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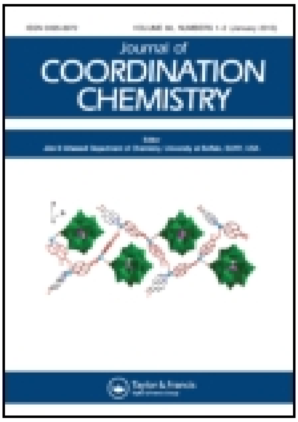

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and characterization of chiral trinuclear cobalt and nickel complexes supported by binaphthol-derived bis(salicylaldimine) ligands

Lei Zhang[a], Wei Gao[a], Qiaolin Wu[a], Qing Su[a], Jingshun Zhang[a] & Ying Mu[a]

[a] State Key Laboratory of Supramolecular Structure and Materials, School of Chemistry, Jilin University, Changchun, P.R. China

Accepted author version posted online: 01 Aug 2013.Published online: 24 Sep 2013.

To cite this article: Lei Zhang, Wei Gao, Qiaolin Wu, Qing Su, Jingshun Zhang & Ying Mu (2013) Synthesis and characterization of chiral trinuclear cobalt and nickel complexes supported by binaphthol-derived bis(salicylaldimine) ligands, Journal of Coordination Chemistry, 66:18, 3182-3192, DOI: 10.1080/00958972.2013.830716

To link to this article: http://dx.doi.org/10.1080/00958972.2013.830716

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 18, 3182–3192, http://dx.doi.org/10.1080/00958972.2013.830716

Synthesis and characterization of chiral trinuclear cobalt and nickel complexes supported by binaphthol-derived bis (salicylaldimine) ligands

LEI ZHANG, WEI GAO*, QIAOLIN WU, QING SU, JINGSHUN ZHANG and YING MU*

State Key Laboratory of Supramolecular Structure and Materials, School of Chemistry,
Jilin University, Changchun, P.R. China

(*Received 27 January 2013; accepted 12 July 2013*)

Chiral bis(salicylaldimine) ligands derived from binaphthol (**LH$_2$**) were synthesized by condensation of (*R/S*) 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarbaldehyde with 2-anisidine. Cobalt and nickel complexes (Co**L**)$_2$(OAc)$_2$Co (**1**) and (Ni**L**)$_2$(OAc)$_2$Ni (**2**) were synthesized *via* reactions of the ligand with the corresponding metal acetate salt. Both complexes were characterized by elemental analysis, IR, MS, and single-crystal X-ray diffraction analysis. The X-ray analysis reveals linear trinuclear for **1** and **2** and the metal ions in both complexes are octahedral coordination. The two acetates separately bridge the center metal with one of the terminal metals in M–O–C–O–M manner. The magnetic susceptibility of **1** below 150 K suggests the existence of a weak ferromagnetic exchange at low temperatures, while antiferromagnetic interactions among Co(II) cores were observed above 150 K. Complex **2** shows similar magnetic behavior to that of **1**.

Keywords: Schiff base ligand; Chiral; Nickel complexes; Cobalt complexes

1. Introduction

Polynuclear complexes of transition metal ions have attracted attention due to their wide uses in catalysis [1–3], single molecular magnets [4–6], and in modeling multimetal active sites of metalloproteins [7]. Some cobalt complexes are capable of reversibly binding dioxygen and can serve as models in the simulation of natural dioxygen transformation biosystems. Generally, polydentate ligands with suitable configuration are used to construct polynuclear complexes. The tetradentate salen ligands, in which two salicylaldimine moieties were linked through aromatic or aliphatic linkers at the imine positions, have received particular interest in preparing polynuclear complexes with deprotonated phenolic oxygens to bind more than one metal [8–12]. Many trinuclear complexes with salen-type ligands were prepared and investigated [13–19]. Yields of polynuclear complexes are dependent not only on the substituents in the ligands but also on reaction conditions such as the concentrations of the reactants and temperature. In some cases, mononuclear complexes are favored

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*Corresponding authors. Email: gw@jlu.edu.cn (Wai Gao); ymu@jlu.edu.cn (Ying Mu) due to flexibilities of the linkers in the ligands [20]. Recently, the Li group developed biphenol/binaphthol diimine ligands for supporting neutral nickel complexes for norbornene polymerization [21]. Such ligands were composed of two salicylaldimine moieties linked at the *ortho* positions of two aromatic rings. In complexation with metal precursors, the large dihedral angle of the two aromatic rings prohibits formation of mononuclear complexes. Chirality of these ligands can be maintained and render a chiral enviroment at the metal centers. To extend use of binaphthol-derived bis(salicylaldimine) ligands in polynuclear chemistry, we introduced methoxy groups in imine moieties which can serve as additional coordinating sites in forming polynuclear complexes. Herein, we report the synthesis of linear, trinuclear cobalt, and nickel complexes $(Co\mathbf{L})_2(OAc)_2Co$ (**1**) and $(Ni\mathbf{L})_2(OAc)_2Ni$ (**2**) supported by chiral binaphthol diimine ligands. The molecular structures of **1** and **2** were characterized by single-crystal X-ray diffraction analysis and preliminary studies on the magnetic properties were also reported.

