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cis-Aquachlorobis(1,10-phenanthroline)nickel(II) chloride 4-hydroxybenzoic acid dihydrate

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Key indicators

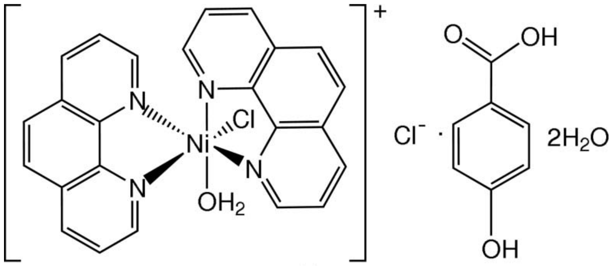
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.041
wR factor = 0.145
Data-to-parameter ratio = 17.0

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

The title compound, $[NiCl(C_{12}H_8N_2)_2(H_2O)]Cl\cdot C_7H_6O_3\cdot 2H_2O$, is composed of Ni^{II} complex cations, uncoordinated chloride anions, 4-hydroxybenzoic acid (HBA) and uncoordinated water molecules. The Ni^{II} atom is surrounded by two phenanthroline (phen) molecules, a chloride anion and a water molecule in a distorted octahedral geometry. π–π stacking occurs between parallel phen ligands and between the nearly parallel carboxyl groups of HBA and the phen ligands.

Comment

As part of our ongoing investigation on the nature of π–π stacking in metal complexes (Su & Xu, 2005), the title compound, (I), incorporating phenanthroline (phen), has been prepared and its crystal structure is presented here.



(I)

The crystal structure of (I) consists of Ni^{II} complex cations, uncoordinated chloride anions, free 4-hydroxybenzoic acid (HBA) and uncoordinated water molecules. The molecular structure of (I) is shown in Fig. 1; the Ni atom is surrounded by two phen ligands, a coordinated chloride anion and one coordinated water molecule in a distorted octahedral geometry (Table 1). The coordination is similar to that found in *cis*-aquachlorobis(1,10-phenanthroline)nickel(II) chloride ethanol solvate monohydrate (Brewer *et al.*, 2003).

An overlapping arrangement of parallel phen ligands of neighbouring cations is observed (Fig. 2). The face-to-face separations between N1-phen and $N1^{vi}$-phen and between N3-phen and $N3^{vii}$-phen are 3.522 (8) and 3.433 (7) Å, respectively [symmetry codes: (vi) $1 - x, 1 - y, 2 - z$; (vii) $2 - x, 1 - y, 1 - z$]. The separations suggest the existence of π–π stacking.

Adjacent HBA molecules are linked, *via* an O—H···O hydrogen bond that involves the carboxyl group, to form a supramolecular dimer (Fig. 3); the hydrogen-bonded HBA dimer is nearly parallel to the N3/N4-phen mean plane [dihedral angle = 5.4 (3)°]. The partially overlapped arrangement between the HBA dimer and N3/N4-phen is illustrated

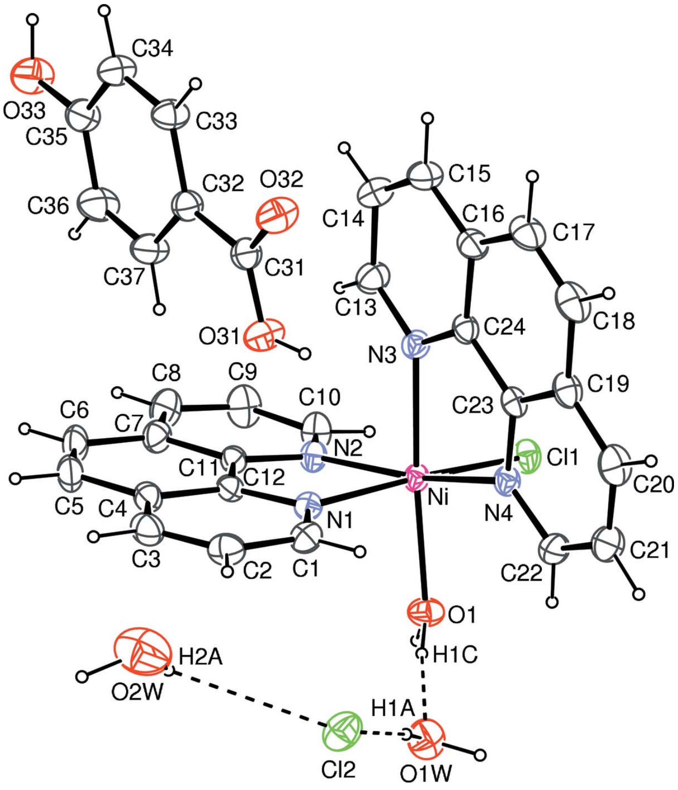


Figure 1
The asymmetric unit of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate hydrogen bonds.

