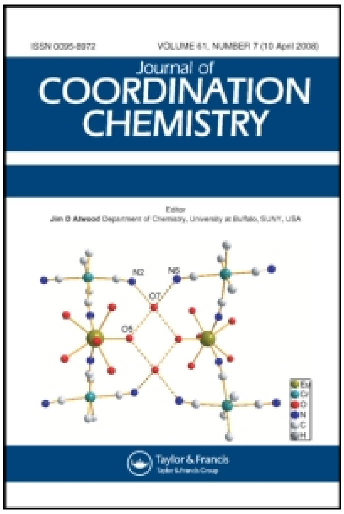

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Synthesis, crystal structures and magnetic properties of two new nickel(II) complexes with α-amino acid Schiff base

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Synthesis, crystal structures and magnetic properties of two new nickel(II) complexes with α-amino acid Schiff base

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Two nickel(II) complexes $[Ni(napgly)(MeOH)]_n$ (**1**) and $[Ni(napphe)(H_2O)_2(MeOH)] \cdot H_2O$ (**2**), where the tridentate Schiff-base ligands H_2napgly and H_2napphe are condensed from 2-hydroxyl-1-naphthaldehyde with glycine and L-phenylalanine, respectively, were prepared and structurally characterized. In **1**, two inversion-related Ni(II) ions were bridged by two O atoms from the phenolate groups of two napgly anions, forming a centrosymmetric dimeric unit which was further linked by carboxylate groups to give a two-dimensional network. Magnetic susceptibility studies performed on the complex revealed anti-ferromagnetic coupling between the metal centers. In **2**, the crystal structures of the complex displayed a distorted octahedral coordination geometry in which the ONO-donor Schiff base was bonded to the metal. Intermolecular H-bonds linked the compound into a 2-D layer structure.

Keywords: Amino acid Schiff base; Nickel(II) complex; Crystal structure

1. Introduction

A large number of Schiff bases and their complexes have been studied for their interesting properties, *e.g*. their ability to reversibly bind oxygen [1], catalytic activity in the hydrogenation of olefins [2], transfer of amino group [3], photochromic properties [4], and complex formation with toxic metals [5]. Metal complexes of amino acid Schiff bases have attracted attention as models for vitamin B_6 and its analogues in catalyzed non-enzymatic transamination reactions in solution [6, 7].

Our interest in complexes of Schiff-base ligands derived from 2-hydroxyl-1-naphthaldehyde and α-amino acids, stems from their wide application in chemistry [8–14]. As a tridentate chelating ligand with multiple donor sites, such Schiff-base ligands coordinate to transition metals by different types of protonated and deprotonated hydroxyl and carboxyl sites [9–11, 15]. Though many efforts have been made to synthesize and investigate metal complexes with these ligands [8–18], few crystal structures of Ni(II) complexes have been reported. In this article, we report the synthesis, crystal structure, and properties of two nickel(II) complexes with the

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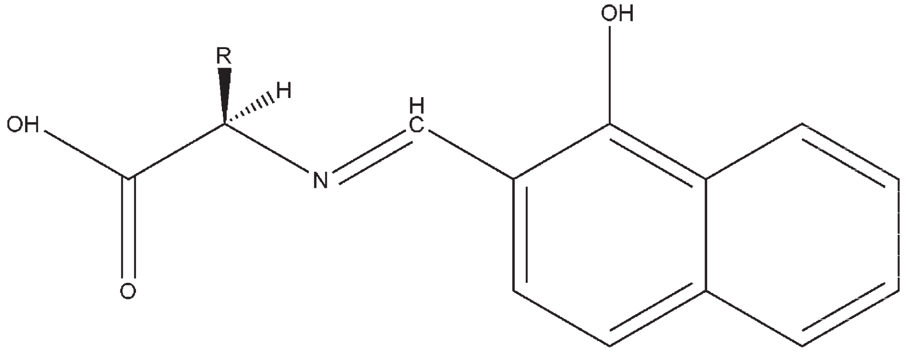

R = H H$_2$napgly
R = CH$_2$Ph H$_2$napphe

Scheme 1. The structures of the ligands.

