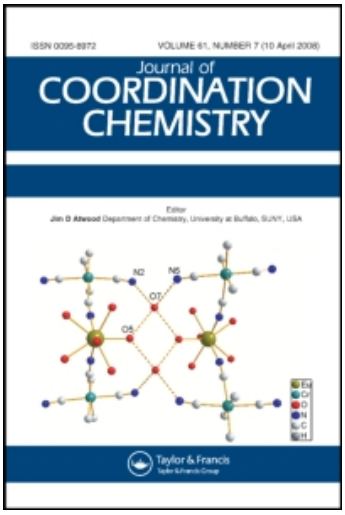


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Bent and linear trinuclear nickel complexes with ligands derived from N-acylsalicylhydrazide ligands: structural characterization and bioactivity

Wei Luo[a]; Xiang-Gao Meng[b]; Gong-Zhen Cheng[a]; Zhen-Ping Ji[a]
[a] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, P. R. China [b] Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, Hubei 430079, P. R. China

To cite this Article Luo, Wei , Meng, Xiang-Gao , Cheng, Gong-Zhen and Ji, Zhen-Ping(2009) 'Bent and linear trinuclear nickel complexes with ligands derived from **N**-acylsalicylhydrazide ligands: structural characterization and bioactivity', Journal of Coordination Chemistry, 62: 9, 1492 — 1501
To link to this Article: DOI: 10.1080/00958970802609830
URL: http://dx.doi.org/10.1080/00958970802609830

Journal of Coordination Chemistry
Vol. 62, No. 9, 10 May 2009, 1492–1501

Bent and linear trinuclear nickel complexes with ligands derived from *N*-acylsalicylhydrazide ligands: structural characterization and bioactivity

WEI LUO*†, XIANG-GAO MENG‡,
GONG-ZHEN CHENG† and ZHEN-PING JI†

†College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, P. R. China
‡Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, Hubei 430079, P. R. China

(*Received 20 April 2008; in final form 1 August 2008*)

Two trinuclear Ni(II) complexes $Ni_3(L_1)_2(py)_2(DMF)(H_2O)$ (**1**) and $Ni_3(L_2)_2(py)_2(DMF)_2$ (**2**) with two new trianionic pentadentate ligands *N*-(3,5-dimethylbenzoyl)-salicylhydrazide (H_3L_1) and *N*-(phenylacetyl)-5-nitrosalicylhydrazide (H_3L_2) have been synthesized and characterized by X-ray crystallography. Nickel ions in the two complexes have square-planar/octahedral/square-planar coordination. Central metal ion and two terminal metal ions in the two complexes are combined by two bridging deprotonated ligands, forming a trinuclear structural unit with an M–N–N–M–N–N–M core. Studies on the trinuclear Ni(II) complexes show that the β-branched *N*-acylsalicylhydrazide ligands with sterically flexible Cα methylene groups yield linear trinuclear Ni(II) complexes, while α-branched *N*-acylsalicylhydrazide ligands tend to form bent trinuclear Ni(II) complexes. Antibacterial screening data in a previous study indicates that bent trinuclear Ni(II) compound **1** is more active than linear compound **2** and less active than a tetranuclear nickel compound.

Keywords: Trinuclear; Crystal structure; Bent; Linear; Antimicrobial activity

1. Introduction

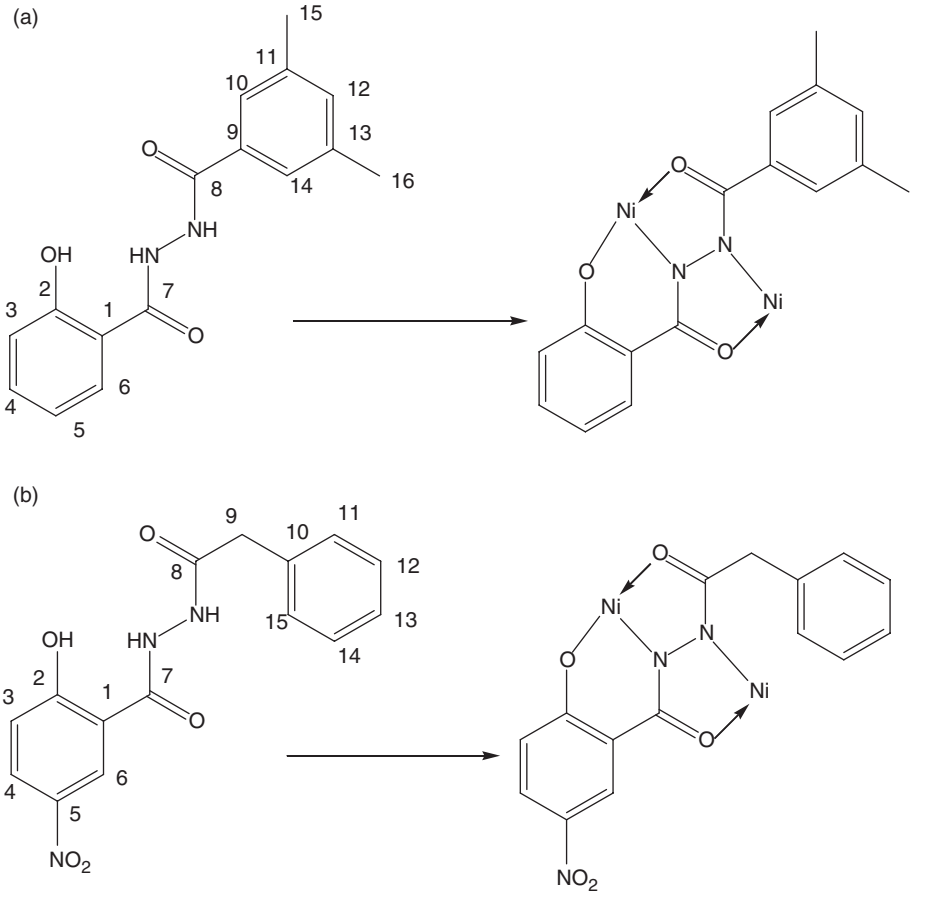
Polynuclear coordination complexes of relatively simple ligands which exhibit unusual structural complexity [1–5] containing nitrogen and phenolic oxygen donors are of interest in inorganic and bioinorganic chemistry due to application in catalysis, biological relevance, and potentially interesting magnetic properties [6–9]. The trianionic pentadentate *N*-acyl-salicylhydrazide ligands have been utilized to construct polynuclear complexes. Trivalent metal ions such as Ga, Co, Fe, and Mn form stable octahedral coordination giving hexanuclear, octanuclear, decanuclear and dodecanuclear metallamacrocycles with such ligands, known as metallacrowns [10–21].

