

Mononuclear nickel(II) and zinc(II) complexes with deprotonated forms of the tripodal hexadentate ligand 1,3-bis(2-hydroxybenzylidene)-2-(2-hydroxybenzylideneaminomethyl)-2-methylpropane-1,3-diamine

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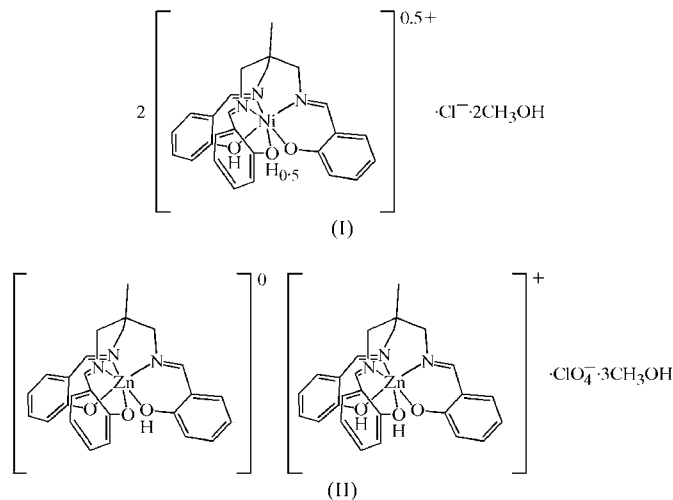
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In the crystal structures of both title compounds, [1,3-bis(2-hydroxybenzylidene)-2-methyl-2-(2-oxidobenzylideneaminomethyl)propane-1,3-diamine]nickel(II) [2-(2-hydroxybenzylideneaminomethyl)-2-methyl-1,3-bis(2-oxidobenzylidene)propane-1,3-diamine]nickel(II) chloride methanol disolvate, $[\text{Ni}(\text{C}_{26}\text{H}_{25.5}\text{N}_3\text{O}_3)]_2\text{Cl}\cdot 2\text{CH}_4\text{O}$, and [1,3-bis(2-hydroxybenzylidene)-2-methyl-2-(2-oxidobenzylideneaminomethyl)propane-1,3-diamine]zinc(II) perchlorate [2-(2-hydroxybenzylideneaminomethyl)-2-methyl-1,3-bis(2-oxidobenzylidene)propane-1,3-diamine]zinc(II) methanol trisolvate, $[\text{Zn}(\text{C}_{26}\text{H}_{25.5}\text{N}_3\text{O}_3)]\cdot \text{ClO}_4\cdot [\text{Zn}(\text{C}_{26}\text{H}_{26}\text{N}_3\text{O}_3)]\cdot 3\text{CH}_4\text{O}$, the 3d metal ion is in an approximately octahedral environment composed of three facially coordinated imine N atoms and three phenol O atoms. The two mononuclear units are linked by three phenol-phenolate $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to form a dimeric structure. In the Ni compound, the asymmetric unit consists of one mononuclear unit, one-half of a chloride anion and a methanol solvent molecule. In the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, two H atoms are located near the centre of $\text{O}\cdots\text{O}$ and one H atom is disordered over two positions. The Ni^{II} compound is thus formulated as $[\text{Ni}(\text{H}_1.5\text{L})]_2\text{Cl}\cdot 2\text{CH}_3\text{OH}$ [H_3L is 1,3-bis(2-hydroxybenzylidene)-2-(2-hydroxybenzylideneaminomethyl)-2-methylpropane-1,3-diamine]. In the analogous Zn^{II} compound, the asymmetric unit consists of two crystallographically independent mononuclear units, one perchlorate anion and three methanol solvent molecules. The mode of hydrogen bonding connecting the two mononuclear units is slightly different, and the formula can be written as $[\text{Zn}(\text{H}_2\text{L})]\text{ClO}_4\cdot [\text{Zn}(\text{HL})]\cdot 3\text{CH}_3\text{OH}$. In both compounds, each mononuclear unit is chiral with either a Δ or a Λ configuration because of the screw coordination arrangement of the achiral tripodal ligand around the 3d metal ion. In the dimeric structure,

molecules with $\Delta-\Delta$ and $\Lambda-\Lambda$ pairs co-exist in the crystal structure to form a racemic crystal. A notable difference is observed between the $M-\text{O}(\text{phenol})$ and $M-\text{O}(\text{phenolate})$ bond lengths, the former being longer than the latter. In addition, as the ionic radius of the metal ion decreases, the $M-\text{O}$ and $M-\text{N}$ bond distances decrease.

