Poly[di-μ_2-aqua-hexaquabis(μ_4-benzene-1,3,5-tricarboxylato)trinickel(II)]

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.085
Data-to-parameter ratio = 11.9

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

The solvothermal reaction of nickel[II] acetate with H_3BTC (benzene-1,3,5-tricarboxylic acid) in water gave the title complex, $[Ni_3(C_9H_3O_6)_2(H_2O)_8]_n$. Single-crystal X-ray analysis shows that the structure contains four crystallographically unique Ni atoms. Two of these each lie at a center of symmetry and each is coordinated by two water molecules and four O atoms from four carboxylate groups. The other two are each coordinated by four water molecules and two O atoms from two carboxylate groups. The different types of chemically unique Ni atoms are connected by μ_2-H_2O and carboxylate groups of BTC ligands to form two two-dimensional networks. The hydrogen-bonding interactions between the layers further connected these two-dimensional layers into a three-dimensional frame work in a parallel fashion.

Comment

In recent years, intense research activity has been directed toward the assembly of coordination polymers due to their intriguing structural motifs and potential applications (Sato *et al.*, 1996). The three carboxylate groups of 1,3,5-H_3BTC (benzene-1,3,5-tricarboxylic acid) have a very versatile coordination behavior. Much of the work has so far been focused on coordination polymers with this ligand (Chui *et al.*, 1999; Chen *et al.*, 2005). Although the construction of complexes from 1,3,5-H_3BTC and Ni[II] metal has been extensively studied (Michaelides *et al.*, 1997; Kepert & Rosseinsky, 1998; Choi & Suh, 1998; Kepert *et al.*, 2000a,b; Prior & Rosseinsky, 2001a,b; Choi *et al.*, 2001; Zhang *et al.*, 2003), the title trinuclear Ni[II] coordination polymer, (I), has never been reported. Its structure is presented here.

(I)
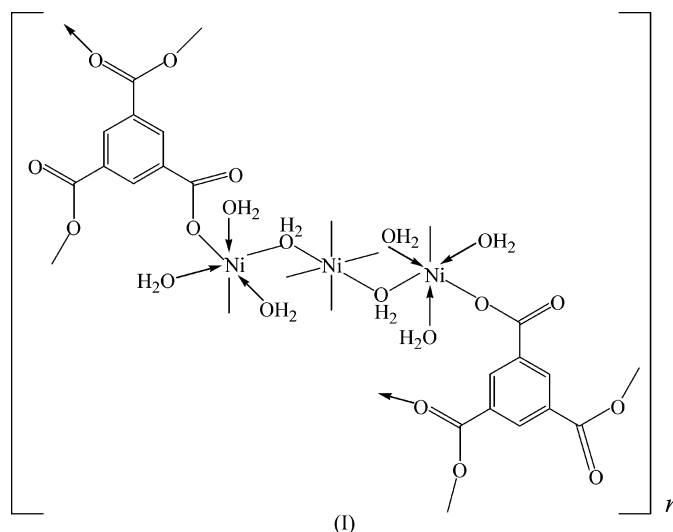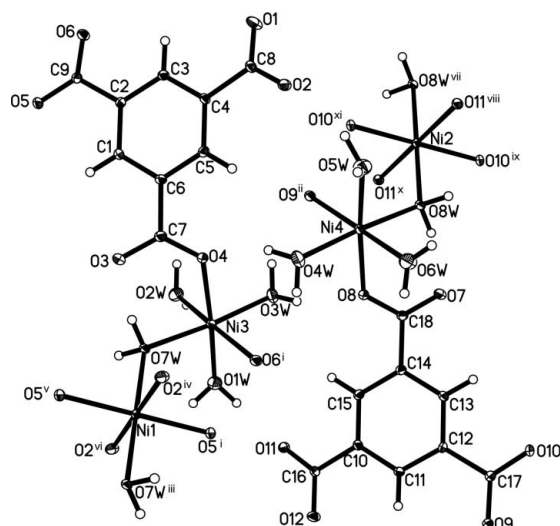
Figure 1
View of the coordination environments of the four independent Ni atoms in (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $1 + x, y, z$; (ii) $-1 + x, y, z$; (iv) $-1 - x, 1 - y, -z$; (v) $-1 - x, -y, -z$; (vi) $1 + x, -1 + y, z$; (vii) $-1 - x, 2 - y, -1 - z$; (viii) $-x, 1 - y, -1 - z$; (ix) $-1 + x, y, z$; (x) $-1 + x, 1 + y, z$; (xi) $-x, 2 - y, -1 - z$.]
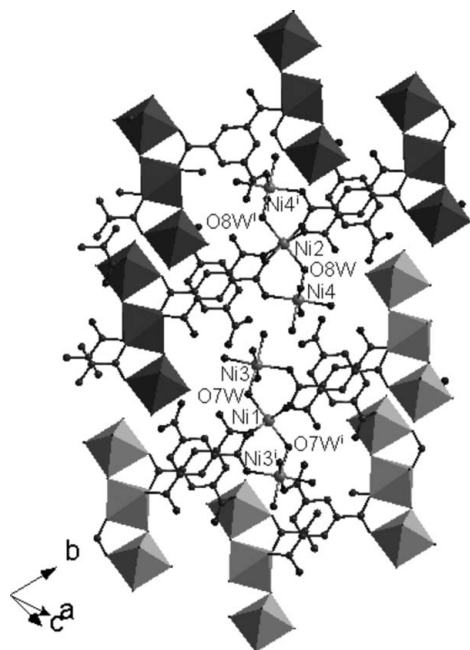
Figure 2
A polyhedral representation of the layers of (I).