*Corresponding author. Email: chemicalluo@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802609830

For bivalent metal complexes, only a few trinuclear Ni(II), Cu(II) and Zn(II) compounds with *N*-acyl-salicylhydrazide ligands have been obtained [22–27].

Trinuclear compounds could have linear or nonlinear arrangement of the metal centers. Nonlinear trinuclear structures could be equilateral triangular or bent [28–36]. Trinuclear complexes with linear or equilateral triangular structures are common; however, trinuclear Ni complexes with bent structures are rare. Thus, the rational design and preparation of such trinuclear complexes remains a challenge. The nature of *N*-acyl groups influence the size and nuclearity of metallacrowns [14]. As part of our efforts to understand the steric effect of *N*-acyl side chains on the arrangement and coordination geometry of metal ions, and develop a better understanding of the antimicrobial activity in trinuclear complexes, two new pentadentate ligands *N*-(3,5-dimethylbenzoyl)-salicylhydrazide (H_3L_1) [scheme 1(a)] and *N*-(phenylacetyl)-5-nitrosalicylhydrazide (H_3L_2) [scheme 1(b)] and their trinuclear complexes $Ni_3(L_1)_2(py)_2(DMF)(H_2O)$ (**1**) and $Ni_3(L_2)_2(py)_2(DMF)_2$ (**2**) were synthesized and their antimicrobial activities against *Stophylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, and *Proteus vulgaris* were studied.



Scheme 1. Ligands and their bonding sites in the trinuclear complexes; (a) compound **1** and (b) compound **2**.

2. Experimental

2.1. *General*

All reagents for the syntheses were obtained commercially of analytical grade and were used without purification. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer at 25°C. Chemical shifts were referenced to residual solvent. IR spectra were recorded on an AVATAR 360 FT-IR spectrophotometer. Elemental analyses were performed on a Perkin–Elmer 2400 elemental analyzer. TG analysis was performed on a Perkin–Elmer DF40 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. UV-Vis spectra were recorded on a Shimadzu-UV-2501 spectrophotometer.

2.2. *Syntheses of* N-*(3,5-dimethylbenzoyl)-salicylhydrazide (H_3L_1)*

3,5-Dimethylbenzoyl chloride (3 mL, 19.7 m mol) was added to a solution of chloroform (100 mL) containing water (0.36 mL, 20.0 m mol) and triethylamine (5.7 mL, 40.0 m mol) at 0°C. The reaction mixture was slowly warmed to ambient temperature and a further amount of 3,5-dimethylbenzoyl chloride (3 mL, 19.7 m mol) was added to the mixture and stirred for a further 1 h. Then, salicylhydrazide (2.5 g, 16.4 m mol) was added to the reaction mixture. The resulting solution was stirred at ambient temperature for 1 day. The solution was diluted with hexane (90 mL), refrigerated overnight, filtered and washed with ether (30 mL × 3) and dried *in vacuo* over P_2O_5. Yield: 4.28 g, 92.2%. Anal. Calcd for $C_{16}H_{16}N_2O_3$ (%): C, 67.59; H, 5.67; N, 9.85. Found: C, 67.55; H, 5.65; N, 9.90. IR (KBr pellet, cm^{-1}): 3450 s, broad; 3230 vs, broad; 3020 vs, broad; 1660 vs; 1630 vs; 1590 vs. ^{1}H NMR (300 MHz, DMSO-d_6), δ ppm: 11.96 (s, 1H, Ar–OH); 10.65 (s, 1H); 10.53 (s, 1H) (both amide NH's); 7.93 (m, 1H, Ar); 7.53 (d, 2H, Bz); 7.43 (m, 1H, Ar); 7.21 (s, 1H, Bz); 6.93 (m, 2H, Ar); 2.33 (s, 6H, $(CH_3)_2$Bz). ^{13}C NMR (150.9 MHz, DMSO-d_6), δ ppm: 168.43 (C8); 166.51 (C7); 160.03 (C2); 138.37 (C13, C11); 134.87 (C12); 133.88 (C9); 133.02 (C4); 128.93 (C6); 125.92 (C10); 119.73 (C5); 118.09 (C1); 115.17 (C3); 21.53 (C15, C16).