Comment

Magnetic interactions between paramagnetic metal centres through bridging atoms have been studied extensively to elucidate fundamental factors controlling the exchange interactions (Kahn, 1993). The mononuclear Ni^{II} title compound with H_3L [H_3L is 1,3-bis(2-hydroxybenzylidene)-2-(2-hydroxybenzylideneaminomethyl)-2-methylpropane-1,3-diamine], (I), involves three phenolate O atoms and can be used as a ligand to another metal ion. By using this complex-as-ligand strategy, we were able to prepare face-sharing di-, tri- and tetranuclear complexes. Various 3d-3d and 3d-4f ferromagnetic polynuclear complexes have been prepared with this Ni ligand complex (Ohta *et al.*, 2001; Yamaguchi *et al.*, 2004; Kobayashi *et al.*, 2006). The title Zn^{II} compound, (II), has also been used as a ligand complex. The analogous 3d-4f complexes with this diamagnetic Zn ligand complex have been prepared as reference complexes with respect to the above ferromagnetic complexes (Yamaguchi *et al.*, 2008). However, despite our efforts, we were not able to prepare heterotrimeric $[(\text{Zn}^{\text{II}}\text{L})_2\text{Ln}^{\text{III}}(\text{NO}_3)]$ complexes. For example, the reaction of $[\text{ZnL}]^-$ with $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ yielded only the homometal trimeric $\text{Zn}^{\text{II}}-\text{Zn}^{\text{II}}-\text{Zn}^{\text{II}}$ complex, *viz.* $[\text{Zn}_3\text{L}_2]$ (Ohta *et al.*, 2001). The present crystallographic study was undertaken in order to clarify the molecular structures and coordination geometries of Ni and Zn ligand complexes, which provide fundamental information on ligand activity.



The title Ni^{II} compound, (I), which was prepared by the reaction of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ in methanol with H_3L , had been reported to be $[\text{Ni}(\text{HL})]\cdot \text{H}_2\text{O}\cdot \text{CH}_3\text{OH}$ on the basis of the crystal structure of the Ni^{II} complex with the analogous 5-methoxy ligand, *viz.* 1,3-bis(2-hydroxy-5-methoxybenzylidene)-2-(2-hydroxy-5-methoxybenzylideneaminomethyl)-2-methylpropane-1,3-diamine (Ohta *et al.*, 2001; Kojima & Ohta,

2001). The present X-ray structure analysis of (I), however, showed that it is actually $[\text{Ni}(\text{H}_{1.5}\text{L})]_2\text{Cl}\cdot 2\text{CH}_3\text{OH}$. The existence of Cl^- in (I) was also confirmed by the precipitation of AgCl on the addition of aqueous AgNO_3 , and the formula was supported by CHN analyses and electrical conductivity measurements. The Zn^{II} compound, $[\text{Zn}(\text{H}_2\text{L})]\text{ClO}_4\cdot [\text{Zn}(\text{HL})]\cdot 3\text{CH}_3\text{OH}$, (II), was prepared by a similar method to that used for the preparation of the Ni^{II} compound, (I); $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ was used instead of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and the compound was isolated as the perchlorate salt. The presence of ClO_4^- was confirmed by the IR spectrum.

