, $R\bar{3}$
 $a = 4.8158$ (1) Å
 $c = 16.0488$ (6) Å
 $V = 322.34$ (2) Å³
 $Z = 3$

Mo $K\alpha$ radiation
 $\mu = 2.17$ mm⁻¹
 $T = 295$ K
 $0.20 \times 0.15 \times 0.12$ mm

2.2. Data collection

Bruker SMART Breeze CCD
diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)
 $T_{\min} = 0.621$, $T_{\max} = 0.746$

738 measured reflections
258 independent reflections
257 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.010$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.059$
 $S = 0.96$
258 reflections

20 parameters
1 restraint
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ca1—O1 ⁱ	2.3833 (10)	C1—O1	1.2853 (9)
(Mg1/Co1)—O1 ⁱⁱ	2.0923 (9)		

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008, 2015) and *WinGX* (Farrugia, 2012); molecular graphics: *CrystalMaker* (CrystalMaker, 2010); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

Dr H. Goethals, Royal Belgian Institute for Natural Sciences, is kindly acknowledged for providing the mineral sample.

Supporting information for this paper is available from the IUCr electronic archives (Reference: BR2247).

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supporting information

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Crystal structure study of a cobaltoan dolomite from Kolwezi, Democratic Republic of Congo

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S1. Synthesis and crystallization

Cobaltoan dolomite was picked from a kolwezite sample from Kolwezi (inventory number RC 3987) kindly provided us by H. Goethals, Royal Belgian Institute for Natural Sciences, Brussels. Pale pink euhedral cobaltoan dolomite was associated with kolwezite and cobaltoan malachite. All these minerals occur in the supergene zones of Cu—Co sulfide ore deposits, originating from the alteration of primary sulphides such as carrollite, $\text{Cu}(\text{Co},\text{Ni})_2\text{As}_4$

S2. Refinement

During the refinement, the twinning according to the $(11\bar{2}0)$ common law was detected and accounted for, with a refined BASF parameter of 0.798. The sum of Co and Mg occupancies in Mg site was constrained to be equal to 1, no other constraint was applied.

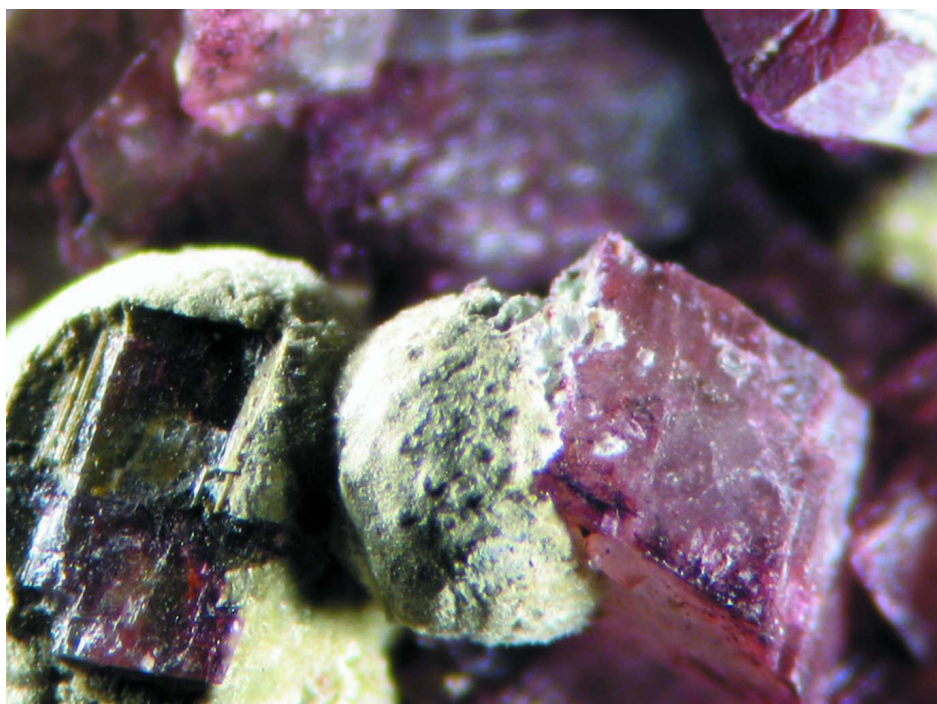


Figure 1

Micro photograph of the cobaltoan dolomite specimen, where pale pink cobaltoan dolomite is associated with pale green cobaltoan malachite.

