metal-organic compounds

Nickel and zinc complexes with a monodentate heterocycle and tridentate Schiff base ligands: self-assembly to one- and two-dimensional supramolecular networks *via* hydrogen bonding

Xiao-Hua Chen,[a]* Qiong-Jie Wu,[b] Zhi-Yu Liang,[a] Chun-Rong Zhan[a] and Jian-Bin Liu[a]

[a]College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, People's Republic of China, and [b]College of Life Science, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, People's Republic of China
Correspondence e-mail: xiaohuachen03@163.com

In the complex (morpholine)[2-hydroxy-N'-(5-nitro-2-oxidobenzylidene)benzohydrazidato]nickel(II), [Ni($C_{14}H_9N_3O_5$)-(C_4H_9NO)], (I), the Ni^{II} center is in a square-planar N_2O_2 coordination geometry. The complex bis[μ-2-hydroxy-N'-(2-oxidobenzylidene)benzohydrazidato]bis[(morpholine)-zinc(II)], [$Zn_2(C_{14}H_{10}N_2O_3)_2(C_4H_9NO)_2$], (II), consists of a neutral centrosymmetric dimer with a coplanar $Zn_2(\mu_2\text{-}O)_2$ core. The two Zn^{II} centers are bridged by phenolate O atoms. Each Zn^{II} center exhibits a distorted square-pyramidal stereochemistry, in which the four in-plane donors come from the O,N,O'-tridentate 2-hydroxy-N'-(2-oxidobenzylidene)-benzohydrazidate(2−) ligand and a symmetry-related phenolate O atom, and the axial position is coordinated to the N atom from the morpholine molecule. There are intramolecular phenol–hydrazide O—H···N hydrogen bonds present in both (I) and (II). In (I), square-planar nickel complexes are linked by intermolecular morpholine–morpholine N—H···O hydrogen bonds, leading to a one-dimensional chain, while in (II) an infinite two-dimensional network is formed *via* intermolecular hydrogen bonds between the coordinated morpholine NH groups and the uncoordinated phenolate O atoms.

Comment

In recent years, self-assemblies of coordination compounds to form one-, two- and three-dimensional supramolecules have been of much interest (Bai *et al.*, 2006; Batten & Robson, 1998; Padhi *et al.*, 2008; Rayati *et al.*, 2008). The general strategies used for self-assemblies into such extended supramolecular

network structures are based on the metal ion's preference for different coordination geometry, use of suitable bridging bidentate ligands such as pyrazine (Warda, 1998*b*) and dioxane (Warda, 1998*a*), and weak intermolecular interactions such as hydrogen bonding and π–π interactions (Bauer & Weber, 2008; Mukhopadhyay *et al.*, 2003; Padhi *et al.*, 2008). Aroylhydrazones have been extensively investigated by chemists in the synthesis of coordination polymers owing to their inherent coordination and hydrogen-bonding donor/acceptor functionalities, as well as their biological activities (Rayati *et al.*, 2008; Dutta *et al.*, 1995; Lian *et al.*, 2008). In the following account, we report two mixed-ligand bivalent nickel/zinc complexes, namely (morpholine)[2-hydroxy-N'-(5-nitro-2-oxidobenzylidene)benzohydrazidato]nickel(II), [Ni(L_1)-(C_4H_9NO)], (I), and bis[μ-2-hydroxy-N'-(2-oxidobenzyl-idene)benzohydrazidato]bis[(morpholine)zinc(II), [Zn(L_2)-(C_4H_9NO)]$_2$, (II). Both complexes contain a tridentate aroylhydrazone ligand, *viz.* 2-hydroxy-N'-(2-hydroxy-5-nitro-benzylidene)benzohydrazide (H_2L_1) in (I) and 2-hydroxy-N'-(2-hydroxybenzylidene)benzohydrazide (H_2L_2) in (II). Neutral N-donor morpholine has been used as the ancillary ligand. The self-assembly of both complex molecules *via* intermolecular hydrogen bonds involving the heterocyclic morpholine NH group has been demonstrated. As far as we know, complex (II) is the first example of a dinuclear zinc hydrazone complex with morpholine as the ancillary ligand; (II) exhibits an infinite two-dimensional supramolecular network structure.
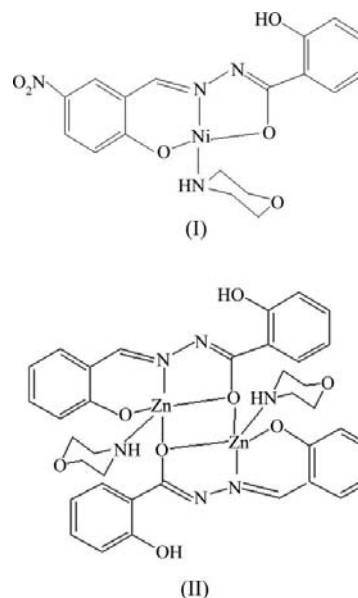
As shown in Fig. 1, in (I), the tridentate L_1^{2-} ligand coordinates the Ni^{II} ion *via* the phenolate O1, carbonyl O4 and hydrazone N2 atoms, forming one five- and one six-membered chelating ring. The fourth site is occupied by atom N4 of the heterocycle to complete a square-planar N_2O_2 geometry around the metal center. There is almost no deviation of the metal center from the N_2O_2 square plane; atom Ni1 deviates from the basal plane by 0.0092 (8) Å. The N—N, N=C and C—O bond distances in the =N—N=C(O$^-$)– fragment of