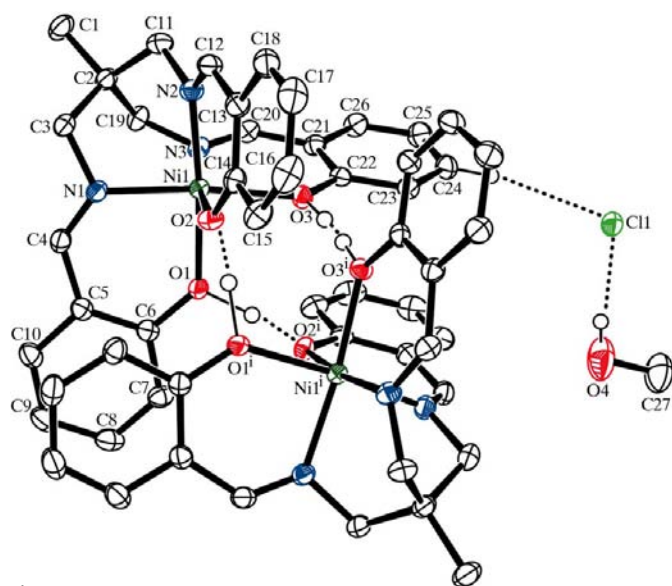


Figure 1
The molecular structure of (I), showing the dimeric unit, linked by O—H...O hydrogen bonds (dotted lines), and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms not involved in the hydrogen bonds have been omitted. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$]

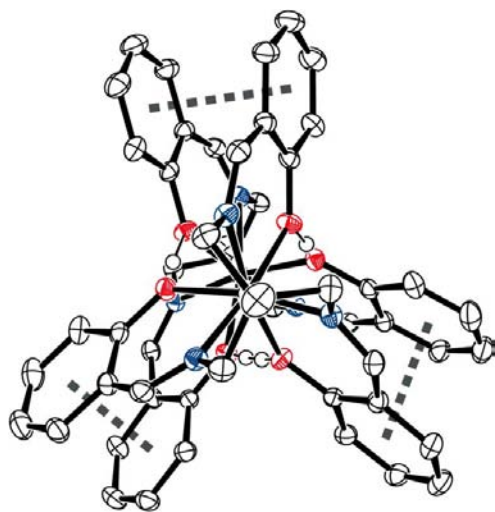


Figure 2
A diagram, viewed along the pseudo-threefold axis, of the dimeric unit of (I), linked by π - π interactions (dotted lines). Displacement ellipsoids are drawn at the 50% probability level. H atoms not involved in the hydrogen bonds have been omitted.

The asymmetric unit of (I) is composed of one $[\text{Ni}(\text{H}_{1.5}\text{L})]^{0.5+}$ cation, one half-occupied (disordered) Cl^- anion and one methanol solvent molecule of crystallization. The Ni^{II} ion displays an approximately octahedral environment composed of three facially coordinated imine N atoms and three phenolic O atoms (Fig. 1). Coordinated bond lengths for (I) are listed in Table 1. Two mononuclear cation units related by a twofold rotation axis are linked by three short phenol-phenolate O—H...O hydrogen bonds (Table 2), forming a dimeric structure. Of the three hydrogen bonds, two are very short [$\text{O1}\cdots\text{O2}^i$ and $\text{O2}\cdots\text{O1}^i = 2.468(2) \text{ \AA}$; symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$]. The H atom is located approximately at the mid-point of the hydrogen bond, which can be described as a proton-centred O...H...O bond in a single-well (SW) potential (Gilli *et al.*, 2004). In the longer hydrogen bond [$\text{O3}\cdots\text{O3}^i = 2.495(2) \text{ \AA}$], the H atom is disordered, with a site-occupancy factor of 0.50; the system can be described as a disordered state between two O—H...O and O...H—O tautomers in a double-well (DW) potential.

Furthermore, there are two weak C—H...O interactions and three π - π stacking interactions between the benzene rings of the ligands in the dimeric structure (Fig. 2). The $\text{Cg1}\cdots\text{Cg1}^i$ distance is $3.4647(15) \text{ \AA}$ [Cg1 is the centroid of ring 1 (C5—C10)]. The perpendicular distance of Cg1 from ring 1ⁱ is 3.424 \AA , with an interplanar angle of $11.81(8)^\circ$. The $\text{Cg2}\cdots\text{Cg3}^i$ (or $\text{Cg3}\cdots\text{Cg2}^i$) distance is $3.5452(15) \text{ \AA}$ [Cg2 and Cg3 are the centroids of rings 2 (C13—C18) and 3 (C21—C26), respectively]. The perpendicular distances of Cg2 from ring 3ⁱ and Cg3 from ring 2ⁱ are 3.268 and 3.357 \AA , respectively, with an interplanar angle of $10.62(11)^\circ$.

