

Formation of a one-dimensional water chain containing two linking patterns of planar water tetramers

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Received 15 August 2007

Accepted 26 September 2007

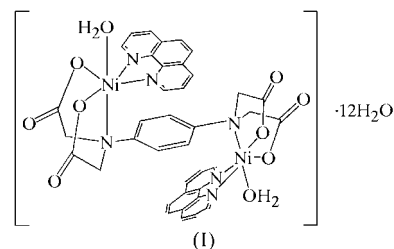
Online 13 October 2007

The self-assembly of the title dinuclear complex, namely (μ -*p*-phenylenediamine-*N,N,N',N'*-tetraacetato)bis[aqua(1,10-phenanthroline)nickel(II)] dodecahydrate, $[\text{Ni}_2(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_8)(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot 12\text{H}_2\text{O}$, through intricate noncovalent interactions results in a two-dimensional sheet-like structure. The dimer lies about an inversion centre at the centre of the *p*-phenylenediamine ring. Uncoordinated water molecules form one-dimensional chains in which cyclic water tetramers act as two types of building blocks. The water molecules play a significant role in the stabilization of the three-dimensional supramolecular framework. Intramolecular 'aryl-metal chelate ring' π - π interactions are also observed.

Comment

Water is one of the most challenging targets in biology and chemistry. In these fields, intense study is currently devoted to a variety of water clusters and low-dimensional polymeric water/ice assemblies (Chacko & Saenger, 1981; Ludwig & Appelhagen, 2005; Moorthy *et al.*, 2002; Wei *et al.*, 2006; Zabel *et al.*, 1986). The number of different water clusters, including dimers (Chand & Bharadwaj, 1998; Manikumari *et al.*, 2002), tetramers (Beobide *et al.*, 2006; Lakshminarayanan *et al.*, 2005; Supriya & Das, 2003), pentamers (Infantes & Motherwell, 2002; Ma *et al.*, 2004a), hexamers (Zhang, Fang & Wu *et al.*, 2005), octamers (Atwood *et al.*, 2001; Blanton *et al.*, 1999), decamers (Barbour *et al.*, 2000, 1998), dodecamers (Neogi *et al.*, 2004), tetradecamers (Ghosh *et al.*, 2005), hexadecamers (Ghosh & Bharadwaj, 2004) and octadecamers (Raghuraman *et al.*, 2003), and infinite one- (Neogi & Bharadwaj, 2005) and two-dimensional (Janiak & Scharman, 2002; Ma *et al.*, 2004b; Zhang, Lin, Huang & Chen, 2005) polymers, has increased dramatically in the past decade. Crystal engineering provides a powerful tool to reveal the nature of the interactions between water molecules. Investigation suggests that the water mol-

ecule is one of the key factors in the formation of organic or metal-organic supramolecular frameworks in which water molecules are encapsulated as guests. The work presented here reports the structural architectural system of hydrogen bonding and π - π stacking interactions which assembles the title complex, $[\text{Ni}_2(\text{dbta})(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 12\text{H}_2\text{O}$ (dbta is *p*-phenylenediamine-*N,N,N',N'*-tetraacetate and phen is 1,10-phenanthroline), (I), in which interesting polymeric water chains are found.



Compound (I) consists of two Ni^{II} cations, two phen ligands, one dbta ligand, two coordinated water molecules and 12 uncoordinated solvent water molecules. Each metal ion is six-coordinated in a slightly distorted octahedral geometry, with equatorial coordination by two carboxylate O atoms from dbta and two N atoms from phen. The axial sites are occupied by an aqua O atom and an N atom from dbta (Table 1).

The complex displays a zigzag-like shape (Fig. 1). In this arrangement, the benzene ring of dbta is fixed between two phen rings, similar to the mixed-ligand Ni or Co complexes (Hao, Li, Chen & Zhang, 2006; Hao, Li, Chen, Zhang *et al.*, 2006). The dimer lies about an inversion centre at the centre of the *p*-phenylenediamine ring. The centroid-to-centroid distance between the Ni-(N-heterocyclic) chelate ring and the benzene ring is 3.45 Å and the dihedral angle between the planes of these rings is 19.3°. These parameters suggest that

