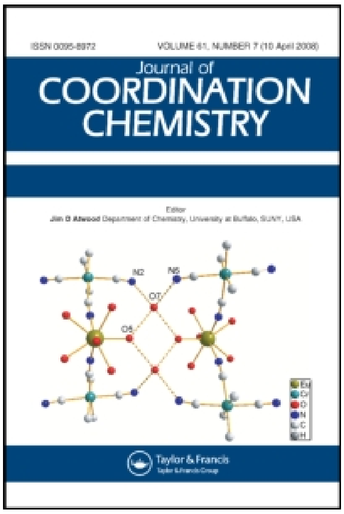

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Bridging chlorides and hydroxides: syntheses and crystal structures of binuclear and tetranuclear Ni^{II} complexes derived from a reduced Schiff-base ligand 2-(2-pyridylmethylamino)ethanesulfonic acid

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To cite this Article Li, Jun-Xia , Jiang, Yi-Min and Chen, Mei-Ji(2008) 'Bridging chlorides and hydroxides: syntheses and crystal structures of binuclear and tetranuclear Ni^{II} complexes derived from a reduced Schiff-base ligand 2-(2-pyridylmethylamino)ethanesulfonic acid', Journal of Coordination Chemistry, 61: 11, 1765 — 1773

To link to this Article: DOI: 10.1080/00958970701744274

URL: http://dx.doi.org/10.1080/00958970701744274

Journal of Coordination Chemistry
Vol. 61, No. 11, 10 June 2008, 1765–1773

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Bridging chlorides and hydroxides: syntheses and crystal structures of binuclear and tetranuclear Ni^{II} complexes derived from a reduced Schiff-base ligand 2-(2-pyridylmethylamino)ethanesulfonic acid

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(*Received 26 May 2007; in final form 12 July 2007*)

Two complexes, [Ni(pmt)(Cl)] (**1**) and $[Ni_4(pmt)_4(OH)_4]\cdot 8H_2O$ (**2**) [Hpmt = 2-(2-pyridylmethylamino)ethanesulfonic acid], were synthesized by different experimental methods in methanol-water mixed solution. Compound **1** crystallizes in triclinic, space group *P*-1 with unit cell parameters: $a = 8.315(2)$ Å, $b = 8.383(2)$ Å, $c = 9.128(2)$ Å, $\alpha = 103.654(2)^\circ$, $\beta = 98.125(2)^\circ$, $\gamma = 113.154(2)^\circ$, $V = 548.6(2)$ Å^3, $Z = 2$. A pair of chlorides is μ_2-bridges linking two Ni^{II} atoms in forming binuclear complex **1**. The coordination environment at Ni^{II} is distorted square-pyramidal geometry. Compound (**2**) belongs to monoclinic, space group *C2*/*c*, with $a = 16.5168(15)$ Å, $b = 18.3718(17)$ Å, $c = 17.5473(16)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 93.3820(10)^\circ$, $V = 5315.3(8)$ Å^3, $Z = 4$. Four hydroxides are μ_3-bridges joining four Ni^{II} atoms to generate a cubic framework as a tetranuclear complex. The configuration at each Ni^{II} is distorted octahedral. Both π–π stacking of pyridine rings and intermolecular hydrogen bonds stabilize the solid state structures for **1** and **2**.

Keywords: Nickel(II)complexes; Binuclear; Tetranuclear; 2-(2-pyridylmethylamino)ethanesulfonic acid; Crystal structure

1. Introduction

Schiff-base complexes containing sulfur and amino acid functionality have received interest due to their antibacterial, anticancer and antiviral activities [1–3]. 2-Aminoethanesulfonic acid, known as taurine, plays an important part in physiological functions. Casella and coworkers [4] have found that zinc and copper complexes of Schiff-base ligands, prepared by the condensation of 2-pyridinecarboxaldehyde with non-polar amino acids, are unstable. This has been attributed to the rigidity of the C=N double bond in the free Schiff bases later confirmed by Wagner *et al.* [5]. In order to explore complexes that are more stable and have stronger biological activities, we have focused our research on coordination complexes based on the reduced Schiff-base ligand 2-(2-pyridylmethylamino)ethanesulfonic acid (Hpmt). Four complexes derived from

