Poly[[μ2-aqua-bis[(1,10-phenanthroline)nickel(II)]]-di-μ2,μ4-5-nitro-1,3-benzenedicarboxylato]

Hong-Yin He,[a] Yi-Li Zhou[a] and Long-Guan Zhu[b]*

[a]Department of Chemical Engineering, Jiaxing College, Jiaxing 314001, People's Republic of China, and [b]Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China
Correspondence e-mail: chezlg@zju.edu.cn

The reaction of $Ni(CH_3COO)_2\cdot 4H_2O$, 5-nitro-1,3-benzenedicarboxylic acid (H_2nmbdc), 1,10-phenanthroline and water under hydrothermal conditions yields the first reported two-dimensional nickel coordination polymer with water- and carboxylate-bridged dimeric units, viz. $[Ni_2(C_8H_3NO_6)_2(C_{12}H_8N_2)_2(H_2O)]_n$. The coordination polyhedron of the Ni^{II} ion in the title structure is an octahedron defined by an N_2O_4 donor set. The water molecule is positioned on a mirror plane and the 5-nitro-1,3-benzenedicarboxylate group is located on a twofold axis. Two types of nmbdc^{2-} coordination mode are observed: one is a bis-monodentate mode, μ2-nmbdc^{2-}, and the other is a bis-bridging mode, μ4-nmbdc^{2-}. The dimeric unit in the title compound is similar to the structural moiety in urease. In the two-dimensional framework in the title compound, strong stacking interactions between benzene rings (μ2-nmbdc^{2-} and μ4-nmbdc^{2-}) and 1,10-phenanthroline ligands are observed.

Comment

Binuclear nickel units with both water and carboxylate bridging ligands have been found to be important structural moieties in some metalloenzymes, such as urease; these units can catalyze the hydrolysis of urease to form ammonia and carbamate (Person et al., 1997; Jabri et al., 1995). Recently, several binuclear complexes have been prepared as models for urease in order to explore the nature of urea hydrolysis (Sung et al., 2001; Barrios & Lippard, 1999; Barrios & Lippard, 2000). However, only a few such nickel binuclear carboxylate complexes have been structurally characterized and all were synthesized using ligands with one carboxyl group. In the present study, we use a dicarboxylic acid (5-nitro-1,3-benzenedicarboxylic acid, H_2nmbdc) to prepare the first reported two-dimensional compound with a μ2-aqua dimeric motif, namely $[Ni_2(nmbdc)_2(phen)_2(H_2O)]_n$, (I) (phen is 1,10-phenanthroline).

Compound (I) consists of a two-dimensional Ni^{II} complex in which the Ni atom has a six-coordinate geometry completed by two N atoms from one phen group, one O atom from the coordinated water molecule and three O atoms from three nmbdc^{2-} ligands (Fig. 1 and Table 1). The water molecule occupies a special position in a mirror plane and the 5-nitro-1,3-benzenedicarboxylate group occupies a special position on a twofold axis. There are two nmbdc^{2-} coordination modes in the title compound: one is a bis-monodentate mode, μ2-nmbdc^{2-}, and the other is a bis-bridging mode, μ4-nmbdc^{2-}. The basic motif in the two-dimensional framework is a dimeric unit, viz. $[Ni_2(μ_2\text{-nmbdc})(μ_4\text{-nmbdc})(phen)_2(μ_2\text{-}H_2O)]$, in which the water molecule bridges two Ni atoms, with an Ni···Ni distance of 3.5042 (8) Å; this value agrees well with the Ni···Ni distance observed in urease (3.5 Å).

(I)
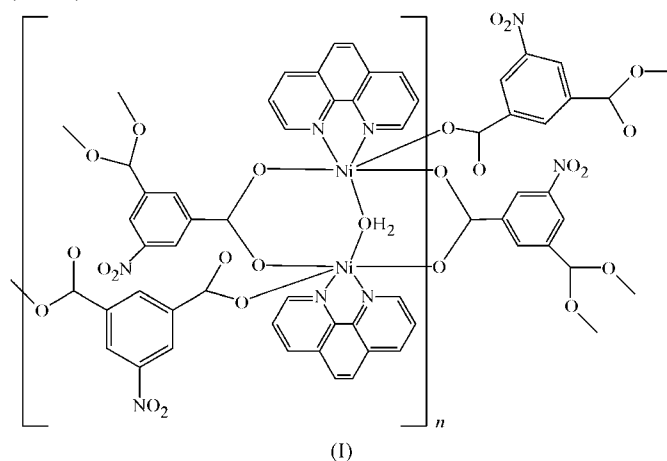
In general, a binuclear unit constructed from bridging carboxylate groups has four carboxyl groups around two metal centres, with short metal–metal distances; a paddle-wheel motif is expected (Braqun et al., 2001; Li et al., 1998; Gao et al., 2003). In (I), the dimeric unit comprises two bridging and two monodentate carboxyl groups. The bridging water molecule and intramolecular hydrogen bonds assemble the mono-
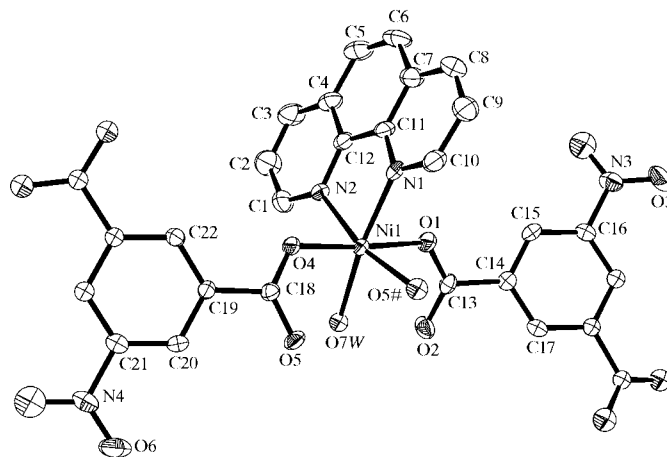