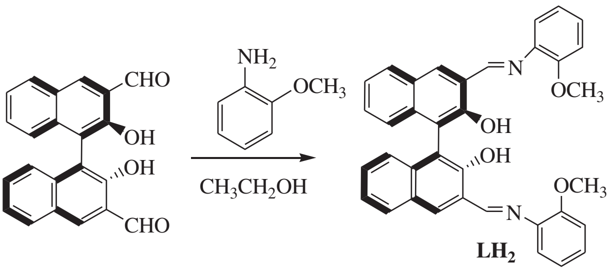
2. Results and discussion

2.1. *Synthesis and characterization of LH₂*

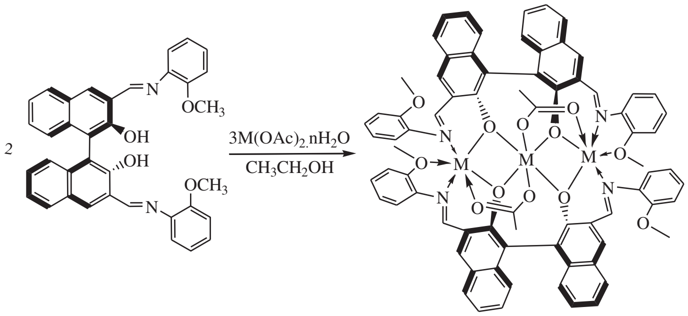
Chiral binaphthol bis(salicylaldimine) was synthesized in high yield by reacting (*R*)-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarbaldehyde with 2-anisidine in ethanol (scheme 1). The ligand was characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum shows typical resonances at δ 13.47 and 9.01 ppm for –OH and the imine N=CH, respectively [22]. Correspondingly, ^{13}C NMR resonances for C–OH and N=CH were found at δ 154.9 and 162.7 ppm, respectively. In a similar procedure, $\mathbf{LH_2}$ (*S*) was also synthesized and identified by ^1H NMR (scheme 1).

2.2. *Synthesis and characterization of the complexes*

Reactions of the ligand with an equivalent of cobalt acetate or nickel acetate in hot ethanol afford the products as red powders which were identified as trinuclear cobalt complex (**1**) and trinuclear nickel complex (**2**). In the complexes, the ratios of the ligands to the metal were determined to be 2 : 3 and the yields were improved by adjusting the ligand to metal acetate ratios (2 : 3). Further increase of the ratios of ligand to metal result in decrease of the yields probably due to formation of insoluble linear



Scheme 1. Synthesis of the ligand.



1, M = Co;
2, M = Ni

Scheme 2. Synthetic procedure of complexes.

multinuclear complexes linked with binaphthol moieties. The complexes were all characterized with IR and were compared with reported cobalt complexes [10, 23]. The Ar–O and C=N stretching bands at 1252 and 1618 cm^{-1} in free **LH$_2$** shift to lower frequencies by ca. 31 and 8 cm^{-1} in **1** and **2**, respectively, upon complexation with metals [16, 18]. The red shift of these Ar–O and C=N absorptions on going from free **LH$_2$** results from M–O and M–N interactions. The new signals of **1** at 418 and 481 cm^{-1} are assigned to *ν*(Co–O) and *ν*(Co–N), respectively. Correspondingly, the new signal of **2** at 486 cm^{-1} is assigned to *ν*(Ni–N). Co(R) (**1**), Co(S), and Ni(R) (**2**) were characterized with UV–vis spectroscopy. Co(R) (**1**) and Co(S) show similar spectra in which three π–π* transitions were found with slight bathochromic shift (~16 nm) at ~248 nm, ~285 nm, and ~351 nm with respect to that of free **LH$_2$**(R) and **LH$_2$**(S). For all the spectra of Co(R) (**1**), Co(S), and Ni(R) (**2**), a new band around 450 nm was observed, probably ascribed to LMCT

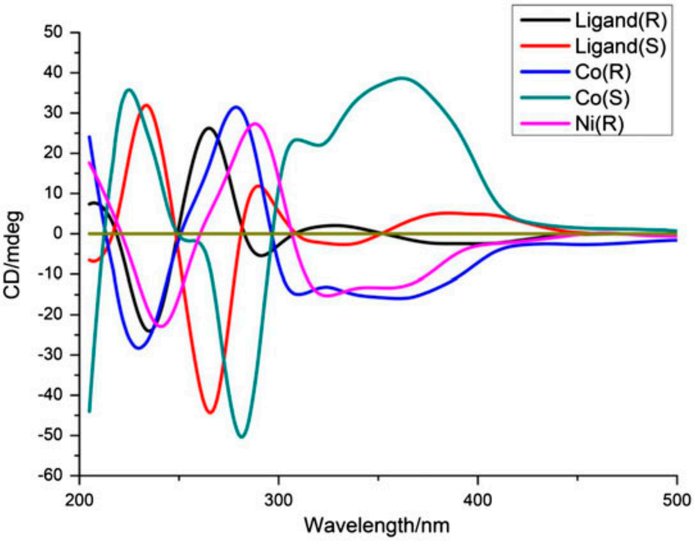


Figure 1. Circular-dichromism spectroscopy of the trinuclear cobalt complex (1.0 × 10^{-5} M/L in methanol).

