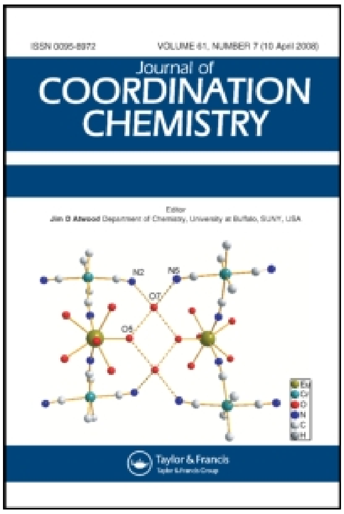

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Synthesis and structural characterization of new trinuclear cobalt(II) and nickel(II) complexes possessing five- and six-coordinated geometry

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Tri-nuclear cobalt and nickel complexes ($[(CoL)_2(OAc)_2Co]\cdot THF$ (**I**) and $[(NiL)_2(OAc)_2(THF)_2Ni]\cdot THF$ (**II**)) have been synthesized by reaction of a new Salen-type bisoxime chelating ligand of 2,2′-[ethylenedioxy*bis*(nitrilomethylidyne)]dinaphthol(H_2L) with cobalt(II) acetate tetrahydrate or nickel(II) acetate tetrahydrate, respectively. Complexes **I** and **II** were characterized by elemental analyses, IR, TG-DTA and ^{1}H-NMR *etc*. The X-ray crystal structures of **I** and **II** reveal that two acetate ions coordinate to three cobalt or nickel ions through M–O–C–O–M (M = Co or Ni) bridges and four μ-naphthoxo oxygen atoms from two [ML] units also coordinate to cobalt(II) or nickel(II). Complex **I** has two distorted square-pyramidal coordination spheres and an octahedral geometry around Co1. In complex **II** all three nickel ions are six-coordinate.

Keywords: 2,2′-[Ethylenedioxy*bis*(nitrilomethylidyne)]dinaphthol; Co(II) complex; Ni(II) complex; Synthesis; Crystal structure

1. Introduction

Cobalt(II) and nickel(II) Schiff-base complexes have been studied for their interesting and important properties, including optical features [1], catalytic activity in hydration of acrylonitrile [2] and magnetic properties [3]. Coordination chemistry of cobalt is of considerable interest since cobalt complexes derived from Schiff bases are reported to be biologically active. Vitamin B12 is a cobalt complex with a substituted corrin macrocycle [4]. Nickel complexes with a wide variety of tetradentate ligands having N_2O_2, N_4 and N_2S_2 donor atoms are important because these complexes can be applied as catalysts for carbonylation, hydrogenation, hydroformylation and epoxidation reactions [5–9]. Therefore, synthesis of new Schiff bases and their cobalt(II) and nickel(II) complexes are the goal of many investigations [10–12]. Here, in continuation of our previous studies on characterization of transition metal complexes [13, 14], we report the synthesis and characterization of a new Salen-type ligand,

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2,2′-[ethylenedioxy*bis*(nitrilomethylidyne)]dinaphthol (H_2L) and its tri-cobalt complex $[(CoL)_2(OAc)_2Co] \cdot THF$ (**I**) and tri-nickel complex $[(NiL)_2(OAc)_2(THF)_2Ni] \cdot THF$ (**II**).

2. Experimental

2.1. *Reagents and physical measurements*

2-Hydroxy-1-naphthaldehyde from Alfa Aesar was used without further purification. 1,2-Dibromoethane was dried and redistilled before using. 1,2-*bis*(aminooxy)ethane was synthesized by a method reported earlier [15]. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. Elemental analyses for Co and Ni were detected by an IRIS ER/S · WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VarioEL V3.00 automatic elemental analyzer. IR spectra in the range 400–4000 cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. The ^1H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using $CDCl_3$ as solvent. TG-DTA analyses were carried out on a ZRY-1P thermal analyzer at a heating rate of 3°C min^{-1}. X-ray single crystal structures were determined on a Bruker Smart APEX CCD area detector. Melting points were measured by the use of **a × 10** microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

