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Aqua(2,4-dihydroxybenzoato-κO^1)bis(1,10-phenanthroline-$\kappa^2 N,N'$)nickel(II) 2,4-dihydroxybenzoate monohydrate

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The crystal structure of the title compound, $[Ni(C_7H_5O_4)(C_{12}H_8N_2)_2(H_2O)](C_7H_5O_4)\cdot H_2O$, consists of Ni^{II} complex cations, 2,4-dihydroxybenzoate (dHBA) anions and solvent water molecules. The Ni^{II} complex cation assumes a distorted octahedral coordination geometry formed by two 1,10-phenanthroline (phen) ligands, one dHBA ion and a water molecule. π–π Stacking is observed between partially overlapped, parallel phen ligands and between a nearly parallel phen ligand and benzene ring of dHBA.

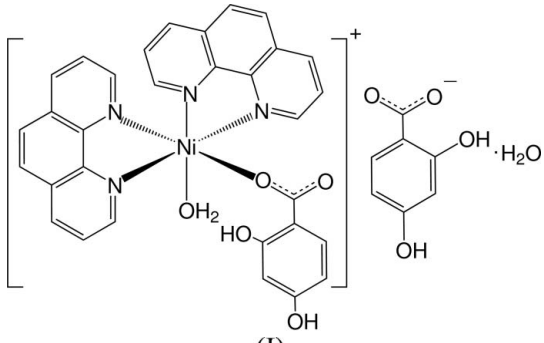
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.097
Data-to-parameter ratio = 15.8

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

Comment

As part of our ongoing investigation on the nature of π–π stacking in metal complexes (Liu *et al.*, 2004; Li *et al.*, 2005), the title Ni^{II} compound, (I), has recently been prepared and its crystal structure is presented here.



(I)

The crystal structure of (I) consists of Ni^{II} complex cations, uncoordinated 2,4-dihydroxybenzoate (dHBA) anions and solvent water molecules (Fig. 1). The Ni^{II} ion is coordinated by a dHBA anion, a water molecule and two 1,10-phenanthroline (phen) molecules with a distorted octahedral coordination geometry (Table 1). The coordinated water molecule is hydrogen bonded with the adjacent coordinated carboxylate group, resulting a larger Ni—O1—C25 bond angle of 133.46 (12)°. The two phen ligands are nearly perpendicular to each other, with a dihedral angle of 88.08 (4)°.

Aromatic π–π stacking between phen ligands is commonly observed in metal complexes (Pan & Xu, 2005; Su & Xu, 2005); it also occurs in the crystal structure of (I). A partially overlapped arrangement of parallel phen ligands is observed in the crystal structure (Fig. 2). The face-to-face separations between N3-phen and N3^{iv}-phen and between N2-phen and N2^{v}-phen are 3.494 (11) and 3.445 (5) Å, respectively [symmetry codes: (iv) $-x, 1-y, 1-z$; (v) $1-x, 2-y, 2-z$]. Moreover, the benzene ring of the uncoordinated C33^{iii}-

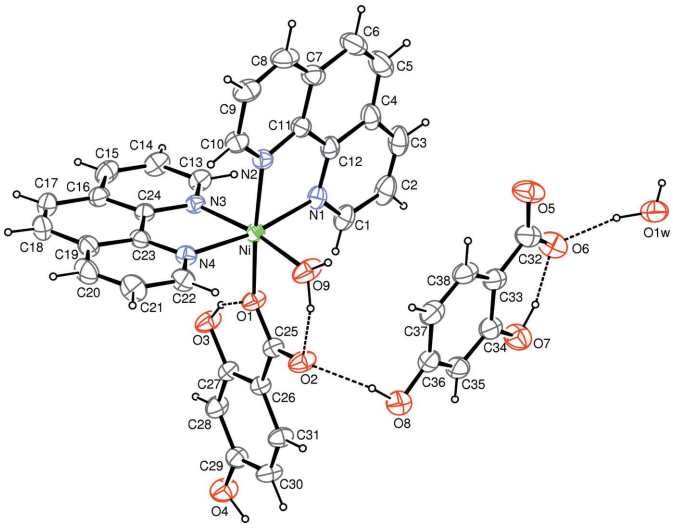


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate the hydrogen bonding.

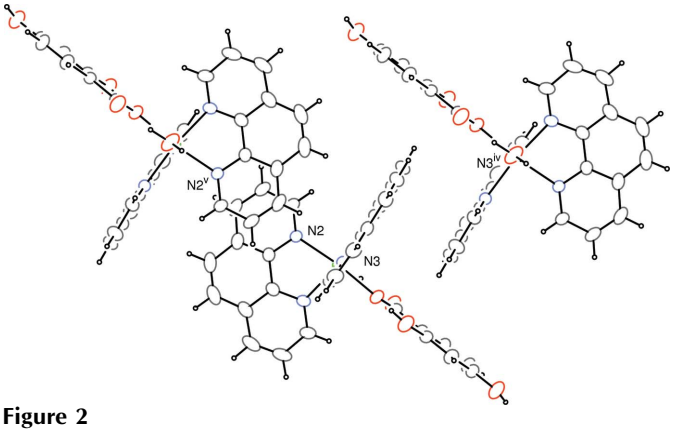


Figure 2
π–π Stacking between phen ligands [symmetry codes: (iv) $-x, 1-y, 1-z$; (v) $1-x, 2-y, 2-z$].