Figure 1
An ORTEP-3 diagram (Farrugia, 1997) of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The atom labeled with a hash (#) is at the symmetry position ($\frac{1}{2} - x$, $1 - y$, z).

dentate carboxyl groups into pseudo-bridging linkers. Therefore, the dimeric motif in (I) could be considered as a pseudo-paddle-wheel motif; even the nmbdc^{2-} ligands are roughly parallel (the dihedral angle is 6.19°). This dimeric motif in (I) is found in several reported binuclear water-bridged nickel complexes, such as [Ni$_2$\{OOCC(CH$_3$)$_3$\}$_2$\{μ_2-OOCC(CH$_3$)$_3$\}$_2$-(2,2′-bipy)$_2$(μ_2-H$_2$O)], (II) (Eremenko *et al.*, 1999). The difference between the coordination geometries in (I) and (II) is the orientation of the carboxylate ligands with respect to the Ni atoms.

In the two-dimensional framework in (I) (Fig. 2), the Ni(μ_4-nmbdc) building blocks form a one-dimensional chain (Fig. 3*a*), while the Ni(μ_2-nmbdc) blocks form dimeric species; the dimeric units are held together by μ_2-aqua molecules and extend into a one-dimensional chain (Fig. 3*b*). The combination of Ni(μ_4-nmbdc) and Ni(μ_2-nmbdc)(μ_2-H$_2$O) units leads to the assembly of a two-dimensional architecture. The Ni···Ni separations in these two one-dimensional chains are 8.7326 (8), 10.2223 (5), 10.5166 (8) and 10.5884 (8) Å.

Two complexes based on the M^{2+}–phen–H$_2$nmbdc system have been reported by Zhou *et al.* (2004). The copper compound, [Cu(nmbdc)(phen)]$_n$, (III), comprises a two-dimensional network with a square-pyramidal copper center, in which the nmbdc^{2-} ligand has a μ_3-bridging monoatomic monodentate coordination mode. The cobalt compound, [Co$_2$(nmbdc)$_2$(phen)$_2$]$_n$, (IV), comprises a one-dimensional chain and the nmbdc^{2-} ligand has a chelating–bridging coordination mode. The μ_2-nmbdc^{2-} and μ_4-nmbdc^{2-} coordination modes in (I) create a new assembly that differs from the topologies of (III) and (IV). Moreover, in (I), the ability of the water molecule to serve as a bridge between two Ni^{II} ions seems to be both an unexpected and a remarkable phenomenon, accounting for the absence of coordination water molecules in (III) and (IV).

Intramolecular hydrogen bonds exist between water molecules and uncoordinated carboxylate O atoms [O7W···O2 = 2.509 (2) Å; Table 2]. There are abundant strong π–π interactions in the two-dimensional network. As well as a π–π stacking interaction (3.23 Å) between μ_2-nmbdc^{2-} and μ_4-nmbdc^{2-} ligands in the dimeric motif, π–π stacking interactions exist between pairs of μ_2-nmbdc^{2-} and neighboring μ_4-nmbdc^{2-} ligands. Moreover, π–π stacking of phen ligands among neighbouring dimeric motifs is observed (3.48 and 3.60 Å).