The extended crystal structure of (I) involves several hydrogen bonds involving CH_3OH and Cl^- (Table 2). Fig. 3 shows the three-dimensional hydrogen-bond network. The Cl^- anion is disordered over two positions with equal occupancies. The hydroxyl group of the methanol molecule is also disordered over two orientations, each pointing towards one

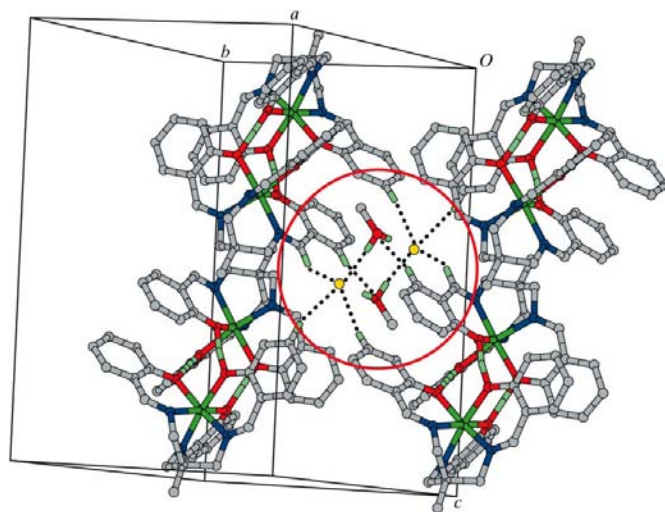


Figure 3
A packing view of (I), showing the molecules linked by O—H...Cl, C—H...O and C—H...Cl hydrogen bonds (dotted lines). The hydroxyl H atom of the methanol molecule is disordered over two positions.

site of the disordered Cl⁻ anion. Fig. 4 shows an enlarged view of the circled area of Fig. 3.

In (II), the asymmetric unit consists of two crystallographically independent mononuclear Zn units, one perchlorate anion and three methanol solvent molecules. Each Zn^{II} ion is coordinated by the ligand in an N₃O₃ coordination sphere (Fig. 5). Coordinate bond lengths for (II) are listed in Table 3. The two mononuclear Zn units are linked by three phenol-phenolate O–H···O hydrogen bonds (Table 4), forming a dimeric structure in a similar fashion to (I). However, the mode of hydrogen bonding connecting the two mononuclear units is slightly different. The hydrogen-bond distances are slightly longer than those in (I) and the three phenolic H atoms are located near atoms O1, O3 and O6. Therefore, atoms O2, O4 and O5 are the phenolate O atoms and the dimeric structure is described as [Zn(H₂L)][Zn(HL)]. Although the O6–H6 bond length is long, as described below, the Zn1–O2 and Zn2–O6 bond lengths imply that atoms O2 and O6 are phenolate and phenol O atoms, respectively.

The benzene rings of the ligands in the dimer are also stacked through π–π interactions. The Cg1···Cg5 distance is 3.571 (2) Å [Cg1 and Cg5 are the centroids of rings 1 (C5–C10) and 5 (C39–C44), respectively], with an average perpendicular distance of ca 3.3 Å and an interplanar angle of 11.28 (13)°. The Cg2···Cg4 distance is 3.772 (2) Å [Cg2 and Cg4 are the centroids of rings 2 (C13–C18) and 4 (C31–C36), respectively], with an average perpendicular distance of ca 3.5 Å and an interplanar angle of 17.96 (13)°. The Cg3···Cg6 distance is 3.590 (2) Å [Cg3 and Cg6 are the centroids of rings 3 (C21–C26) and 6 (C47–C52), respectively], with an average perpendicular distance of ca 3.4 Å and an interplanar angle of 13.04 (12)°.

In the crystal structure of (II), there are also several hydrogen bonds involving CH₃OH and ClO₄⁻ (Table 4). Fig. 6

shows hydrogen bonds forming a three-dimensional structure. One perchlorate anion and three methanol molecules connected by C–H···O hydrogen bonds are connected in the shape of a curve. Furthermore, methanol molecules and a perchlorate anion are linked with neighbouring Zn dimeric units *via* C–H···O hydrogen bonds.