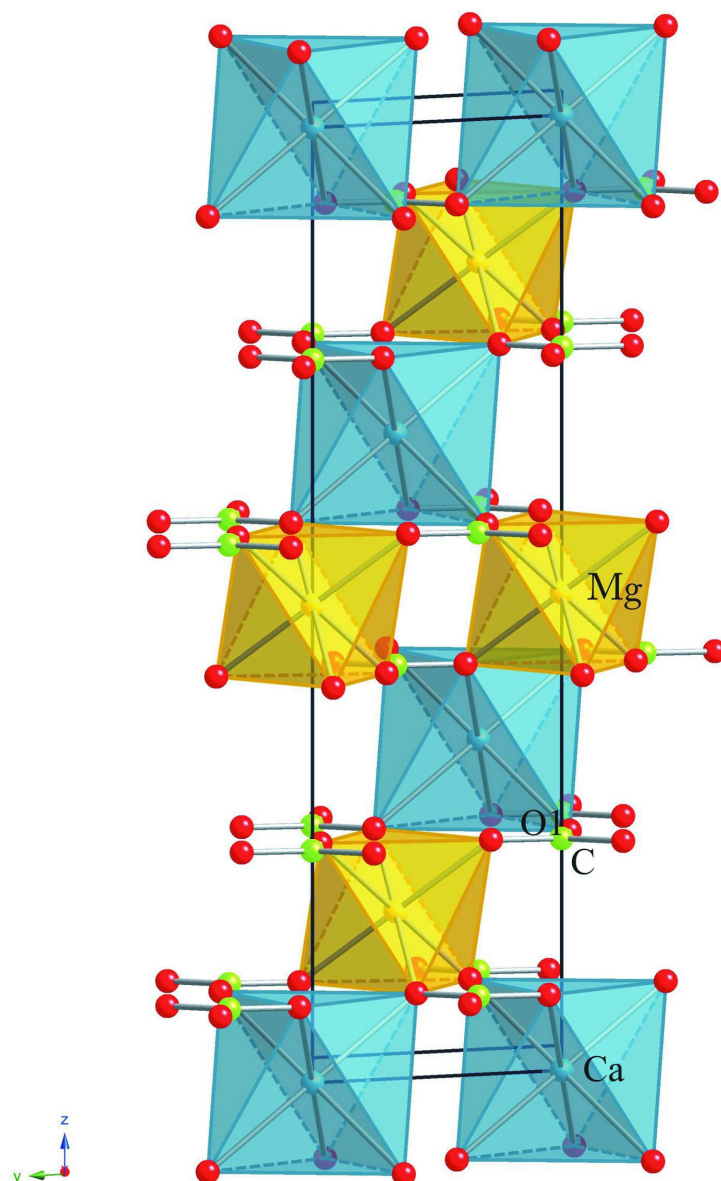
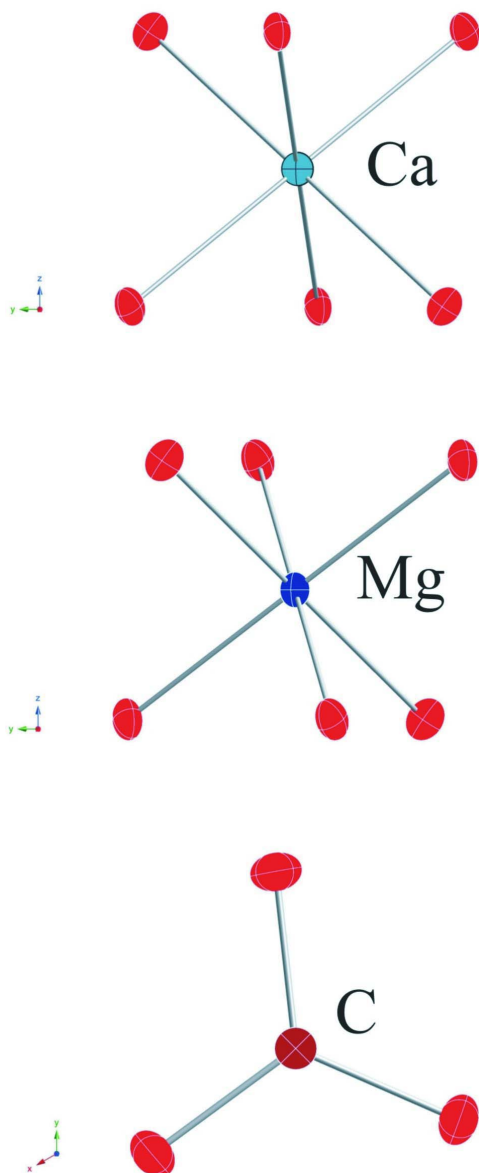


