

Tris(2,2'-biimidazole)nickel(II) phthalate

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A novel three-dimensional hydrogen-bonded complex, $[\text{Ni}(\text{C}_6\text{H}_6\text{N}_4)_3](\text{C}_8\text{H}_4\text{O}_4)$, was synthesized. Each Ni atom is six-coordinate, in a pseudo-octahedral geometry, formed by six N atoms of three chelating biimidazole ligands. It has a three-dimensional network structure, formed by extensive hydrogen bonds between $[\text{Ni}(\text{H}_2\text{biim})_3]^{2+}$ cations and phthalate anions. There are two cations and two anions in the asymmetric unit.

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Key indicators

Single-crystal X-ray study

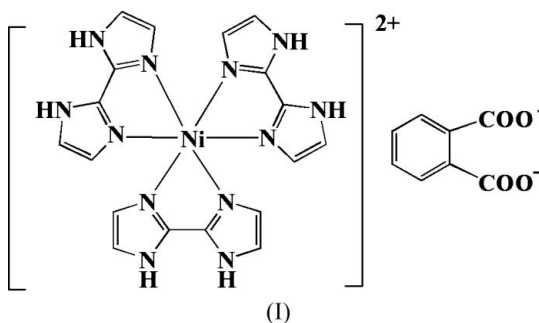
 $T = 298 \text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ R factor = 0.043 wR factor = 0.146

Data-to-parameter ratio = 16.7

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

Comment

In recent years, the controlled assembly of molecular building blocks to give three-dimensional nets connected *via* coordinate, hydrogen or covalent bonds, has been an important area for the development of molecular-based materials science (Ferey, 2001; Moulton & Zaworotko, 2002). 2,2'-Biimidazole (H_2biim) possesses dual properties, namely coordination to metal centres and the ability to act as a donor in hydrogen-bonding interactions (Fortin & Beauchamp, 2001; Sang *et al.*, 2002; Atencio *et al.*, 2004).



The structure of the title compound, (I), consists of $[\text{Ni}(\text{H}_2\text{biim})_3]^{2+}$ cations hydrogen bonded to phthalate dianions (Fig. 1). There are two cations and two anions in the asymmetric unit. The coordination geometry of the nickel(II) centres can be described as distorted octahedral, formed by six N atoms from three chelating H_2biim ligands. The main distortion results from the small N–Ni–N bite angles of the H_2biim ligands, *viz.* $78.57(8)–79.31(8)^\circ$ for $[\text{Ni1}(\text{H}_2\text{biim})_3]^{2+}$ and $79.07(8)–79.57(8)^\circ$ for $[\text{Ni2}(\text{H}_2\text{biim})_3]^{2+}$ (Table 1). The Ni–N bond lengths are in the range $2.072(2)–2.137(2) \text{ \AA}$. A similarly distorted octahedron has been reported previously for the analogous complex $[\text{Ni}^{\text{II}}(\text{Hbiim})_3](\text{NMe}_4)$ (NMe_4 is tetramethylammonium), in which the Ni–N bond lengths are in the range $1.96(3)–2.19(2) \text{ \AA}$ (Tadokoro *et al.*, 1999).

Each $[\text{Ni1}(\text{H}_2\text{biim})_3]^{2+}$ complex cation is connected to three phthalate dianions through seven $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds,

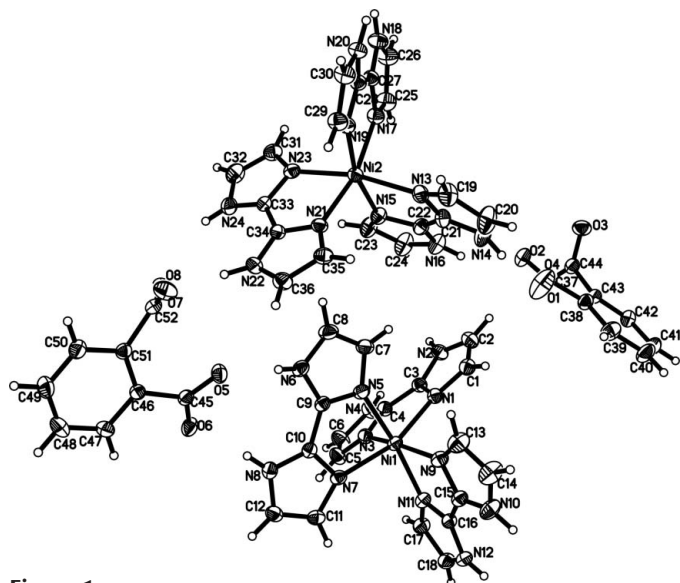


Figure 1
View of the asymmetric unit of the title complex with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