In (I) and (II), each mononuclear unit is chiral with either a Δ or a Λ configuration because of the screw coordination arrangement of the achiral tripodal ligand around the 3d metal ion. When two chiral units associate to form a dimeric structure, homochiral (Δ–Δ or Λ–Λ) and heterochiral (Δ–Λ) pairs are possible. As shown in Figs. 1 and 5, both the Ni and Zn dinuclear units are homochiral pairs. The stability of the homochiral pairs is supported by examination of molecular models, which indicates that the heterochiral pair involves severe steric repulsion between the units. On the other hand, strong hydrogen bonding is possible in the homochiral pair. Moreover, in the homochiral pair, aromatic rings in neighbouring molecules can stack efficiently. Because compounds (I) and (II) crystallize in centrosymmetric space groups, the Δ–Δ and Λ–Λ pairs co-exist in the crystal structure to form a racemic crystal.

In (I) and (II), a remarkable difference between the *M*–O(phenol) and *M*–O(phenolate) bond lengths is observed, as pointed out by Okabe & Muranishi (2002) and Sokolowski *et al.* (1997). For (I), the nickel-phenol Ni1–O1 bond [2.0926 (15) Å] is longer than the nickel-phenolate Ni1–O2 bond [2.0594 (15) Å]. The Ni1–O3 bond [2.0754 (14) Å] is approximately intermediate between these lengths because of the disordering of the H atom. For (II), the difference is apparent; the zinc-phenol Zn1–O1 [2.1507 (19) Å], Zn1–O3 [2.2036 (18) Å] and Zn2–O6 [2.1622 (18) Å] bonds are longer than the zinc-phenolate Zn1–O2 [2.0860 (17) Å], Zn2–O4 [2.1243 (17) Å] and Zn2–O5 [2.1043 (18) Å] bonds. This difference has also been observed in Ni (Adams *et al.*,

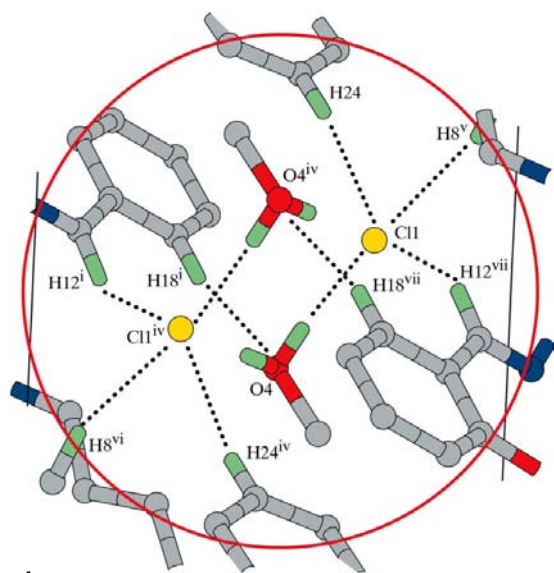


Figure 4
An enlarged view of the circled area of Fig. 3 showing the packing of (I). Intermolecular hydrogen bonds are shown as dotted lines. [Symmetry codes: (i) $-x+1, y, -z+\frac{1}{2}$; (iv) $-x+1, -y, -z+1$; (v) $x, y-1, z$; (vi) $-x+1, -x+1, -y+1, -z+1$; (vii) $x, -y, z+\frac{1}{2}$.]

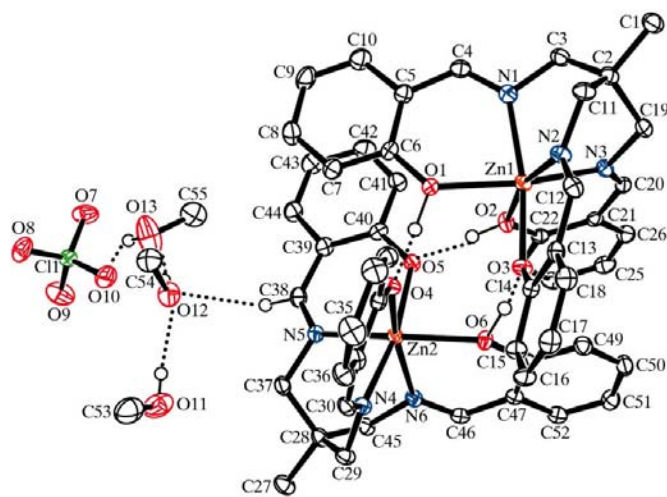


Figure 5
The molecular structure of (II), showing the dimeric unit, linked by O–H···O hydrogen bonds (dotted lines), and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms not involved in the hydrogen bonds have been omitted.