L_1^{2-} are consistent with the enolate form of the hydrazone functionalities (Chen, 2008; Lin *et al.*, 2007; Lian *et al.*, 2008). The Ni1—N2, Ni1—O1 and Ni1—O4 bond distances (Table 1) are normal, as observed in some similar square-planar Ni^{II} complexes with aroylhydrazone ligands (Chen, 2008; Lin *et al.*, 2007; Lian *et al.*, 2008). The Ni1—N4 bond length is comparable to the distance observed in the lone example of a four-coordinated Ni^{II} complex (Lian *et al.*, 2008) containing a monodentate neutral morpholine ligand.

Both the six-membered chelate ring [r.m.s. deviation = 0.0332 (1) Å] and the five-membered chelate ring [r.m.s. deviation = 0.0338 (8) Å] are close to being planar, and the dihedral angle between them is 3.6 (1)°. The dihedral angle between the benzene ring and the substituent –NO$_2$ group is 4.1 (4)°. However, the dihedral angle between the two benzene rings of the hydrazone ligand in complex (I) is 12.6 (1)°, indicating a slight twist of the whole ligand.

There exists a weak O5—H5B···N3 intramolecular contact (Table 2). In the crystal structure, the asymmetric units are linked by intermolecular N4—H4B···O6^i interactions (symmetry code as in Table 2), forming a one-dimensional zigzag supramolecular network (Fig. 2). The Ni···Ni distance in this uniform arrangement is 8.935 (3) Å.
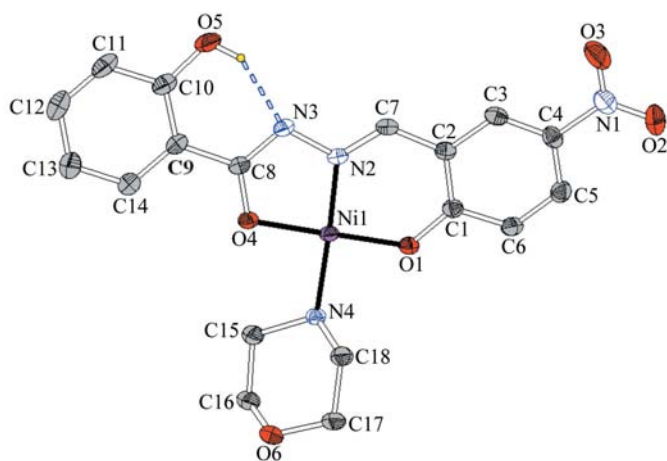
As shown in Fig. 3, the structure of (II) consists of a centrosymmetric binuclear entity with a coplanar $Zn_2(\mu_2\text{-O})_2$ fragment. Phenolate O atoms bridge the Zn^{II} ions, with Zn1—O1^i and Zn1—O1 bonds of 2.007 (2) and 2.079 (2) Å, respectively [symmetry code: (i) $-x$, $-y + 1$, $-z + 1$]. Each Zn^{II} ion is well described as having a distorted square-pyramidal configuration, as evidenced by the structural index parameter τ of 12.7% (Addison *et al.*, 1984). The basal plane is occupied by one N atom from the hydrazone group and three O atoms (two bridging phenolate O atoms and one from the carbonyl group), with an r.m.s. deviation from the mean plane of 0.0735 (2) Å. The apical position at each Zn^{II} ion is occupied by the N atom from the heterocyclic morpholine ligand. Atom Zn1 deviates from the basal plane by a distance of 0.449 (1) Å towards the apical atom N3.