2.2. *Synthesis*

2.2.1. Synthesis of H_2L. 2,2′-[Ethylenedioxy*bis*(nitrilomethylidyne)]dinaphthol (H_2L) was prepared by modification of the reported method [16]. To an ethanol solution of 2-hydroxy-1-naphthaldehyde (349.5 mg, 2.01 mmol) was added an ethanol solution of 1,2-*bis*(aminooxy)ethane (92.1 mg, 1.00 mmol). The mixture was stirred at 55°C for 4 h. After cooling to room temperature, the precipitate was filtered and washed successively with ethanol and ethanol/hexane (1 : 4), respectively. The product was dried under vacuum, giving 221.1 mg of pearl-colored microcrystals. Yield, 55.2%. m.p. 157.5–158.5°C. ^1H NMR (400 MHz, $CDCl_3$) 4.61 (s, 4H), 7.20 (d, J = 8.8 Hz, 2H), 7.27 (s, 2H) 7.37 (*t*, J = 3.6 Hz, 2H), 7.51 (*t*, J = 4.2 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 9.20 (s, 2H), 10.90 (s, 2H). Anal. Calcd for $C_{24}H_{20}N_2O_4$ (%): C, 71.99; H, 5.03; N, 7.00. Found: C, 71.72; H, 5.05; N, 6.91.

Needle-shaped crystals of H_2L suitable for X-ray crystal analysis were grown from ethanol solution by slow evaporation of the solvent at room temperature.

2.2.2. Synthesis of complex I. A solution of cobalt(II) acetate tetrahydrate (24.9 mg, 0.10 mmol) in ethanol (10 ml) was added dropwise to a solution of H_2L (40.1 mg, 0.10 mmol) in tetrahydrofuran/acetonitrile (3 : 2) (20 ml) at room temperature. The color of the mixing solution turns to claret immediately, and stirring was continued for 4 h at room temperature. The mixture was filtered and the filtrate allowed to stand at room temperature for one week; the solvent was partially evaporated and obtained several reddish-brown block-shaped single crystals suitable for X-ray crystallographic analysis. Anal. Calcd for $C_{56}H_{50}Co_3N_4O_{13}$ (%): C, 57.79; H, 4.33; N, 4.81; Co, 15.19. Found: C, 57.72; H, 4.55; N, 4.85; Co, 15.01.

2.2.3. Synthesis of complex II.

Complex **II** was prepared by the same method as that of complex **I** except $Co(CH_3COO)_2 \cdot 4H_2O$ was replaced by $Ni(CH_3COO)_2 \cdot 4H_2O$ (24.8 mg, 0.10 mmol). Prismatic dark-green crystals were isolated after four weeks following partial evaporation of the solvent. Anal. Calcd for $C_{64}H_{66}N_4Ni_3O_{15}$ (%): C, 58.80; H, 5.09; N, 4.29; Ni, 13.47. Found: C, 58.72; H, 4.95; N, 4.35; Ni, 13.40.

2.3. *IR spectra*

Complexes **I** and **II** have similar IR spectra indicating similar structures (see the supporting information). The free ligand H_2L exhibits Ar–O and C=N stretching bands at 1240 and 1602 cm^{-1}, which shift to lower frequencies by *ca.* 49 and 4 cm^{-1} upon complexation from the M–O and M–N interaction upon complexation [13]. In addition, infrared spectra of **I** and **II** show the expected absorption band due to the stretching mode of THF at *ca.* 1099 cm^{-1}, evidence for the existence of THF.

2.4. *TG-DTA analyses*

Thermal decomposition of **I** occurs in three stages. The initial weight loss occurs in the range 46 to 68°C. The TG curve shows that weight loss corresponding to this temperature range is 5.96% consistent with 6.19%, calculated for loss of one tetrahydrofuran. The second stage degradation temperature is in the range 235 to 260°C with mass loss of 10.2%, in which two coordinated acetate ions decompose with theoretical loss of 10.1%. The solid remains stable up to 342°C and the third weight loss starts at around 345 to 353°C with further decomposition of the compound.

The TG trace of **II** shows loss of one crystallizing and two coordinated tetrahydrofuran molecules in the range 60–240°C. Then, two acetates are lost (9.4% weight loss) from 243 to 270°C. The third weight loss from 272 to 380°C gives decomposition of the compound. The TG curve shows 81.9% weight loss at 380°C indicating complete removal of organic fragments and NiO with a residual value of 18.3% (theoretical residual value was 17.2%).

2.5. *X-ray crystallography*

The single crystals of H_2L, **I** and **II** with approximate dimensions of $0.66 \times 0.27 \times 0.07$, $0.58 \times 0.46 \times 0.43$, $0.60 \times 0.48 \times 0.21$mm were placed on a Bruker Smart diffractometer equipped with an Apex CCD area detector. The diffraction data were collected using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2), 298(2), and 298(2) K, respectively. The structures were solved by using SHELXL-97 and Fourier difference techniques, and refined by full-matrix least-squares on F^2. Details of the data collection and refinement are given in table 1. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically.