2.3. *Syntheses of* N-*(phenylacetyl)-5-nitrosalicylhydrazide (H_3L_2)*

The ligand was prepared in a manner analogous to that used for N-(3,5-dimethylbenzoyl)-salicylhydrazide, except that phenylacetyl chloride and 5-nitrosalicylhydrazide were used instead of 3,5-dimethylbenzoyl chloride and salicylhydrazide. Yield: 4.04 g, 78.1%. Anal. Calcd for $C_{15}O_5N_3H_{13}$ (%): C, 57.14; H, 4.16; N, 13.33. Found: C, 56.82; H, 3.78; N, 13.45. IR (KBr pellet, cm^{-1}): 3440 vs, broad; 2980 s; 2940 s; 2740 s; 2670 s; 1640 s; 1610 s; 1490 s. ^{1}H NMR (300 MHz, DMSO-d_6), δ ppm: 11.27 (s, 1H); 10.72 (s, 1H) (both amide NH's); 10.30 (b, 1H, Ar–OH); 8.70 (s, 1H, Ar); 8.15 (m, 1H, Ar); 7.29 (m, 1H, Ar); 7.18 (t, 2H, Bz); 7.05 (d, 2H, Bz); 6.94 (s, 1H, Bz); 3.99 (s, 2H, –CH_2–). ^{13}C NMR (150.9 MHz, DMSO-d_6), δ ppm: 169.08 (C8); 167.70 (C7); 164.41 (C2); 138.40 (C5); 136.78 (C10); 130.18 (C11, C15); 129.34 (C12, C14); 127.63 (C13); 125.73 (C4); 120.18 (C6); 117.98 (C1); 110.54 (C3); 46.37 (C9).

2.4. *Synthesis of $C_{45}H_{45}N_7Ni_3O_8$ (1)*

H_3L_1 (28.4 mg, 0.1 m mol) was dissolved in 30 mL of 1 : 1 methanol : DMF, and nickel acetate tetrahydrate (24.8 mg, 0.1 m mol) was added, followed by 2 ml of pyridine. The mixture was stirred for 1 h and the resulting solution filtered. After slow evaporation of the mother liquor for several days, red needles suitable for X-ray diffraction were obtained. Yield: 68.2%. Anal. Calcd for $C_{45}H_{45}N_7Ni_3O_8$ (%): C, 54.71; H, 4.59; N, 9.92. Found: C, 54.1; H, 4.2; N, 10.3. IR (KBr pellet, cm^{-1}): 1660 m; 1600 m; 1520 s; 1380 m; 758 m; 696 m.

2.5. *Synthesis of $C_{46}H_{44}N_{10}Ni_3O_{12}$ (2)*

Compound **2** was prepared in a manner analogous to that of **1**. H_3L_2 (31.5 mg, 0.1 m mol) was used instead of H_3L_1. Yield: 85.3%. Anal. Calcd for $C_{46}H_{44}N_{10}Ni_3O_{12}$ (%): C, 50.00; H, 4.01; N, 12.68. Found: C, 49.6; H, 3.7; N, 13.3. IR (KBr pellet, cm^{-1}): 1650 m; 1610 m; 1530 s; 1450 m; 735 m; 696 m.

2.6. *Crystal structure determinations*

X-ray single-crystal diffraction data for **1** and **2** were collected on a Bruker Smart APEX diffractometer at 293(2) K with Mo-Kα radiation ($\lambda = 0.71073$ Å). There was no evidence of crystal decay during data collection. Semiempirical absorption corrections were applied using SADABS; SAINT was used for integration of the diffraction profiles. The structures were solved by direct methods using SHELXS of the SHELXTL package and refined with SHELXL [37, 38]. All non-hydrogen atoms were modeled with anisotropic displacement parameters and refined by full-matrix least-squares on F^2. Crystallographic data and selected bond lengths and angles of **1** and **2** are summarized in tables 1 and 2.

2.7. *Antimicrobial activities*

The antimicrobial activities were assessed by the ability to inhibit the growth of *S. aureus*, *E. coli*, *B. subtilis* and *P. vulgaris* in Mueller–Hinton broth medium. The minimum inhibitory concentrations in micrograms per milliliters against the four bacteria species were measured. The bacteria concentration was $5 \times (10^5 - 10^6)$ cfu mL^{-1} and concentrations of 1600, 800, 400, 200, 100, 50, and 25 μg mL^{-1} of the complexes in DMF were tested. The solvent showed no antimicrobial action.