The distances in the coordination plane (Table 3) are comparable to those found in the similar compounds bis{μ-N-[1-(2-oxidophenyl)ethylidene]benzohydrazido}bis[(dimethyl sulfoxide)zinc(II)], (III) (Ali *et al.*, 2003), and bis(μ-2,4-dihydroxyacetophenone salicylhydrazidato)bis[pyridine-zinc(II)] dimethylformamide disolvate, (IV) (Huang *et al.*, 2005). The Zn1···Zn1^i separation within the binuclear unit is 3.144 (1) Å. The Zn—O(Ph)—Zn bridging angle is 100.6 (1)°, which is in the range observed for five-coordinated Zn^{II} complexes of related ligands with a coplanar $Zn_2(\mu_2\text{-O})_2$ fragment. For the purpose of comparison, the dimensions of the $Zn_2(\mu_2\text{-O})_2$ fragment in some binuclear zinc complexes of similar O,N,O'-tridentate ligands are shown in Table 5. Structurally characterized mononuclear Zn^{II} complexes containing neutral morpholine as a ligand are rare (Ivanov *et al.*, 2001), and complex (II) is the first example of a binuclear Zn^{II} complex with a coordinated heterocyclic morpholine ligand. In (II), the apical Zn—N(morpholine) bond distance is 2.072 (3) Å, similar to those found in the above mononuclear Zn^{II} complexes ranging from 2.061 (6) to 2.106 (5) Å. The C8—O2 and C8=N2 bond distances suggest that the L_2^{2-} ligands also take the enolate form of the hydrazone functionality, similar to that of (I).

Figure 1
A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonding. Only H atoms involved in hydrogen bonds have been included.
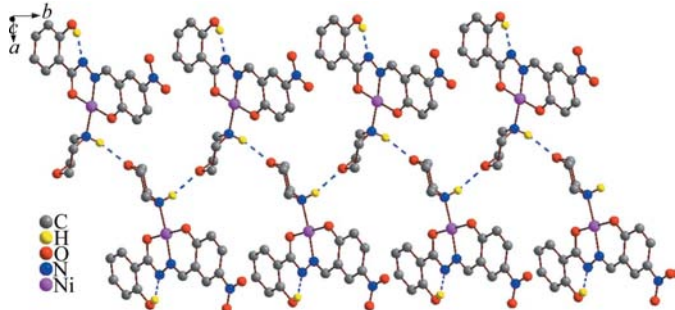