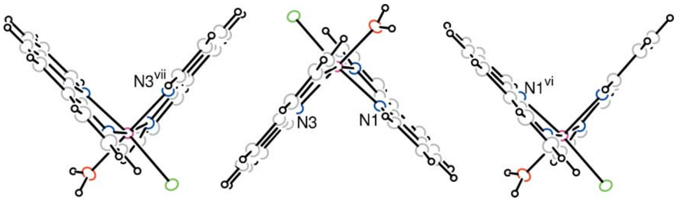


Figure 2
A diagram showing the parallel arrangement of phen rings.

in Fig. 3. The somewhat short distances to the N3/N4-phen mean plane [O31 3.318 (3), C31 3.435 (4) and O32^{iv} 3.364 (4) Å] suggest the existence of π–π stacking between the carboxyl groups and the phen ligands.

Extensive hydrogen bonding occurs in the crystal structure. Neighbouring complex cations are also linked by O—H···Cl hydrogen bonds. The uncoordinated chloride anion is simultaneously hydrogen bonded to four uncoordinated water molecules (Table 2).

Experimental

An aqueous solution (10 ml) containing $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol), HBA (0.14 g, 1 mmol) and Na_2CO_3 (0.05 g, 0.25 mmol) was added to an ethanol solution (10 ml) of phen (0.20 g, 1 mmol). The mixture was refluxed for 5 h and then filtered. Green crystals were obtained after about six months.

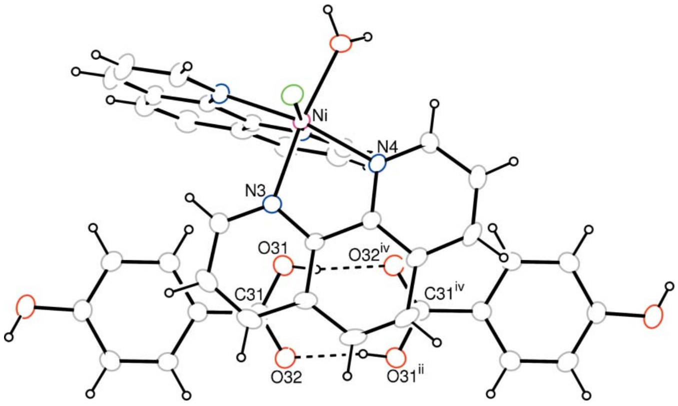


Figure 3
A diagram showing the overlapped arrangement between phen and hydrogen-bonded (dashed lines) HBA dimer.

Crystal data

$[NiCl(C_{12}H_8N_2)_2(H_2O)]Cl \cdot C_7H_6O_3 \cdot 2H_2O$
$M_r = 682.18$
Triclinic, $P\overline{1}$
$a = 10.670$ (5) Å
$b = 12.553$ (5) Å
$c = 13.505$ (5) Å
$\alpha = 115.242$ (12)°
$\beta = 93.281$ (17)°
$\gamma = 110.841$ (17)°
$V = 1481.7$ (11) Å^3
$Z = 2$
$D_x = 1.529$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12708 reflections
$\theta = 3.0$–26.6°
$\mu = 0.89$ mm^{-1}
$T = 295$ (3) K
Block, green
0.35 × 0.30 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.736$, $T_{max} = 0.849$
14658 measured reflections
6737 independent reflections
5197 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 15$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.145$
$S = 1.03$
6737 reflections
397 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0988P)^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—O1	2.087 (2)	Ni—N3	2.105 (2)
Ni—N1	2.095 (2)	Ni—N4	2.072 (2)
Ni—N2	2.092 (2)	Ni—Cl1	2.4246 (12)
O1—Ni—N1	87.56 (9)	N1—Ni—Cl1	171.40 (6)
O1—Ni—N2	95.69 (9)	N2—Ni—N3	91.15 (9)
O1—Ni—N3	172.87 (8)	N2—Ni—N4	168.35 (9)
O1—Ni—N4	93.57 (9)	N2—Ni—Cl1	93.62 (7)
O1—Ni—Cl1	87.88 (7)	N3—Ni—N4	79.39 (9)
N1—Ni—N2	79.59 (9)	N3—Ni—Cl1	93.71 (7)
N1—Ni—N3	91.72 (9)	N4—Ni—Cl1	93.77 (7)
N1—Ni—N4	93.79 (9)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···Cl2	0.94	2.29	3.221 (4)	174
O1*W*—H1*B*···Cl2$^{\rm i}$	0.85	2.34	3.183 (4)	169
O2*W*—H2*A*···Cl2	0.90	2.79	3.449 (5)	131
O2*W*—H2*B*···Cl2$^{\rm ii}$	0.99	2.41	3.286 (5)	148
O1—H1*C*···O1*W*	0.85	1.89	2.731 (4)	171
O1—H1*D*···Cl1$^{\rm iii}$	0.87	2.36	3.227 (3)	171
O31—H31···O32$^{\rm iv}$	0.81	1.88	2.652 (4)	160
O33—H33···Cl1$^{\rm v}$	0.86	2.26	3.099 (3)	164

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

The H atoms on the aromatic rings were placed in calculated positions, with C—H = 0.93 Å, and were included in the final cycles of refinement in riding mode, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Other H atoms were located in a difference Fourier map and refined riding in their as-found positions relative to the O atoms, with a fixed isotropic displacement parameter of 0.08 Å^2.

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: *ORTEP3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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