3. Results and discussion

3.1. *IR spectra*

In IR spectra of H_3L_1, stretching bands attributed to C=O, PhO–H (phenolic, including intramolecular and intermolecular hydrogen bonds) and N–H were shown at 1600, 1640, 3020–3230, 3450 cm^{-1}, respectively [39]. The N–C=O framework at 1590 cm^{-1} in

Table 1. Crystallographic data and structure refinement summary for **1** and **2**.

	1	**2**
Formula	$C_{45}H_{45}N_7Ni_3O_8$	$C_{46}H_{44}N_{10}Ni_3O_{12}$
M_r	988.01	1105.04
Crystal size (mm)	$0.44 \times 0.23 \times 0.17$	$0.35 \times 0.27 \times 0.10$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$
Units of dimensions (Å, °)		
a	14.4141(14)	14.2691(9)
b	17.5047(16)	8.7421(6)
c	19.8428(19)	19.9857(13)
α	69.250(2)	90
β	78.938(2)	104.893(1)
γ	72.670(2)	90
Cell volume (Å^3)	4448.4(7)	2409.3(3)
Z	4	2
D_{Calcd} (g cm^{-3})	1.475	1.523
μ (mm^{-1})	1.318	1.233
F (000)	2048	1140
Parameters	1163	325
R_{int}	0.0325	0.02
R indices [$I > 2\sigma(I)$]	0.0485, 0.0923	0.0392, 0.0962
Goodness-of-fit on F^2	1.01	1.06
Residuals (e Å^{-3})	−0.517, 0.575	−0.325, 0.709

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

1				**2**	
Bond lengths					
Ni(1)–N(2)	2.059(3)	Ni(2)–N(9)	2.086(3)	Ni(1)–O(4)#1	2.0210(15)
Ni(1)–N(5)	2.106(3)	Ni(2)–N(11)	2.066(3)	Ni(1)–O(4)	2.0210(15)
Ni(1)–O(5)	2.030(3)	Ni(2)–O(11)	2.016(3)	Ni(1)–N(3)#1	2.0753(16)
Ni(1)–O(2)	2.038(3)	Ni(2)–O(12)	2.057(3)	Ni(1)–N(3)	2.0753(16)
Ni(1)–O(7)	2.051(3)	Ni(2)–O(15)	2.091(3)	Ni(1)–O(6)#1	2.1253(16)
Ni(1)–O(8)	2.180(3)	Ni(2)–O(16)	2.093(3)	Ni(1)–O(6)	2.1253(16)
Ni(3)–N(4)	1.822(3)	Ni(4)–N(8)	1.830(3)	Ni(2)–O(3)	1.8233(16)
Ni(3)–N(6)	1.930(4)	Ni(4)–N(13)	1.946(4)	Ni(2)–N(2)	1.8329(16)
Ni(3)–O(4)	1.806(3)	Ni(4)–O(9)	1.810(3)	Ni(2)–O(5)	1.8489(15)
Ni(3)–O(6)	1.816(3)	Ni(4)–O(10)	1.833(3)	Ni(2)–N(4)	1.9329(18)
Ni(5)–N(1)	1.818(3)	Ni(6)–N(10)	1.813(3)		
Ni(5)–N(3)	1.932(3)	Ni(6)–N(12)	1.933(4)		
Ni(5)–O(1)	1.816(3)	Ni(6)–O(14)	1.820(3)		
Ni(5)–O(3)	1.833(3)	Ni(6)–O(13)	1.846(3)		
Bond angles					
O(5)–Ni(1)–O(2)	94.00(10)	O(11)–Ni(2)–O(12)	92.51(10)	O(4)#1–Ni(1)–N(3)#1	78.93(6)
O(5)–Ni(1)–N(2)	171.42(11)	O(11)–Ni(2)–N(11)	170.58(11)	O(4)–Ni(1)–N(3)#1	101.07(6)
O(5)–Ni(1)–N(5)	77.31(11)	O(11)–Ni(2)–N(9)	79.13(12)	O(4)#1–Ni(1)–N(3)	101.07(6)
O(5)–Ni(1)–O(8)	84.94(12)	O(11)–Ni(2)–O(15)	86.21(12)	O(4)#1–Ni(1)–O(6)#1	87.61(7)
O(4)–Ni(3)–O(6)	176.87(13)	O(9)–Ni(4)–N(8)	95.63(14)	O(4)#1–Ni(1)–O(6)	92.39(7)
N(4)–Ni(3)–N(6)	172.75(16)	N(8)–Ni(4)–N(13)	174.49(15)	N(3)#1–Ni(1)–O(6)	90.97(7)
O(1)–Ni(5)–O(3)	177.90(13)	O(14)–Ni(6)–O(13)	178.22(13)	N(2)–Ni(2)–N(4)	176.43(8)
N(1)–Ni(5)–N(3)	173.48(15)	N(10)–Ni(6)–N(12)	174.90(15)	O(3)–Ni(2)–N(2)	94.84(7)