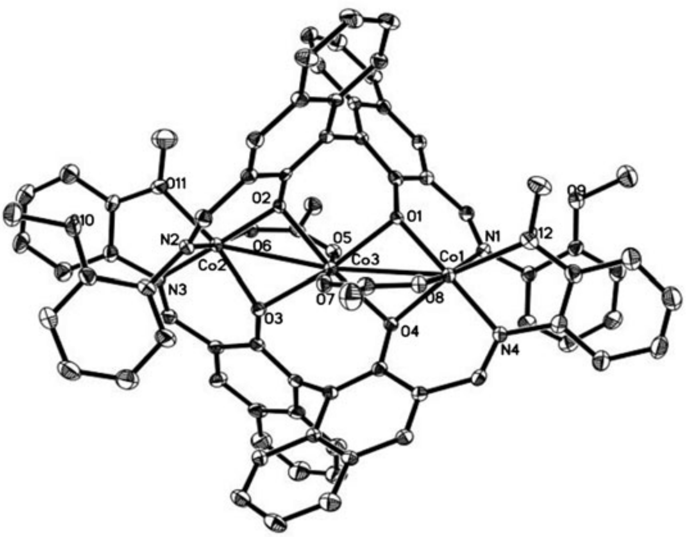


Figure 2. Perspective view of **1** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvents are omitted for clarity.

excitations. Circular dichromism (figure 1) spectra of **1** and **2** exhibit three major bands similar to that of the ligand, but with much higher intensities. Due to LMCT excitations, the CD spectra of **1** and **2** exhibit a broad and strong band at 360 nm.

2.3. *Crystal structure of complexes*

Crystals of **1** and **2** suitable for X-ray diffraction analysis were grown from toluene and ethanol. The molecular structure of **1** and **2** are depicted in figures 2 and 3. Crystal data are collected in table 1 and selected bond lengths and angles in table 2. Complexes **1** and **2** are isomorphous and crystallized in the monoclinic space group *P2(1)*. Both of them are composed of three metal ions, two L^{2-} moieties and two acetates. All the metal centers in **1** and **2** are six-coordinate in slightly distorted octahedral geometries due to the restrictions imposed by the two bridged acetates. The internal metal ions in **1** and **2** were coordinated by O_2O_2 donors of the two binaphthol ligands and two oxygens of two different acetates. The six O–Co bond lengths around Co(3) (2.0346–2.1375 Å) are similar to those in the other trinuclear cobalt complex with similar structure [16] and are typical for high-spin Co(II)–O distances [24]. The Ni–O bond distances involving Ni(3) (2.017(3)–2.079(4) Å) are similar to those observed in the nickel complexes bearing N,O-bidentate ligands and those in linear trinuclear nickel complexes with 2-[(3-dimethylamino-propylimino)-methyl]-phenol [25]. The bridging angles of Co–O–Co (87.9(2)–91.5(2)°) and Ni–O–Ni (88.6(2)–92.6(3)°) are close to the right angle and are smaller than those (94.01(5)–95.71(7)°) in the linear trinuclear cobalt cluster bearing salen-type bisoxime ligands [15] and those (97.22(16)–99.97(16)°) in linear trinuclear cobalt complexes with 1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene ligands [16]. The two terminal metals are in similar environments coordinated with two ON donor sets from two different binaphthol ligands, one O from

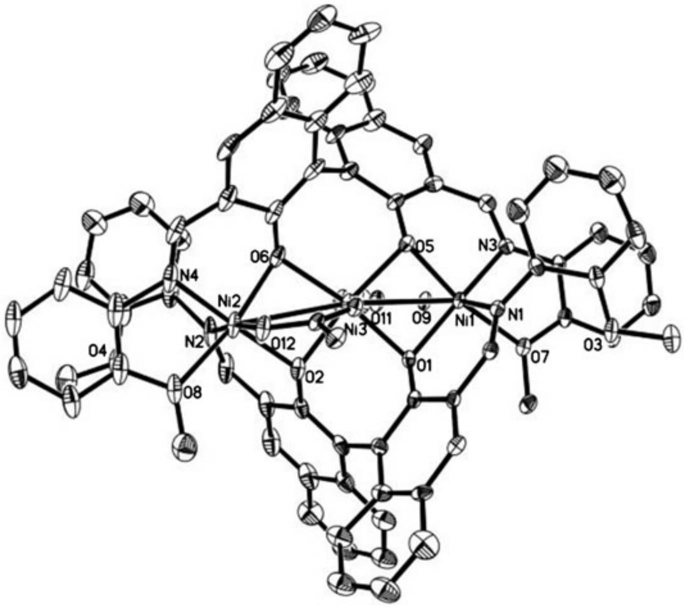


Figure 3. Perspective view of **2** with thermal ellipsoids drawn at 15% probability level. Hydrogens and uncoordinated solvent are omitted for clarity.

Table 1. Crystal data and structure refinement for **1**·C_2H_5OH and **2**·C_7H_8.