Figure 2
A packing diagram for (I), with hydrogen bonds shown as dashed lines. Only H atoms involved in hydrogen bonds have been included.
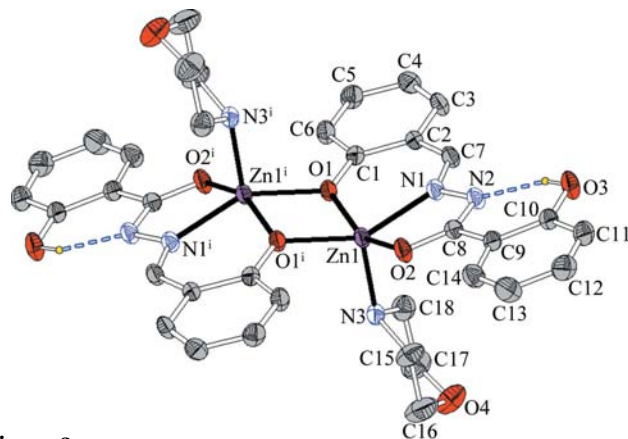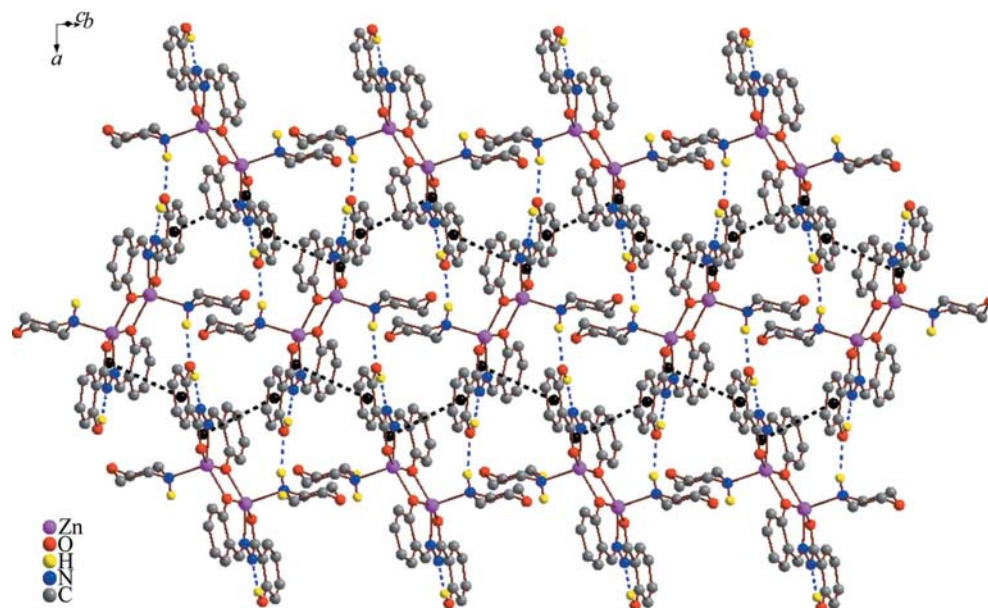

Figure 3
A view of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonding. Only H atoms involved in hydrogen bonds have been included. [Symmetry code: (i) $-x$, $-y + 1$, $-z + 1$.]

Figure 4
A packing diagram for (II), with hydrogen bonds and π–π stacking interactions [with $Cg\cdots Cg$ distances of 3.991 (3) Å] shown as dashed lines. Only H atoms involved in hydrogen bonds have been included.

All the non-H atoms of each ligand are nearly coplanar, with a mean deviation of 0.0726 (3) Å from the mean plane. There exists one intramolecular phenol–hydrazone O—H$\cdots$N hydrogen bond in each ligand, forming a six-membered ring (H3C/O3/C10–C8/N2; Table 4). On the other hand, in contrast to the one-dimensional assemblies of the complexes (III), (IV) and [Zn(SHSH)(2-Me-py)]$_2$ [SHSH is 2-hydroxy-N'-(2-oxidobenzylidene)benzohydrazide; Hu *et al.*, 2007], and the discrete entity of the complex bis[μ-2-hydroxy-N'-(4-hydroxy-2-oxidobenzylidene)benzohydrazide]bis[pyridinezinc(II)] dimethylformamide disolvate (Huang & Li, 2007), each complex molecule of (II) is linked to four adjacent molecules by two pairs of intermolecular morpholine–phenol N—H$\cdots$O$^{\mathrm{ii}}$ hydrogen bonds [symmetry code: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$] to form an infinite two-dimensional supramolecular network (see Table 4 and Fig. 4). It is interesting that the packing in the unit cell is also stabilized by weak π–π interactions. The centroid $Cg1$ (C9–C14) is involved in a weak π–π interaction with $Cg2^{\mathrm{iii}}$ [C8/N1/N2/Zn1/O2; symmetry code: (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$], the distance between the interleaved ligands being 3.993 (1) Å (see Fig. 4).

