

Tris(phenanthroline- κ^2N,N')nickel(II) dibromosuccinate heptahydrateDai-Xi Li,[‡] Duan-Jun Xu* and
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The crystal structure of the title compound, $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3] \cdot (\text{C}_4\text{H}_2\text{Br}_2\text{O}_4) \cdot 7\text{H}_2\text{O}$, consists of discrete nickel(II) complex cations, dibromosuccinate dianions and uncoordinated water molecules. The Ni^{II} atom is surrounded by three phenanthroline ligands in a distorted octahedral geometry. The overlapped arrangement and short face-to-face distances of 3.525 (12) and 3.369 (5) Å between parallel phen planes of neighboring complexes indicate π - π stacking. The dibromosuccinate dianions are located on inversion centers and are linked to uncoordinated water molecules *via* hydrogen bonds.

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Key indicators

Single-crystal X-ray study

 $T = 295 \text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$

Disorder in solvent or counterion

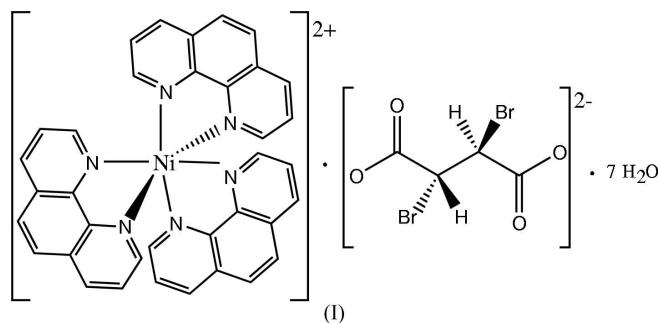
 R factor = 0.052 wR factor = 0.133

Data-to-parameter ratio = 13.8

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

Comment

Recently, we have been interested in the nature of π - π stacking as it plays an important role in some biological processes (Deisenhofer & Michel, 1989). A series of metal complexes incorporating different aromatic ligands has been prepared and their crystal structures provide useful information about π - π stacking (Wu *et al.*, 2003; Pan & Xu, 2004; Li *et al.*, 2005). As part of ongoing investigations, the title complex, incorporating 1,10-phenanthroline (phen), (I), has been prepared.



The crystal structure of (I) consists of nickel(II) complex cations, dibromosuccinate (DBrS) dianions and uncoordinated water molecules, as shown in Fig. 1. The Ni^{II} atom is coordinated by three phen ligands in a distorted octahedral geometry. The DBrS dianions are each located on an inversion center and the carbon skeletons are thus planar. DBrS dianions link the Ni^{II} complex cations *via* weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2). Water molecules and DBrS dianions are held together *via* classical $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a hydrophilic layer, which is inserted between hydrophobic layers formed by Ni^{II} complexes to form a sandwich crystal structure, as shown in Fig. 2.

An overlapped arrangement of phen rings of neighboring complexes is observed (Fig. 3); face-to-face distances of 3.525 (12) Å between parallel N1-phen and N1-phen^{viii}

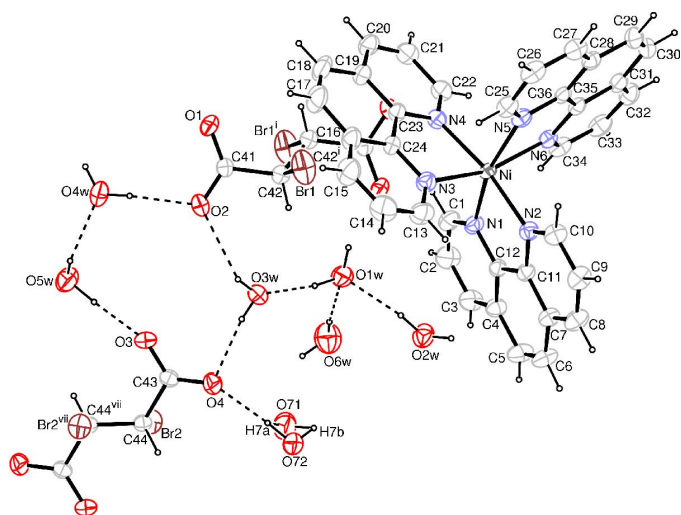


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate classical hydrogen bonds [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (vii) $2 - x, -y, 2 - z$].