Table 1. Crystal data and structure refinement for H_2L, complex **I** and **II**.

	H_2L	**I**	**II**
Empirical formula	$C_{24}H_{20}N_2O_4$	$C_{56}H_{50}Co_3N_4O_{13}$	$C_{64}H_{66}N_4Ni_3O_{15}$
Formula weight	400.42	1163.79	1307.34
Temperature (K)	293(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2(1)/c$	Monoclinic, $P2(1)/c$	Monoclinic, $P2(1)/c$
Unit cell dimensions (Å, °)			
a	14.608(3)	11.130(3)	9.7636(18)
b	4.6696(19)	25.123(7)	19.206(2)
c	28.751(3)	10.193(3)	17.464(2)
β	90.464(3)	115.691(3)	91.020(3)
Volume (Å^3)	1961.1(9)	2568.4(12)	3274.2(8)
Z, Calculated density (Mg m^{-3})	4, 1.356	2, 1.505	2, 1.326
Absorption coefficient (mm^{-1})	0.093	1.028	0.919
$F(000)$	840	1198	1364
Crystal size (mm^{-3})	0.66 × 0.27 × 0.07	0.58 × 0.46 × 0.43	0.65 × 0.50 × 0.37
Theta range for data collection	1.39 to 25.01°	1.62 to 25.01°	1.58 to 25.01
Limiting indices	$-16 \leq h \leq 17$, $-5 \leq k \leq 5$, $-34 \leq l \leq 9$	$-13 \leq h \leq 12$, $-29 \leq k \leq 29$, $-7 \leq l \leq 12$	$-10 \leq h \leq 11$, $-22 \leq k \leq 22$, $-20 \leq l \leq 15$
Reflections collected/unique	9547/3945 [$R_{\text{int}} = 0.0614$]	13138/4514 [$R_{\text{int}} = 0.0353$]	12418/5459 [$R_{\text{int}} = 0.1560$]
Completeness to theta 25.01°	99.60%	99.70%	94.40%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9935 and 0.9410	0.6661 and 0.5869	0.7272 and 0.5863
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3459/0/271	4514/65/367	5459/244/440
Goodness-of-fit on F^2	1.02	1.032	1.068
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0481$, $wR_2 = 0.1017$	$R_1 = 0.0522$, $wR_2 = 0.1436$	$R_1 = 0.0959$, $wR_2 = 0.1891$
R indices (all data)	$R_1 = 0.1304$, $wR_2 = 0.1367$	$R_1 = 0.0809$, $wR_2 = 0.1777$	$R_1 = 0.2117$, $wR_2 = 0.2613$
Largest diff. peak and hole e. (Å^{-3})	0.156 and −0.170	0.725 and −0.290	1.144 and −0.813

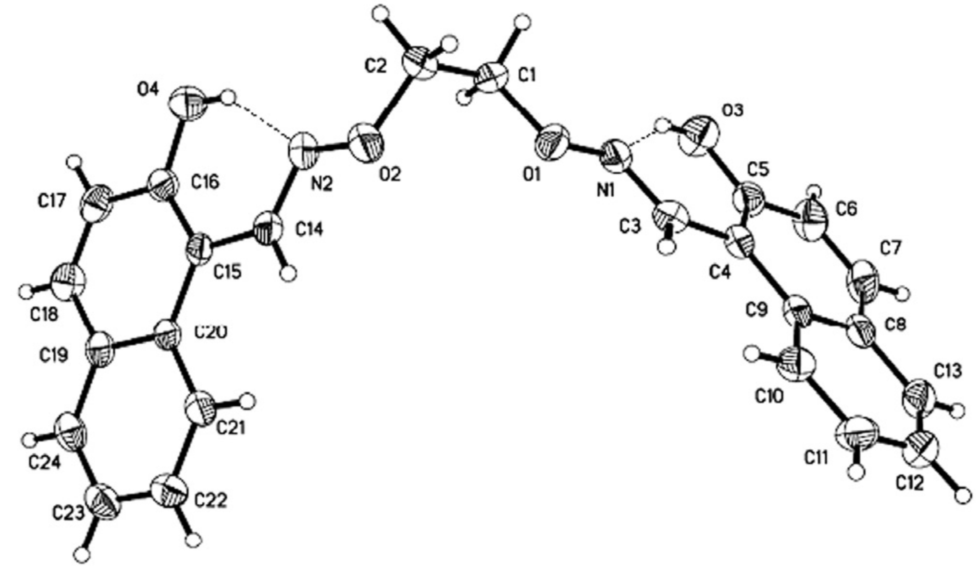

Figure 1. The molecular structure and intramolecular hydrogen bonds of H_2L with atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

Table 2. Selected bond distances (Å) and bond angles (°) for H_2L.