Data	**1**·C_2H_5OH	**2**·C_7H_8
Formula	$C_{78}H_{64}Co_3N_4O_{13}$	$C_{90}H_{74}N_4Ni_3O_{12}$
Fw	1442.12	1579.66
Temperature/K	185	185
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)*	*P2(1)*
a/Å	12.3360(15)	13.2082(14)
b/Å	21.605(3)	21.096(2)
c/Å	14.8114(18)	15.7818(3)
α/°	90.00	90.00
β/°	95.761(3)	109.425(2)
γ/°	90.00	90.00
Volume (Å^3)	3927.6(8)	4147.1(8)
Z	2	2
D_{Calcd} (Mg m^{-3})	1.219	1.265
F (000)	1490.0	1544
θ range for data collection	1.38–510°	1.37–26.08°
Limiting indices	$-14 \le h \le 7$, $-25 \le k \le 25$, $-17 \le l \le 17$	$-16 \le h \le 16$, $-26 \le k \le 20$, $-16 \le l \le 19$
Data/restraints/parameters	13422/589/891	15035/636/860
Goodness-of-fit on F^2	0.973	1.026
Final *R* indices [I>2σ(I)]	$R_1^{a} = 0.0821$, $wR_2^{b} = 0.1935$	$R_1^{a} = 0.0857$, $wR_2^{b} = 0.2392$
Largest diff. peak and hole/e.A^{-3}	1.614 and –0.332	1.674 and –0.722

$^{a}R_1 = \sum||F_o|-|F_c|| / \sum|F_o|$.
$^{b}wR_2 = [\sum[w(F_o^2-F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

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

1		**2**	
Co(1)–O(1)	1.978(6)	Ni(1)–O(1)	1.976(5)
Co(1)–N(4)	2.009(8)	Ni(1)–N(3)	1.973(7)
Co(1)–O(4)	2.081(6)	Ni(1)–O(5)	2.033(5)
Co(1)–N(1)	2.100(8)	Ni(1)–N(1)	2.073(6)
Co(1)–O(8)	2.111(7)	Ni(1)–O(10)	2.016(5)
Co(1)–O(12)	2.289(7)	Ni(1)–O(7)	2.202(6)
Co(1)–Co(3)	2.9170(17)	Ni(1)–Ni(3)	2.8649(14)
Co(2)–O(2)	1.986(5)	Ni(2)–O(2)	1.956(6)
Co(2)–N(3)	2.027(7)	Ni(2)–N(4)	1.995(11)
Co(2)–O(3)	2.030(6)	Ni(2)–O(6)	2.034(7)
Co(2)–O(6)	2.098(6)	Ni(2)–O(12)	2.068(6)
Co(2)–N(2)	2.100(7)	Ni(2)–N(2)	2.060(9)
Co(2)–O(11)	2.193(7)	Ni(2)–O(8)	2.175(9)
Co(2)–Co(3)	2.9339(16)	Ni(2)–Ni(3)	2.8774(15)
Co(3)–O(7)	2.042(7)	Ni(3)–O(11)	2.008(5)
Co(3)–O(5)	2.079(6)	Ni(3)–O(10)	2.016(5)
Co(3)–O(3)	2.099(6)	Ni(3)–O(1)	2.078(6)
Co(3)–O(2)	2.111(6)	Ni(3)–O(6)	2.066(6)
Co(3)–O(4)	2.113(7)	Ni(3)–O(5)	2.070(6)
Co(3)–O(1)	2.137(6)	Ni(3)–O(2)	2.024(7)
O(1)–Co(1)–N(4)	171.8(3)	O(1)–Ni(1)–N(3)	171.4(2)
O(1)–Co(1)–O(4)	91.7(2)	O(1)–Ni(1)–O(5)	91.5(2)
N(4)–Co(1)–O(4)	90.6(3)	N(3)–Ni(1)–O(9)	85.6(3)
O(1)–Co(1)–N(1)	87.9(3)	O(1)–Ni(1)–N(1)	89.0(2)
N(4)–Co(1)–N(1)	99.4(3)	N(3)–Ni(1)–N(1)	98.4(3)
O(4)–Co(1)–N(1)	99.5(3)	O(5)–Ni(1)–N(1)	91.8(2)
O(1)–Co(1)–O(8)	86.2(2)	O(1)–Ni(1)–O(9)	86.7(2)
N(4)–Co(1)–O(8)	85.9(3)	N(3)–Ni(1)–O(7)	76.6(3)
O(4)–Co(1)–O(8)	93.3(2)	O(5)–Ni(1)–O(9)	92.9(2)
N(1)–Co(1)–O(8)	166.1(3)	N(1)–Ni(1)–O(9)	173.7(3)
O(1)–Co(1)–O(12)	104.0(3)	O(1)–Ni(1)–O(7)	99.4(2)
N(4)–Co(1)–O(12)	73.6(3)	N(3)–Ni(1)–O(7)	76.6(3)
O(4)–Co(1)–O(12)	164.2(3)	O(5)–Ni(1)–O(7)	169.1(2)
N(1)–Co(1)–O(12)	82.7(3)	N(1)–Ni(1)–O(7)	88.4(2)
O(8)–Co(1)–O(12)	86.5	O(9)–Ni(1)–O(7)	87.8(2)
O(2)–Co(2)–O(11)	101.2(2)	O(2)–Ni(2)–O(6)	89.2(3)
O(2)–Co(2)–O(3)	90.4(2)	N(4)–Ni(2)–O(6)	90.5(4)
N(3)–Co(2)–O(3)	92.0(3)	O(2)–Ni(2)–O(12)	86.1(2)
O(2)–Co(2)–O(6)	83.5(2)	N(4)–Ni(2)–O(12)	87.2(3)
N(3)–Co(2)–O(6)	87.3(3)	O(6)–Ni(2)–O(12)	93.9(3)
O(3)–Co(2)–O(6)	94.4(2)	O(2)–Ni(2)–N(2)	87.9(4)
O(2)–Co(2)–N(2)	86.1(2)	N(4)–Ni(2)–N(2)	98.9(4)
N(3)–Co(2)–N(2)	102.8(3)	O(6)–Ni(2)–N(2)	90.9(4)
O(6)–Co(2)–N(2)	168.0(3)	O(12)–Ni(2)–N(2)	172.3(4)
O(7)–Co(3)–O(5)	177.0(3)	O(11)–Ni(3)–O(10)	179.5(3)
O(7)–Co(3)–O(3)	87.5(3)	O(11)–Ni(3)–O(1)	91.8(2)
O(5)–Co(3)–O(3)	92.4(2)	O(10)–Ni(3)–O(1)	88.2(2)
O(7)–Co(3)–O(2)	91.2(3)	O(11)–Ni(3)–O(10)	179.5(3)
O(5)–Co(3)–O(2)	85.8(2)	O(11)–Ni(3)–O(2)	87.3(2)
O(3)–Co(3)–O(2)	85.2(2)	O(10)–Ni(3)–O(2)	92.1(3)
O(7)–Co(3)–O(4)	92.1(3)	O(11)–Ni(3)–O(6)	92.2(2)
O(5)–Co(3)–O(4)	90.8(2)	O(10)–Ni(3)–O(6)	87.7(2)
O(3)–Co(3)–O(4)	102.5(3)	O(2)–Ni(3)–O(6)	86.4(3)
O(2)–Co(3)–O(4)	171.7(3)	O(11)–Ni(3)–O(5)	89.2(2)
O(7)–Co(3)–O(1)	89.0(3)	O(10)–Ni(3)–O(5)	91.4(2)
O(5)–Co(3)–O(1)	90.5(2)	O(5)–Ni(3)–O(2)	171.8(3)
O(3)–Co(3)–O(1)	170.4(3)	O(6)–Ni(3)–O(5)	101.1(3)
O(2)–Co(3)–O(1)	85.9(2)	O(6)–Ni(3)–O(1)	170.4(3)
O(4)–Co(3)–O(1)	86.6(2)	O(5)–Ni(3)–O(1)	87.7(2)
Co(1)–Co(3)–Co(2)	170.05(6)	Ni(2)–Ni(3)–Ni(1)	170.91(6)

