Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

$Cs_2Co^{II}(C_2O_4)_2 \cdot 4H_2O$

Karolina Schwendtner and Uwe Kolitsch*

Universität Wien, Institut für Mineralogie und Kristallographie, Geozentrum, Althanstraße 14, A-1090 Wien, Austria

Correspondence e-mail:
uwe.kolitsch@univie.ac.at

Received 13 April 2004
Accepted 20 April 2004
Online 24 April 2004

Dicaesium cobalt(II) dioxalate tetrahydrate [tetraaquabis(μ-oxalato)cobalt(II)dicaesium(I)], $Cs_2Co^{II}(C_2O_4)_2 \cdot 4H_2O$, has a layered structure and is isotypic with $Cs_2Mg(C_2O_4)_2 \cdot 4H_2O$. The unique Co atom shows octahedral coordination, with a mean Co—O bond length of 2.084 Å. The Cs atom is irregularly coordinated by nine O atoms. Layers of $CoO_4(H_2O)_2$ octahedra, whose non-water O ligands belong to nearly planar bidentate oxalate groups, are separated by corrugated layers of Cs atoms. Medium-strong hydrogen bonds provide connections within the layer planes. All atoms are in general positions except the Co atom, which lies on a twofold axis.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.017
wR factor = 0.042
Data-to-parameter ratio = 23.3

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

Comment

As part of recent work on the crystal chemistry and topology of double metal oxalates (Kolitsch, 2004; Fleck & Kolitsch, 2004), the title compound has been prepared by crystallization from an aqueous solution at room temperature, and its crystal structure has been determined from single-crystal X-ray intensity data collected at 293 K.

$Cs_2Co^{II}(C_2O_4)_2 \cdot 4H_2O$ is isotypic with $Cs_2Mg(C_2O_4)_2 \cdot 4H_2O$, the new structure type that was recently described by Kolitsch (2004). The title compound crystallizes in space group $C2/c$ and exhibits a layered atomic arrangement. The asymmetric unit contains one unique Cs atom, one Co, two C, six O atoms and four H atoms. Only the Co atom is located on a special

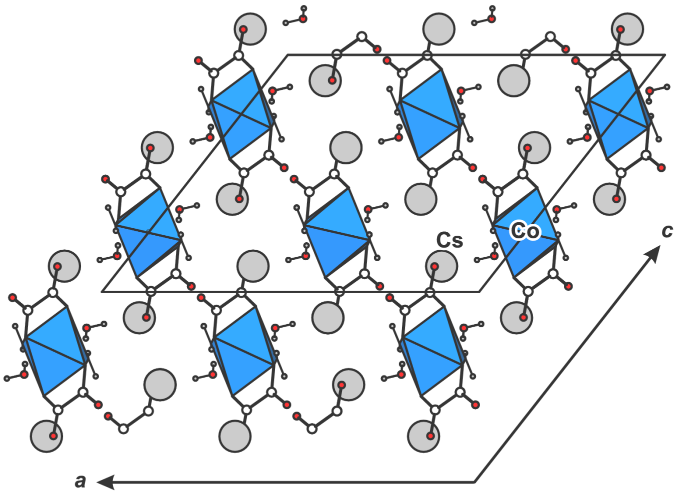

Figure 1
The layered structure of $Cs_2Co(C_2O_4)_2 \cdot 4H_2O$, in a view along [010]. Layers of $CoO_4(H_2O)_2$ octahedra (blue) parallel to $(10\overline{1})$ are separated by corrugated layers of nine-coordinate Cs atoms (large dark-grey spheres); oxalate groups link these units together in different directions. The unit cell is outlined.

DOI: 10.1107/S1600536804009626

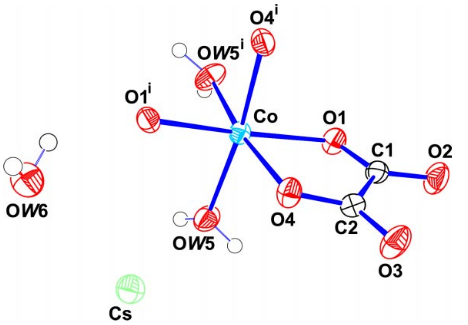

Figure 2

The connectivity in $Cs_2Co(C_2O_4)_2 \cdot 4H_2O$, with displacement ellipsoids at the 50% probability level. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

position, *viz*. a twofold rotation axis (4*e* in the Wyckoff notation).

$CoO_4(H_2O)_2$ octahedra are located in layers parallel to $(10\bar{1})$, which are separated by somewhat corrugated layers of Cs atoms (Figs. 1 and 2). The slightly distorted $CoO_4(H_2O)_2$ octahedron (Table 1 and Fig. 2) consists of four O atoms from bidentate oxalate groups and two *cis* water molecules (O*W*5). The average Co—O bond length is 2.084 Å, which is slightly shorter than the average value for CoO_6 octahedra in inorganic cobalt(II) compounds of 2.11 (6) Å (Wildner, 1992). In the Mg analogue, $Cs_2Mg^{II}(C_2O_4)_2 \cdot 4H_2O$ (Kolitsch, 2004), the average Mg—O bond length (2.066 Å) is also slightly shorter than the average value in inorganic Mg compounds (2.085 Å; Baur, 1981). These specific observations are in good agreement with the general observation that average metal–oxygen distances in metal-organic compounds are consistently smaller than those in inorganic compounds (Trzesowska *et al.*, 2004, and references therein).

