

Poly[tetra- μ -aqua-hexaaquadi- μ_3 -malonato-dinitratodibarium(II)nickel(II)]

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Received 22 June 2006

Accepted 31 July 2006

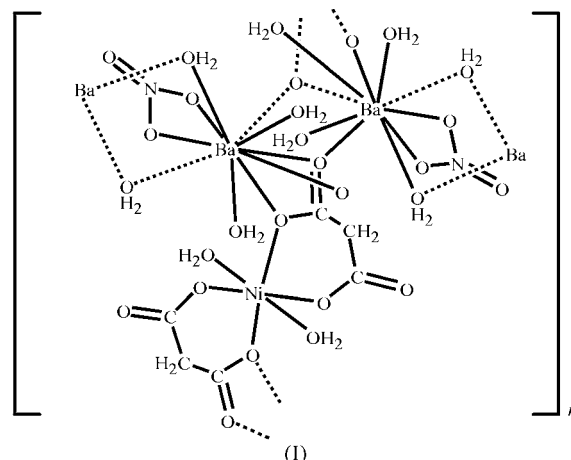
Online 23 August 2006

The title complex, $[\text{Ba}_2\text{Ni}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{NO}_3)_2(\text{H}_2\text{O})_{10}]_n$, has a two-dimensional layer structure. The Ni atom lies on a crystallographic centre of symmetry in an octahedral NiO_6 environment, and is coordinated by four malonate O atoms in a planar arrangement and by two water molecules in axial positions. The coordination of the unique Ba atom involves two nitrate O atoms, five water molecules and three malonate O atoms.

Comment

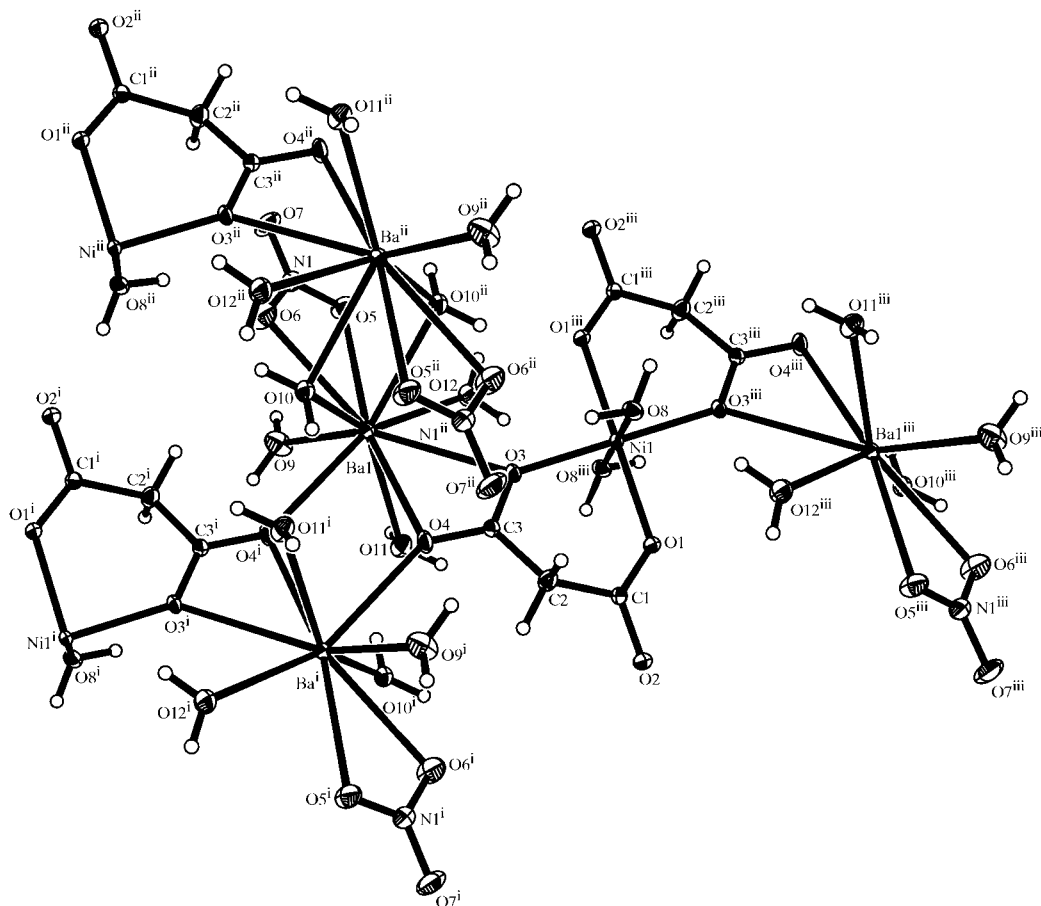
There has been considerable interest in the design and synthesis of coordination polymers based on assemblies of transition metal ions and α,ω -dicarboxylate ligands, because carboxylates can give rise to different coordination modes with metal ions in the construction of coordination polymers with specific architectures (Rodriguez-Martin *et al.*, 2002), and there is increasing recognition of the role of metals in biological systems (Maji *et al.*, 2003). The malonate (mal) ligand, with two neighbouring carboxylate groups, is very flexible. 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 non-chelating O atoms makes the formation of polymeric networks possible (Djeghri *et al.*, 2005). With its versatile coordinating ability as a monodentate, chelated bidentate or bridging ligand, malonate can create various patterns (Delgado *et al.*, 2004; Gil de Muro *et al.*, 2000; Djeghri *et al.*, 2006; Wang *et al.*, 2004). Our interest in heterobimetallic malonate complexes involving transition and alkaline-earth metals stems from their potential application in molecular-based magnetism, catalysis, supramolecular chemistry and materials science (Gil de Muro *et al.*, 1998, 2004). We have recently reported the crystal structure of poly[tetraaquadidi- μ_4 -malonato-barium(II)zinc(II)] (Guo & Guo, 2006). Using nickel chloride, we expected a structure similar to or isotopic with that of the zinc compound, but interestingly, a completely different crystal structure was obtained, the title bimetallic malonate complex, (I), and we report its crystal structure here.