acetate and one O from the *ortho* methoxy. The other methoxy group in the adjacent ligand is away from the metal centers. Each acetate bridges the terminal metal and central metal in a *syn–syn* fashion. The Co–$O_{methoxy}$ bond distances of 2.290(6) and 2.193(7) Å are slightly longer than the other Co–O bonds of 1.984(6)–2.101(6) Å to the same cobalt. The Co–N bond lengths at 2.017(7)–2.106(7) Å are slightly longer than those in the Co(III)/Co(II)/Co (III) trinuclear complexes bearing pyrazolate bridges [26]. The Ni–O bond lengths (1.949 (4)–2.079(4) Å) and Ni–N bond lengths (2.017(6)–2.046(5) Å) are comparable to those in salen nickel complexes [27]. The three metal centers in the trinuclear complexes are linear with big M(1)–M(3)–M(2) angles of 170.05(6)° and 170.76(4)° for **1** and **2**, respectively. The bond lengths of Co–Co (Co1–Co3 (2.917(2) Å) and Co2–Co3 (2.933(2) Å)) are slightly shorter than that of 3.043(3) Å in the trinuclear cobalt complex bearing salen-type bisoxime ligands [15]. Bond lengths of Ni–Ni (Ni1–Ni3 (2.875(1) Å) and Ni2–Ni3 (2.864(1) Å)), although slightly shorter than 3.072(2) Å in salen-type bisoxime trinuclear nickel complex [28], suggest the existence of weak intermetallic interactions.

2.4. *Magnetic measurement*

The temperature dependent dc magnetic susceptibility of **1** is shown in figure 4. The room temperature $\chi_M T$ of **1** is 5.99 $cm^3\,K\,M^{-1}$, corresponding to an effective magnetic movement 6.92 µB, which is larger than the spin-only value of 4.74 µB for three high-spin Co(II) ions. This value is indicative of an appreciable orbital contribution to the magnetic moment of the high-spin Co(II) in octahedral coordination. The magnetic data of Co(II) complex above 150 K obeys the Curie-Weiss law with a Weiss constant θ of –44.91 K and a Curie constant C of 6.87 $cm^3\,K\,M^{-1}$. The negative θ value may reveal antiferromagnetic interactions among Co(II) above 150 K. Nevertheless, weak ferromagnetic exchange may exist in the low temperature range due to the fact that $\chi_M T$ increased steadily below 150 K.