The Cs atom has a geometrically irregular, but otherwise clearly defined, coordination sphere involving nine O atoms (average Cs—O = 3.290 Å), two of which belong to water molecules (Table 1); atom O*W*6 is only bonded to Cs, while the less strongly bonded atom O*W*5 is shared with the Co atom. The average Cs—O bond length in the Mg analogue is very similar (3.303 Å; Kolitsch, 2004).

The oxalate group is nearly planar and shows expected bond distances and angles (Table 1). Hydrogen bonding in $Cs_2Co(C_2O_4)_2 \cdot 4H_2O$ involves the water molecules O*W*5 and O*W*6 bonded to the Co and Cs atoms. The four hydrogen bonds are medium-strong, with O···O distances between 2.685 (2) and 2.752 (2) Å (Table 2). In the Mg analogue (Kolitsch, 2004), the hydrogen-bonding scheme is identical and shows a very similar range of O···O bond distances [2.684 (2)–2.760 (2) Å]. The three strongest hydrogen bonds are all directed along vectors approximately in the $(10\bar{1})$ plane, *i.e.* in the plane of the layers in the structure.

Experimental

$Cs_2Co(C_2O_4)_2 \cdot 4H_2O$ crystallized at room temperature by slow evaporation of an alkaline aqueous solution containing dissolved $CsCO_3$, $Co(OH)_2$, HCl, and oxalic acid dihydrate at a pH of about 9. The title compound was obtained as very few dark pink tabular well formed small crystals on an uninvestigated pink crystalline crust. The crystals are stable in air.

Crystal data

$Cs_2Co(C_2O_4)_2 \cdot 4H_2O$
$M_r = 572.85$
Monoclinic, $C2/c$
$a = 16.949$ (3) Å
$b = 7.368$ (1) Å
$c = 13.540$ (3) Å
$\beta = 128.09$ (3)°
$V = 1330.8$ (7) Å^3
$Z = 4$
$D_x = 2.859$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2582 reflections
$\theta = 2.0$–32.6°
$\mu = 6.74$ mm^{-1}
$T = 293$ (2) K
Irregular, dark pink
0.19 × 0.18 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.338$, $T_{max} = 0.545$
4679 measured reflections
2423 independent reflections
2290 reflections with $I > 2\sigma(I)$
$R_{int} = 0.008$
$\theta_{max} = 32.6°$
$h = -25 \rightarrow 25$
$k = -11 \rightarrow 11$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.042$
$S = 1.08$
2423 reflections
104 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 2.66P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00154 (10)

Table 1

Selected geometric parameters (Å, °).

Cs···O2^{iii}	3.108 (2)	Co—O*W*5	2.0701 (14)
Cs···O3^{ii}	3.1391 (15)	Co—O4	2.0881 (13)
Cs···O*W*6	3.157 (2)	Co—O1	2.0927 (14)
Cs···O1^{i}	3.2887 (15)	C1—O2	1.242 (2)
Cs···O*W*5	3.3146 (17)	C1—O1	1.265 (2)
Cs···O1^{iv}	3.3193 (14)	C1—C2	1.554 (2)
Cs···O2^{v}	3.3396 (19)	C2—O3	1.235 (2)
Cs···O3^{v}	3.4503 (17)	C2—O4	1.268 (2)
Cs···O4	3.4978 (14)		
O*W*5—Co—O*W*5^{i}	94.59 (9)	O1^{i}—Co—O1	169.53 (7)
O*W*5—Co—O4^{i}	171.00 (5)	O2—C1—O1	125.88 (16)
O*W*5—Co—O4	88.29 (6)	O2—C1—C2	117.82 (15)
O4^{i}—Co—O4	90.15 (8)	O1—C1—C2	116.27 (14)
O*W*5—Co—O1^{i}	92.28 (6)	O3—C2—O4	125.44 (16)
O*W*5^{i}—Co—O1^{i}	94.81 (6)	O3—C2—C1	119.19 (15)
O4^{i}—Co—O1^{i}	78.96 (5)	O4—C2—C1	115.36 (14)
O4—Co—O1^{i}	93.59 (6)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*5—H1···O*W*6^{vi}	0.80 (4)	1.91 (4)	2.685 (2)	162 (4)
O*W*5—H2···O3^{iii}	0.86 (3)	1.88 (3)	2.730 (2)	172 (3)
O*W*6—H3···O2^{i}	0.81 (3)	1.93 (3)	2.733 (2)	173 (3)
O*W*6—H4···O4^{vii}	0.77 (4)	1.99 (4)	2.752 (2)	177 (4)

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

For comparison purposes, the atomic coordinates of the isotypic compound $Cs_2Mg(C_2O_4)_2 \cdot 4H_2O$ (Kolitsch, 2004) were used as starting parameters in the final refinement. The H atoms were freely refined, resulting in O—H distances ranging between 0.77 (4) and 0.86 (3) Å.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999); *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Financial support by the Austrian Science Foundation (FWF) (grant P15220-N06) and the International Centre for Diffraction Data (grant 90-03 ET) are gratefully acknowledged.

References

Baur, W. H. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe and A. Navrotsky, pp. 31–52. New York: Academic Press.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fleck, M. & Kolitsch, U. (2004). In preparation.

Kolitsch, U. (2004). *Acta Cryst.* C**60**, m129–m133.

Nonius (2003). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Shape Software (1999). *ATOMS for Windows and Macintosh*. Version 5.0.4. Shape Software, Kingsport, TN 37663, USA.

Trzesowska, A., Kruszynski, R. & Bartczak, T. J. (2004). *Acta Cryst.* B**60**, 174–178.

Wildner, M. (1992). *Z. Kristallogr.* **202**, 51–70.