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701744274

Hpmt have been reported in our earlier research [6–9]. In this article, we describe the syntheses and crystal structures of a binuclear Ni^{II} complex **1** and a tetranuclear Ni^{II} complex **2**, prepared with the same proportion of Hpmt and $NiCl_2 \cdot 6H_2O$ but by different experimental methods in methanol–water mixed solvent. In compound **1**, a pair of chlorides is μ_2-bridges. In compound **2**, four hydroxides are μ_3-bridges joining four Ni^{II} atoms in a cubical framework similar to cubane. Complexes **1** and **2** are stabilized by π–π stacking of pyridine rings and intermolecular hydrogen bonding interactions.

2. Experimental

2.1. *Materials and apparatus*

2-(2-pyridylmethylamino)ethanesulfonic acid (Hpmt) was prepared by a literature procedure [6]. Other chemicals were of reagent grade obtained from commercial sources and used as received without further purification. The C, H, N, S elemental analyses were preformed on a Elementar Vario EL elemental analyzer. The IR spectrum was recorded with a Shimadzu IR-408 spectrophotometer using KBr pellets in the range 4000–400 cm^{-1}.

2.2. *Synthesis of [Ni(pmt)(Cl)] (1)*

To Hpmt (1 mmol, 0.216 g) dissolved in 7 mL water was added a solution of $NiCl_2 \cdot 6H_2O$ (1 mmol, 0.238 g) in 8 mL methanol and the resulting mixture was stirred at 333 K for 3 h, then cooled to room temperature. Several weeks later, blue claviform crystals suitable for X-ray diffraction were obtained by slow evaporation. Yield: 148.5 mg (48%). Anal. Calcd for $C_8H_{11}Cl\ N_2NiO_3S$ (%): C, 31.03; H, 3.55; N, 9.05; S, 10.34. Found: C, 31.09; H, 3.48; N, 9.02; S, 10.37. IR (cm^{-1}): 3222.8m, 1611.2m, 1572.1m, 1161.2s, 1145.0s, 1031.5s, 781.3s, 754.3m.

2.3. *Synthesis of [Ni$_4$(pmt)$_4$(OH)$_4$]·8H$_2$O (2)*

A solution of $NiCl_2 \cdot 6H_2O$ (1 mmol, 0.238 g) in methanol (8 mL) was dropped into a solution (7 mL) of ligand Hpmt (1.0 mmol, 0.216 g) in water and the mixture was treated with KOH (1 mol l^{-1}) to a pH of 7.5–8.0 and stirred at 333 K for 4 h. Then the solution was cooled to room temperature, filtered and kept at room temperature to obtain green block-shaped crystals 5 days later. Yield: 784.8 mg (62%). Anal. Calcd for $C_{32}H_{64}N_8Ni_4O_{24}S_4$ (%): C, 29.36; H, 4.89; N, 4.28; S, 9.78. Found: C, 29.31; H, 4.82; N, 4.33; S, 9.81. IR (cm^{-1}): 3445.2s, 3214.8m, 1609.7m, 1573.3m, 1189.4s, 1151.3s, 1041.7s, 771.7s, 747.4m.

2.4. *X-ray diffraction determination*

Single crystal X-ray data collections for the title complexes were performed with a Bruker APEX-II CCDC area detector diffractometer, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS [10].

The structure was solved by direct methods [11] and refined by full-matrix least squares on F^2 using SHELXL97 [12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The crystallographic data for complexes **1** and **2** are listed in table 1, selected bond lengths (Å) and angles (°) are listed in table 2; details of the hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. *Structural description of [Ni(pmt)(Cl)] (1)*

Single crystal X-ray diffraction analysis reveals that **1** is a dinuclear complex and the asymmetric unit contains a Ni, a Cl^- and a deprotonated pmt anionic ligand. The Ni^{II} is five-coordinate through two N and one O atoms of the tridentate chelating pmt and two chlorides in a deformed square-pyramid (figure 1) [Ni1–O1 = 1.9838(15) Å, Ni1–N1 = 2.0079(17) Å, Ni1–N2 = 2.0307(18) Å, Ni1–Cl1 = 2.2930(7) Å, Ni1–Cl1A = 2.6873(8) Å]. N1, N2, O1 and Cl1 atoms occupy the plane, with Cl1A at the apex. Ni1 deviates from the least-squares plane of the basal plane N1/N2/O1/Cl1 by 0.1688 Å toward Cl1A. A pair of chlorides is μ_2-bridges with Ni$\cdots$Ni distance of 3.472 Å. The function of chlorides here is similar to "catena-[bis(μ_2-chloro)-bis(N-(2-pyridylmethyl)glycinato)-di-copper(II) dihydrate]" [13] in which one chloride