Complex **2** shows similar magnetic behavior to that of **1**. The room temperature $\chi_M T$ of **2** is 3.01 $cm^3\,K\,M^{-1}$, corresponding to an effective magnetic moment of 4.91 µB, almost the same as the spin-only value 4.90 µB for three Ni(II) cations. The magnetic data of **2** above 150 K obey Curie-Weiss law with a Weiss constant θ of –53.31 K and a Curie constant C of 3.53 $cm^3\,K\,M^{-1}$ (figure 5).

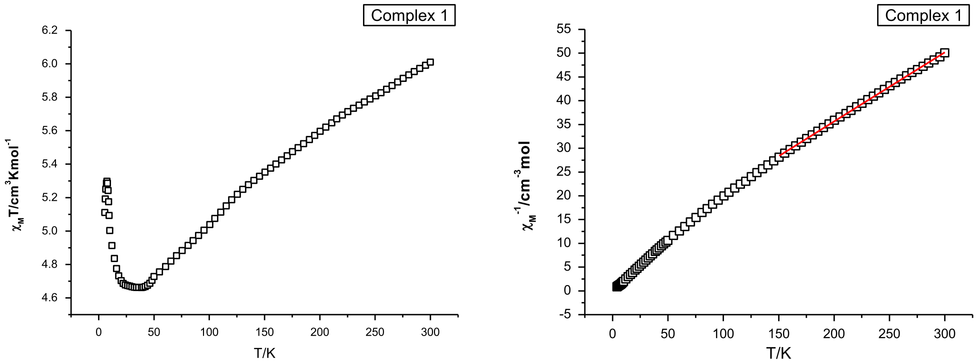


Figure 4. Temperature dependence of the magnetic susceptibility of **1** from 4.0 to 300 K.

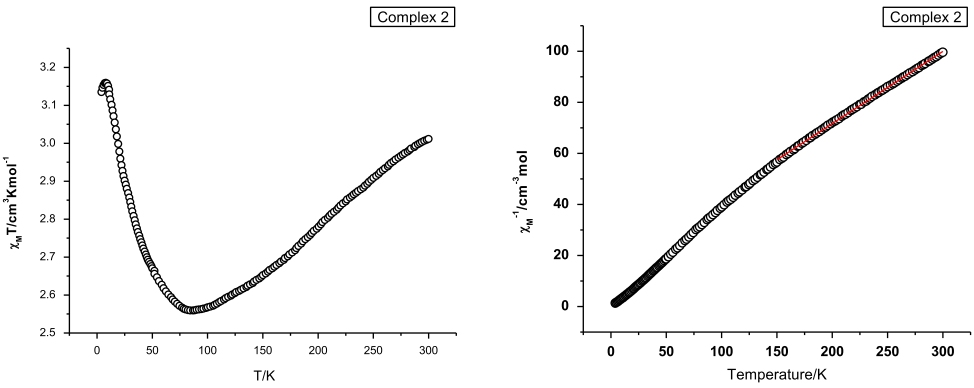


Figure 5. Temperature dependence of the magnetic susceptibility of **2** from 2.0 to 300 K.

3. Experimental

3.1. *General remarks and materials*

(*R/S*)-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarbaldehyde was synthesized by starting with a methoxymethyl ether protected optically active (*R/S*)-BINOL according to the literature procedure [29]. The NMR data of the ligands were obtained on a Bruker 300 MHz spectrometer at ambient temperature with $CDCl_3$ as solvent. The elemental analysis was performed on a Perkin–Elmer 2400 analyzer. FT-IR was performed on a Nicolet FT-IR 360 spectrometer (Nicolet, USA). MS spectra were recorded on a Bruker HTC spectrometer. UV–vis and CD were preformed on a Biologic PMS 450. Magnetic measurements were performed on SQUID Magnetic Property Measurement System.

3.2. *Synthesis of LH_2 (R)*

To a stirred solution of (*R*)-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarbaldehyde (1.0 g, 2.9 mM) in methanol (20 mL) were added 2-methoxyaniline (0.76 g, 6.1 mM) and formic acid (1 drop) as a catalyst. The mixture was refluxed for 4 h to yield an orange precipitate. The crude product was filtered at room temperature and washed with ice-cold ethanol to afford pure ligand as an orange solid in 85% yield (1.37 g). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 13.47 (s, 2H, OH), 9.01 (s, 2H, CH=NAr), 8.12 (s, 2H, Ar-H), 7.92 (m, 2H, Ar-H), 7.30 (m, 6H, Ar-H), 6.53 (m, 6H, Ar-H), 3.81 (s, 6H, –OCH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 55.6, 111.7, 116.9, 120.4, 120.8, 121.7, 123.3, 124.9, 127.6, 128.0, 128.5, 128.9, 134.4, 135.69, 137.0, 153.0, 154.9, 162.7 ppm. Anal. Calcd for $C_{36}H_{28}N_2O_4$: C, 78.24; H, 10.01; N, 4.97. Found: C, 78.20; H, 10.05; N, 5.00.