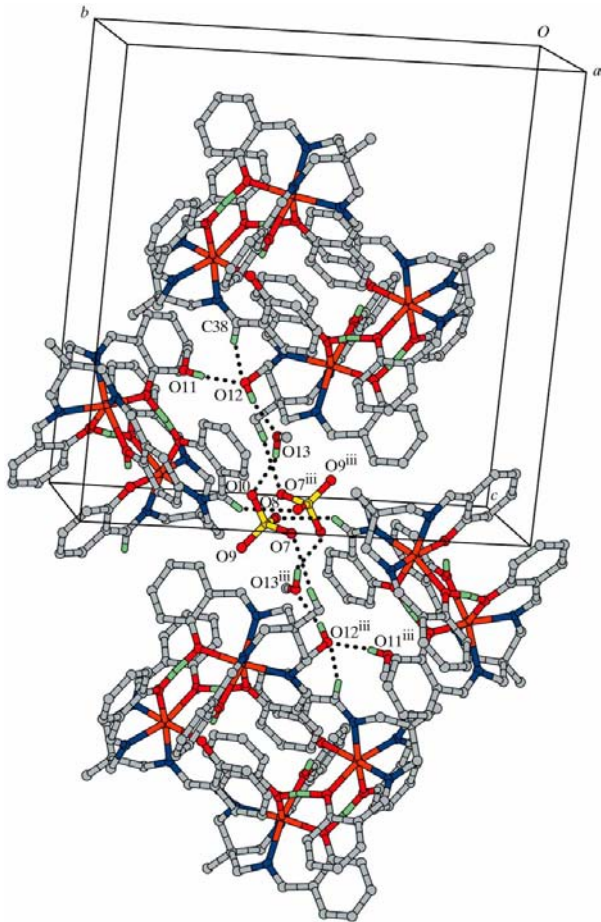


Figure 6
A packing view of (II), showing the molecules linked by hydrogen bonds (dotted lines). [Symmetry code: (iii) $-x + 1, -y + 1, -z + 2$.]

2004; Chaudhuri *et al.*, 2006; You & Chi, 2006) and Zn complexes (Flassbeck *et al.*, 1992).

As expected from the difference in ionic radii (Shannon, 1976) between Ni^{2+} (0.83 Å, six-coordinate) and Zn^{2+} (0.88 Å, six-coordinate), the coordinate bond lengths of (II) (mean $\text{Zn}-\text{O} = 2.139$ Å and mean $\text{Zn}-\text{N} = 2.135$ Å) are slightly longer than those of (I) (mean $\text{Ni}-\text{O} = 2.076$ Å and mean $\text{Ni}-\text{N} = 2.047$ Å). The same is true for other metal complexes, *e.g.* Ga^{3+} (0.62 Å, six-coordinate), with mean $\text{Ga}-\text{O} = 1.920$ Å and mean $\text{Ga}-\text{N} = 2.131$ Å (Liu *et al.*, 1993), and Fe^{3+} (0.785 Å, six-coordinate in high-spin state), with mean $\text{Fe}-\text{O} = 1.944$ Å and $\text{Fe}-\text{N} = 2.150$ Å (Deeney *et al.*, 1998). As the ionic radius of a metal ion decreases, the $M-\text{O}$ and $M-\text{N}$ bond distances decrease. The difference in reactivity between Ni and Zn ligand complexes, as observed in the synthesis of heteronuclear complexes $[(M^{\text{II}}L)_2\text{Ln}^{\text{III}}(\text{NO}_3)]$ ($M = \text{Ni}$ and Zn ; $\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$ and Dy ; Yamaguchi *et al.*, 2008), may be related to the difference in coordinate bond lengths.