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)–C(3)	1.272(3)	C(4)–C(9)	1.436(4)	C(15)–C(16)	1.391(4)
N(1)–O(1)	1.405(3)	C(5)–C(6)	1.408(4)	C(15)–C(20)	1.424(4)
N(2)–C(14)	1.277(4)	C(6)–C(7)	1.343(4)	C(16)–C(17)	1.409(4)
N(2)–O(2)	1.411(3)	(7)–C(8)	1.417(4)	C(17)–C(18)	1.341(4)
O(1)–C(1)	1.427(3)	C(8)–C(13)	1.412(4)	C(18)–C(19)	1.415(4)
O(2)–C(2)	1.438(3)	C(8)–C(9)	1.416(4)	C(19)–C(24)	1.407(4)
O(3)–C(5)	1.363(4)	C(9)–C(10)	1.411(4)	C(19)–C(20)	1.418(4)
O(4)–C(16)	1.350(4)	C(10)–C(11)	1.367(4)	C(20)–C(21)	1.415(4)
C(1)–C(2)	1.496(4)	C(11)–C(12)	1.394(5)	C(21)–C(22)	1.359(4)
C(3)–C(4)	1.447(4)	C(12)–C(13)	1.346(5)	C(22)–C(23)	1.396(4)
C(4)–C(5)	1.372(4)	C(14)–C(15)	1.446(4)	C(23)–C(24)	1.355(4)
Bond	Angles	Bond	Angles	Bond	Angles
C(3)–N(1)–O(1)	111.3(2)	C(13)–C(8)–C(9)	119.4(3)	O(4)–C(16)–C(17)	115.8(3)
C(14)–N(2)–O(2)	110.5(3)	C(13)–C(8)–C(7)	121.7(3)	C(15)–C(16)–C(17)	120.8(3)
N(1)–O(1)–C(1)	109.5(2)	C(9)–C(8)–C(7)	118.9(3)	C(18)–C(17)–C(16)	120.2(3)
N(2)–O(2)–C(2)	110.3(2)	C(10)–C(9)–C(8)	117.2(3)	C(17)–C(18)–C(19)	122.1(3)
O(1)–C(1)–C(2)	107.0(3)	C(10)–C(9)–C(4)	123.7(3)	C(24)–C(19)–C(18)	121.7(3)
O(2)–C(2)–C(1)	112.6(3)	C(8)–C(9)–C(4)	119.2(3)	C(24)–C(19)–C(20)	120.0(3)
N(1)–C(3)–C(4)	122.2(3)	C(11)–C(10)–C(9)	121.7(3)	C(18)–C(19)–C(20)	118.2(3)
C(5)–C(4)–C(9)	118.6(3)	C(10)–C(11)–C(12)	120.2(3)	C(21)–C(20)–C(19)	116.3(3)
C(5)–C(4)–C(3)	121.3(3)	C(13)–C(12)–C(11)	120.0(3)	C(21)–C(20)–C(15)	123.8(3)
C(9)–C(4)–C(3)	120.1(3)	C(12)–C(13)–C(8)	121.4(4)	C(19)–C(20)–C(15)	119.8(3)
O(3)–C(5)–C(4)	122.5(3)	N(2)–C(14)–C(15)	122.1(3)	C(22)–C(21)–C(20)	122.4(3)
O(3)–C(5)–C(6)	115.5(3)	C(16)–C(15)–C(20)	118.9(3)	C(21)–C(22)–C(23)	120.3(3)
C(4)–C(5)–C(6)	122.0(3)	C(16)–C(15)–C(14)	120.5(3)	C(24)–C(23)–C(22)	119.6(3)
C(7)–C(6)–C(5)	119.6(3)	C(20)–C(15)–C(14)	120.5(3)	C(23)–C(24)–C(19)	121.3(3)
C(6)–C(7)–C(8)	121.7(3)	O(4)–C(16)–C(15)	123.5(3)		

3. Results and discussion

The crystal structure of H_2L was determined by X-ray crystallography (figure 1 and table 2). H_2L is sufficiently stable to resist scrambling of the C=N bonds, which may be ascribed to lower reactivity of the oxime C=N bonds toward nucleophiles. The molecule adopts an extended conformation where the two naphthaldoxime moieties are apart. The oxime groups and naphtholic alcohols have *cis*-conformations, and there are intramolecular hydrogen bonds between O3–H3 ⋯ N1 and O4–H4 ⋯ N2 table 3, Three C atoms, one N atom, one O atom and one H atom generate a six-membered ring through this hydrogen bond, which stabilizes the three-dimensional network.