There are four kinds of crystallographically independent Ni atoms in (I), and all of them adopt six-coordinate environments (Fig. 1). Atoms Ni1 and Ni2 are chemically identical, and each of them lies at a center of symmetry and is coordinated by two water molecules and four O atoms from four carboxylate groups. Atoms Ni3 and Ni4 are chemically identical, and each of them is coordinated by four water molecules and two O atoms from two carboxylate groups. The bond distances of Ni—O(carboxylate) and Ni—O(water) are 2.034 (2)–2.146 (2) and 2.045 (2)–2.087 (2) Å respectively, which are in agreement with the normal distances in the

related compound $[Ni_3(C_9H_3O_6)_2(H_2O)_{18}]$ (Zhang *et al.*, 2003). All carboxylate groups of the two crystallographically independent H_3BTC ligands are deprotonated, and display two different kinds of coordination modes, *viz.* bidentate bridging and monodentate mode. Based on its connection modes, each BTC ligand coordinates to four Ni^{II} centers.

The trinuclear cluster, which consists of two nickel octahedra of Ni3 and Ni3^i, linked by μ_2-O7W/O7W^i to the octahedron of Ni1 (or octahedra of Ni4 and Ni4^i linked by μ_2-O8W/O8W^i to the octahedron of Ni2), acts as the repeating structural motif, together with carboxylate groups of BTC ligands, forming two two-dimensional networks [Fig. 2; symmetry code: (i) $-x, -y, -z$]. The non-bonding Ni$\cdots$Ni distances are 3.596 (1) and 3.624 (1) Å for Ni1$\cdots$Ni3 and Ni2$\cdots$Ni4, respectively. The layers are stacked in an $-ABAB-$ sequence along the c axis to form a three-dimensional structure through hydrogen bonds (Fig. 3). The hydrogen-bond distances and angles are listed in Table 2. It can be seen that there are eight H atoms involved in hydrogen-bonding in the asymmetric unit. All of them belong to water molecules. The carboxylate O atoms play the role of acceptors. The hydrogen-bonding interactions within the layer and between the layers enhance the stability of the compound (I) and lead to a three-dimensional structure.

Experimental

A mixture of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.1867 g, 0.75 mmol) and H_3BTC (0.1051 g, 0.5 mmol) in water (10 ml) was sealed in a 15 ml Teflon-lined stainless steel bomb and heated to 433 K for 3 d; very fine green crystals were obtained after slow cooling to room temperature at a rate of 10 K h^{-1}. Yield 74% (based on Ni). Analysis calculated for $C_{18}H_{22}Ni_3O_{20}$: C 29.43, H 3.03%; found: C 29.29, H 3.11%.

