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Key indicators

Single-crystal X-ray study
 T = 295 K
 Mean $\sigma(C-C)$ = 0.004 Å
 R factor = 0.034
 wR factor = 0.084
 Data-to-parameter ratio = 11.6

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

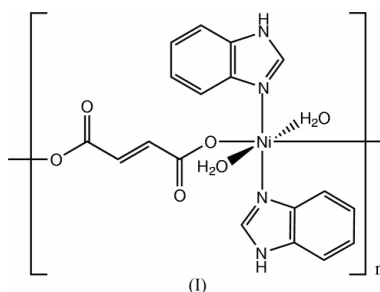
**catena-Poly[[diaquabis(1*H*-benzimidazole- κ N³)-
 nickel(II)]- μ -fumarato- κ^2 O:O']**

The title compound, $[Ni(\mu-C_4H_2O_4)(C_7H_6N_2)_2(H_2O)_2]_n$, is a one-dimensional polymeric complex bridged by fumarate dianions. The Ni atom lies on one inversion centre and the fumarate on another. The molecular chains are linked by hydrogen bonding. π - π stacking between parallel benzimidazole rings exists in the crystal structure.

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Comment

The aromatic π - π stacking interaction has been shown to be correlated with electron transfer in some biological systems (Deisenhofer & Michel, 1989). As part of an investigation of π - π stacking interactions in metal complexes (Chen *et al.*, 2003), the crystal structure of the title benzimidazole (BZIM) complex of Ni^{II}, (I), is presented here.



The title Ni^{II} complex is polymeric and displays a similar structure to that of the Co^{II} analogue (Liu *et al.*, 2003). The Ni^{II} atom in (I) is located on an inversion centre and assumes normal octahedral coordination geometry (Table 1), formed

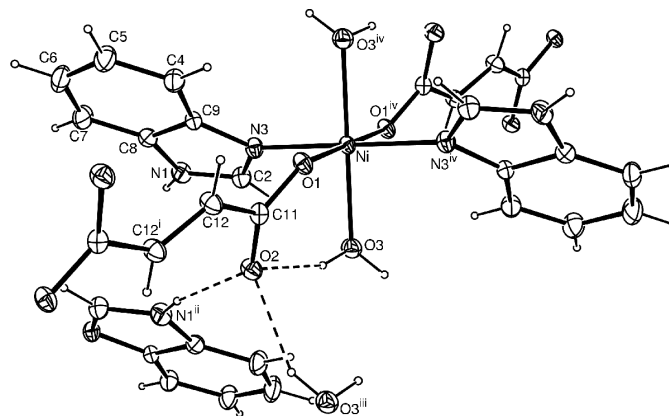


Figure 1
 The coordination environment around the Ni^{II} atom in (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate the hydrogen bonding involving the uncoordinated carboxy O2 atom. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, 1-y, 2-z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$.]

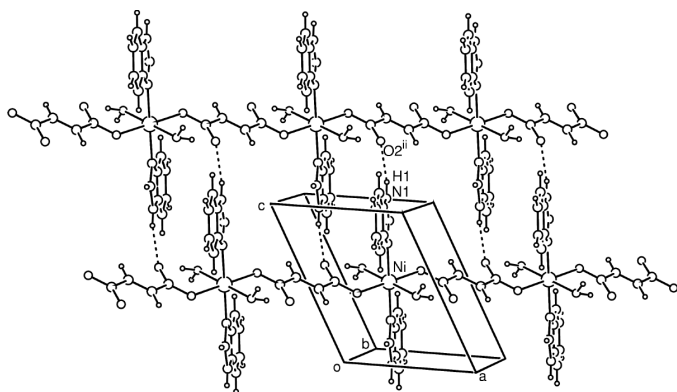


Figure 2
The molecular packing of (I); dashed lines indicate the N—H...O hydrogen bonding between adjacent polymeric chains. [Symmetry code: (ii) $1 - x, 1 - y, 2 - z$.]

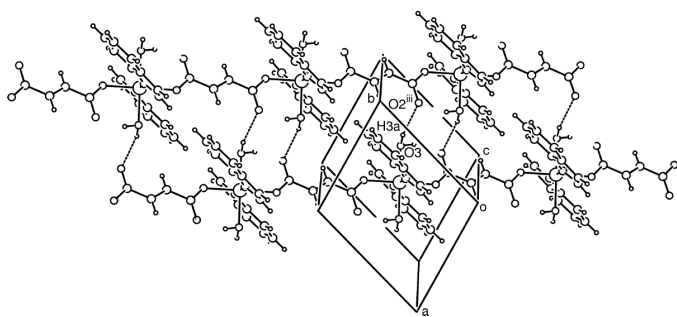


Figure 3
The molecular packing of (I); dashed lines indicate the O—H...O hydrogen bonding between adjacent polymeric chains. [Symmetry code: (iii) $-x, 1 - y, 1 - z$.]

by fumarate anions, BZIM and coordinated water molecules, as shown in Fig. 1. The fumarate anion is located on another inversion centre and the carboxy groups are coplanar with the carbon skeleton, the maximum atomic deviation being 0.035 (2) Å (for C12). Each carboxy group coordinates in a monodentate fashion to the Ni^{II} atom, and the uncoordinated carboxy O atom (O2) links with BZIM and coordinated water molecules *via* three hydrogen bonds, as shown in Fig. 1 and Table 2.