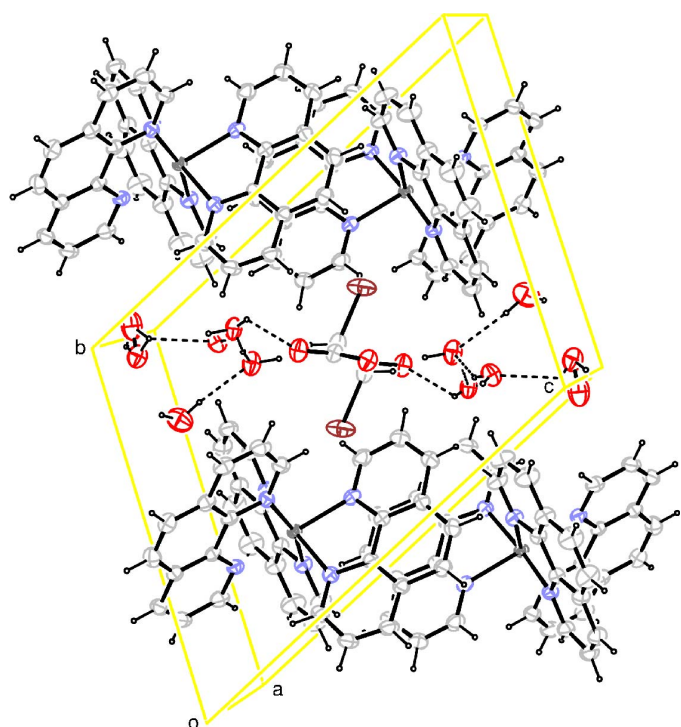
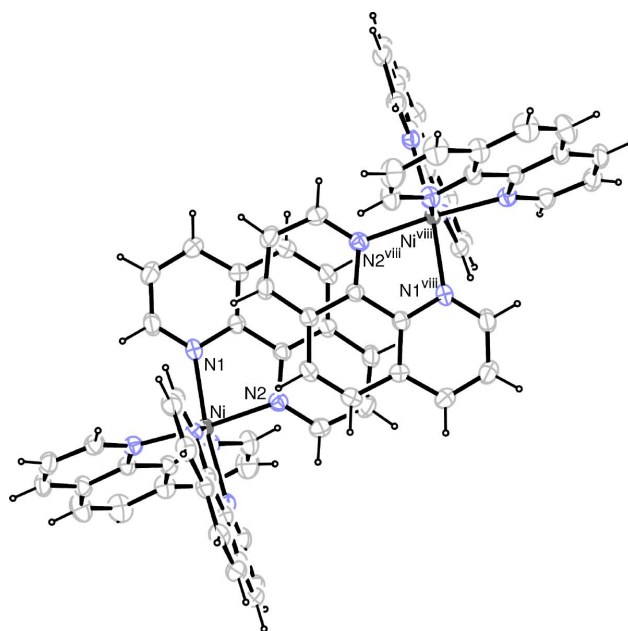


Figure 2
The packing, showing the sandwich structure formed by hydrophilic and hydrophobic layers. Dashed lines indicate hydrogen bonds.

[symmetry code: (viii) $-x, -y, 1 - z$] and $3.369(5) \text{ \AA}$ between parallel N5-phen and N5-phen^{ix} [symmetry code: (ix) $-x, 1 - y, -z$] indicate the existence of π - π stacking.

Experimental

An aqueous solution (5 ml) of NiCl₂·6H₂O (0.24 g, 1 mmol) was mixed with an aqueous solution (5 ml) containing H₂DBrS (0.55 g, 2 mmol) and Na₂CO₃ (0.21 g, 2 mmol). The solution was refluxed for

Figure 3
 π - π stacking between phen rings of neighboring complex cations [symmetry codes: (viii) $-x, -y, 1 - z$; (ix) $-x, 1 - y, -z$].

30 min, then phen (0.36 g, 2 mmol) was added. The mixture was refluxed for a further 30 min and filtered. Green single crystals of (I) were obtained from the filtrate after 5 d.