The single crystal structures of **I** and **II** were confirmed by X-ray crystallography figures 2 and 3. Complexes **I** and **II** crystallize in the same space group as summarized in table 1, and are isomorphous and isostructural.

Table 3. Hydrogen bonds for H_2L.

D–H ⋯ A	d(D–H)	d(H..A)	∠DHA	d(D ⋯ A)
O3–H3 ⋯ N1	0.820	1.875	145.95	2.596
O4–H4 ⋯ N2	0.820	1.896	145.49	2.613

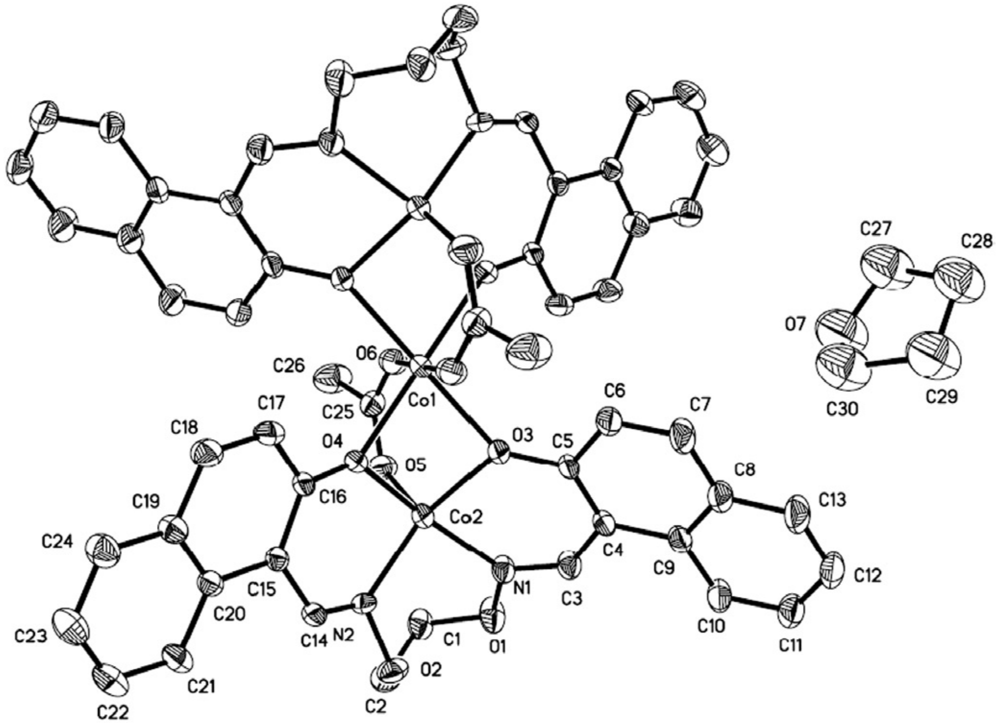

Figure 2. The molecular structure of **I** with atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