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

Complex	**1**	**2**
Empirical formula	$C_8H_{11}Cl\ N_2NiO_3S$	$C_{32}H_{64}N_8Ni_4O_{24}S_4$
Formula weight	309.41	1307.99
Temperature (K)	291(2)	291(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	8.315(2)	16.5168(15)
b (Å)	8.383(2)	18.3718(17)
c (Å)	9.128(2)	17.5473(16)
α (°)	103.654(2)	90
β (°)	98.125(2)	93.3820(10)
γ (°)	113.154(2)	90
V (Å^3)	548.6(2)	5315.3(8)
Z	2	4
D_{cal} (Mg m^{-3})	1.873	1.634
Absorption coefficient (mm^{-1})	2.193	1.637
F (000)	316	2720
Crystal size (mm^3)	0.38 × 0.22 × 0.21	0.36 × 0.26 × 0.23
θ Range (°)	2.38–27.49	2.33–27.50
Limiting indices $h/k/l$ (max, min)	−10, 10/−10, 10/−11, 11	−21, 21/−16, 23/−22, 22
Reflections collected	4700	15804
Independent reflections (R_{int})	2460(0.0121)	5987(0.0227)
Completeness to θ	98.1%	97.9%
Max. and Min. transmission	0.6596 and 0.4888	0.7086 and 0.5918
Data/restraints/parameters	2460/0/149	5987/56/341
Goodness-of-fit on F^2	1.049	1.038
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0248$, $wR_2 = 0.0636$	$R_1 = 0.0426$, $wR_2 = 0.1181$
R indices (all data)	$R_1 = 0.0273$, $wR_2 = 0.0653$	$R_1 = 0.0577$, $wR_2 = 0.1286$
Largest diff. peak and hole (e Å^{-3})	0.695 and −0.48	0.740 and −0.915