Schiff bases derived from 2-hydroxyl-1-naphthaldehyde with glycine and L-phenylanin (scheme 1).

2. Experimental

2.1. *Chemical reagents*

Chemicals were purchased from commercial sources; 2-hydroxyl-1-naphthaldehyde, glycine and L-phenylalanine were obtained from Aldrich. Solvents were purified by standard procedures [19]. The Schiff-base ligands were prepared by a literature method [20, 21].

2.2. *Measurements*

The IR spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer in the 4000–400 cm^{-1} region by using KBr pellets. Elemental analyses for C, H and N atoms were carried out on a Model 2400 Π Perkin-Elmer elemental analyzer. The variable temperature susceptibility measurements were carried out with a MagLab System 2000 magnetometer in the temperature range 2–300 K at a magnetic field of 1000 G; diamagnetic corrections were made using Pascal's constants.

2.3. *Syntheses*

2.3.1. Synthesis of [Ni(napgly)(MeOH)]$_n$ (1). A mixture of Ni(CH$_3$COO)$_2$ · 4H$_2$O (1.0 mmol), H$_2$napgly (1.0 mmol), dichloromethane (2 mL), and methanol (14 mL) was stirred for 15 min. The mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel and heated under autogenous pressure at 60°C for 6 days, and then slowly cooled to room temperature. The dark green crystals obtained were recovered

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{14}H_{13}NNiO_4$	$C_{21}H_{25}NNiO_7$
Formula weight (M)	317.96	462.13
Temperature, T (K)	293(2)	293(2)
Wavelength, Mo-Kα (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
a (Å)	13.088(4)	7.011(5)
b (Å)	7.049(2)	7.696(5)
c (Å)	14.137(4)	19.897(12)
β (°)	101.206	97.027(12)
V (Å^3)	1279.3(7)	1065.5(12)
Z	4	2
D_c (mg m^{-3})	1.651	1.440
Absorption coefficient, μ (mm^{-1})	1.529	0.95
$F(000)$	656	484
Crystal size (mm^3)	$0.26 \times 0.20 \times 0.12$	$0.20 \times 0.18 \times 0.12$
θ range for data collection (°)	$1.59 \leq \theta \leq 26.41$	$2.84 \leq \theta \leq 25.01$
Limiting indices	$-16 \leq h \leq 15$, $-7 \leq k \leq 8$, $-9 \leq l \leq 17$	$-8 \leq h \leq 7$, $-9 \leq k \leq 8$, $-23 \leq l \leq 13$
Reflections collected/unique	7084/2617 [$R_{(int)} = 0.0444$]	5561/3475 [$R_{(int)} = 0.0562$]
Data/restraints/parameters	2617/0/182	3475/10/273
Goodness-of-fit on F^2	0.996	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0369$, $wR_2 = 0.0946$	$R_1 = 0.0627$, $wR_2 = 0.1282$
R indices (all data)	$R_1 = 0.0593$, $wR_2 = 0.1147$	$R_1 = 0.0932$, $wR_2 = 0.1418$
Largest diff. peak and hole (e Å^{-3})	0.504 and −0.514	1.054 and −0.568

by filtration, washed with methanol and dried in air. Yield: 85%. Calcd (%) for $C_{14}H_{13}NNiO_4$: C, 52.88; H, 4.12; N, 4.40. Found (%): C, 52.84; H, 4.09; N, 4.40. IR (cm^{-1}, KBr): 3422(w), 1637(m), 1631(s), 1603(s), 1580(m), 1545(m), 1512(s), 1461(s), 1395(m), 849(s), 773(m), 446(m), 413(w).