Note: Symmetry codes for (**2**): #1: $-x+1, -y+1, -z$

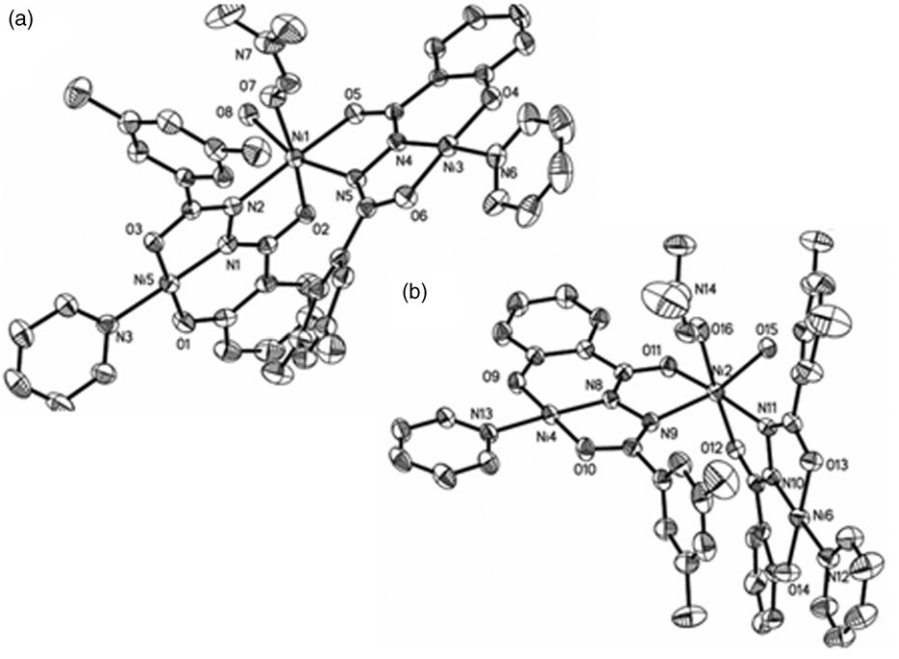


Figure 1. Molecular structure of $Ni_3(L_1)_2(py)_2(DMF)(H_2O)$ with the atom-labeling scheme.

the ligand shifts to 1530 cm^{-1} in **1** due to the coordination to Ni and its relative intensity decreased [40]. The absence of the N–H band and the weakness of the C=O stretching bands in **1** are consistent with deprotonation of CONH and coordination to Ni. Deprotonation and coordination are also confirmed by bands at 735 cm^{-1}, attributed to Ni–O, and the bands at 696 cm^{-1} assigned to Ni–N [41]. In the IR spectra of H_3L_2, bands at 1610, 1640, 2490–2980 and 3440 cm^{-1} were attributed to C=O, PhO–H and N–H groups. Infrared stretching bands for **1** and **2** are quite similar. In **2**, disappearance of N–H, the decrease of C=O band and the presence of Ni–O and Ni–N bands at 758 and 696 cm^{-1} indicate the same chelating mode of the two ligands to Ni.

3.2. *Crystal structures*

Two independent molecules comprise the crystallographic asymmetric unit of **1** that differ only in terms of minor conformational changes. The arrangement of the two molecules is pseudo-centrosymmetric, however, no further symmetry element was found by ADDSYMM in PLATON [42]. An ORTEP diagram of the bent trinuclear **1** is shown in figure 1. The deprotonated ligand L_1^{3-} is trianionic pentadentate with phenolate oxygen, carbonyl oxygen, and hydrazide nitrogen in the ligand bound to the terminal Ni(II) cations with the fourth sites occupied by the pyridine nitrogens; other carbonyl oxygen plus the other hydrazide nitrogen in the two ligands are chelated to the central Ni(II) cation as a bidentate ligand for the central nickel, while tridentate for the two terminal nickel ions. Central nickel Ni(I)/Ni(II) and two terminal nickel ions Ni(III)/Ni(IV) and Ni(V)/Ni(VI) are connected by two bridging deprotonated L_1^{3-} ligands, forming a bent trinuclear nickel structure with an Ni–N–N–Ni–N–N–Ni core.

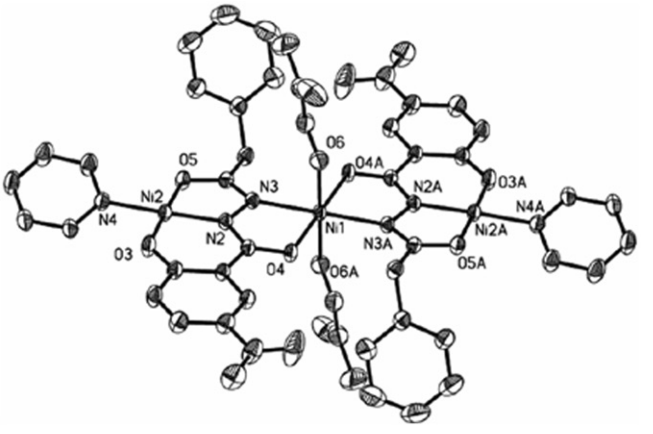


Figure 2. Molecular structure of $Ni_3(L_2)_2(py)_2(DMF)_2$ with the atom-labeling scheme. Symmetry operation used to generate equivalent atoms: a $-x+1, -y+1, -z$.