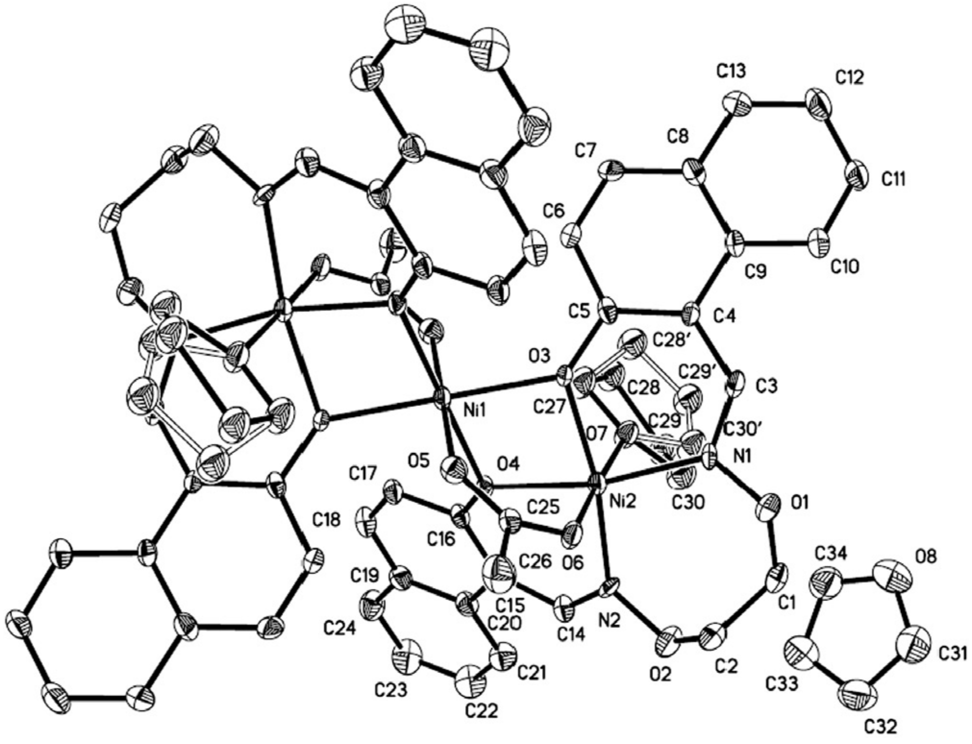

Figure 3. The molecular structure of **II** with atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Each nickel has octahedral geometry.

The molecular structure of **I** consists of three cobalt(II) ions, two L^{2-} units, two acetate ions and one crystallizing tetrahydrofuran molecule. The X-ray crystal structure of **I** shows that Co2 and Co2# are five-coordinate by N_2O_2 donors of L^{2-} and one oxygen atom of the acetate. Cobalt ion (Co1) is six-coordinate by four oxygen atoms of deprotonated naphtholic alcohol in two [CoL] chelates and two oxygen atoms of the acetate ions. Two L^{2-} units serve as tetradentate N_2O_2 ligands for two cobalt ions (Co2 and Co2#) and at the same time bidentate ligands for the third cobalt ion (Co1). One acetate ion is bidentate for Co2 and Co1, and another one coordinates to Co2# and Co1 *via* a Co–O–C–O–Co bridge. Co2 or Co2# is located on a distorted pentahedral center with N_2O_2 donors from the ligand and one O donor of the acetate. The double μ-acetato bridges adopt the more familiar μ O–C–O connecting the Co2–Co1 and Co1–Co2# so tetra μ-naphthoxo oxygens from two L^{2-} moieties and the two oxygen atoms from μ-acetato give an octahedral geometry around Co1.

Comparing **I** and **II**, the ratio of ligand : metal are 2 : 3, and completing the octahedral geometry at Co1 and Ni1 aligns the N_2O_2 donor set such that the ligand is in the meridial plane of the metal. The acetates adopt their familiar role to reinforce the structure by bridging between adjacent nickel or cobalt. The coordination number of cobalt is generally four or six with tetrahedral or octahedral coordination geometry [17, 18]. However, there are a few reports of the five-coordinate cobalt complexes [16, 19] with distorted square-pyramidal or trigonal-bipyramidal configurations. Here, two cobalt ions have coordination number five and the third one has coordination

Table 4. Selected bond distances (Å) and angles (°) for **I** and **II**.