Figure 2

The crystal structure of cobaltoan dolomite, in a projection along [100], slightly tilted by 5° about along the x Cartesian rotation axis. Ca-centered octahedra are cyan, whereas Mg-centered octahedra are yellow; carbon and oxygen atoms are represented as green and red spheres, respectively.

**Figure 3**

Coordination polyhedra in cobaltoan dolomite. Displacement ellipsoids are drawn at the 50% probability.

Calcium magnesium cobalt dicarbonate

Crystal data

$\text{CaMg}_{0.83}\text{Co}_{0.17}(\text{CO}_3)_2$

$M_r = 190.38$

Trigonal, $R\bar{3}$

$a = 4.8158 (1) \text{ \AA}$

$c = 16.0488 (6) \text{ \AA}$

$V = 322.34 (2) \text{ \AA}^3$

$Z = 3$

$F(000) = 284$

$D_x = 2.930 \text{ Mg m}^{-3}$

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

$\mu = 2.17 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Cleavage rhombohedron, pale pink

$0.2 \times 0.15 \times 0.12 \text{ mm}$

Data collection

Bruker SMART Breeze CCD diffractometer	738 independent reflections
ω scans	257 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$R_{\text{int}} = 0.010$
$T_{\text{min}} = 0.621$, $T_{\text{max}} = 0.746$	$\theta_{\text{max}} = 32.4^\circ$, $\theta_{\text{min}} = 3.8^\circ$
258 measured reflections	$h = -7 \rightarrow 3$
	$k = 0 \rightarrow 7$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.562P]$
$R[F^2 > 2\sigma(F^2)] = 0.019$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.96$	$\Delta\rho_{\text{max}} = 0.46 \text{ e } \text{\AA}^{-3}$
258 reflections	$\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$
20 parameters	

Special details

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

Refinement. Refined as a 2-component twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ca1	0.0000	0.0000	0.0000	0.01249 (17)	
Mg1	0.0000	0.0000	0.5000	0.0104 (3)	0.828 (4)
Co1	0.0000	0.0000	0.5000	0.0104 (3)	0.172 (4)
C1	0.0000	0.0000	0.24297 (12)	0.0106 (4)	
O1	0.2482 (2)	-0.0341 (2)	0.24403 (6)	0.0143 (2)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0121 (2)	0.0121 (2)	0.0133 (3)	0.00605 (10)	0.000	0.000
Mg1	0.0091 (3)	0.0091 (3)	0.0130 (4)	0.00456 (15)	0.000	0.000
Co1	0.0091 (3)	0.0091 (3)	0.0130 (4)	0.00456 (15)	0.000	0.000
C1	0.0103 (5)	0.0103 (5)	0.0112 (8)	0.0051 (3)	0.000	0.000
O1	0.0117 (4)	0.0156 (4)	0.0183 (4)	0.0088 (3)	-0.0024 (3)	-0.0033 (3)