The angles of the three nickel ions are 134.2° in **1**, and 108.7° in **1**a. The coordination geometry of the three Ni ions is square–planar/octahedral/square–planar. The coordination of the central Ni(I)/Ni(II) is completed by one H_2O and one DMF. The N_4O_2 donor set of the central Ni(I)/Ni(II) ion forms a distorted octahedral coordination geometry. The terminal Ni–N and Ni–O bond lengths are shorter than corresponding values of the central Ni, attributed to the difference in stereochemistry between the central and terminal Ni (octahedral versus square planar).

An ORTEP diagram of linear trinuclear **2** is shown in figure 2. The central Ni(II) possesses an octahedral coordination environment, while the other two metal cations are square planar. The whole molecule is connected by two bridging deprotonated L_1^{3-} ligands, forming a linear trinuclear nickel structure. The trinuclear nickel molecule is strictly linear, with the central nickel lying on a crystallographic center of symmetry. The equatorial plane of the octahedron is perfectly planar and the nickel lies in this plane. Axial coordination sites are occupied by two DMF molecules.

Compared to known trinuclear complexes, the β-branched *N*-acylsalicylhydrazide (H_3L_2, H_3acbshz [19], H_3acshz [21], H_3pabshz [22]) with sterically flexible Cα methylene groups yield linear trinuclear Ni(II) complexes, while α-branched *N*-acylsalicylhydrazides (H_3L_1, H_3-*p*-nbzshz [20], $H_3$3-*t*-bbznshz, $H_3$3-*t*-bbzshz and $H_3$3,5dmb-bshz [22]) tend to form bent Ni(II) complexes. The different molecular configurations in **1** and **2** may be attributed to the spatial effect of the substituent on two ends of the ligands, e.g., the benzyl in ligand H_3L_2 can better expand away than 3,5-dimethylphenyl in H_3L_1. Further research on how substituents correlate with the molecular configuration is undertaken in our lab.

3.3. *Integrity and stability*

To explore the solution integrity and stability of complexes in DMF, concentration-dependent absorbances were measured at 346 and 330 nm for **1** and **2**, respectively (figures 3 and 4). For **1**, the absorbance increases linearly with the concentration in the

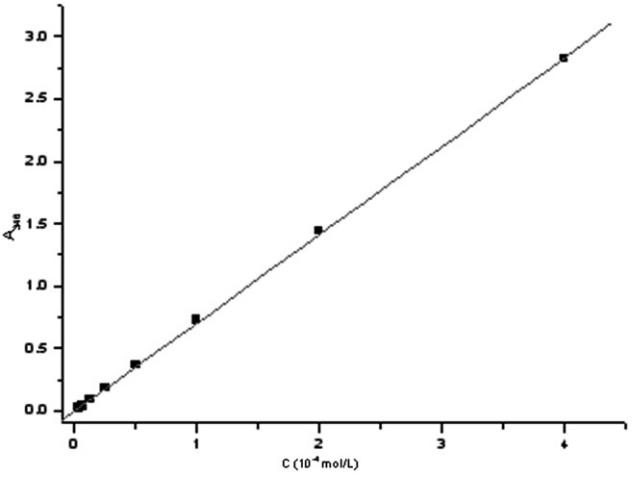


Figure 3. The concentration dependent absorbance of **1** in DMF at 346 nm.

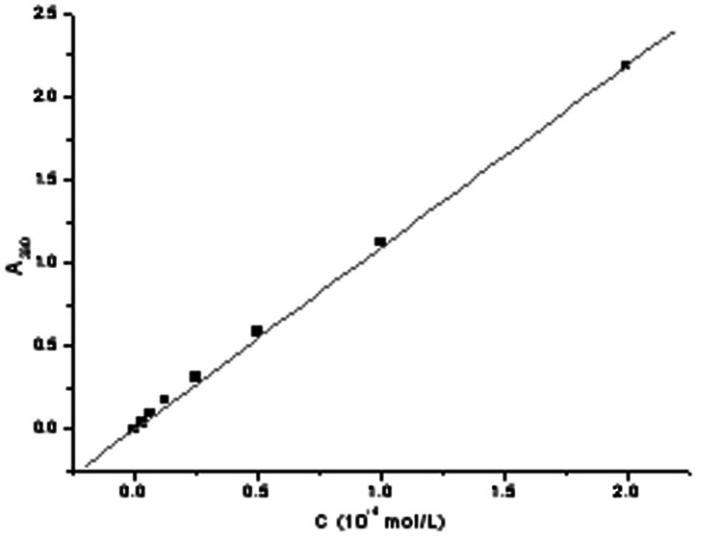


Figure 4. The concentration dependent absorbance of **2** in DMF at 330 nm.

range of 3.1–400 μM, while for **2**, the concentration is between 3.1 and 200 μM. No change was observed for the absorption of the two solutions after two weeks. The results indicate that **1** and **2** retain the trinuclear structure and are stable at least in these concentration ranges in DMF.

3.4. *TG analysis*

The TG curves of **1** and **2** exhibit three steps of weight loss. For **1**, the first weight loss is about 8.8% in the range of 30–140°C, corresponding to loss of one DMF and one water; the second is 16.2% from 140°C to 360°C, corresponding to the loss of two

Table 3. Minimum inhibitory concentration (MIC) of ligands and complexes in $\mu g\,mL^{-1}$.