Bond	Dist.	Bond	Dist.	Bond	Dist.
Co(1)–O(6)#1	2.070(4)	Co(1)–O(3)#1	2.178(3)	Co(2)–N(2)	2.006(4)
Co(1)–O(6)	2.070(4)	Co(1)–O(3)	2.178(3)	Co(2)–N(1)	2.047(4)
Co(1)–O(4)#1	2.112(3)	Co(2)–O(3)	1.973(3)	Co(2)–O(4)	2.077(3)
Co(1)–O(4)	2.112(3)	Co(2)–O(5)	1.994(4)		
Ni(1)–O(5)#1	2.013(7)	Ni(1)–O(4)#1	2.102(6)	Ni(2)–O(3)	2.032(6)
Ni(1)–O(5)	2.013(7)	Ni(1)–O(4)	2.102(6)	Ni(2)–N(2)	2.060(8)
Ni(1)–O(3)#1	2.093(5)	Ni(2)–O(6)	1.998(7)	Ni(2)–N(1)	2.061(7)
Ni(1)–O(3)	2.093(5)	Ni(2)–O(4)	2.025(6)	Ni(2)–O(7)	2.171(7)
Bond	Angles	Bond	Angles	Bond	Angles
O(6)#1–Co(1)–O(6)	180.000(1)	O(4)–Co(1)–O(3)	76.7(1)	C(3)–N(1)–Co(2)	125.7(3)
O(6)#1–Co(1)–O(4)#1	88.2 (1)	O(3)#1–Co(1)–O(3)	180	O(1)–N(1)–Co(2)	124.6(3)
O(6)–Co(1)–O(4)#1	91.8(1)	O(3)–Co(2)–O(5)	106.8(2)	C(14)–N(2)–Co(2)	129.0(3)
O(6)#1–Co(1)–O(4)	91.8(1)	O(3)–Co(2)–N(2)	141.9(2)	O(2)–N(2)–Co(2)	117.6(3)
O(6)–Co(1)–O(4)	88.2(1)	O(5)–Co(2)–N(2)	110.0(2)	C(5)–O(3)–Co(2)	127.5(3)
O(4)#1–Co(1)–O(4)	180	O(3)–Co(2)–N(1)	87.9(1)	C(5)–O(3)–Co(1)	136.3(3)
O(6)#1–Co(1)–O(3)#1	89.7(1)	O(5)–Co(2)–N(1)	100.5(2)	Co(2)–O(3)–Co(1)	94.6(1)
O(6)–Co(1)–O(3)#1	90.3(1)	N(2)–Co(2)–N(1)	94.9(2)	C(16)–O(4)–Co(2)	131.6(3)
O(4)#1–Co(1)–O(3)#1	76.7(1)	O(3)–Co(2)–O(4)	82.2(1)	C(16)–O(4)–Co(1)	132.5(3)
O(4)–Co(1)–O(3)#1	103.3(1)	O(5)–Co(2)–O(4)	93.4(2)	Co(2)–O(4)–Co(1)	93.6(1)
O(6)#1–Co(1)–O(3)	90.3(1)	N(2)–Co(2)–O(4)	86.0(1)	C(25)–O(5)–Co(2)	121.2(4)
O(6)–Co(1)–O(3)	89.7(1)	N(1)–Co(2)–O(4)	164.8(2)	C(25)–O(6)–Co(1)	134.0(3)
O(4)#1–Co(1)–O(3)	103.3(1)				
O(5)#1–Ni(1)–O(5)	180.0(2)	O(6)–Ni(2)–O(4)	92.0(3)	C(3)–N(1)–Ni(2)	123.4(7)
O(5)#1–Ni(1)–O(3)#1	89.1(3)	O(6)–Ni(2)–O(3)	92.9(3)	O(1)–N(1)–Ni(2)	126.6(6)
O(5)–Ni(1)–O(3)#1	90.9(3)	O(4)–Ni(2)–O(3)	82.1(2)	C(14)–N(2)–Ni(2)	122.9(7)
O(5)#1–Ni(1)–O(3)	90.9(3)	O(6)–Ni(2)–N(2)	91.7(3)	O(2)–N(2)–Ni(2)	127.4(6)
O(5)–Ni(1)–O(3)	89.1(3)	O(4)–Ni(2)–N(2)	86.5(3)	C(5)–O(3)–Ni(2)	125.4(5)
O(3)#1–Ni(1)–O(3)	180.000(1)	O(3)–Ni(2)–N(2)	167.9(3)	C(5)–O(3)–Ni(1)	133.7(6)
O(5)#1–Ni(1)–O(4)#1	89.0(3)	O(6)–Ni(2)–N(1)	90.8(3)	Ni(2)–O(3)–Ni(1)	96.3(2)
O(5)–Ni(1)–O(4)#1	91.0(3)	O(4)–Ni(2)–N(1)	168.4(3)	C(16)–O(4)–Ni(2)	127.5(6)
O(3)#1–Ni(1)–O(4)#1	78.8(2)	O(3)–Ni(2)–N(1)	86.6(3)	C(16)–O(4)–Ni(1)	133.0(6)
O(3)–Ni(1)–O(4)#1	101.2(2)	N(2)–Ni(2)–N(1)	104.6(3)	Ni(2)–O(4)–Ni(1)	96.2(2)
O(5)#1–Ni(1)–O(4)	91.0(3)	O(6)–Ni(2)–O(7)	177.9(3)	C(25)–O(5)–Ni(1)	131.7(6)
O(5)–Ni(1)–O(4)	89.0(3)	O(4)–Ni(2)–O(7)	89.6(3)	C(25)–O(6)–Ni(2)	127.6(7)
O(3)#1–Ni(1)–O(4)	101.2(2)	O(3)–Ni(2)–O(7)	88.7(3)	C(27)–O(7)–Ni(2)	125.2(6)
O(3)–Ni(1)–O(4)	78.8(2)	N(2)–Ni(2)–O(7)	87.1(3)	C(30′)–O(7)–Ni(2)	129.0(1)
O(4)#1–Ni(1)–O(4)	180.0(2)	N(1)–Ni(2)–O(7)	87.9(3)	C(30)–O(7)–Ni(2)	1.17(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$ for **I**; #1 $-x+1$, $-y$, $-z+1$ for **II**.