2.3.2. Preparation of [Ni(napphe)(H_2O)$_2$(MeOH)]·H_2O (2). H_2napphe (1.0 mmol), $Ni(CH_3COO)_2 \cdot 4H_2O$ (1.0 mmol) were dissolved in a water/methanol solution (20 mL, 1 : 1). The solution was stirred for 3 h at 60°C and filtered. Dark green block crystals were obtained from the filtrate after 4 days. Yield: 68%. Calcd (%) for $C_{21}H_{25}NNiO_7$: C, 54.58; H, 5.45; N, 3.03. Found (%): C, 54.84; H, 5.85; N, 3.40. IR (cm^{-1}, KBr): 3382(w), 1625(s), 1596(s), 1581(m), 1542(m), 1509(w), 1460(s), 1406(m), 1325(m), 860(m), 826(m), 561(w), 492(m).

2.4. *X-ray structure determination*

Suitable crystals of **1** and **2** were used for the structure determination. Data collection was carried out on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation. Details of data collection and procession are given in table 1. The structures were solved by direct methods with SHELXL-97 and refined by full-matrix least-squares on F^2 with SHELXL-97 [22]. All non-hydrogen atoms were assigned anisotropic thermal parameters. The coordinates of the hydrogen atoms were obtained from difference Fourier maps and refined with a common isotropic thermal parameter.

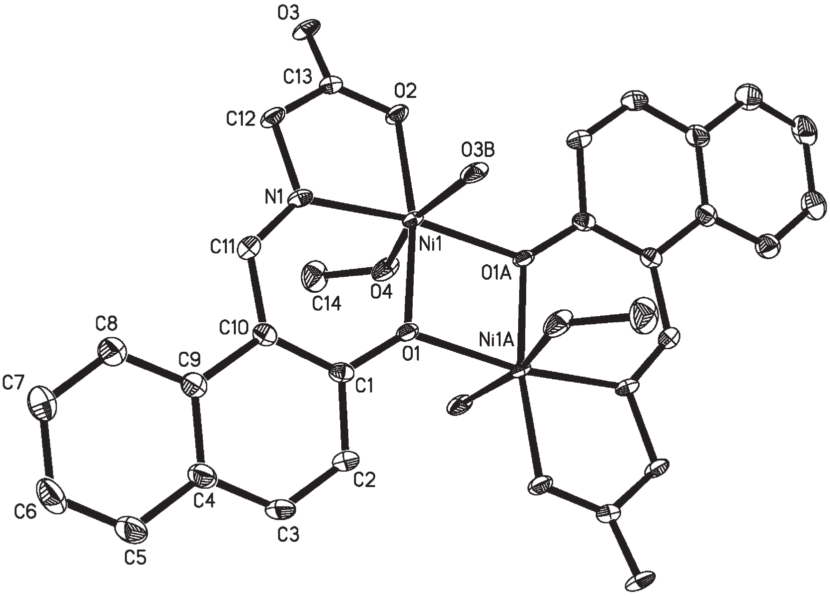

Figure 1. View of the dimeric unit of **1** (hydrogen atoms are omitted for clarity). Symmetry codes: (a): $-x+2$, $-y+2$, $-z+2$; (b): $-x+2$, $y-1/2$, $-z+5/2$.