Experimental

The H_3L ligand was prepared according to the method of Fleischer *et al.* (1971). For the preparation of compound (I), a methanol solution

(100 ml) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48 g, 2.0 mmol) was added slowly with stirring to a dichloromethane solution (50 ml) of H_3L (0.90 g, 2.0 mmol). After the addition was complete, water (50 ml) was added and the organic solvents were removed using a rotary evaporator. A pale-green precipitate was collected by filtration and recrystallized from methanol (yield 0.71 g, 72%). Analysis calculated for $[\text{Ni}(\text{H}_{1.5}\text{L})_2]\text{Cl} \cdot 4\text{H}_2\text{O} = \text{C}_{52}\text{H}_{59}\text{ClN}_3\text{Ni}_2\text{O}_{10}$: C 57.78, H 5.50, N 7.78%; found: C 57.70, H 5.18, N 7.48%. IR (KBr disk): $\nu(\text{C}=\text{N})$ 1635 cm^{-1} . Λ_{M} : 37.2 $\text{S mol}^{-1} \text{cm}^2$ in methanol (10^{-3}M). For the preparation of compound (II), a methanol solution (100 ml) of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.49 g, 4.0 mmol) was added slowly with stirring to a dichloromethane solution (50 ml) of H_3L (1.72 g, 4.0 mmol). After the addition was complete, water (50 ml) was added and the organic solvents were removed using a rotary evaporator. A pale-yellow precipitate was collected by filtration and recrystallized from methanol (yield 0.947 g, 44%). Analysis calculated for $\text{C}_5\text{H}_6\text{ClN}_6\text{O}_{13}\text{Zn}_2 = [\text{Zn}(\text{H}_2\text{L})]\text{ClO}_4 \cdot [\text{Zn}(\text{HL})] \cdot 3\text{CH}_3\text{OH}$: C 55.87, H 5.37, N 7.10%; found: C 55.88, H 4.45, N 7.43%. IR (KBr disk): $\nu(\text{C}=\text{N})$ 1636 cm^{-1} , $\nu(\text{ClO}_4^-)$ 1093 cm^{-1} .

Compound (I)

Crystal data

$[\text{Ni}(\text{C}_{26}\text{H}_{25.5}\text{N}_3\text{O}_3)]_2\text{Cl} \cdot 2\text{CH}_4\text{O}$	$V = 4911.3 (15) \text{ \AA}^3$
$M_r = 1072.95$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.530 (4) \text{ \AA}$	$\mu = 0.88 \text{ mm}^{-1}$
$b = 13.409 (2) \text{ \AA}$	$T = 173 (1) \text{ K}$
$c = 19.792 (3) \text{ \AA}$	$0.40 \times 0.20 \times 0.15 \text{ mm}$
$\beta = 92.969 (7)^\circ$	

Data collection

Rigaku R-Axis RAPID-II diffractometer	47265 measured reflections
Absorption correction: numerical (ABSCOR; Higashi, 1999)	7140 independent reflections
$T_{\text{min}} = 0.767, T_{\text{max}} = 0.876$	6018 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.146$	$\Delta\rho_{\text{max}} = 2.00 \text{ e \AA}^{-3}$
$S = 1.09$	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
7140 reflections	
335 parameters	

Table 1

Selected bond lengths (Å) for (I).

$\text{Ni1}-\text{N1}$	2.0514 (18)	$\text{Ni1}-\text{O1}$	2.0926 (15)
$\text{Ni1}-\text{N2}$	2.0496 (17)	$\text{Ni1}-\text{O2}$	2.0594 (15)
$\text{Ni1}-\text{N3}$	2.0409 (18)	$\text{Ni1}-\text{O3}$	2.0754 (14)

Table 2

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

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1} \cdots \text{O2}^{\text{i}}$	1.21 (4)	1.27 (4)	2.468 (2)	170 (3)
$\text{O3}-\text{H3} \cdots \text{O3}^{\text{i}}$	0.87 (6)	1.63 (6)	2.495 (2)	174 (5)
$\text{O4}-\text{H4A} \cdots \text{Cl1}$	0.82	2.11	2.925 (3)	173
$\text{C7}-\text{H7} \cdots \text{O2}^{\text{i}}$	0.95	2.49	3.134 (3)	125
$\text{C8}-\text{H8} \cdots \text{Cl1}^{\text{ii}}$	0.95	2.73	3.622 (3)	158
$\text{C12}-\text{H12} \cdots \text{Cl1}^{\text{iii}}$	0.95	2.75	3.504 (2)	137
$\text{C18}-\text{H18} \cdots \text{O4}^{\text{i}}$	0.95	2.50	3.435 (4)	170
$\text{C24}-\text{H24} \cdots \text{Cl1}$	0.95	2.75	3.679 (3)	167

Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $x, -y, z - \frac{1}{2}$.