number six in the cobalt complex, but the nickel complex has three six-coordinate Ni(II) ions, similar to those of previously reported salen-type analogues of {[Ni(H_4Salpr)(X)]$_2$(OAc)$_2$Ni} ($X = NC_5H_5$, DMSO, DMF) [20–23] and {[Ni(Salpr)(DMF)]$_2$(NO_3)$_2$Ni} [24].

The selected bond distances (Å) and angles (°) for **I** and **II** are shown in table 4. Complex **I** has Co–O and Co–N distances from 1.973(3) to 2.178(3) Å and from 2.006(4) to 2.047(4) Å, respectively, which are close to those of previously reported cobalt complexes [25, 26]. The equatorial plane of Co2 is defined by N1, N2, O4, O3 atoms with the largest deviation of Co2 at 0.444(2) Å. The apical position is occupied by O5 from acetate. The distorted square-pyramidal coordination sphere around Co2 has equatorial angles in the range 82.18(13)–94.94(17)°, and an axial angle O5–Co2–O4 of 93.39(15)°.

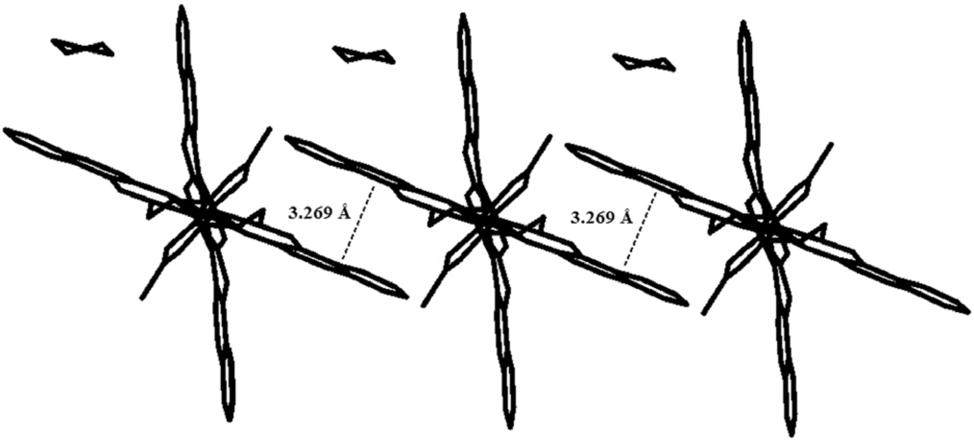

Figure 4. A view of the π-π stacking in **I**; H atoms are omitted for clarity.

In **II**, the Ni–N bonds (in the range 2.060(8)–2.061(7) Å) are longer than Co–N. The Ni2 and Co2 form two six-membered rings with two ligands. The dihedral angle of the two planes [Ni2–N1–O3, Ni2–N2–O4] (5.02°) is smaller than the dihedral angle of [Co2–N1–O3, Co2–N2–O4] (39.3°), attributed to the THF molecule coordinated to Ni2 making the steric hindrance larger. The ethylenedioxime carbons C1 and C2 are buckled asymmetrically from the Ni2–N1–N2 plane, with the displacement for C1 being 0.561(3) Å toward the plane and for C2, 1.290(3) Å in the same direction, while the displacement for C1 is only 1.824(2) Å and for C2, 1.268(3) Å toward the Co2–N1–N2 plane in **I**.

The unit cell packing of **I** and **II** show the roomy space formed by packing of the molecules (see the supporting information). There is one crystallizing THF molecule in the two complexes. The distance between nearest parallel naphthalene rings is about 3.269(2) Å in **I**, exhibiting obvious strong intermolecular π–π stacking interactions, which forms the three-dimensional structure of **I** figure 4.

Supplementary data

Further details of the crystal structure investigation(s) may be obtained from the Cambridge Crystallographic Data Centre, E-mail: deposit@ccdc.cam.ac.uk on quoting the depository number CCDC Nos: 626924 for H_2L, 630624 for **I** and 636044 for **II**.

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