3. Results and discussion

3.1. *Crystal structure of [Ni(napgly)(MeOH)]$_n$ (1)*

Each Ni(II) atom adopts a distorted octahedral configuration defined by one methanol O atom, four O atoms and one N atom from three different fully deprotonated napgly anions (figure 1). Four O atoms (O1, O2, O4, and O3B (symmetry code B: $-x+2$, $y-1/2$, $-z+5/2$)) comprise the equatorial plane, while N1 and O1A (symmetry code A: $-x+2$, $-y+2$, $-z+2$) atoms lie in the axial positions with bond distance 1.974(3) and 2.074(2) Å, respectively. The Ni–O and Ni–N bond lengths (table 2) are in agreement with values found in other Ni(II) complexes with Schiff-base amino acids [23–28]. In the complex, each Ni(II) center is linked to another inversion-related Ni(II) center by two O atoms of phenolate groups to give a centrosymmetric dimeric unit and a planar four-membered ring [Ni1–O1–Ni1A–O1A] is completed as shown in figure 1. The Ni1–O1–Ni1A bond angle is 98.738(11)° and the Ni1 ··· Ni1A distance is 3.0999(8) Å. The carboxylate groups bridge nickel(II) atoms by *syn-anti* conformation with the Ni ··· Ni separation of 5.439 Å, leading to a two-dimensional network in the *bc* plane (figure 2).

The value 1.4568(4) Å for C12–N1 bond, which is shorter than the usual C–N single bond, and the double bond C11–N1 length of 1.2770(3) Å agree well with the values of Schiff-base type ligands [29]. The carboxylate group shows the expected trigonal geometry with the values of carbon–oxygen bond distance and O–C–O intracarboxylate bond angle, 1.243 Å [C13–O2], 1.264 Å [C13–O3], and 125.1° [O2–C13–O3], respectively.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Ni1–N1	1.974(3)	Ni1–N1	1.974(5)
Ni1–O2	2.056(2)	Ni1–O1	1.978(5)
Ni1–O3B	2.077(2)	Ni1–O2	2.049(5)
Ni1–O1	2.010(2)	Ni1–O5	2.076(4)
Ni1–O1A	2.074(2)	Ni1–O6	2.100(5)
Ni1–O4	2.143(3)	Ni1–O4	2.116(5)
N1–Ni1–O1	90.08(10)	N1–Ni1–O1	91.2(2)
N1–Ni1–O2	81.90(10)	N1–Ni1–O2	81.7(2)
O1–Ni1–O2	168.72(10)	O1–Ni1–O2	172.9(2)
N1–Ni1–O1A	171.21(10)	N1–Ni1–O5	175.74(17)
O1–Ni1–O1A	81.26(10)	O1–Ni1–O5	92.6(2)
O2–Ni1–O1A	106.45(9)	O2–Ni1–O5	94.52(19)
N1–Ni1–O3B	97.92(11)	N1–Ni1–O6	95.8(3)
O1–Ni1–O3B	92.08(10)	O1–Ni1–O6	90.2(2)
O2–Ni1–O3B	96.85(10)	O2–Ni1–O6	90.0(2)
O1A–Ni1–O3B	84.02(9)	O5–Ni1–O6	86.1(2)
N1–Ni1–O4	97.01(11)	N1–Ni1–O4	89.1(3)
O1–Ni1–O4	87.54(10)	O1–Ni1–O4	91.3(2)
O2–Ni1–O4	85.60(10)	O2–Ni1–O4	89.2(2)
O1A–Ni1–O4	81.16(9)	O5–Ni1–O4	88.9(2)
O3B–Ni1–O4	165.06(10)	O6–Ni1–O4	174.9(2)

Symmetry codes for **1**: A: $-x+2$, $-y+2$, $-z+2$; B: $-x+2$, $y-1/2$, $-z+5/2$.

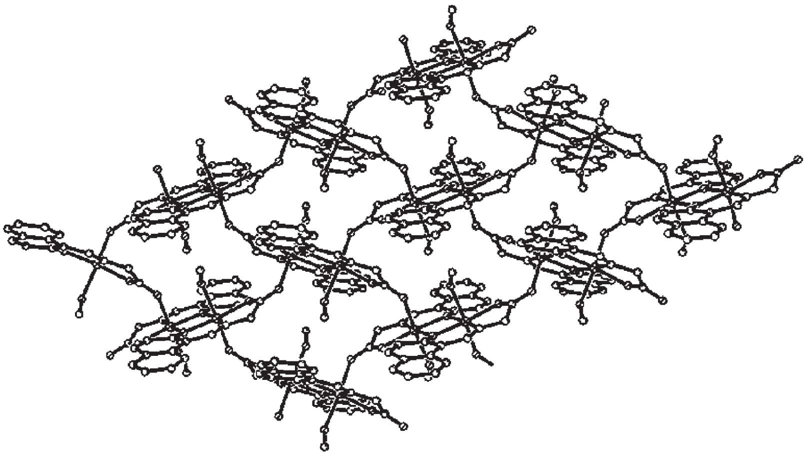

Figure 2. Perspective view of the 2D network structure of **1**.