Compound (II)

Crystal data

[Zn(C ₂₆ H ₂₅ N ₃ O ₃)]ClO ₄ ·	$\beta = 106.270 (7)^\circ$
[Zn(C ₂₆ H ₂₆ N ₃ O ₃)]·3CH ₄ O	$V = 5457 (3) \text{ \AA}^3$
$M_r = 1182.35$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.626 (5) \text{ \AA}$	$\mu = 1.00 \text{ mm}^{-1}$
$b = 19.383 (6) \text{ \AA}$	$T = 103 (1) \text{ K}$
$c = 21.522 (7) \text{ \AA}$	$0.40 \times 0.30 \times 0.10 \text{ mm}$

Data collection

Rigaku R-AXIS RAPID-II diffractometer	31274 measured reflections
Absorption correction: numerical (ABSCOR; Higashi, 1999)	11737 independent reflections
$T_{\min} = 0.834$, $T_{\max} = 0.905$	9143 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.124$	$\Delta\rho_{\text{max}} = 0.90 \text{ e \AA}^{-3}$
$S = 1.12$	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
11737 reflections	
711 parameters	

Table 3

Selected bond lengths (Å) for (II).

Zn1—N1	2.139 (2)	Zn2—N4	2.145 (2)
Zn1—N2	2.120 (2)	Zn2—N5	2.119 (2)
Zn1—N3	2.136 (2)	Zn2—N6	2.148 (2)
Zn1—O1	2.1507 (19)	Zn2—O4	2.1243 (17)
Zn1—O2	2.0860 (17)	Zn2—O5	2.1043 (18)
Zn1—O3	2.2036 (18)	Zn2—O6	2.1622 (18)

Table 4

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O4	1.04 (4)	1.46 (5)	2.494 (3)	168 (5)
O3—H3 \cdots O5	0.92 (4)	1.60 (4)	2.513 (3)	175 (4)
O6—H6 \cdots O2	1.17 (4)	1.34 (4)	2.499 (2)	175 (4)
O11—H11 \cdots O12	0.82	2.01	2.830 (4)	173
O12—H12 \cdots O13	0.82	1.93	2.738 (4)	169
O13—H13 \cdots O10	0.82	2.00	2.746 (3)	151
C1—H1A \cdots O7 ⁱ	0.97	2.57	3.502 (4)	161
C7—H7 \cdots O4	0.95	2.55	3.200 (3)	126
C15—H15 \cdots O6	0.95	2.57	3.225 (3)	126
C23—H23 \cdots O5	0.95	2.55	3.207 (4)	126
C38—H38 \cdots O12	0.95	2.56	3.460 (4)	159
C46—H46 \cdots O8 ⁱⁱ	0.95	2.56	3.365 (3)	143
C49—H49 \cdots O2	0.95	2.54	3.199 (3)	126

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

For both compounds, the hydroxyl H atoms of the methanol solvent molecules and the phenolic H atoms of the ligands were located in a difference Fourier map. The hydroxyl H atoms were then treated as riding, with O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$, while the phenolic H atoms were refined isotropically. The methyl groups of the ligand and of the methanol molecule were refined as rigid groups, with C—H = 0.97 Å and tetrahedral angles, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, allowing for rotation around the C—O and C—C bond axes, respectively. Other H atoms attached to C atoms were treated as riding, with C—H distances of 0.98 (CH₂) and 0.95 Å (CH), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. For (I), atom H3, one of the phenolic H atoms, was found to be disordered over two sites from the difference Fourier map, where two peaks of almost equal height related approximately

by a crystallographic twofold rotation axis were observed between atoms O3 and O3ⁱ. The occupancy factor was constrained to 0.5. The hydroxyl H atom of the methanol molecule was also found to be disordered over two positions from two peaks of almost equal height in the difference Fourier map. Again, the occupancy factors were fixed at 0.5 in the refinement. In (I), the highest residual electron-density peak is located 0.27 Å from atom Cl1.

For both compounds, data collection: *PROCESS-AUTO* (Rigaku/MSK, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3116). Services for accessing these data are described at the back of the journal.

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