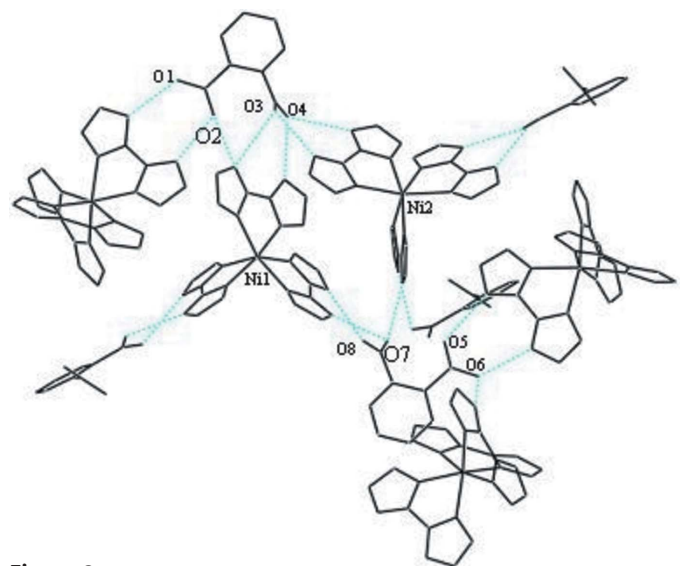


Figure 2
View of the hydrogen-bonded interactions (turquoise lines) in the title complex. H atoms have been omitted.

with N—O distances of 2.693 (3)–3.028 (3) Å (Table 2). In the hydrogen-bond environment of Ni2, however, each [Ni2(H₂biim)₃]²⁺ complex cation is connected through six strong N—H···O hydrogen bonds, with N—O distances of 2.674 (3)–2.788 (3) Å, to four phthalate dianions (Fig. 2). Through this complicated and dense three-dimensional network of hydrogen bonds, the crystal packing is formed (Fig. 3).

Experimental

All reagents were of AR grade from commercial sources and used without further purification. Biimidazole was prepared following a slightly modified procedure (Ramirez *et al.*, 2002) of Fieselmann *et al.*

(1978). Ni(CH₃COO)₂ (124.43 mg, 0.5 mmol), phthalic acid (83.074 mg, 0.5 mmol) and H₂biim (67.07 mg, 0.5 mmol) in a 1:1:1 molar ratio were added directly as solids suspended in deionized water (10 ml); after the mixture was stirred at room temperature for 30 min, a purple precipitate was obtained. The pH was adjusted to 7.0 using aqueous KOH solution. The mixture was then placed in a 25 ml Teflon-lined stainless steel vessel and heated at 433 K for 4 d. The reaction vessel was allowed to cool to room temperature slowly, and purple crystals of the title complex were obtained and collected by filtration and washed with water (yield 60%).

Crystal data

[Ni(C₆H₆N₄)₃](C₈H₄O₄)
M_r = 625.27
 Monoclinic, *P*2₁/*c*
a = 23.5242 (18) Å
b = 11.1168 (9) Å
c = 23.8578 (19) Å
 β = 115.325 (1)°
V = 5639.5 (8) Å³
Z = 8

D_x = 1.473 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 7467 reflections
 θ = 2.4–24.2°
 μ = 0.74 mm⁻¹
T = 298 (2) K
 Block, purple
 0.49 × 0.19 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
T_{min} = 0.712, *T_{max}* = 0.897
 34502 measured reflections

13575 independent reflections
 9366 reflections with *I* > 2σ(*I*)
R_{int} = 0.029
 θ_{max} = 28.3°
h = -15 → 30
k = -14 → 14
l = -31 → 27