3.3. *Synthesis of LH_2 (S)*

A procedure analogous to that used for **LH_2** (*R*) was used, but starting from (S)-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarbaldehyde. Yield (1.40 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 13.49 (s, 2H, OH), 9.00 (s, 2H, CH=NAr), 8.12 (s, 2H, Ar-H), 7.92 (m, 2H, Ar-H), 7.29 (m, 6H, Ar-H), 6.53 (m, 6H, Ar-H), 3.81 (s, 6H, –OCH_3) ppm. ^{13}C NMR

($CDCl_3$, 75 MHz, 298 K): δ 55.6, 111.7, 116.9, 120.4, 120.8, 121.7, 123.3, 124.9, 127.6, 128.1, 128.5, 128.9, 134.4, 135.7, 137.0, 153.0, 154.9, 162.8 ppm. Anal. Calcd for $C_{36}H_{28}N_2O_4$: C, 78.24; H, 10.01; N, 4.97. Found: C, 78.21; H, 10.06; N, 4.99.

3.4. *Synthesis of complexes*

3.4.1. Complex 1 (R). A solution of cobalt(II) acetate tetrahydrate (0.747 g, 3.0 mM) in ethanol (20 mL) was added dropwise to a solution of ligand (0.985 g, 2.0 mM) in ethanol (20 mL) and NEt_3 (1 mL) at reflux. The mixture turned red at once and stirred for 4 h. Filtering and evaporating the solvent to dryness affords **1** as red powder. The crystals suitable for X-ray diffraction analysis were grown from toluene and ethanol (10 : 1). Data for $C_{76}H_{58}N_4Co_3O_{12}$ (1396.05): yield, 0.911 g (65.3%). Anal. Calcd for $C_{76}H_{58}N_4Co_3O_{12}$: C, 65.38; H, 4.19; N, 4.01. Found: C, 65.35; H, 4.21; N, 4.04. MS (*m*/*z*): Calcd for $[(Co\mathbf{L})_2(OAc)_2Co\text{-}(OAc)_2]^+$: 1276.05, Found: 1276.1.

3.4.2. Complex 1 (S). A procedure analogous to that used to **1** (*R*) was used, but starting from $\mathbf{LH_2}$ (S). Yield (0.942 g, 67.5%). Anal. Calcd for $C_{76}H_{58}N_4Co_3O_{12}$: C, 65.38; H, 4.19; N, 4.01. Found: C, 65.34; H, 4.23; N, 4.06.

3.4.3. Complex 2 (R). A solution of nickel(II) acetate tetrahydrate (0.746 g, 3.0 mM) in ethanol (20 mL) was added dropwise to a solution of $\mathbf{LH_2}$ (0.985 g, 2.0 mM) in ethanol (20 mL) and NEt_3 (1 mL) at refluxing temperature. The mixture turned orange at once. The mixture was stirred for 4 h and the solution was filtered. Filtering and evaporating the solvent to dryness afford **2** (*R*) as red powder. Crystals suitable for X-ray diffraction analysis were grown from mixed solution of toluene and ethanol (10 : 1). Data for $C_{76}H_{58}N_4Ni_3O_{12}$ (1395.37): yield, 0.980 g (70.2%). Anal. Calcd for $C_{76}H_{58}N_4Ni_3O_{12}$: C, 65.42; H, 4.19; N, 4.02. Found: C, 65.39; H, 4.21; N, 4.04. MS (*m*/*z*): Calcd for $[(Ni\mathbf{L})_2(OAc)_2Ni\text{-}OAc]^+$: 1335.37, Found: 1335.2.

3.5. *X-ray crystal structural determination*

Crystals were mounted on a glass fiber using an oil drop. Data obtained with the ω–2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods, with further refinement with full-matrix least squares on F^2 obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogens were introduced in calculated positions with displacement factors of the host carbons. Complexes **1** and **2** crystallize from toluene/ethanol mixed solution and have lost solvent prior to X-ray measurement. PLATON suggests the existence of large solvent accessible voids in both **1** and **2**, which lower the qualities greatly. Due to the big structure and lower quality caused by the large voids, some aromatic rings in **2** are seriously disordered and necessary constraints were used.

4. Conclusions

Two trinuclear nickel and cobalt complexes were synthesized by reaction of chiral binaphthol bis(salicylaldimine) with metal acetate. Both complexes have trinuclear configuration with the three metals in a linear array. The metal centers are octahedral and two acetates coordinate to the three metal ions *via* a familiar M–O–C–O–M mode. Temperature dependence of magnetic susceptibility of **1** suggests the existence of antiferromagnetic interactions among Co(II) cores at 150 K. Weak ferromagnetic exchanges were found at low temperature. Similar magnetic behavior of **2** was also observed.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers: 921224 (**1**); 921225 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44–1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccd.cam.ac.uk).

Acknowledgment

This study was supported by the National Science Foundation of China (Nos. 51173061, 21074043 and 21274050).