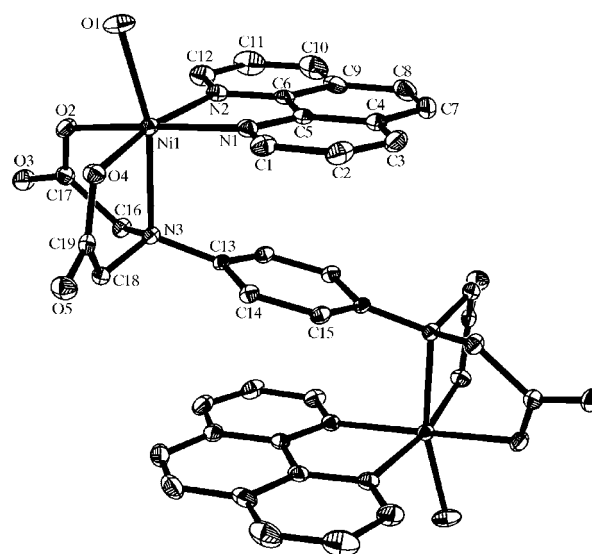


Figure 1

A perspective view of the zigzag-like structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and uncoordinated water molecules have been omitted for clarity. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x + 1, -y + 1, -z)$.

there are intramolecular ‘metal-chelate ring–aromatic ring’ π – π interactions. These structural features can be viewed as evidence of metalloaromaticity (Castiñeiras *et al.*, 2002; Masui, 2001). Weak intra- and intermolecular π – π stacking interactions between benzene rings (3.53–3.69 Å) (Fig. 2), accompanied by double hydrogen bonds between the coordinated water molecule and a carboxylate O atom of an adjacent complex [O1···O4(–*x*, –*y*, –*z*) = 2.776 (2) Å and O1–H1A···O4 = 177°], connect the complexes to form a two-dimensional sheet.

Uncoordinated solvent water molecules are trapped in the host framework as infinite parallel chains. A closer view of the water chain is depicted in Fig. 3, and important bond distances and angles related to the water chain are given in Table 1. The primary parts of the chain are two tetrameric cyclic rings formed by atoms O6 and O8 and their symmetry-related atoms O6ⁱ and O8ⁱ (ring A), and by atoms O9 and O10 and

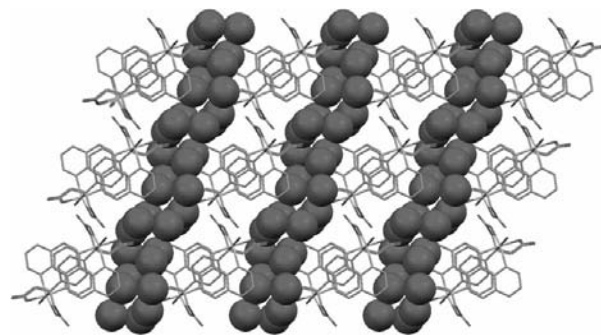


Figure 4
A space-filling view, along the *b* axis, of the one-dimensional water chains in the structure of (I).

their symmetry-related atoms O9ⁱⁱⁱ and O10ⁱⁱⁱ (ring B) (see Fig. 3 for symmetry codes). It is interesting that the cyclic water tetramer can provide a model for understanding liquid water and ice in theoretical and experimental studies (Ludwig, 2001; Herbert & Head-Gordon, 2006). The H and O atoms involved in these rings are almost coplanar. The configurations of the cyclic water tetramers, rings A and B, are uudd (u is up and d is down; Long *et al.*, 2004; Ugalde *et al.*, 2000). For ring A, the H atoms on atoms O6 and O8 not included in the ring are 0.43 and 0.76 Å above the ring, respectively, while the H atoms of atoms O6ⁱ and O8ⁱ are 0.43 and 0.76 Å, respectively, below the ring. For ring B, the H atoms on atoms O9 and O10ⁱⁱⁱ are 0.46 and 0.40 Å, respectively, above the ring, while the H atoms on atoms O9ⁱⁱⁱ and O10 are 0.46 and 0.40 Å, respectively, below the ring. In the ring, each water molecule acts as both hydrogen-bond donor and acceptor. Water molecules containing atoms O8, O10 and O11 are tetrahedrally connected by means of four hydrogen-bonding interactions and atoms O6, O7 and O9 are involved in three hydrogen bonds. As a building block, the planar water tetramer ring A exhibits a side-linking pattern and ring B exhibits a diagonal-linking pattern. Atoms O7 and O11^{iv} bridge rings A and B to form a chain *via* hydrogen bonds [O6···O7 = 2.834 (3) Å and O6–H6A···O7 = 174°; O7···O10 = 2.781 (3) Å and O7–H7B···O10 = 171°; O8ⁱ···O11^{iv} = 2.896 (3) Å and O8ⁱ–H8Aⁱ···O11^{iv} = 170°; O10ⁱⁱⁱ···O11^{iv} = 2.789 (3) Å and O10ⁱⁱⁱ–H10ⁱⁱⁱB···O11^{iv} = 175°; for symmetry codes, see the caption to Fig. 3].

