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Poly[μ-aqua-diaqua-μ_4-malonato-μ_3-malonato-barium(II)nickel(II)]

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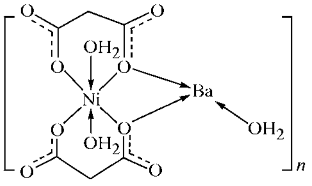
The title complex, $[BaNi(C_3H_2O_4)_2(H_2O)_3]_n$, is polymeric, with two non-equivalent malonate dianions bridging one Ni atom and five different Ba atoms. The Ni atoms have a distorted octahedral (NiO_6) environment, and are coordinated by four malonate O atoms in a planar arrangement and two water molecules in axial positions. The Ba atom may be described as a BaO_9 polyhedron in a monocapped square-antiprismatic environment, which involves two water molecules and seven O atoms from different malonate ligands. The three-dimensional structure is further maintained and stabilized by hydrogen bonds.

Comment

Heterobimetallic malonate (mal) complexes involving transition and alkaline-earth metals have attracted much attention recently in the area of topology design and for their potential applications in molecular-based magnetism, catalysis, supramolecular chemistry and materials science (Gil de Muro *et al.*, 1998, 2004; Fu *et al.*, 2006). The use of dicarboxylate ligands as small building blocks to generate metal–organic frameworks of different dimensionalities may lead to interesting network architectures (Rodriguez-Martin *et al.*, 2002). From a coordination standpoint, the malonate ligand, with two neighbouring carboxylate groups, is a very flexible ligand. Its basic coordination mode is as a chelate *via* two distal carboxylate O atoms to form a six-membered ring, and the coordinating ability of the nonchelating O atoms makes the formation of polymeric networks possible (Djeghri *et al.*, 2005, 2006). In the course of our study of heterobimetallic malonate complexes involving transition and alkaline-earth metals, we have recently reported the crystal structures of poly[tetraaquadi-μ_4-malonato-barium(II)zinc(II)], (II) (Guo & Guo, 2006), and poly-[tetra-μ-aqua-hexaaquadi-μ_3-malonato-dinitratodibarium(II)-nickel(II)], (III) (Guo & Cao, 2006). Interestingly, when nickel chloride was used in an attempt to obtain a product similar or isotypic to that of the zinc compound, a completely different crystal structure was obtained. We report here the structure of the bimetallic malonate complex (I).



(I)

The asymmetric unit of (I) comprises one Ni atom, one Ba atom, two complete malonate dianions (C1–C3/O1–O4 and C4–C6/O5–O8) and three non-equivalent water molecules (O9–O11), and is shown in Fig. 1 in a symmetry-expanded view that displays the full coordination of the Ba and Ni atoms. Selected geometric parameters are given in Table 1.

The Ba atom is surrounded by an O_9 donor set in an approximate monocapped square-antiprismatic environment (Fig. 1). The four coordination sites of the basal plane are occupied by atom O6^{iii} from a malonate dianion, atom O4^{iv} from a second malonate ligand and two coordinated water molecules (O11 and O11^{i}; see Fig. 1 for symmetry codes). The opposite plane contains two O atoms (O1 and O5) from two malonate ligands, a bridging O atom (O4^{ii}) from a third malonate ligand and a chelating carboxylate O atom (O7^{v}) from a fourth malonate ligand. Finally, the capping site is occupied by the chelating atom O8^{v}. Of the Ba—O distances (Table 1), Ba—O7^{v} and Ba—O8^{v} are the longest, probably as a result of strain in the four-membered chelate ring. The Ba—O(water) bonds are slightly shorter than those in (III) (Guo & Cao, 2006), while the Ba—O(malonate) bond distances correspond well with the sum of the ionic radii (1.21 + 1.66 = 2.87 Å for 10-coordinate Ba^{2+} ions; Bauer *et al.*, 2005) and are comparable to the values reported for barium oxydiacetates (Baggio *et al.*, 2004). The BaO_9 polyhedra share edges to form zigzag chains propagated in the *c* direction *via* pairs of water

