metal-organic compounds

Poly[tetraaquadi-μ_3-malonato-cobalt(II)calcium(II)]

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The structure of the polymeric title compound, [CaCo-$(C_3H_2O_4)_2(H_2O)_4]_n$, consists of CaO_8 and CoO_6 polyhedra linked together by malonate groups. The Co atom lies on a centre of symmetry in an octahedral arrangement, and is coordinated by four malonate O atoms in a planar arrangement and two water molecules in a *trans* conformation. The geometry around the Ca atom, which lies on a twofold axis, may be described as a distorted square antiprism, which involves two water molecules and six malonate O atoms. The Co—O and Ca—O bond lengths are in the ranges 2.0711 (12)–2.1004 (14) and 2.3775 (12)–2.6329 (12) Å, respectively.

Comment

The most commonly employed synthetic design strategy that is used to assemble coordination frameworks is the building-block methodology, which relies on utilizing the specific geometries of both metal cations and ligands. Typically, dicarboxylate ligands, such as malonate, have been used to construct coordination polymers by acting as chelating bidentate ligands or as simple bridges between metal centres. Consequently, a great number of homo- or heteronuclear malonate complexes are well known and structurally characterized (Alderighi *et al.*, 1999; Barbaro *et al.*, 1997; Benmerad *et al.*, 2000; Filippova *et al.*, 2000; Gil de Muro *et al.*, 1998, 1999, 2000; Hodgson & Asplund, 1991; Rodriguez-Martin *et al.*, 2002; Ruiz-Perez, Hernandez-Molina *et al.*, 2000; Ruiz-Perez, Sanchiz *et al.*, 2000; Tapparo *et al.*, 1996; Zhang *et al.*, 2000). In the course of our study of heterobimetallic malonate complexes involving transition and alkaline-earth metals, we have synthesized the complex poly[tetraaquadi-μ_3-malonato-cobalt(II)calcium(II)], (I), which has already been reported (Gil de Muro *et al.*, 2000), although its crystal structure has not been determined until now.

A single-crystal X-ray diffraction study reveals that the title compound consists of a honeycomb framework built up from calcium(II), cobalt(II) malonate and water molecules. A view

of the coordination around the two metal centres is shown in Fig. 1. The Co atom lies on a crystallographic inversion centre and has an octahedral coordination, involving four O atoms from two bidentate malonate ligands in a planar arrangement and two water O atoms in axial positions. The bond lengths in

(I)
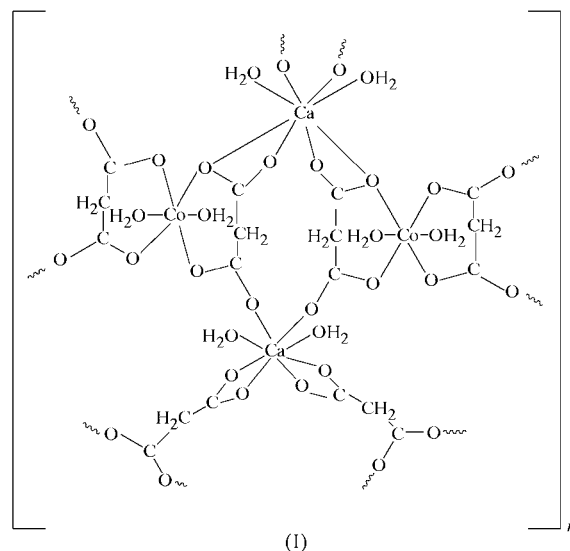
the coordination polyhedron of the Co[II] atoms are quite similar. The equatorial Co—O bonds, ranging from 2.0711 (12) to 2.0900 (11) Å, have a mean value of 2.081 (9) Å, while the axial Co—O distances are 2.1004 (14) Å (Table 1). The O—Co—O bond angles range from 87.30 (5) to 92.70 (5)° and deviate little from ideal octahedral geometry. These bond lengths and angles agree well with those previously reported for other cobalt(II) complexes containing carboxylate ligands (Gil de Muro *et al.*, 1998, 1999; Livage *et al.*, 1998, 1999; Suresh *et al.*, 1997; Zheng & Lin, 2000; Zheng *et al.*, 2000). The six-membered chelate rings Co/O2/C1–C3/O3 and Co/O2[ii]/C1[ii]–
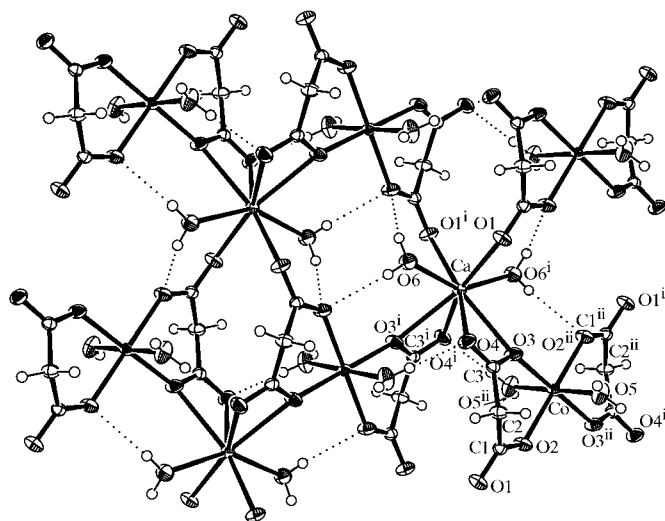
Figure 1
A view of the coordination polyhedra for calcium and cobalt ions in (I), showing the atom numbering (50% probability displacement ellipsoids). Hydrogen bonds are shown as dotted lines. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $-x, -y, -z$.]