The IR spectra of the free ligand H$_2$L$_2$ displays three bands attributed to C=O, C=N and N—H at 1637, 1619 and 3260 cm^{-1}, respectively, indicative of its ketonic nature. In (II), these bands are absent, but a new C—O$^-$ stretch appears at 1420 cm^{-1} (Rao *et al.*, 1999). In addition, a strong band found at 1600 cm^{-1} is attributed to the >C=N—N=C< group (Kuriakose *et al.*, 2007). Such behavior is considered diagnostic for the enolization of the hydrazone residue. Out of the two ν(C—OH) bands, observed at 1158 and 1231 cm^{-1} in the free ligand, the latter exhibits a shift to 1259 cm^{-1}, while the former remains unchanged in complex (II). This indicates that one of the phenolate O atoms has undergone deprotonation and coordinated to the metal center (Rao *et al.*, 1999). Thus,

the Schiff ligand acts as a dianionic tridentate ligand in complex (II), corresponding to the X-ray structure determination. A band also appears at 3500 cm^{-1}, which may be attributed to the hydrogen-bond interaction. Additionally, in complex (II), coordination of the N and O atoms to the Zn atom is observed by the presence of bands at 460–535 cm^{-1}, assignable to ν(Zn—N) and ν(Zn—O) (Hu *et al.*, 2007).

Experimental

The Schiff base ligands H$_2$L$_1$ and H$_2$L$_2$ were prepared according to a procedure previously reported by Chen (2008). H$_2$L$_1$ (0.2 mmol) and [Ni(CH$_3$COO)$_2$]·4H$_2$O (0.2 mmol) were dissolved in C$_2$H$_5$OH (15 ml). After stirring for 15 min, morpholine (1 ml) was added to the solution, which was then stirred for another 1 h and filtered. Red single crystals of (I) were obtained after 2 d. Analysis calculated for C$_{18}$H$_{18}$N$_4$NiO$_6$: C 48.58, H 4.08, N 12.59%; found: C 48.69, H 4.03, N 12.52%. H$_2$L$_2$ (0.2 mmol) and [Zn(CH$_3$COO)$_2$]·H$_2$O (0.2 mmol) were dissolved in a mixture of DMF (5 ml) and C$_2$H$_5$OH (5 ml). After stirring for 15 min, morpholine (1 ml) was added to the mixed solution, which was then stirred for another 1 h and filtered. Yellow single crystals of (II) were obtained after one week. Analysis calculated for C$_{36}$H$_{38}$N$_6$O$_8$Zn$_2$: C 53.16, H 4.71, N 10.33%; found: C 53.29, H 4.67, N 10.25%. The molar conductance values of the two complexes measured in DMF solutions are 6.32 and 5.21 S cm^2 mol^{-1}, respectively, indicating that both are nonconducting in DMF solutions.

Compound (I)

Crystal data

[Ni(C$_{14}$H$_9$N$_3$O$_5$)(C$_4$H$_9$NO)]	$V = 3640.8$ (19) Å^3
$M_r = 445.07$	$Z = 8$
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation
$a = 11.548$ (4) Å	$\mu = 1.11$ mm^{-1}
$b = 8.479$ (2) Å	$T = 293$ K
$c = 37.184$ (10) Å	$0.45 \times 0.28 \times 0.15$ mm

Table 1
Selected geometric parameters (Å, °) for (I).

Ni1—O1	1.8280 (16)	O3—N1	1.218 (3)
Ni1—N2	1.8325 (19)	O4—C8	1.298 (3)
Ni1—O4	1.8442 (15)	N2—C7	1.290 (3)
Ni1—N4	1.9422 (19)	N2—N3	1.394 (2)
O1—C1	1.304 (3)	N3—C8	1.315 (3)
O2—N1	1.219 (3)		
O1—Ni1—N2	95.50 (7)	O1—Ni1—N4	87.47 (7)
O1—Ni1—O4	178.15 (7)	N2—Ni1—N4	175.92 (8)
N2—Ni1—O4	83.99 (7)	O4—Ni1—N4	93.13 (7)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$B\cdots$N3	0.822 (18)	1.86 (3)	2.578 (3)	145 (4)
N4—H4$B\cdots$O6^i	0.900 (10)	2.202 (11)	3.081 (3)	166 (2)

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, z$.