3.2. *Crystal structure of* $[Ni(napphe)(H_2O)_2(MeOH)]\cdot H_2O$ *(2)*

The independent unit of **2** is composed of a mononuclear Ni(II) unit and a lattice water molecule (figure 3). The central Ni(II) has a distorted octahedral coordination geometry with one N atom and two O atoms from a deprotonated ligand, one O atom from a methanol molecule, and two waters. The Ni–O and Ni–N bond lengths are similar to those in **1**. The Schiff-base ligand is tridentate forming five-membered and six-membered chelate rings. The dihedral angle between the two related mean planes is 7.1°. In the ligand the dihedral angle between naphthyl and phenyl ring is 49.7°. Similar

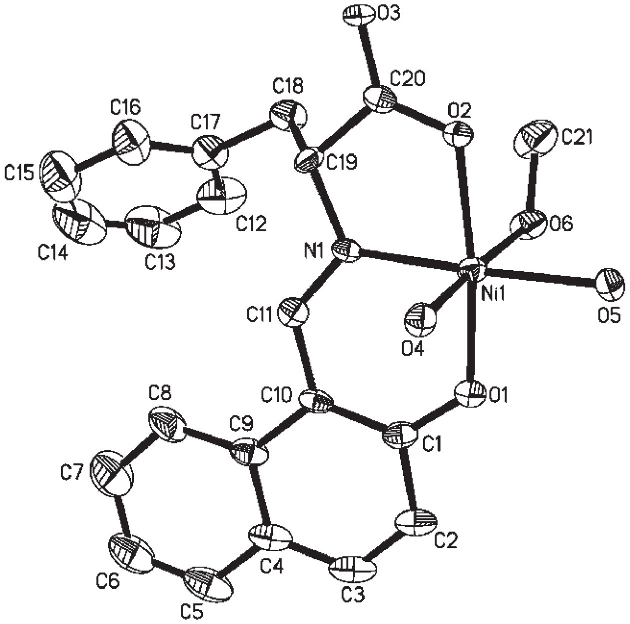

Figure 3. View of the molecular structure of **2** with the atom-numbering scheme and 30% displacement ellipsoids (the lattice water molecule and hydrogen atoms are omitted for clarity).

Table 3. Selected Hydrogen-bond geometry (Å, °) for **2**.

D–H···A	D–H	H···A	D···A	D–H···A
O4–H4C···O7	0.85	2.05	2.795(8)	146
O4–H4D···O2^{i}	0.85	1.94	2.759(6)	161
O5–H5C···O3^{i}	0.85	1.84	2.657(8)	161
O5–H5D···O7^{ii}	0.85	2.03	2.792(8)	150
O6–H6A···O3^{iii}	0.93	2.03	2.639(8)	122
O7–H7C···O1^{iv}	0.85	1.82	2.664(8)	175
O7–H7D···O5^{i}	0.85	1.95	2.792(8)	167

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

to **1**, C19–N1 and C11–N1 bond lengths in **2** are 1.466(8) and 1.286 Å. In the carboxylate group of **2**, the carbon–oxygen bond distances of 1.265 Å (C20–O2) and 1.245 Å (C20–O3) are close to the values in **1**.

Neighboring molecules are connected by hydrogen bonds involving the napphe anions, methanol molecules, coordinated water molecules and lattice water molecules. The hydrogen bonds, summarized in table 3, link the molecules along the *bc* plane to form 2-D layers (figure 4).