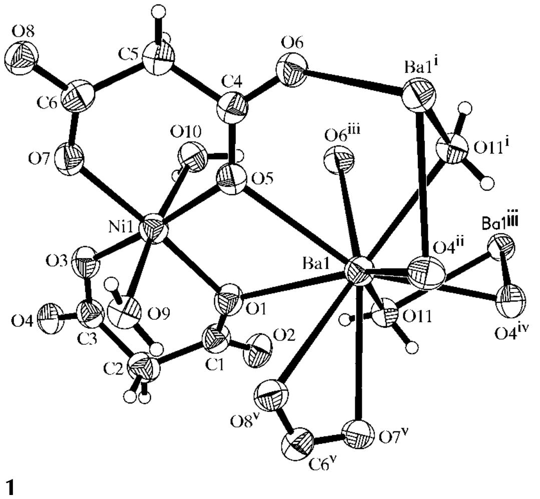


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and coordination polyhedra for Ni and Ba atoms; displacement ellipsoids were drawn at the 30% probability level. [Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $x, -y+1, z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.]

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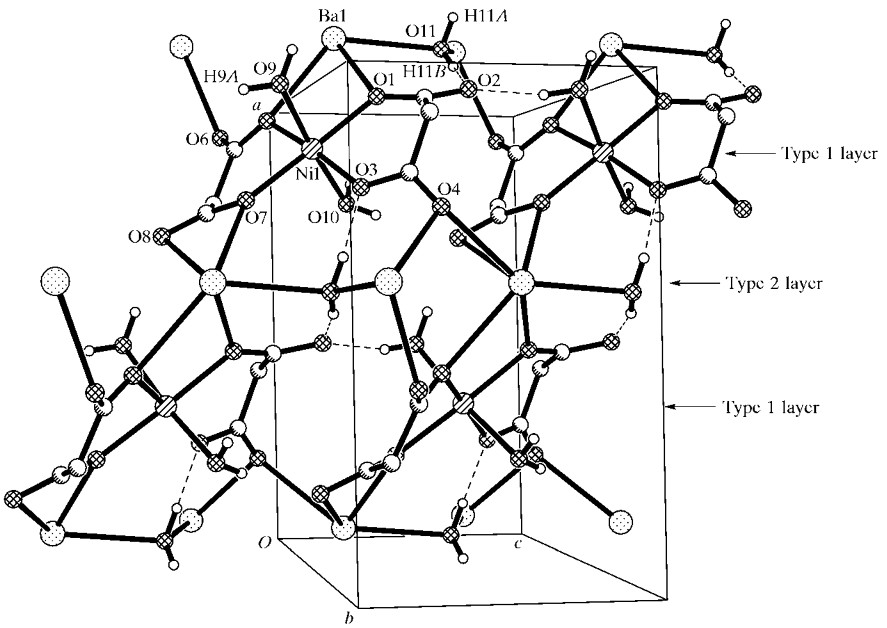

Figure 2
The packing of (I), showing hydrogen-bonding interactions within a type 1 layer parallel to the *bc* plane, viewed down the *a* axis.