The asymmetric unit in the structure of (I) comprises half an Ni atom, one Ba atom, one nitrate anion, one complete malonate dianion and five non-equivalent water molecules, and is shown in Fig. 1 in a symmetry-expanded view, which displays the full coordination geometry of the Ba and Ni atoms. Selected geometric parameters are given in Table 1.

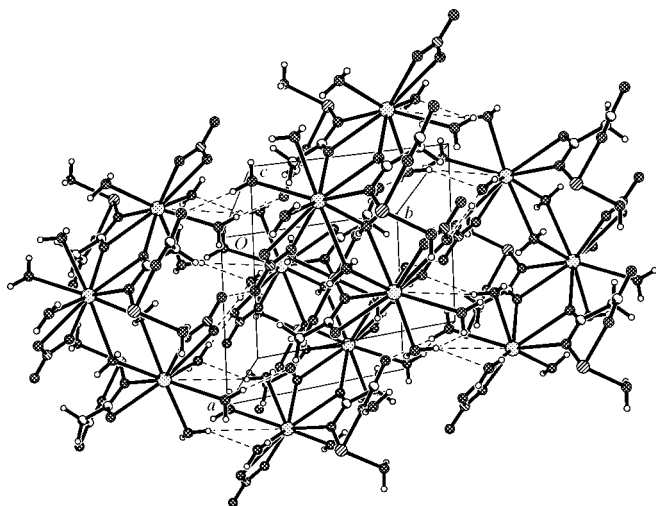


The Ni atom, lying on a crystallographic centre of symmetry, is octahedrally coordinated, with atoms O1 and O3 of two malonate anions in a planar arrangement [$\text{Ni}-\text{O} = 2.047(2)$ and $2.021(2)$ Å] and two O8 atoms [$\text{Ni}-\text{O} = 2.098(2)$ Å] from two water molecules forming the opposing apices of the octahedron. The $\text{Ni}-\text{O}_{\text{water}}$ bonds are slightly longer and the $\text{Ni}-\text{O}_{\text{mal}}$ bonds are somewhat shorter than those in the $[\text{CaNi}(\text{mal})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ complex (Gil de Muro *et al.*, 2000). All the *cis*-O-Ni-O bond angles are close to 90° [in the range $86.77(10)$ – $93.23(10)^\circ$] and, because of the site symmetry of Ni, all the *trans* angles are exactly 180° . Thus, the coordination octahedra of the Ni atoms can be visualized as having a slightly elongated axial distortion.