Crystal data

[Ni(C ₁₂ H ₈ N ₂) ₃](C ₄ H ₂ Br ₂ O ₄)·7H ₂ O	Z = 2
<i>M_r</i> = 999.27	<i>D_x</i> = 1.562 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo K α radiation
<i>a</i> = 12.3571 (11) Å	Cell parameters from 9880 reflections
<i>b</i> = 12.6397 (12) Å	θ = 2.0–25.0°
<i>c</i> = 15.3369 (12) Å	μ = 2.40 mm ⁻¹
α = 67.286 (3)°	<i>T</i> = 295 (2) K
β = 89.668 (3)°	Prism, green
γ = 75.133 (2)°	0.52 × 0.48 × 0.43 mm
<i>V</i> = 2124.0 (3) Å ³	

Data collection

Rigaku R-AXIS RAPID
diffractometer
 ω scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.286$, $T_{\max} = 0.352$
12401 measured reflections

7599 independent reflections
5543 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 25.2^\circ$
 $h = -14 \rightarrow 14$
 $k = -15 \rightarrow 15$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.133$
 $S = 1.01$
7599 reflections
550 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 4.025P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.09 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.39 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (\AA).

Ni—N1	2.120 (4)	Ni—N4	2.087 (4)
Ni—N2	2.082 (4)	Ni—N5	2.195 (4)
Ni—N3	2.152 (4)	Ni—N6	2.165 (4)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1A \cdots O3W	0.92	1.84	2.750 (6)	172
O1W—H1B \cdots O1 ⁱ	0.90	1.89	2.767 (6)	161
O2W—H2A \cdots O5W ⁱⁱ	0.81	2.17	2.804 (6)	136
O2W—H2B \cdots O1W	0.92	1.95	2.781 (6)	149
O3W—H3A \cdots O4	0.86	1.96	2.794 (5)	163
O3W—H3B \cdots O2	0.87	2.30	2.930 (6)	130
O4W—H4A \cdots O2	0.86	2.00	2.799 (6)	154
O4W—H4B \cdots O4W ⁱⁱⁱ	0.87	2.46	2.838 (6)	107
O5W—H5A \cdots O3	0.97	1.77	2.734 (6)	172
O5W—H5B \cdots O4W	0.88	2.08	2.816 (6)	141
O6W—H6A \cdots O1W	0.88	2.11	2.981 (7)	171
O6W—H6B \cdots O71	0.88	2.54	3.198 (16)	132
O71—H7A \cdots O4	0.96	1.99	2.774 (13)	137
O71—H7B \cdots O71 ^{iv}	0.91	2.49	2.955 (19)	113
O72—H7A \cdots O4	0.91	2.00	2.844 (11)	155
O72—H7B \cdots O72 ^{iv}	0.83	2.48	2.904 (13)	113
C2—H2 \cdots O1 ⁱ	0.93	2.44	3.172 (8)	135
C9—H9 \cdots O3 ^v	0.93	2.52	3.319 (7)	144
C21—H21 \cdots O3 ⁱ	0.93	2.35	3.223 (8)	155
C26—H26 \cdots O2W ^{vi}	0.93	2.59	3.517 (7)	175
C33—H33 \cdots O1 ⁱⁱ	0.93	2.30	3.170 (7)	155
C42—H42 \cdots O3W	0.98	2.54	3.376 (7)	143

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

As the initial anisotropic refinement showed unusually large displacement parameters for O7W, this was separated into two atoms (O71 and O72). The occupancies of O71 and O72 were refined and converged to 0.487 (4) and 0.513 (4), respectively; they were fixed as 0.5 each in the final cycles of refinement. A difference Fourier map showed that O71 and O72 share the same H atoms (H7A and H7B), which were included in the structure-factor calculations with fixed positional parameters and isotropic displacement parameters of 0.06 \AA^2 . H atoms on ordered water molecules were located in a difference Fourier map and refined as riding in their as-found positions relative to O atoms, with fixed isotropic displacement parameters of 0.06 \AA^2 . H atoms on aromatic rings were placed in calculated positions, with C—H = 0.93 \AA and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atoms. The highest peak and deepest hole in the final difference Fourier map lie 0.94 and 0.92 \AA , respectively, from atom Br1.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK and Rigaku, 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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