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

Complex **1**			
Ni(1)–O(1)	1.9838(15)	Ni(1)–N(1)	2.0079(17)
Ni(1)–N(2)	2.0307(18)	Ni(1)–Cl(1)	2.2930(7)
Ni(1)–Cl(1)#1	2.6873(8)	O(1)–Ni(1)–N(1)	169.83(7)
N(1)–Ni(1)–N(2)	81.09(7)	O(1)–Ni(1)–N(2)	92.71(7)
N(1)–Ni(1)–Cl(1)	95.64(5)	O(1)–Ni(1)–Cl(1)	89.05(5)
O(1)–Ni(1)–Cl(1)#1	96.09(5)	N(2)–Ni(1)–Cl(1)	169.68(6)
N(2)–Ni(1)–Cl(1)#1	97.93(6)	N(1)–Ni(1)–Cl(1)#1	92.77(5)
Ni(1)–Cl(1)–Ni(1)#1	88.01(2)	Cl(1)–Ni(1)–Cl(1)#1	91.99(2)
Complex **2**			
Ni(1)–O(7)	2.038(2)	Ni(1)–N(1)	2.062(3)
Ni(1)–O(8)	2.068(3)	Ni(1)–O(7)#2	2.072(2)
Ni(1)–N(2)	2.095(3)	Ni(1)–O(1)	2.129(2)
Ni(2)–O(8)#2	2.049(2)	Ni(2)–O(7)	2.053(2)
Ni(2)–O(8)	2.066(3)	Ni(2)–N(3)	2.089(3)
Ni(2)–N(4)	2.106(3)	Ni(2)–O(6)	2.125(3)
O(7)–Ni(1)#2	2.072(2)	O(8)–Ni(2)#2	2.049(2)
O(7)–Ni(1)–N(1)	100.23(12)	O(7)–Ni(1)–O(8)	81.74(10)
N(1)–Ni(1)–O(8)	177.06(11)	O(7)–Ni(1)–O(7)#2	81.49(9)
N(1)–Ni(1)–O(7)#2	97.21(11)	O(8)–Ni(1)–O(7)#2	80.88(9)
O(7)–Ni(1)–N(2)	174.01(11)	N(1)–Ni(1)–N(2)	81.08(15)
O(8)–Ni(1)–N(2)	96.75(13)	O(7)#2–Ni(1)–N(2)	92.56(11)
O(7)–Ni(1)–O(1)	90.94(9)	N(1)–Ni(1)–O(1)	89.10(11)
O(8)–Ni(1)–O(1)	93.06(10)	O(7)#2–Ni(1)–O(1)	170.87(9)
N(2)–Ni(1)–O(1)	94.93(11)	O(8)#2–Ni(2)–O(7)	81.79(10)
O(8)#2–Ni(2)–O(8)	80.15(11)	O(7)–Ni(2)–O(8)	81.40(10)
O(8)#2–Ni(2)–N(3)	102.54(12)	O(7)–Ni(2)–N(3)	175.43(11)
O(8)–Ni(2)–N(3)	97.80(12)	O(8)#2–Ni(2)–N(4)	175.08(12)
O(7)–Ni(2)–N(4)	95.53(11)	O(8)–Ni(2)–N(4)	95.40(12)
N(3)–Ni(2)–N(4)	80.05(14)	O(8)#2–Ni(2)–O(6)	90.85(10)
O(7)–Ni(2)–O(6)	91.82(11)	O(8)–Ni(2)–O(6)	169.39(10)
N(3)–Ni(2)–O(6)	89.59(13)	N(4)–Ni(2)–O(6)	93.35(13)
Ni(1)–O(7)–Ni(2)	98.37(10)	Ni(1)–O(7)–Ni(1)#2	97.96(9)
Ni(2)–O(7)–Ni(1)#2	97.87(10)	Ni(2)#2–O(8)–Ni(2)	99.40(11)
Ni(2)#2–O(8)–Ni(1)	98.15(11)	Ni(2)–O(8)–Ni(1)	96.99(11)

Symmetry codes: #1: $-x+1$, $-y$, $-z$; #2: $-x+1$, y, $-z+1/2$.

Table 3. Hydrogen bonds (Å, °) for **1** and **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
Complex **1**				
N(2)–H(1N)···O(3)#1	0.99(4)	2.15(3)	2.973(3)	139(3)
Complex **2**				
O(7)–H(1X)···O(10)	0.86(5)	2.14(5)	2.981(4)	168(5)
O(8)–H(2X)···O(9)	0.71(6)	2.18(6)	2.879(7)	171(7)
O(9)–H(1W)···O(3)	0.96	2.23	3.145(8)	158.7
O(9)–H(2W)···O(8)	0.91	2.27	2.879(7)	123.4
O(10)–H(3W)···O(10)#2	0.84	2.37	2.939(8)	126.2
O(10)–H(4W)···O(11)	0.85	1.95	2.790(6)	169.4
O(11)–H(5W)···O(2)	0.85	2.11	2.941(5)	168.9
O(11)–H(5W)···O(1)	0.85	2.65	3.259(4)	130.5
O(11)–H(6W)···O(12)	0.86	2.43	2.859(8)	111.7
O(12)–H(7W)···O(9)#3	0.89	2.03	2.926(10)	178.7

Symmetry codes: #1: $-x+1$, $-y+1$, $-z$; #2: $-x+1$, $-y+1$, $-z+1$; #3: $-x+3/2$, $y+1/2$, $-z+1/2$.

links two Cu^{II} atoms into a one-dimensional polymer. The geometric parameters are in good agreement.

The NH and S=O groups participate in weak hydrogen bonds and join binuclear units into a one-dimensional infinite chain along *b* (figure 2). In addition, there are weak π–π stacking interactions between parallel pyridine rings of neighboring chains along the *b* axis (figure 3). The interplanar average distance and ring-centroid separation distance are 3.503 Å and 4.109 Å, respectively. Thus the one-dimensional chain is extended into a two-dimensional layer in the *bc* plane, stabilized by hydrogen bonds and π–π stacking.