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer	32687 measured reflections
Absorption correction: multi-scan (TEXRAY; Molecular Structure Corporation, 1999)	4139 independent reflections
	3196 reflections with $I > 2\sigma(I)$
$T_{min} = 0.635$, $T_{max} = 0.851$	$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.088$	
$S = 1.03$	
4139 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
270 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
2 restraints	

Compound (II)

Crystal data

[Zn$_2$(C$_{14}$H$_{10}$N$_2$O$_3$)$_2$(C$_4$H$_9$NO)]	$V = 3518.3$ (19) Å^3
$M_r = 813.46$	$Z = 4$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 17.004$ (5) Å	$\mu = 1.43$ mm^{-1}
$b = 11.130$ (4) Å	$T = 293$ K
$c = 18.590$ (5) Å	$0.38 \times 0.26 \times 0.08$ mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer	28663 measured reflections
Absorption correction: multi-scan (TEXRAY; Molecular Structure Corporation, 1999)	3994 independent reflections
	2484 reflections with $I > 2\sigma(I)$
$T_{min} = 0.614$, $T_{max} = 0.895$	$R_{int} = 0.087$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.138$	
$S = 1.07$	
3994 reflections	$\Delta\rho_{max} = 1.38$ e Å^{-3}
243 parameters	$\Delta\rho_{min} = -0.73$ e Å^{-3}
2 restraints	

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—O1^i	2.007 (2)	O2—C8	1.269 (4)
Zn1—O2	2.046 (2)	N1—C7	1.274 (4)
Zn1—N1	2.048 (3)	N1—N2	1.396 (4)
Zn1—N3	2.072 (3)	N2—C8	1.329 (4)
Zn1—O1	2.079 (2)		
O1^i—Zn1—O2	105.34 (10)	N1—Zn1—N3	107.59 (11)
O1^i—Zn1—N1	148.80 (11)	O1^i—Zn1—O1	79.42 (10)
O2—Zn1—N1	77.73 (10)	O2—Zn1—O1	156.40 (10)
O1^i—Zn1—N3	102.15 (11)	N1—Zn1—O1	86.52 (10)
O2—Zn1—N3	101.97 (12)	N3—Zn1—O1	99.47 (11)

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$B\cdots$O3^{ii}	0.899 (10)	2.113 (14)	2.992 (4)	165 (3)
O3—H3$C\cdots$N2	0.82 (3)	1.80 (4)	2.547 (4)	149 (6)

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

Table 5
Comparative geometric parameters (Å, °) for the Zn$_2$(μ_2-O)$_2$ fragment in zinc complexes.

Complex	Zn—O^i	Zn—O	Zn$\cdots$Zn^i	Zn—O—Zn^i
(II)^a	2.007 (2)	2.079 (2)	3.144 (1)	100.6 (1)
[Zn(C$_{15}$H$_{12}$N$_2$O$_2$)(C$_2$H$_6$OS)]$_2$^{b}	2.004 (1)	2.068 (2)	3.137 (1)	100.76 (5)
[Zn(C$_{15}$H$_{12}$N$_2$O$_3$)(py)]$_2$·2DMF^c	2.022 (2)	2.023 (3)	3.141 (2)	101.9 (1)
[Zn(SHSH)(2-Me-py)]$_2$^{d}	1.991 (2)	2.118 (4)	3.161 (2)	100.57 (6)
[Zn(C$_{14}$H$_{10}$N$_2$O$_4$)(py)]$_2$·2DMF^e	1.998 (2)	2.080 (2)	3.149 (2)	100.67 (7)

References: (a) this work; (b) Ali et al. (2003); (c) Huang et al. (2005); (d) Hu et al. (2007); (e) Huang & Li (2007).

H atoms bonded to C atoms in (I) and (II) were positioned geometrically and refined using a riding model [C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C)]. H atoms bonded to phenolate O and morpholine N atoms were located in a difference Fourier map and were refined isotropically with O—H and N—H distance restraints of 0.82 and 0.90 Å, respectively.

For both compounds, data collection: TEXRAY (Molecular Structure Corporation, 1999); cell refinement: TEXRAY; data reduction: TEXSAN (Molecular Structure Corporation, 1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEX (McArdle, 1995); software used to prepare material for publication: SHELXL97/2 (Sheldrick, 2008).

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