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR (*F*²) = 0.146
S = 1.05
 13575 reflections
 811 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.086P)^2 + 0.3746P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.052$
 $\Delta\rho_{max} = 0.85 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.41 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—N11	2.072 (2)	Ni2—N19	2.076 (2)
Ni1—N5	2.090 (2)	Ni2—N21	2.088 (2)
Ni1—N3	2.102 (2)	Ni2—N23	2.097 (2)
Ni1—N9	2.119 (2)	Ni2—N13	2.098 (2)
Ni1—N1	2.123 (2)	Ni2—N17	2.107 (2)
Ni1—N7	2.137 (2)	Ni2—N15	2.124 (2)
N11—Ni1—N5	169.97 (8)	N19—Ni2—N21	92.13 (8)
N11—Ni1—N3	88.58 (8)	N19—Ni2—N23	99.52 (8)
N5—Ni1—N3	96.75 (8)	N21—Ni2—N23	79.07 (8)
N11—Ni1—N9	78.90 (8)	N19—Ni2—N13	91.66 (9)
N5—Ni1—N9	96.76 (8)	N21—Ni2—N13	94.35 (8)
N3—Ni1—N9	165.43 (8)	N23—Ni2—N13	167.17 (8)
N11—Ni1—N1	101.58 (8)	N19—Ni2—N17	79.57 (8)
N5—Ni1—N1	87.79 (8)	N21—Ni2—N17	165.64 (8)
N3—Ni1—N1	79.31 (8)	N23—Ni2—N17	90.67 (8)
N9—Ni1—N1	95.82 (8)	N13—Ni2—N17	97.57 (8)
N11—Ni1—N7	92.87 (8)	N19—Ni2—N15	166.75 (8)
N5—Ni1—N7	78.57 (8)	N21—Ni2—N15	98.11 (8)
N3—Ni1—N7	91.25 (8)	N23—Ni2—N15	90.70 (8)
N9—Ni1—N7	96.73 (8)	N13—Ni2—N15	79.25 (8)
N1—Ni1—N7	162.44 (8)	N17—Ni2—N15	91.98 (8)

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>
N2—H2A···O8 ⁱ	0.85 (2)	1.84 (2)	2.693 (3)	175 (4)
N4—H4A···O7 ⁱ	0.88 (2)	1.97 (2)	2.832 (3)	169 (3)
N6—H6A···O5	0.86 (2)	1.94 (2)	2.788 (3)	169 (4)
N8—H8A···O6	0.86 (2)	1.91 (2)	2.745 (3)	165 (3)
N10—H10A···O2 ⁱⁱ	0.89 (2)	2.40 (3)	2.990 (3)	124 (3)
N10—H10A···O3 ⁱⁱⁱ	0.89 (2)	2.22 (2)	3.028 (3)	152 (3)
N12—H12A···O4 ⁱⁱ	0.84 (2)	1.96 (2)	2.792 (3)	169 (4)
N14—H14A···O1	0.87 (2)	1.84 (2)	2.674 (3)	161 (4)
N16—H16A···O2	0.85 (2)	1.94 (2)	2.723 (3)	154 (4)
N18—H18A···O4 ⁱⁱⁱ	0.85 (2)	1.94 (2)	2.781 (3)	169 (4)
N20—H20A···O3 ⁱⁱⁱ	0.87 (2)	1.86 (2)	2.728 (3)	175 (3)
N22—H22A···O7	0.90 (2)	1.84 (2)	2.733 (3)	174 (3)
N24—H24A···O6 ^{iv}	0.84 (2)	1.99 (2)	2.788 (3)	158 (4)

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $x, -y + \frac{5}{2}, z - \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

H atoms on C atoms were treated as riding, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom. H atoms on N atoms were refined with $U_{\text{iso}}(\text{H}) = 0.08$ Å and N—H distances in the range 0.84 (2)–0.90 (2) Å. The final electron-density maximum and minimum are closest to atoms H39 and Ni2, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2000); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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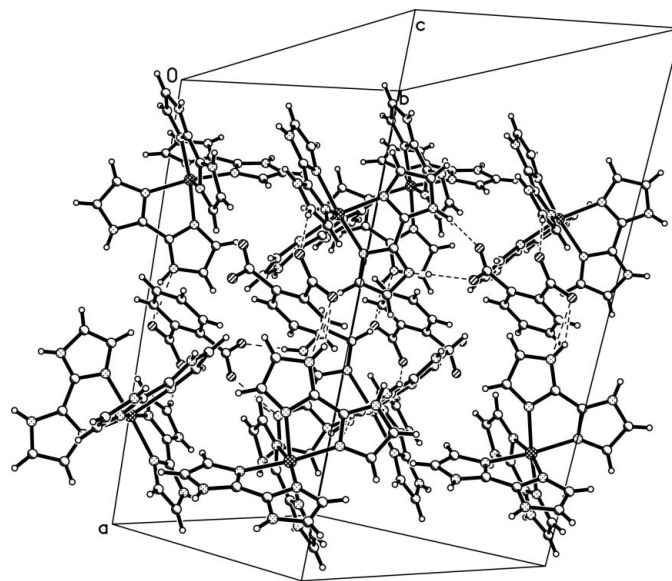


Figure 3

A packing diagram of the title complex. Hydrogen bonds are shown as dashed lines.

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