Experimental

A mixture of Ni(CH$_3$COO)$_2$·4H$_2$O (0.0376 g, 0.15 mmol), 5-nitro-1,3-benzenedicarboxylic acid (0.0318 g, 0.15 mmol), 1,10-phenanthroline (0.0304 g, 0.15 mmol) and water (10 ml) in a molar ratio of *ca* 1:1:1:3700 was sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 453 K for 72 h. After cooling, blue plate-like crystals of (I) were collected by filtration. Analysis calculated for C$_{40}$H$_{46}$N$_6$-Ni$_2$O$_{13}$: C 51.70, H 2.65, N 9.19%; found: C 51.64, H 2.70, N 9.36%. A weight loss in the temperature range 574–637 K corresponds to the release of the water molecule (calculated 1.97%, found 1.73%).
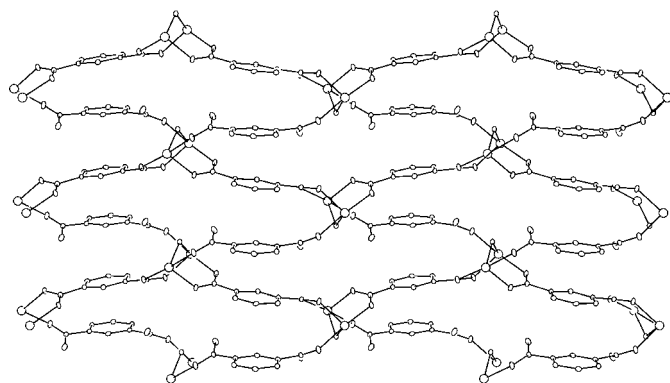

Figure 2
A view of the two-dimensional framework in (I). Phen ligands, nitro groups and H atoms have been omitted for clarity.
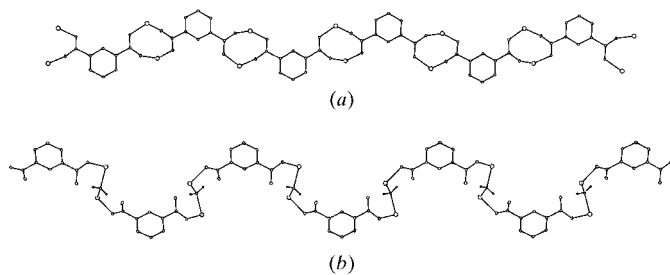

(a)

(b)

Figure 3
(*a*) A view of the one-dimensional chain constructed from Ni(μ_4-nmbdc) building blocks. (*b*) A view of the one-dimensional chain constructed from Ni(μ_2-nmbdc)(μ_2-H$_2$O) building blocks. H atoms and nitro groups have been omitted for clarity.

Crystal data

[Ni$_2$(C$_8$H$_3$NO$_6$)$_2$(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)]	Mo $K\alpha$ radiation
M_r = 914.03	Cell parameters from 3176
Orthorhombic, $Pnna$	reflections
a = 29.5645 (13) Å	θ = 2.6–50.4°
b = 18.0613 (7) Å	μ = 1.15 mm^{-1}
c = 6.5961 (3) Å	T = 293 (2) K
V = 3522.1 (3) Å^3	Plate, blue
Z = 4	0.54 × 0.45 × 0.06 mm
D_x = 1.724 Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	3176 independent reflections
	2953 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.034
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 25.2°
	h = −23 → 35
T_{min} = 0.575, T_{max} = 0.934	k = −21 → 21
17 323 measured reflections	l = −7 → 7

Table 1
Selected geometric parameters (Å, °).

Ni1—O5^i	2.027 (2)	Ni1—O7	2.0762 (17)
Ni1—O4	2.052 (2)	Ni1—N2	2.104 (3)
Ni1—N1	2.067 (3)	Ni1—O1	2.172 (2)
O5^i—Ni1—O4	98.38 (9)	N1—Ni1—N2	80.04 (10)
O5^i—Ni1—N1	88.80 (10)	O7—Ni1—N2	100.83 (10)
O4—Ni1—N1	96.15 (9)	O5^i—Ni1—O1	86.81 (9)
O5^i—Ni1—O7	89.08 (9)	O4—Ni1—O1	174.63 (9)
O4—Ni1—O7	93.17 (7)	N1—Ni1—O1	82.52 (9)
N1—Ni1—O7	170.65 (8)	O7—Ni1—O1	88.27 (8)
O5^i—Ni1—N2	166.85 (10)	N2—Ni1—O1	84.89 (10)
O4—Ni1—N2	89.76 (10)		

Symmetry code: (i) $\frac{1}{2} - x, 1 - y, z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 7.1492P]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} = 0.001$
3176 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
282 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H-atom parameters constrained	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H7A···O1	0.85 (3)	2.47 (4)	2.959 (2)	117 (3)
O7—H7A···O2	0.85 (3)	1.68 (3)	2.509 (2)	163 (4)

H atoms attached to C atoms were positioned geometrically and treated as riding, with C—H distances of 0.93 Å and U_{iso}(H) values of $1.2U_{eq}$(C). Water H atoms were found in a difference Fourier map and included in the refinement with an O—H distance restraint (0.85 Å) and with U_{iso}(H) values set at 0.05 Å^2.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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