The water chains are gathered between the two-dimensional sheets by means of hydrogen bonds involving the coordinated water and the dbta ligand O atoms (Fig. 4 and Table 1).

The broad IR band of (I) centred around 3466 and 3400 cm^{–1} can be attributed to the O–H stretching frequency of the coordinated water molecules and water tetramer (Zuhayra *et al.*, 2006).

Experimental

All reagents were commercial grade materials and were used as received. H₄dbta was obtained by the direct reaction of *p*-phenylenediamine with sodium chloroacetate in alkaline aqueous solution. Elemental analyses were determined on an Elementar Vario EL elemental analyser. IR spectra were measured as KBr pellets on a

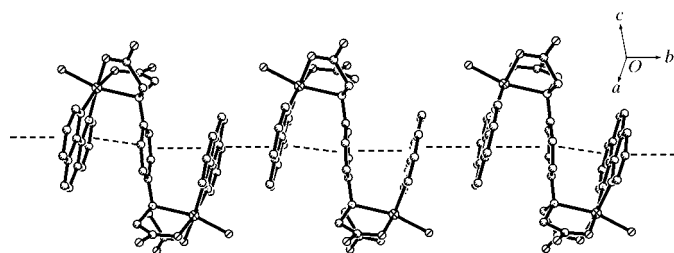


Figure 2
The intra- and intermolecular π – π interactions in (I), indicated as dashed lines.

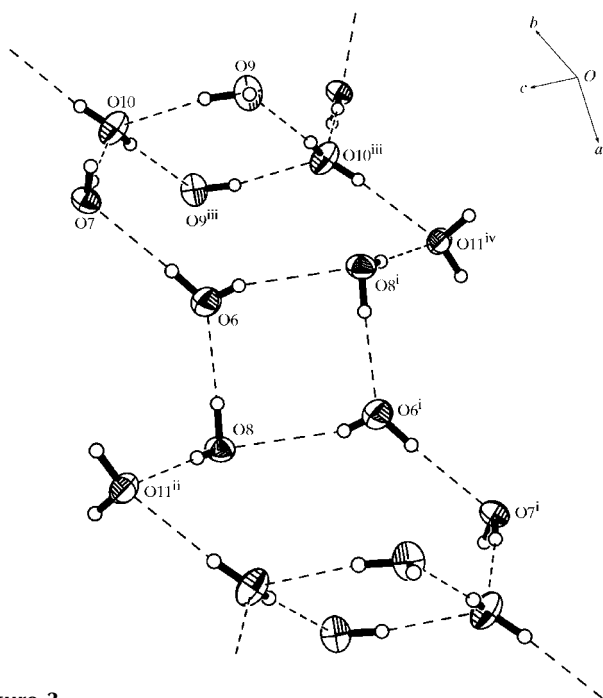


Figure 3
The water chain in the structure of (I), showing the hydrogen-bonding environment of water molecules in the chain. Displacement ellipsoids are drawn at the 50% probability and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines [Symmetry codes: (i) –*x* + 1, –*y*, –*z* + 1; (ii) –*x* + 1, –*y* + 1, –*z* + 1; (iii) –*x*, –*y*, –*z* + 1; (iv) *x*, *y* – 1, *z*.]