$C3^{ii}/O3^{ii}$ [symmetry code: (ii) $-x$, $-y$, $-z$] have boat conformations, with atoms Co and C2 lying 0.44 and 0.48 Å, respectively, out of the C1/O2/C3/O3 mean plane.

The Ca atom, lying on a twofold axis, is coordinated by two water molecules (O6 and O6^i), two bridging carboxyl O atoms [O1 and O1^i; symmetry code: (i) $-x$, y, $-z + \frac{1}{2}$] and the O atoms of two chelated carboxyl groups (O3/C3/O4 and O3^i/C3^i/O4^i). The geometry around the Ca^{II} atom may be described as a distorted square antiprism. The four-membered chelate ring linked to the Ca atom is bonded to the six-membered ring involving the Co atom *via* the C3—O3 bond. The Ca—O bond lengths differ in the chelating and bridging malonate groups. While the bridging carboxylate Ca—O1 bond lengths [2.3775 (12) Å] are similar to the Ca—O$_{water}$ distances [Ca—O6 = 2.3970 (14) Å], the Ca—O bonds of the chelating malonate ligands are quite different [2.4410 (13) to 2.6329 (12) Å]. The longest Ca—O distance is observed for the Ca—O3 bond, atom O3 being three-coordinated to one Ca atom, one Co atom and one C atom. The increase of these bond lengths is related to the requirements of the conformation of the fused-ring system.

Each Ca atom is connected to two Ca atoms through bis-carboxylate bridges, defining infinite chains of CaO$_8$ polyhedra, running parallel to the [010] axis and forming 12-membered binuclear rings, *viz.* [Ca/O1/C1–C3/O4]$_2$. The Ca$\cdots$Ca separation within these rings is 7.531 (12) Å. The same carboxylate bridges bind each Ca atom to four Co atoms, leading to the formation of 12-membered tetranuclear rings, *viz.* [Ca/Co/O1/C1/O2/O3]$_2$. The Ca$\cdots$Ca and Co$\cdots$Co separations within these rings are, respectively, 7.054 (1) and 7.531 (1) Å, while the Ca$\cdots$Co distances are shorter at 5.7945 (6) and 4.4340 (5) Å. The two carboxylate groups have the same dimensions, with a mean value of 1.257 (2) Å, and are inclined at 40.4 (1)° to each other.

The crystal structure may be described as a three-dimensional network. The two different 12-membered rings create wide channels. The two crystallographically independent water molecules are hydrogen bonded to the carboxyl O atoms, and the supramolecular assembly of this heterobinuclear complex is realized by this hydrogen bonding (Table 2 and Fig. 1).

Experimental

Malonic acid (0.208 g, 2 mmol), CoCl$_2$·6H$_2$O (0.238 g, 1 mmol) and Ca(OH)$_2$·8H$_2$O (0.315 g, 1 mmol) were successively dissolved in water (100 ml) under continuous stirring. A pink solution was obtained after filtration and the filtrate was kept at 313 K. Pink prismatic crystals had grown after several weeks.