In the present structure, the variability of the malonate ligand can be clearly seen (Fig. 1). Monodentate, bidentate-chelating, chelated six-membered and bridging bonding modes are all present. Atom O1 of the O1/C1/O2 carboxylate group adopts a monodentate mode. Atoms O3 and O4 of the O3/C3/O4 carboxylate group have both a bidentate 1,2-chelating mode, to connect with the Ba atom, and a bridging bonding mode, atom O3 being coordinated to one Ni atom and one Ba atom, while atom O4 is connected to two Ba atoms. Furthermore, the whole molecule chelates the Ni atom to form a six-membered ring. The resulting six-membered Ni/O1/C1/C2/C3/O3 chelate ring has a boat conformation, with atoms Ni and C2 lying 0.4769 and 0.4176 Å, respectively, out of the O1/C1/C3/O3 mean plane. The O–C–O angle for the monodentate carboxylate group is $123.2(3)^\circ$, slightly larger than the value of $121.9(3)^\circ$ for the chelating carboxylate group. The two C–O bond distances (O1–C1 and O2–C1) of the monodentate carboxylate group are 1.255(4) and 1.260(4) Å, respectively, while the two C–O bond distances (O4–C3 and O3–C3) of the chelating carboxylate group are 1.240(4) and 1.277(4) Å, respectively.


Figure 1

A view of the structure of (I), showing the atom-numbering scheme and the coordination polyhedra for Ni and Ba atoms. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x, 1 - y, -z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, 1 - y, 1 - z$.]


Figure 2

A packing diagram of (I), showing the hydrogen bonds (dashed lines) and the alternating layers in the direction of b , viewed down the c axis.

This indicates that the mesomeric effect for the monodentate carboxylate group is larger than that of the chelating carboxylate group.

The Ba atom is coordinated by two nitrate O atoms, five water molecules and three malonate O atoms. The Ba—O distances for Ba—O_{nitrate} range from 2.886 (3) to 2.902 (3) Å, those for Ba—O_{water} range from 2.805 (3) to 2.897 (2) Å and those for Ba—O_{mal} range from 2.752 (2) to 2.941 (2) Å. Of these Ba—O distances, Ba—O3 and Ba—O5 are the longest, and the increase of these bond lengths is related to the requirements of the conformation of the fused ring system. These Ba—O distances correspond well with the sum of the ionic radii ($1.21 + 1.66 = 2.87$ Å for ten-coordinated Ba²⁺ ions; Bauer *et al.*, 2005) and are comparable with the values reported for barium malonate (Hodgson & Asplund, 1991). The Ba polyhedra share edges to form zigzag BaO₈ polyhedral chains propagating along [100] via pairs of water molecules, O10 and O10ⁱⁱ atoms or bridging malonate O4 and O4ⁱ atoms (see Table 1 for symmetry codes). This results in Ba1ⁱ··Ba1ⁱ and Ba1ⁱ··Ba1ⁱⁱⁱ distances of 4.6867 (7) and 4.7877 (8) Å, respectively, and a Ba1ⁱ··Ba1ⁱ··Ba1ⁱⁱⁱ angle of 97.422 (16)°. Each Ni atom is connected to two Ba atoms through atoms O3 and O3ⁱⁱⁱ of the carboxylate group in the c direction, defining infinite chains of BaO₈ polyhedra. The Ni··Ba distance is 4.6731 (9) Å and the Ba··Ni··Ba angle is 180°. Thus, a complete two-dimensional polymeric layer is formed in the direction of the ac plane.

In the crystal structure of (I), symmetry-related molecules are linked by hydrogen bonds (Table 2). Hydrogen bonding plays an important role in the stabilization of the extended structure. The structure consists of alternating layers in the *b* direction. Neighbouring layers are linked together *via* these hydrogen bonds to build up a three-dimensional network (Fig. 2).

Experimental

The title complex was prepared under continuous stirring with successive addition of malonic acid (0.43 g, 4 mmol), NiCl₂·6H₂O (0.47 g, 2 mmol), barium nitrate (0.52 g, 2 mmol) and Ba(OH)₂·8H₂O (0.63 g, 2 mmol) to distilled water (30 ml) at room temperature. After filtration, slow evaporation over a period of three weeks at room temperature provided green plate-shaped crystals of (I).