	Ligands		Complexes	
Microorganisms	H_3L_1	H_3L_2	**1**	**2**
S. aureus ($Gram^+$)	800	800	12.5	400
E. coli ($Gram^-$)	1600	1600	25	400
B. subtilis ($Gram^+$)	>1600	1600	12.5	200
P. vulgaris ($Gram^-$)	800	800	12.5	400

pyridines. For **2**, the first weight loss is 13.6% in the range of 30–207°C, corresponding to loss of two DMF molecules; the second is 14.2% between 207 and 415°C, which assigned to the removal of two pyridine molecules. The observed total weight losses in the first and second step (25.0% and 27.8%) are in agreement with the calculated values (25.2% and 27.4%). The third weight losses are 32.6% for **1** from 360°C to 700°C and 42.4% for **2** from 415°C to 700°C, resulting from decomposition of the ligands.

3.5. *Antimicrobial activities*

Data on antibacterial activity of the ligands and complexes against *S. aureus*, *E. coli*, *B. subtilis*, and *P. vulgaris* are listed in table 3. The ligands are inactive to the entire array of tested microorganism, while **1** has strong antimicrobial activities. Until now, only limited polynuclear nickel complexes have been tested as antibacterial agents. Compared to the linear trinuclear **2** and $[Ni_3(H_2O)_2(DMA)_2(acbshz)_2]\cdot 2DMF$ [19] with high-MIC values (200–400 and 400–800 $\mu g\,mL^{-1}$), the MIC value in the bent **1** is lower. Although it is risky to correlate the bioactivity of these complexes to the structural features, the different arrangement and coordination geometry of the three metal ions in the complexes are important. Compared to the tetranuclear Ni(II) complex ($[12\text{–}MC_{Ni(II)N(Hshi)2(pko)2}\text{–}4](NNN)_2(DMF)(CH_3OH)$) with MIC value of 12–25 $\mu g\,mL^{-1}$ [43], the MIC value in these trinuclear Ni(II) compounds are much higher. It is still not possible to correlate the nuclearity and antibacterial activity. Preparation of more polynuclear compounds to correlate the relationship between nuclearity or structural features and antibacterial activity is in progress in our lab.

4. Conclusion

In this article, we present the syntheses and crystal structures of two new trinuclear Ni(II) complexes $C_{45}H_{45}N_7Ni_3O_8$ (**1**) and $C_{46}H_{44}N_{10}Ni_3O_{12}$ (**2**) with two new trianionic pentadentate ligands *N*-(3,5-dimethylbenzoyl)-salicylhydrazide (H_3L_1) and *N*-(phenylacetyl)-5-nitrosalicylhydrazide (H_3L_2). The three nickel ions within **1** and **2** are linked by two bridging deprotonated L^{3-} ligands, forming a bent/linear trinuclear metal structure unit with an M–N–N–M–N–N–M–N–N–M core due to the steric effects of the *N*-acyl side chains. Antibacterial screening data indicate that bent trinuclear Ni(II) compound **1** is more active than linear compound **2**, but less active than tetranuclear nickel compound in the previous study.