Crystal data

[CaCo(C$_3$H$_2$O$_4$)$_2$(H$_2$O)$_4$]
$M_r = 375.17$
Monoclinic, $C2/c$
$a = 13.874$ (2) Å
$b = 7.531$ (1) Å
$c = 13.615$ (2) Å
$\beta = 122.94$ (2)°
$V = 1193.9$ (4) Å^3
$Z = 4$

$D_x = 2.087$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.4–13.6°$
$\mu = 1.93$ mm^{-1}
$T = 298$ K
Prism, pink
$0.26 \times 0.22 \times 0.14$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.660$, $T_{max} = 0.768$
1353 measured reflections
1300 independent reflections
1177 reflections with $I > 2\sigma(I)$

$R_{int} = 0.007$
$\theta_{max} = 27.0°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 9$
$l = -17 \rightarrow 14$
3 standard reflections
  frequency: 60 min
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.050$
$S = 1.11$
1300 reflections
110 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 0.8504P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0020 (4)

Table 1
Selected geometric parameters (Å, °).

Ca—O1	2.3775 (12)	O1—C1	1.2500 (18)
Ca—O6	2.3970 (14)	O2—C1	1.2681 (19)
Ca—O4^{iii}	2.4410 (13)	O3—C3	1.2623 (19)
Ca—O3^{iii}	2.6329 (12)	O4—C3	1.2476 (19)
Co—O3	2.0711 (12)	C2—C3	1.509 (2)
Co—O2	2.0900 (11)	C2—C1	1.511 (2)
Co—O5	2.1004 (14)		
O1^{iv}—Ca—O1	88.80 (6)	O3—Co—O2	87.30 (5)
O1^{iv}—Ca—O6	78.05 (5)	O2—Co—O5^{vi}	88.59 (5)
O1—Ca—O6	78.29 (5)	O3—Co—O5	90.68 (6)
O6^{iv}—Ca—O6	146.66 (7)	C1—O1—Ca	135.95 (10)
O1—Ca—O4^{iii}	89.93 (4)	C1—O2—Co	127.49 (10)
O6—Ca—O4^{iii}	77.99 (5)	C3—O3—Co	127.06 (10)
O1—Ca—O4^v	155.76 (4)	C3—O3—Ca^{vii}	88.26 (9)
O6—Ca—O4^v	125.01 (5)	Co—O3—Ca^{vii}	140.69 (5)
O4^{iii}—Ca—O4^v	100.82 (6)	C3—O4—Ca^{vii}	97.63 (10)
O1—Ca—O3^v	153.40 (4)	C3—C2—C1	116.97 (13)
O6—Ca—O3^v	77.03 (4)	O1—C1—O2	123.31 (14)
O4^{iii}—Ca—O3^v	75.38 (4)	O1—C1—C2	116.83 (13)
O4^v—Ca—O3^v	50.73 (4)	O2—C1—C2	119.81 (13)
O1^{iv}—Ca—O3^{iii}	153.40 (4)	O4—C3—O3	120.61 (14)
O1—Ca—O3^{iii}	95.65 (4)	O4—C3—C2	117.91 (13)
O6—Ca—O3^{iii}	128.54 (4)	O3—C3—C2	121.47 (14)
O3^v—Ca—O3^{iii}	92.00 (6)		

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O5—H5$A\cdots$O1^{viii}	0.77 (3)	2.16 (3)	2.920 (2)	173 (3)
O5—H5$B\cdots$O4^{ix}	0.78 (3)	2.00 (3)	2.773 (2)	169 (3)
O6—H6$A\cdots$O2^{iv}	0.84 (3)	1.98 (3)	2.7905 (18)	161 (2)
O6—H6$B\cdots$O2^x	0.75 (3)	2.33 (3)	3.0388 (19)	159 (3)

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

H atoms bonded to C atoms were included in geometrically idealized positions using a riding model, with C—H distances of 0.95 Å and U_{iso}(H) values of $1.2U_{eq}$(C). H atoms bonded to O atoms were found by difference Fourier methods and refined isotropically.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97*

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(Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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