References

[1] A. Kilic, A.A. Palali, M. Durgun, Z. Tasci, M. Ulusoy, M. Dagdevren, I. Yilmaz. *Inorg. Chim. Acta*, **394**, 635 (2013).

[2] M. Ulusoy, O. Sahin, A. Kilic, O. Buyukgungor. *Catal. Lett.*, **141**, 717 (2011).

[3] K. Endo, D. Hamada, S. Yakeishi, M. Ogawa, T. Shibate. *Org. Lett.*, **14**, 2342 (2012).

[4] K. Katoh, H. Isshiki, T. Komeda, M. Yamashita. *Chem. Asian J.*, **7**, 1154 (2012).

[5] C. Lydon, M.M. Sabi, M.D. Symes, D.L. Long, M. Murrie, S. Yoshii, H. Nojiri, L. Cronin. *Chem. Commun.*, **48**, 9819 (2012).

[6] J.M. Zadrozny, J.R. Long. *J. Am. Chem. Soc.*, **133**, 20732 (2011).

[7] R. Salzmann, M.T. McMahon, N. Godbout, L.K. Sanders, M. Wojdelski, E. Oldfield. *J. Am. Chem. Soc.*, **121**, 3818 (1999).

[8] P. Seth, L. Das, M. Drew, A. Ghosh. *Eur. J. Inorg. Chem.*, **13**, 2232 (2012).

[9] S. Akine, W.K. Dong, T. Nabeshima. *Inorg. Chem.*, **45**, 4677 (2006).

[10] W. Feng, Y. Zhang, Z. Zhang, X. Lu, H. Liu, G. Shi, D. Zou, J. Song, D. Fan, W.K. Wong, R.A. Jones. *Inorg. Chem.*, **51**, 11377 (2012).

[11] W. Feng, Y. Hui, G. Shi, D. Zou, X. Lu, J. Song, D. Fan, W. Wong, R. Jones. *Inorg. Chem. Commun.*, **20**, 33 (2012).

[12] S. Biswas, R. Saha, A. Ghosh. *Organometallics*, **31**, 3844 (2012).

[13] F. Yang, P. Yan, Q. Li, P. Chen, G. Li. *Eur. J. Inorg. Chem.*, **27**, 4287 (2012).

[14] J. Welby, L.N. Rusere, J.M. Tanski, L.A. Tyler. *Inorg. Chim. Acta*, **362**, 1405 (2009).

[15] W.K. Dong, L. Li, C.F. Li, L. Xu, J.G. Duan. *Spectrochim. Acta, Part A*, **71**, 650 (2008).

[16] S. Chattopadhyay, G. Bocelli, A. Musatti, A. Ghosh. *Inorg. Chem. Commun.*, **9**, 1053 (2006).

[17] L. Mechi, P. Siega, R. Dreos, E. Zangrando, L. Randaccio. *Eur. J. Inorg. Chem.*, **18**, 2629 (2009).

[18] W.K. Dong, J.G. Duan, L.Q. Chai, G.L. Liu, H.L. Wu. *J. Coord. Chem.*, **61**, 1306 (2008).

[19] W. Bi, T. Wei, X. Lue, Y. Hui, J. Song, S. Zhao, W.K. Wong, R.A. Jones. *New J. Chem.*, **33**, 2326 (2009).

[20] W.M. Ren, X. Zhang, Y. Liu, J.F. Li, H. Wang, X.B. Lu. *Macromolecules*, **43**, 1396 (2010).

[21] T. Hu, Y.G. Li, Y.S. Li, N.H. Hu. *J. Mol. Catal. A: Chem.*, **253**, 155 (2006).

[22] T.Q. Xu, Y. Pan, X.B. Lu. *Dalton Trans.*, 8643 (2011).
[23] S. Djebbar-Sid, O. Benali-Baitich, J.P. Deloume. *J. Mol. Struct.*, **569**, 121 (2001).
[24] (a) C. Fukuhara, E. Asato, T. Simoji, K. Kastura, M. Mori, K. Matsumoto, S. Ooi. *J. Chem. Soc. Dalton Trans.*, 1305 (1987); (b) A. Gerli, K.S. Hagen, L.G. Marzilli. *Inorg. Chem.,* **30**, 4673 (1991).
[25] (a) M. Dey C.P. Rao, P.K. Saarenketo K. Rissanen. *Inorg. Chem. Commun.*, **5**, 924 (2002); (b) S. Giri, R. Biswas, A. Ghosh, S.K. Saha. *Polyhedron*, **30**, 2717 (2011).
[26] T.S. Billson, J.D. Crane, O.D. Fox, S.L. Heath. *Inorg. Chem. Commun.*, **3**, 718 (2000).
[27] A. Kumar Singh, S. Kumari, T.N. Guru Row, J. Prakash, K. Ravi Kumar, B. Sridhar, T.R. Rao. *Polyhedron*, **27**, 3710 (2008).
[28] W.K. Dong, X. Chen, Y.X. Sun, Y.H. Yang, L. Zhao, L. Xu, T.Z. Yu. *Spectrochim. Acta, Part A*, **74**, 719 (2009).
[29] H.C. Zhang, W.S. Huang, L. Pu. *J. Org. Chem.*, **66**, 481 (2001).