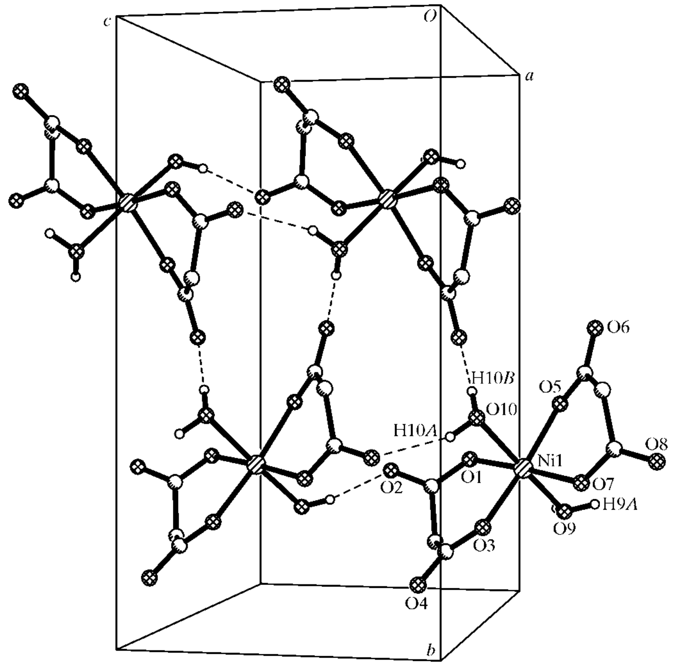

Figure 3
The packing of (I), viewed down the *b* axis, showing the alternation of type 1 and type 2 layers along the *a* axis.

bridges (O11 and O11^{i}) or bridging malonate O4^{ii} and O4^{iv} atoms. This results in Ba1···Ba1^{i} separations of 4.3362 (8) Å.

The Ni atom has octahedral coordination, with atoms O1, O3, O5 and O7 of two non-equivalent malonate dianions in a planar arrangement, and atoms O9 and O10 from two water molecules in a *trans* conformation. The Ni—O(water) bonds are slightly longer while the Ni—O(mal) bonds are somewhat shorter than those in $[CaNi(mal)_2(H_2O)_4]\cdot 2H_2O$ (Gil de Muro *et al.*, 2000). Thus, the coordination octahedra of the Ni atoms can be visualized as having a slightly elongated axial distortion.

Also evident in Fig. 1 is the variability of the coordination modes of the malonate ligand. Monodentate, bidentate chelating, chelated six-membered and bridging coordination modes are all present. In the case of the C1–C3/O1–O4 malonate dianion, atom O1 adopts both a monodentate mode bonding to Ni and a bridging bonding mode to Ni and Ba. Atom O4 adopts a bridging mode to connect two Ba atoms. Furthermore, two carboxylate groups (atoms O1 and O3) adopt a six-membered chelating mode, forming a ring around Ni with an envelope conformation, with atom C2 displaced by 0.65 Å from the plane defined by the other atoms in the ring. For the C4–C6/O5–O8 malonate dianion, the coordination modes of atom O5 are the same as for atom O1; atom O6 adopts a monodentate mode, coordinating another Ba atom. Atoms O7 and O8 from the same carboxylate function chelate the Ba atom at $(x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2})$ to form a four-membered ring. Atoms O7 and O5 from different carboxylate groups form a six-membered chelate (Ni1/O5/C4–C6/O7) with a boat conformation; atoms Ni1 and C5 lie 0.52 and 0.42 Å, respectively, out of the O5/C4/C6/O7 plane. The Ni1···Ba1 separation of 3.8059 (14) Å, mediated by the O1,O5 double bridge, is much less than the sum of their van der Waals radii (2.30 + 2.14 = 4.44 Å).

The structure as a whole consists of two distinct types of layer (Fig. 2), both perpendicular to [100] and stacked alternately in the *a* direction. The first of these (Fig. 3) is composed entirely of Ni atoms, malonate dianions and water molecules (O9 atom O10). Hydrogen bonding plays an important role in the stabilization of the extended layers. The noncoordinated O2 atom is involved in forming strong hydrogen bonds (O9—H9*A*···O2^{vi}; symmetry codes as in Table 2) (Brown, 1976). Within this layer, and along the *c* direction, O9—H9*A*···O2^{vi}

and O10—H10$A\cdots$O8$^{\rm vii}$ hydrogen bonds are responsible for the formation of a 12-membered hydrogen-bonded $R_2^2(12)$ ring (Bernstein *et al.*, 1995). In the *b* direction, the neighbouring Ni coordination octahedra are linked together *via* O10—H10$B\cdots$O6$^{\rm iii}$ hydrogen bonds and 14-membered hydrogen-bonded $R_2^2(14)$ rings. In this way, a complete two-dimensional connectivity is achieved parallel to the *bc* plane.

