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## Key indicators

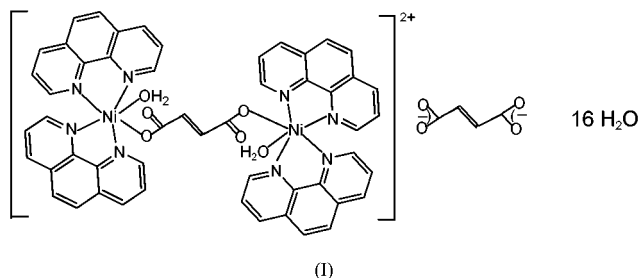
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$   
 $R$  factor = 0.057  
 $wR$  factor = 0.143  
Data-to-parameter ratio = 13.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.A nickel(II) fumarate complex with  
*o*-phenanthroline

In the dinuclear and centrosymmetric title complex,  $\mu$ -fumarato-bis[aquabis(1,10-phenanthroline)nickel(II)] fumarate hexadecahydrate,  $[\text{Ni}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)_4(\text{H}_2\text{O})_2] \cdot (\text{C}_4\text{H}_2\text{O}_4) \cdot 16\text{H}_2\text{O}$  or  $[\text{Ni}_2(\text{phen})_4\text{L}(\text{H}_2\text{O})_2]\text{L} \cdot 16\text{H}_2\text{O}$ , where phen = 1,10-phenanthroline and  $\text{L}^{2-}$  = fumarate, the nickel(II) cation is six-coordinated by two O atoms, one from a water molecule and the other from one end of a bridging  $\text{L}^{2-}$  anion, and four N atoms from two bidentate phen ligands. Each of the two independent  $\text{L}^{2-}$  anions is located about an inversion centre. Interestingly, one  $\text{L}^{2-}$  anion is bridging and the other acts as a counter-ion. The  $[\text{Ni}_2(\text{phen})_4\text{L}(\text{H}_2\text{O})_2]^{2+}$  cations, water molecules and  $\text{L}^{2-}$  anions are connected through complex hydrogen-bonding interactions to form a three-dimensional structure.

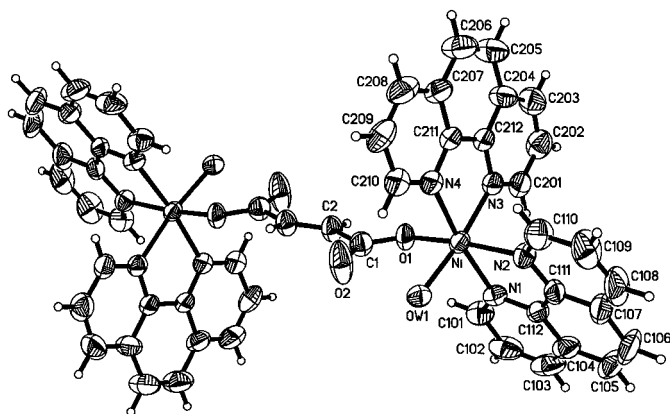
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## Comment

Recently, studies on metal-dicarboxylate complexes with aromatic *N*-donor chelating ligands have attracted special attention because of their interesting structural and chemical properties (Robl, 1992). It is well established that fumaric acid is a versatile ligand and that the coordination mode for fumarate,  $\text{L}^{2-}$ , can be tailored by introducing different neutral ligands to the complex (Young *et al.*, 1998). In our previous work, we have studied the effects of phen on cobalt(II), zinc(II) and cadmium(II) fumarate complexes, respectively (Ma *et al.*, 2003; Yang, Ma, Li & Liu, 2003; Yang, Ma & Liu, 2003). In this paper, we present the preparation and crystal structure of a nickel(II) complex of 1,10-phenanthroline containing  $\text{L}^{2-}$  anions (Fig. 1 and Table 1).



In the structure of (I), the coordination environment of each nickel(II) cation is defined by two O atoms, one from a water molecule and the other from one end of a bridging  $\text{L}^{2-}$  anion, and four N atoms from two chelating phen molecules. The distance between Ni and O2 is 3.288 (4) Å, an observation that confirms the monodentate coordination mode of each end of the  $\text{L}^{2-}$  anion. The charge balance of the dinuclear dication is provided by an uncoordinated fumarate ion, located about a centre of inversion. It is interesting that one  $\text{L}^{2-}$  anion bridges



**Figure 1**  
View of the local coordination of dinuclear (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

two nickel(II) centres to form a dinuclear cation, and the other acts as a counter-ion. The Ni...Ni ( $-x, -y, -z$ ) distance is 9.730 (3) Å. In the reported structures of  $[M(\text{phen})_2(-2\text{O})_2]L \cdot 4\text{H}_2\text{O}$ ,  $M = \text{Zn}$  and  $\text{Cd}$ , the  $L^{2-}$  anions do not coordinate the central metal cation but, rather, act as counter-ions. There are sixteen non-coordinating water molecules in the unit cell of (I).

The constituents of (I) are linked through hydrogen bonds to form a complicated three-dimensional network (Table 2). The water molecules play a role as both acceptors and donors, while the carboxylate-O atoms function only as acceptors, confirming their deprotonation.