Supplementary data

CCDC 664913 and 664912 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

References

[1] M.J. Hannon, S. Bunce, A.J. Clarke, N.W. Alcock. *Angew. Chem. Int. Ed*, **38**, 1277 (1999).
[2] C. Piguet, G. Bernardinelli, G. Hopfgartner. *Chem. Rev.*, **97**, 2005 (1997).
[3] J. Rojo, J.M. Lehn, G. Baum, D. Fenske, O. Waldmann, P. Müller. *Eur. J. Inorg. Chem.*, 517 (1990).
[4] A. Neels, H. Stoeckli-Evans. *Inorg. Chem.*, **38**, 6164 (1999).
[5] X.H. Bu, H. Morishita, K. Tanaka, K. Biradha, S. Furusho, M. Shiiionoya. *Chem. Commun.*, 971 (2000).
[6] E.I. Solomon, R.K. Szilagyi, S.D. George, L. Basumallick. *Chem. Rev.*, **104**, 419 (2004).
[7] S. Leininger, B. Olenyuk, P.J. Stang. *Chem. Rev.*, **100**, 853 (2000).
[8] D.C. Smith, C.H. Lake, G.M. Gray. *Chem. Commun.*, 2771 (1998).
[9] M. Du, X.-J. Zhao, J.-H. Guo, X.H. Bu, J. Ribas. *Eur. J. Inorg. Chem.*, 294 (2005).
[10] B. Kwak, H. Rhee, S. Park, M.S. Lah. *Inorg. Chem.*, **37**, 3599 (1998).
[11] F.-P. Xiao, L.-F. Jin, W. Luo, G.-Z. Cheng, Z.-P. Ji. *Inorg. Chim. Acta*, **360**, 3341 (2007).
[12] W. Luo, B. Li, F.-P. Xiao, G.-Z. Cheng, Z.-P. Ji. *J. Coord. Chem.*, **60**, 1037 (2007).
[13] B. Li, D.-D. Han, G.-Z. Cheng, Z.-P. Ji. *Inorg. Chem. Commun.*, **8**, 216 (2005).
[14] W. Luo, X.-Z. Sun, K. Hu, Z.-P. Ji, G.-Z. Cheng. *Transition Met. Chem.*, **33**, 295 (2008).
[15] I. Kim, B. Kwak, M.S. Lah. *Inorg. Chim. Acta*, **317**, 12 (2001).
[16] L.-F. Jin, F.-P. Xiao, G.-Z. Cheng, Z.-P. Ji. *Inorg. Chem. Commun.*, **9**, 758 (2006).
[17] F.-P. Xiao, L.-F. Jin, G.-Z. Cheng, Z.-P. Ji. *Polyhedron*, **26**, 2695 (2007).
[18] S. Lin, S.-X. Liu, B.-Z. Lin. *Inorg. Chim. Acta*, **328**, 69 (2002).
[19] S.-X. Liu, S. Lin, B.-Z. Lin, C.-C. Lin, J.-Q. Huang. *Angew. Chem. Int. Ed.*, **40**, 1084 (2001).
[20] D. Moon, K. Lee, R.P. John, G.H. Kim, B.J. Suh, M.S. Lah. *Inorg. Chem.*, **45**, 7991 (2006).
[21] S. Lin, S.-X. Liu, J.-Q. Huang, C.-C. Lin. *J. Chem. Soc. Dalton Trans.*, 1595 (2002).
[22] W. Luo, X.-G. Meng, X.-Z. Sun, F.-P. Xiao, J.-F. Shen, Y. Zhou, G.-Z. Cheng, Z.-P. Ji. *Inorg. Chem. Commun.*, **10**, 1351 (2007).
[23] S. Lin, M.-X. Yang, S.-X. Liu. *Polyhedron*, **26**, 4793 (2007).
[24] W. Luo, X.-G. Meng, F.-P. Xiao, G.-Z. Cheng, Z.-P. Ji. *Polyhedron*, **27**, 1802 (2008).
[25] W. Luo, X.-G. Meng, J.-F. Xiang, Y. Duan, G.-Z. Cheng, Z.-P. Ji. *Inorg. Chim. Acta*, **361**, 2667 (2008).
[26] W. Luo, X.-T. Wang, X.-G. Meng, G.-Z. Cheng, Z.-P. Ji. *Inorg. Chem. Commun.*, **11**, 1044 (2008).
[27] W. Luo, X.-G. Meng, G.-Z. Cheng, Z.-P. Ji. Inorg. Chim. Acta, doi: 10.1016/j.ica.2008.05.007 (2008).
[28] L.K. Thompson, V. Niel, H. Grove, D.O. Miller, M.J. Newlands, P.H. Bird, W.A. Wickramasinghe, A.B.P. Lever. *Polyhedron*, **23**, 1175 (2004).
[29] A.L. Harris, A.H. Yang, A. Hegmans, L. Povirk, J.J. Ryan, L. Kelland, N.P. Farrel. *Inorg. Chem.*, **44**, 9598 (2005).
[30] L. Cronin, P.H. Walton. *Inorg. Chim. Acta*, **269**, 241 (1998).
[31] T.C. Higgs, K. Spartalian, C.J. O'Connor, B.F. Matzanke, C.J. Carrano. *Inorg. Chem.*, **37**, 2263 (1998).
[32] Z.-N. Chen, H.-X. Zhang, K.-B. Yu, C.-Y. Su, B.-S. Kang. *Polyhedron*, **17**, 1535 (1998).
[33] M.-X. Yang, S. Lin, L.-J. Chen, S.-X. Liu. *Chinese J. Inorg. Chem.*, **19**, 433 (2003).
[34] M.-X. Yang, S. Lin, P. Yu, L.-J. Chen, S.-X. Liu. *Chin. J. Chem.*, **23**, 1407 (2005).
[35] M.-X. Yang, S. Lin. *Acta Cryst.*, **E61**, m1095 (2005).
[36] Z.-X. Yu, Y.-X. Sun. *Acta Cryst.*, **E62**, m3521 (2006).
[37] G.M. Sheldrick. *Acta Crystallogr.*, **A46**, 467 (1990).
[38] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen (1997).
[39] S.N. Rao, K.N. Munshi, N.N. Rao, M.M. Bhadbadc, E. Syresh. *Polyhedron*, **18**, 2491 (1999).
[40] M.A. Ali, A.H. Mirza, R.J. Butcher, M.T.H. Tarafder. *Inorg. Chim. Acta*, **320**, 1 (2001).
[41] G.R. Angel, J.F. Juan, B. Ferran. *Polyhedron*, **15**, 4407 (1996).
[42] A.L. Spek. *J. Appl. Cryst.*, **36**, 7 (2003).
[43] M. Alexiou, I. Tsivikas, C. Dendrinou-Samara, A.A. Pantazaki, P. Trikalitis, N. Lalioti, D.A. Kyriakidis, D.P. Kessissoglou. *J. Inorg. Biochem.*, **93**, 256 (2003).