The other type of layer, *viz*. type 2, consists of Ba atoms and water molecules (Fig. 2). In the crystallographic *a* direction, the connectivity of two layers is achieved by means of O1, O5 and O7 bridging atoms and O6—C4—O5, O4—C3—O3 and O8—C6—O7 bridges between Ni1 coordination octahedra and neighbouring BaO_9 polyhedra. At the same time, the zigzag BaO_9 polyhedral chains in the *c* direction are linked into layers and complete the three-dimensional connectivity of the structure. The interlayer connectivity is further enhanced by hydrogen bonds of the form O11—H11$A\cdots$O3$^{\rm v}$ and O11—H11$B\cdots$O2 (Table 2).

Experimental

The title complex was prepared under continuous stirring with successive addition of malonic acid (0.31 g, 3 mmol), $NiCl_2\cdot6H_2O$ (0.47 g, 2 mmol) and $Ba(OH)_2\cdot8H_2O$ (0.63 g, 2 mmol) to distilled water (20 ml) at room temperature. After filtration, slow evaporation over a period of 3 d at room temperature provided green needle-shaped crystals of (I).

Crystal data

$[BaNi(C_3H_2O_4)_2(H_2O)_3]$
$M_r = 454.19$
Monoclinic, *Cc*
$a = 12.177$ (2) Å
$b = 13.842$ (3) Å
$c = 7.1502$ (14) Å
$\beta = 91.17$ (3)°
$V = 1204.9$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.86$ mm^{-1}
$T = 294$ (2) K
0.12 × 0.10 × 0.06 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\rm min} = 0.558$, $T_{\rm max} = 0.738$
3369 measured reflections
1432 independent reflections
1424 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.099$
$S = 1.09$
1432 reflections
173 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max} = 1.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.65$ e Å^{-3}
Absolute structure: Flack (1983), 365 Friedel pairs
Flack parameter: 0.18 (6)

All difference peaks larger than 1.0 e Å^{-3} are around atom Ba1. The highest difference peak lies 0.85 Å from atom Ba1. All H atoms attached to O atoms were found in difference Fourier maps. During refinement, the H atoms were fixed at O—H distances of 0.85 Å and their $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$(O). H atoms of CH_2 groups were treated as riding [C—H = 0.97 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C)].

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1
Selected geometric parameters (Å).

Ba1—O11	2.724 (10)	Ba1—O8$^{\rm v}$	2.911 (7)
Ba1—O11$^{\rm i}$	2.729 (6)	Ba1—Ni1	3.8059 (14)
Ba1—O4$^{\rm ii}$	2.778 (7)	Ni1—O3	1.989 (6)
Ba1—O1	2.794 (7)	Ni1—O5	2.033 (7)
Ba1—O6$^{\rm iii}$	2.796 (6)	Ni1—O1	2.045 (8)
Ba1—O5	2.825 (7)	Ni1—O7	2.052 (8)
Ba1—O4$^{\rm iv}$	2.857 (7)	Ni1—O9	2.082 (7)
Ba1—O7$^{\rm v}$	2.885 (7)	Ni1—O10	2.117 (7)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O9—H9$A\cdots$O2$^{\rm vi}$	0.85	1.85	2.672 (11)	163
O11—H11$A\cdots$O3$^{\rm v}$	0.85	1.79	2.622 (11)	166
O11—H11$B\cdots$O2	0.85	1.85	2.677 (10)	162
O9—H9$B\cdots$O8$^{\rm v}$	0.85	2.12	2.903 (10)	153
O10—H10$A\cdots$O8$^{\rm vii}$	0.85	2.07	2.886 (10)	160
O10—H10$B\cdots$O6$^{\rm iii}$	0.85	1.92	2.772 (10)	176

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3125). Services for accessing these data are described at the back of the journal.

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