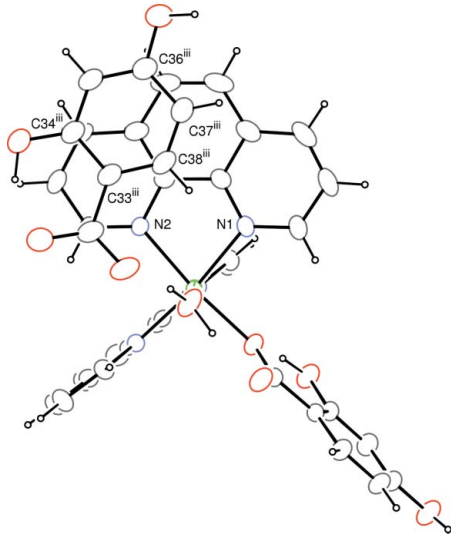


Figure 3
π–π Stacking between the N1-phen ligand and uncoordinated dHBA ion [symmetry code: (iii) $1-x, 1-y, 2-z$].

containing dHBA anion [symmetry code: (iii) $1-x, 1-y, 2-z$] is nearly parallel to the N1-phen ligand [dihedral angle 5.27 (10)°] and partially overlapped with the N1-phen ligand (Fig. 3). The separations of C33^{iii}, C37^{iii} and C38^{iii} from the N1-phen plane are 3.532 (3), 3.321 (3) and 3.426 (3) Å, respectively. These findings suggest the existence of π–π stacking between the N1-phen ligand and the C33^{iii}-benzene ring of the dHBA anion.

Extensive intra- and intermolecular O—H···O hydrogen bonding is observed in the crystal structure (Table 2). Weak C—H···O hydrogen bonding also occurs between Ni^{II} complex cations in the crystal.

Experimental

A water (15 ml) and ethanol (5 ml) mixture containing $Ni(NO_3)_2{\cdot}6H_2O$ (1 mmol), 2,4-dihydroxybenzoic acid (2 mmol), phen (1 mmol) and Na_2CO_3 (1 mmol) was refluxed for 3 h, and filtered after cooling to room temperature. Single crystals of (I) were obtained from the filtrate after 2 d.

Crystal data

$[Ni(C_7H_5O_4)(C_{12}H_8N_2)_2(H_2O)]$-$(C_7H_5O_4){\cdot}H_2O$
M_r = 761.37
Triclinic, $P\overline{1}$
a = 12.347 (4) Å
b = 13.408 (6) Å
c = 13.578 (6) Å
α = 118.829 (14)°
β = 90.106 (14)°
γ = 116.327 (13)°
V = 1697.1 (13) Å^3
Z = 2
D_x = 1.490 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.64 mm^{-1}
T = 295 (2) K
Prism, green
0.35 × 0.19 × 0.13 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.785, T_{max} = 0.920
16731 measured reflections
7612 independent reflections
5990 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.097
S = 1.07
7612 reflections
482 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.1081P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—O1	2.0681 (15)	Ni—N2	2.1002 (17)
Ni—O9	2.0279 (16)	Ni—N3	2.1047 (17)
Ni—N1	2.0723 (16)	Ni—N4	2.0748 (15)
O9—Ni—O1	89.00 (7)	N1—Ni—N2	79.85 (6)
O9—Ni—N1	92.39 (7)	N4—Ni—N2	93.00 (6)
O1—Ni—N1	93.98 (6)	O9—Ni—N3	171.54 (6)
O9—Ni—N4	94.57 (7)	O1—Ni—N3	85.28 (7)
O1—Ni—N4	93.06 (6)	N1—Ni—N3	94.21 (6)
N1—Ni—N4	170.18 (6)	N4—Ni—N3	79.55 (6)
O9—Ni—N2	91.80 (7)	N2—Ni—N3	94.55 (7)
O1—Ni—N2	173.81 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1A···O6	0.99	1.77	2.715 (3)	159
O1W—H1B···O5^{i}	0.91	1.78	2.685 (3)	172
O3—H3···O1	0.99	1.58	2.517 (2)	157
O4—H4···O1W^{ii}	0.92	1.68	2.589 (3)	172
O7—H7···O6	0.96	1.62	2.508 (3)	151
O8—H8···O2	0.94	1.87	2.733 (3)	151
O9—H9A···O2	0.97	1.72	2.632 (3)	155
O9—H9B···O5^{iii}	0.96	1.66	2.611 (3)	167
C20—H20···O3^{iv}	0.93	2.59	3.509 (4)	168

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

H atoms of the water molecules and hydroxy groups were located in a difference Fourier map and refined as riding in their as-found relative positions with $U_{iso}(H) = 1.5U_{eq}(O)$. Aromatic H atoms were placed in calculated positions with C—H = 0.93 Å, and refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (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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