Crystal data

$[Ni_3(C_9H_3O_6)_2(H_2O)_8]$	$V = 1122.5$ (9) Å^3
$M_r = 734.49$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 2.173$ Mg m^{-3}
$a = 10.040$ (5) Å	Mo $K\alpha$ radiation
$b = 10.092$ (5) Å	$\mu = 2.60$ mm^{-1}
$c = 13.165$ (5) Å	$T = 293$ (2) K
$\alpha = 75.719$ (5)°	Block, green
$\beta = 68.643$ (5)°	$0.38 \times 0.28 \times 0.16$ mm
$\gamma = 65.409$ (5)°	

Data collection

Bruker APEX CCD area-detector diffractometer	6913 measured reflections
ω scans	5008 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	4047 reflections with $I > 2\sigma(I)$
$T_{min} = 0.42$, $T_{max} = 0.65$	$R_{int} = 0.013$
	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 0.3629P]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
5008 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
421 parameters	$\Delta\rho_{min} = -0.57$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Ni1—O5^i	2.034 (2)	Ni3—O1W	2.068 (2)
Ni1—O7W	2.046 (2)	Ni3—O4	2.083 (2)
Ni1—O2^{ii}	2.146 (2)	Ni3—O2W	2.087 (2)
Ni2—O10^{iii}	2.049 (2)	Ni4—O9^{iii}	2.036 (2)
Ni2—O8W	2.076 (2)	Ni4—O5W	2.056 (2)
Ni2—O11^{iv}	2.113 (2)	Ni4—O4W	2.066 (2)
Ni3—O6^i	2.040 (2)	Ni4—O8	2.069 (2)
Ni3—O7W	2.045 (2)	Ni4—O6W	2.072 (2)
Ni3—O3W	2.054 (2)	Ni4—O8W	2.072 (2)
O5^i—Ni1—O2^v	87.41 (7)	O9^{iii}—Ni4—O8	97.04 (7)
O10^{vi}—Ni2—O11^{iv}	87.74 (7)	Ni3—O7W—Ni1	123.07 (7)
O6^i—Ni3—O4	96.66 (7)	Ni4—O8W—Ni2	121.78 (7)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2W—H2$A\cdots$O7^{vii}	0.797 (17)	2.121 (19)	2.891 (3)	163 (3)
O5W—H5$B\cdots$O3^v	0.876 (17)	2.025 (19)	2.892 (3)	170 (3)
O1W—H1$A\cdots$O11	0.888 (17)	1.898 (18)	2.781 (3)	172 (3)
O3W—H3$B\cdots$O8	0.860 (17)	1.87 (2)	2.648 (3)	150 (3)
O4W—H4$A\cdots$O4	0.896 (17)	1.86 (2)	2.705 (3)	157 (3)
O5W—H5$A\cdots$O2	0.917 (18)	2.05 (2)	2.909 (3)	156 (3)
O7W—H7$A\cdots$O3	0.865 (16)	1.708 (17)	2.561 (3)	168 (3)
O8W—H8$B\cdots$O7	0.872 (16)	1.760 (18)	2.612 (3)	165 (3)

Symmetry codes: (v) $-x - 1, -y + 1, -z$; (vii) $-x, -y + 1, -z - 1$.

All H atoms bound to carbon were refined using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms. Water H atoms were located in a difference Fourier map and refined without O—H distance restraints and with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.
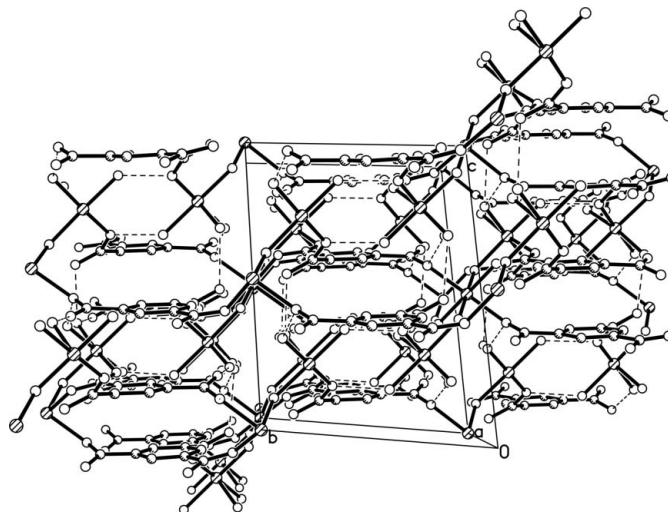
Figure 3
Three-dimensional packing arrangement of (I) through hydrogen bonds. Hydrogen bonds are shown as dashed lines and H atoms have been omitted for clarity.

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