In the synthesis of **2**, water was used and water molecules coordinate to Ni(II), causing the different structure between the two complexes.

3.3. *Magnetic properties*

The magnetic behavior of **1** is shown in figure 5. The value of μ_{eff} at 300 K is 3.85 μ_{B}, smaller than that of two uncoupled $S=1$ centers (theoretical value with

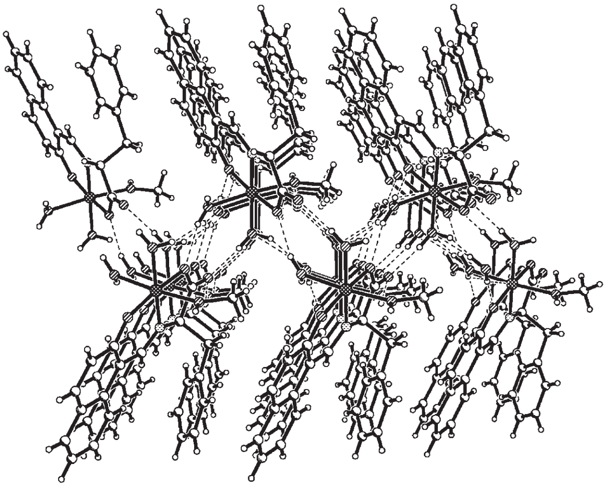

Figure 4. The 2D structure of **2**.

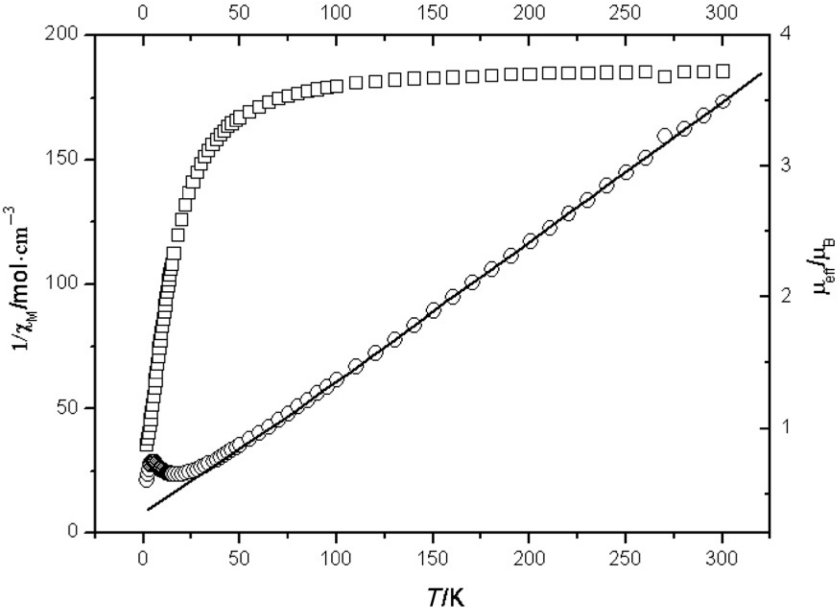

Figure 5. Temperature dependence of $1/\chi_M$ and μ_{eff} for **1** (○, $1/\chi_M$, ϒ, μ_{eff}).

$g = 2$, $\mu_{eff} = 4.0\,\mu_B$). As the temperature is lowered, μ_{eff} decreases to 0.12 μ_B at 2 K. The Weiss constant based on the equation $\chi_M = C/(T - \theta)$ is negative ($\theta = -8.1$) in the range 100–300 K, which suggests an antiferromagnetic interaction between the nickel(II) ions.

Supplementary data

Crystallographic data for **1** and **2** are deposited at the Cambridge Crystallographic Data Center CCDC, the deposition numbers are 626504 and 633449, respectively. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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