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

Ca1—O1 ⁱ	2.3833 (10)	Mg1—O1 ^{ix}	2.0923 (9)
Ca1—O1 ⁱⁱ	2.3833 (10)	Mg1—O1 ^x	2.0923 (9)
Ca1—O1 ⁱⁱⁱ	2.3833 (10)	Mg1—O1 ^{xi}	2.0923 (9)
Ca1—O1 ^{iv}	2.3833 (10)	Mg1—O1 ^{xii}	2.0923 (9)
Ca1—O1 ^v	2.3833 (10)	C1—O1	1.2853 (9)
Ca1—O1 ^{vi}	2.3833 (10)	C1—O1 ^{xiii}	1.2853 (9)

Mg1—O1 ^{vii}	2.0923 (9)	C1—O1 ^{xiv}	1.2853 (9)
Mg1—O1 ^{viii}	2.0923 (9)	C1—Ca1 ^{xv}	3.1359 (9)
O1 ⁱ —Ca1—O1 ⁱⁱ	180.00 (5)	O1 ^{viii} —Mg1—O1 ^{ix}	91.62 (4)
O1 ⁱ —Ca1—O1 ⁱⁱⁱ	92.43 (3)	O1 ^{vii} —Mg1—O1 ^x	91.62 (4)
O1 ⁱⁱ —Ca1—O1 ⁱⁱⁱ	87.57 (3)	O1 ^{viii} —Mg1—O1 ^x	88.38 (4)
O1 ⁱ —Ca1—O1 ^{iv}	87.57 (3)	O1 ^{ix} —Mg1—O1 ^x	180.0
O1 ⁱⁱ —Ca1—O1 ^{iv}	92.43 (3)	O1 ^{vii} —Mg1—O1 ^{xi}	91.62 (4)
O1 ⁱⁱⁱ —Ca1—O1 ^{iv}	180.00 (4)	O1 ^{viii} —Mg1—O1 ^{xi}	88.38 (4)
O1 ⁱ —Ca1—O1 ^v	87.57 (3)	O1 ^{ix} —Mg1—O1 ^{xi}	91.62 (4)
O1 ⁱⁱ —Ca1—O1 ^v	92.43 (3)	O1 ^x —Mg1—O1 ^{xi}	88.38 (4)
O1 ⁱⁱⁱ —Ca1—O1 ^v	92.43 (3)	O1 ^{vii} —Mg1—O1 ^{xii}	88.38 (4)
O1 ^{iv} —Ca1—O1 ^v	87.57 (3)	O1 ^{viii} —Mg1—O1 ^{xii}	91.62 (4)
O1 ⁱ —Ca1—O1 ^{vi}	92.43 (3)	O1 ^{ix} —Mg1—O1 ^{xii}	88.38 (4)
O1 ⁱⁱ —Ca1—O1 ^{vi}	87.57 (3)	O1 ^x —Mg1—O1 ^{xii}	91.62 (4)
O1 ⁱⁱⁱ —Ca1—O1 ^{vi}	87.57 (3)	O1 ^{xi} —Mg1—O1 ^{xii}	180.00 (4)
O1 ^{iv} —Ca1—O1 ^{vi}	92.43 (3)	O1—C1—O1 ^{xiii}	119.984 (5)
O1 ^v —Ca1—O1 ^{vi}	180.00 (8)	O1—C1—O1 ^{xiv}	119.983 (5)
O1 ^{vii} —Mg1—O1 ^{viii}	180.0	O1 ^{xiii} —C1—O1 ^{xiv}	119.981 (5)
O1 ^{vii} —Mg1—O1 ^{ix}	88.38 (4)		

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