Crystal data

[Ba ₂ Ni(C ₃ H ₂ O ₄) ₂ (NO ₃) ₂ (H ₂ O) ₁₀]	<i>V</i> = 584.19 (18) Å ³
<i>M_r</i> = 841.66	<i>Z</i> = 1
Triclinic, <i>P</i> 1̄	<i>D_x</i> = 2.392 Mg m ⁻³
<i>a</i> = 7.1193 (13) Å	Mo <i>K</i> α radiation
<i>b</i> = 9.3307 (16) Å	<i>μ</i> = 4.24 mm ⁻¹
<i>c</i> = 9.8866 (17) Å	<i>T</i> = 294 (2) K
<i>α</i> = 110.428 (2)°	Plate, green
<i>β</i> = 104.240 (2)°	0.22 × 0.14 × 0.10 mm
<i>γ</i> = 95.622 (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	2940 measured reflections
<i>φ</i> and <i>ω</i> scans	2042 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1877 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.492, <i>T_{max}</i> = 0.657	<i>R_{int}</i> = 0.015
	<i>θ_{max}</i> = 25.0°

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.022	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0364 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.056	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 1.06	(Δ/σ) _{max} = 0.001
2042 reflections	Δρ _{max} = 1.01 e Å ⁻³
160 parameters	Δρ _{min} = -0.66 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—O3	2.021 (2)	Ba1—O5	2.902 (3)
Ni1—O1	2.047 (2)	Ba1—O3	2.941 (2)
Ni1—O8	2.098 (2)	Ba1—Ba1 ⁱ	4.6867 (7)
Ba1—O4 ⁱ	2.752 (2)	Ba1—Ba1 ⁱⁱ	4.7877 (8)
Ba1—O9	2.805 (3)	C1—O1	1.255 (4)
Ba1—O12	2.820 (2)	C1—O2	1.260 (4)
Ba1—O11	2.833 (3)	C3—O4	1.240 (4)
Ba1—O4	2.837 (3)	C3—O3	1.277 (4)
Ba1—O10 ⁱⁱ	2.882 (3)	N1—O7	1.227 (4)
Ba1—O6	2.886 (3)	N1—O5	1.250 (4)
Ba1—O10	2.897 (2)	N1—O6	1.257 (4)
Ba1 ⁱ —Ba1—Ba1 ⁱⁱ	97.422 (16)	O3 ⁱⁱⁱ —Ni1—O8	87.48 (9)
O3—Ni1—O1 ⁱⁱⁱ	90.09 (9)	O1 ⁱⁱⁱ —Ni1—O8	86.77 (10)
O3—Ni1—O1	89.91 (9)	O1—C1—O2	123.2 (3)
O3—Ni1—O8 ⁱⁱⁱ	87.48 (9)	O4—C3—O3	121.9 (3)
O3 ⁱⁱⁱ —Ni1—O8 ⁱⁱⁱ	92.52 (9)	O7—N1—O5	121.1 (3)
O1 ⁱⁱⁱ —Ni1—O8 ⁱⁱⁱ	93.23 (10)	O7—N1—O6	120.7 (3)
O3—Ni1—O8	92.52 (9)	O5—N1—O6	118.2 (3)

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2A...O7 ⁱⁱ	0.97	2.56	3.336 (5)	137
O12—H12B...O8 ⁱⁱⁱ	0.85	2.16	2.995 (4)	171
O12—H12A...O5 ^{iv}	0.85	2.00	2.839 (4)	168
O11—H11B...O12 ^v	0.85	2.25	3.024 (4)	152
O11—H11A...O2 ^{vi}	0.85	1.90	2.739 (4)	170
O10—H10B...O1 ^{vii}	0.85	2.06	2.853 (3)	155
O10—H10A...O11 ⁱ	0.85	2.04	2.837 (4)	156
O9—H9B...O7 ^{viii}	0.85	2.16	2.987 (4)	162
O9—H9A...O2 ^{ix}	0.85	2.22	3.058 (4)	172
O8—H8B...O2 ^x	0.85	1.89	2.726 (3)	168
O8—H8A...O6 ^{xi}	0.86	2.02	2.804 (4)	152

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y, -z$; (v) $-x, -y, -z$; (vi) $-x, -y + 1, -z + 1$; (vii) $x, y, z - 1$; (viii) $x - 1, y, z$; (ix) $x, y - 1, z - 1$; (x) $x + 1, y, z$.

The H atoms of the water molecule were found in difference Fourier maps. However, during refinement, they were fixed at O—H distances of 0.847–856 Å and their *U*_{iso} values were set at 1.2*U*_{eq}(O). The H atoms of C—H groups were treated as riding, with C—H = 0.97 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: SMART (Bruker 1997); cell refinement: SAINT (Bruker 1997); data reduction: SAINT; 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.

The authors thank Tianjin Polytechnic University for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3027). Services for accessing these data are described at the back of the journal.

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