## Experimental

A mixture of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.238 g, 1 mmol), fumaric acid (0.116 g, 1 mmol) and  $\text{NaOH}$  (0.080 g, 2 mmol) in water (10 ml) was stirred at room temperature, then 1,10-phenanthroline (0.198 g, 1 mmol) was added to the suspension. Green crystals of (I) were obtained from the solution after several days. Analysis calculated for  $[\text{Ni}_2(\text{phen})_4L(-2\text{O})_2]L \cdot 16\text{H}_2\text{O}$ , C 48.37, H 5.22, N 8.06. Found: C 48.51, H 5.43, N 7.92%.

### Crystal data

$[\text{Ni}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)_4(\text{H}_2\text{O})_2] \cdot (\text{C}_4\text{H}_2\text{O}_4) \cdot 16\text{H}_2\text{O}$   
 $M_r = 1390.60$   
 Triclinic,  $P\bar{1}$   
 $a = 10.736$  (4) Å  
 $b = 10.903$  (3) Å  
 $c = 14.802$  (5) Å  
 $\alpha = 86.68$  (3)°  
 $\beta = 86.27$  (3)°  
 $\gamma = 72.46$  (3)°  
 $V = 1647.3$  (10) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.402$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 22 reflections  
 $\theta = 4.7\text{--}9.3^\circ$   
 $\mu = 0.66$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, green  
 $0.44 \times 0.35 \times 0.32$  mm

### Data collection

Siemens P4 diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.734$ ,  $T_{\max} = 0.810$   
 7676 measured reflections  
 6365 independent reflections  
 3577 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$   
 $\theta_{\text{max}} = 26.0^\circ$   
 $h = -1 \rightarrow 13$   
 $k = -13 \rightarrow 13$   
 $l = -18 \rightarrow 18$   
 3 standard reflections every 97 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.143$   
 $S = 0.88$   
 6365 reflections  
 469 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.63$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.49$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ni—O1	2.070 (3)	Ni—N2	2.102 (4)
Ni—OW1	2.068 (4)	Ni—N3	2.086 (4)
Ni—N1	2.094 (4)	Ni—N4	2.102 (4)
O1—Ni—Ow1	90.76 (13)	OW1—Ni—N4	93.49 (14)
O1—Ni—N1	91.27 (14)	N1—Ni—N2	79.51 (15)
O1—Ni—N2	170.68 (14)	N1—Ni—N3	96.19 (15)
O1—Ni—N3	87.76 (13)	N1—Ni—N4	173.17 (15)
O1—Ni—N4	94.03 (14)	N2—Ni—N3	91.88 (15)
OW1—Ni—N1	90.74 (14)	N2—Ni—N4	95.07 (15)
OW1—Ni—N2	90.70 (14)	N3—Ni—N4	79.74 (15)
OW1—Ni—N3	172.94 (14)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{--}H \cdots A$	$D\text{--}H$	$H \cdots A$	$D \cdots A$	$D\text{--}H \cdots A$
OW1—H12...O2	0.79 (2)	1.88 (2)	2.648 (5)	163 (5)
OW1—H11...O3 <sup>i</sup>	0.80 (2)	1.94 (2)	2.727 (5)	170 (5)
OW2—H22...OW3 <sup>ii</sup>	0.80 (2)	2.00 (2)	2.799 (6)	170 (5)
OW2—H21...OW3 <sup>iii</sup>	0.80 (2)	2.04 (3)	2.789 (6)	157 (5)
OW3—H31...O4 <sup>iv</sup>	0.80 (2)	1.94 (2)	2.735 (6)	178 (5)
OW3—H32...OW7	0.82 (4)	2.04 (2)	2.808 (7)	157 (4)
OW4—H42...O3 <sup>i</sup>	0.84 (2)	2.00 (2)	2.823 (6)	168 (5)
OW4—H41...OW2 <sup>v</sup>	0.82 (2)	2.06 (3)	2.800 (6)	150 (5)
OW5—H52...O4	0.786 (19)	2.18 (3)	2.780 (7)	133 (3)
OW5—H51...OW6	0.81 (4)	2.12 (2)	2.871 (8)	154 (4)
OW6—H62...O2 <sup>vi</sup>	0.824 (19)	2.17 (2)	2.960 (7)	159 (4)
OW7—H71...OW4 <sup>iv</sup>	0.744 (19)	2.30 (3)	2.914 (7)	141 (5)
OW7—H72...OW6 <sup>iv</sup>	0.979 (16)	2.00 (3)	2.815 (8)	139 (4)
OW8—H82...O1 <sup>v</sup>	0.772 (19)	2.22 (2)	2.978 (6)	167 (4)
OW8—H81...OW4	0.716 (19)	2.09 (2)	2.784 (6)	163 (4)
OW9—H92...OW5	0.797 (15)	2.18 (2)	2.755 (8)	129 (2)
OW9—H91...OW8 <sup>vi</sup>	0.765 (19)	2.75 (4)	2.941 (10)	97 (3)

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

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with  $\text{C—H} = 0.93$  Å and  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ . The H atoms of the water molecules were located and refined with  $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$ .

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; 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.

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