Perkin–Elmer spectrophotometer in the 4000–400 cm^{-1} region. 1,10-Phenanthroline (1.5 mmol) and nickel nitrate (1 mmol) were dissolved in water (20 ml) and the solution was refluxed for 1.5 h. After filtration, the solution was added to H_4dbta (0.5 mmol) in water (10 ml), and the mixture was refluxed for 4 h, filtered and left to stand at room temperature. Blue single crystals of (I) were obtained after 12 h (yield 48% based on Ni). Analysis calculated for $\text{C}_{38}\text{H}_{56}\text{N}_6\text{Ni}_2\text{O}_{22}$: C 42.80, H 5.29, N 7.88%; found: C 43.11, H 5.44, N 7.86%. Selected IR frequencies (KBr , ν , cm^{-1}): 3466 (*vs*), 3400 (*vs*), 1623 (*s*), 1519 (*m*), 1431 (*m*), 1385 (*m*), 1328 (*m*), 1272 (*m*), 1208 (*m*), 1151 (*m*), 906 (*m*), 871 (*m*), 858 (*m*).

Crystal data

$[\text{Ni}_2(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_8)(\text{C}_{12}\text{H}_8\text{N}_2)_2 \cdot (\text{H}_2\text{O})_2] \cdot 12\text{H}_2\text{O}$	$\beta = 108.4260 (10)^\circ$
$M_r = 1066.31$	$\gamma = 107.5360 (10)^\circ$
Triclinic, $P\bar{1}$	$V = 1175.71 (14) \text{ \AA}^3$
$a = 10.2082 (7) \text{ \AA}$	$Z = 1$
$b = 10.3481 (7) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 12.4101 (8) \text{ \AA}$	$\mu = 0.89 \text{ mm}^{-1}$
$\alpha = 91.3360 (10)^\circ$	$T = 183 (2) \text{ K}$
	$0.28 \times 0.25 \times 0.19 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	6344 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2001)	4092 independent reflections
$T_{\min} = 0.777$, $T_{\max} = 0.849$	3613 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	307 parameters
$wR(F^2) = 0.083$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
4092 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

Table 1

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{O1---H1A}\cdots\text{O4}^{\text{i}}$	0.85	1.93	2.776 (2)	177
$\text{O1---H1B}\cdots\text{O8}^{\text{ii}}$	0.85	1.93	2.773 (2)	173
$\text{O6---H6A}\cdots\text{O7}$	0.85	1.99	2.834 (3)	174
$\text{O6---H6B}\cdots\text{O8}^{\text{ii}}$	0.85	2.06	2.887 (3)	165
$\text{O7---H7B}\cdots\text{O10}$	0.85	1.94	2.781 (3)	171
$\text{O7---H7A}\cdots\text{O3}$	0.85	2.05	2.887 (2)	170
$\text{O8---H8B}\cdots\text{O6}$	0.84	1.92	2.761 (3)	177
$\text{O8---H8A}\cdots\text{O11}^{\text{iii}}$	0.85	2.05	2.896 (3)	170
$\text{O9---H9A}\cdots\text{O2}$	0.84	2.04	2.874 (2)	170
$\text{O9---H9B}\cdots\text{O10}$	0.85	2.05	2.882 (3)	167
$\text{O10---H10B}\cdots\text{O11}^{\text{iv}}$	0.79	2.00	2.789 (3)	175
$\text{O10---H10A}\cdots\text{O9}^{\text{v}}$	0.76	2.02	2.758 (3)	164
$\text{O11---H11B}\cdots\text{O3}$	0.85	1.93	2.772 (2)	169
$\text{O11---H11A}\cdots\text{O5}^{\text{vi}}$	0.85	1.83	2.665 (2)	164

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

H atoms attached to C atoms were placed in geometrically idealized positions, with $\text{Csp}^2\text{---}H = 0.93 \text{ \AA}$ and $\text{Csp}^3\text{---}H = 0.97 \text{ \AA}$, and refined with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. H atoms attached to O atoms were located in a difference Fourier map and refined as riding in their as-found positions, with $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$. The O—H distances are in the range 0.762–0.853 \AA .

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXL97*.

This project was supported by the Natural Science Foundation of the Education Bureau of Liaoning Province. MLZ acknowledges the National Natural Science Foundation of China (grant No. 20471033), the Provincial Natural Science Foundation of Shanxi Province of China (grant No. 20051013) and the Overseas Returned Scholar Foundation of Shanxi Province of China in 2006 for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3107). Services for accessing these data are described at the back of the journal.

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