The fumarate anions bridge neighbouring Ni^{II} atoms through both terminal carboxy groups to form polymeric molecular chains, extending along the [110] direction. Adjacent polymeric chains are linked by N—H...O (Fig. 2) and O—H...O (Fig. 3) hydrogen bonds to form the three-dimensional supramolecular structure.

An overlapped arrangement of BZIM rings of adjacent complex molecules is observed in the crystal structure (Fig. 4). The distance of 3.404 (13) Å between neighbouring parallel BZIM rings suggests the existence of π – π stacking.

Experimental

An aqueous solution (5 ml) containing fumaric acid (0.12 g, 1 mmol) and NaOH (0.08 g, 2 mmol) was mixed with an aqueous solution (5 ml) of NiCl₂·6H₂O (0.24 g, 1 mmol). The mixture was refluxed for 30 min. An ethanol solution (5 ml) of benzimidazole (0.24 g, 2 mmol)

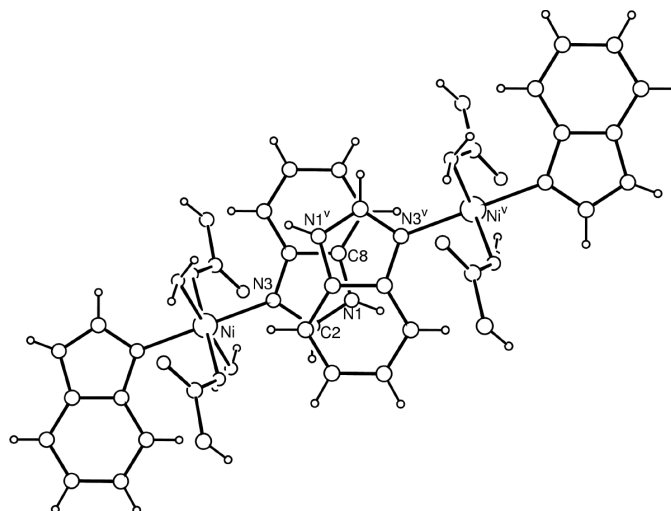


Figure 4
 π – π stacking of benzimidazole rings between neighbouring complex molecules. [Symmetry code: (v) $2 - x, 1 - y, 2 - z$.]

was then added to the above mixture and the resulting solution was refluxed for a further 3 h. After cooling to room temperature, the solution was filtered. Single crystals were obtained from the filtrate after two weeks.

Crystal data

[Ni(C₄H₂O₄)(C₇H₆N₂)₂(H₂O)₂]
 $M_r = 445.07$
 Triclinic, $P\bar{1}$
 $a = 7.0650$ (10) Å
 $b = 8.4842$ (10) Å
 $c = 8.6617$ (9) Å
 $\alpha = 98.471$ (7)°
 $\beta = 112.685$ (4)°
 $\gamma = 103.098$ (4)°
 $V = 450.37$ (10) Å³

$Z = 1$
 $D_x = 1.641$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2668 reflections
 $\theta = 3.0$ – 26.0 °
 $\mu = 1.12$ mm⁻¹
 $T = 295$ (2) K
 Prism, green
 $0.27 \times 0.14 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.74, T_{\max} = 0.89$
 3114 measured reflections

1616 independent reflections
 1511 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 25.2$ °
 $h = -8 \rightarrow 7$
 $k = -10 \rightarrow 10$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.084$
 $S = 1.05$
 1616 reflections
 139 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.3701P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.27$ e Å⁻³
 $\Delta\rho_{\min} = -0.28$ e Å⁻³

Table 1

Selected bond distances (Å, °).

Ni—O1	2.0646 (15)	O2—C11	1.263 (3)
Ni—O3	2.0984 (18)	C11—C12	1.492 (3)
Ni—N3	2.0647 (19)	C12—C12 ⁱ	1.310 (5)
O1—C11	1.257 (3)		

Symmetry code: (i) $-x, -y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O2^{ii}$	0.86	2.05	2.868 (3)	159
$O3-H3A\cdots O2^{iii}$	0.86 (5)	2.11 (5)	2.893 (3)	151 (5)
$O3-H3B\cdots O2$	0.87 (5)	1.87 (5)	2.699 (3)	159 (5)

Symmetry codes: (ii) $1-x, 1-y, 2-z$; (iii) $-x, 1-y, 1-z$.

Water H atoms were located in a difference Fourier map and refined independently with fixed isotropic displacement parameters $U_{iso} = 0.08 \text{ \AA}^2$. Other H atoms were placed in calculated positions, with C–H distances of 0.93 Å and N–H distances of 0.86 Å, and were refined in the riding mode, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR-92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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