3.2. *Structural description of [$Ni_4(pmt)_4(OH)_4$]·$8H_2O$ (2)*

The asymmetric unit of **2** consists of two Ni atoms, two deprotonated pmt ligands, two OH^- and four H_2O molecules. Four Ni^{II} atoms lie in the same coordination

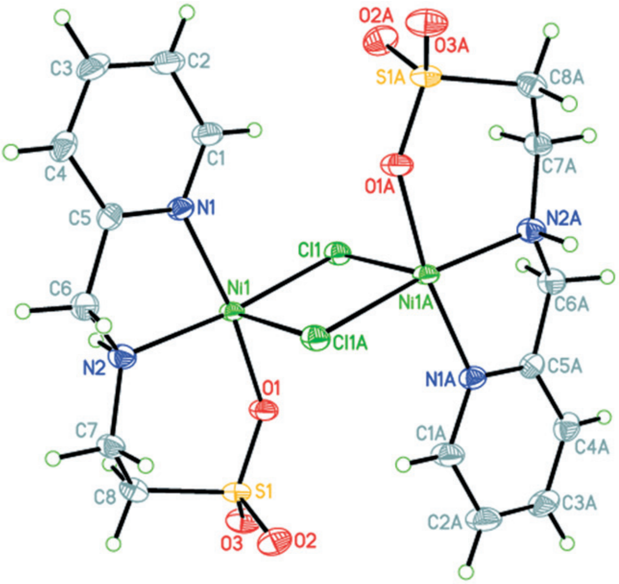

Figure 1. The molecular structure for **1** with thermal ellipsoids drawn at 30% probability level.

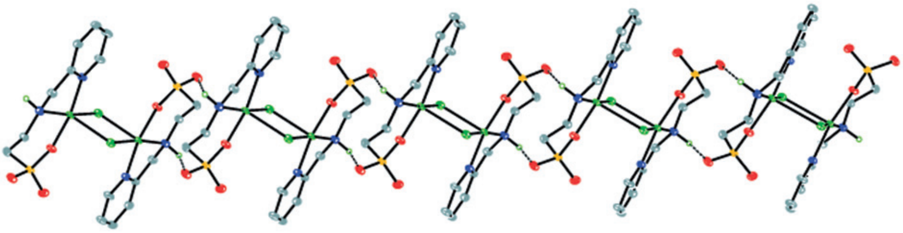

Figure 2. The hydrogen bonds viewed along the *b* axis in **1**. H atoms bonded to C atoms have been omitted.

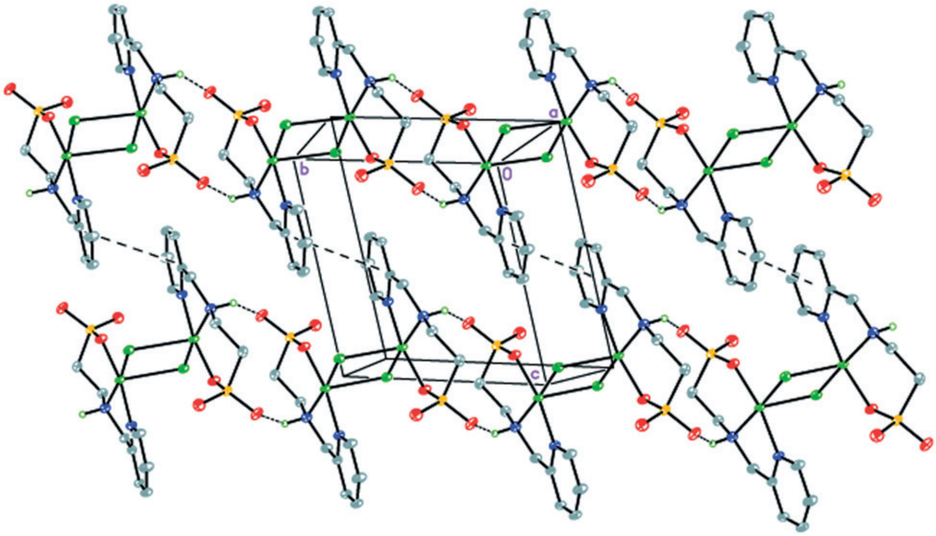

Figure 3. The π–π stacking between adjacent chains in **1** projected on the *bc* plane. H atoms have been omitted for clarity.

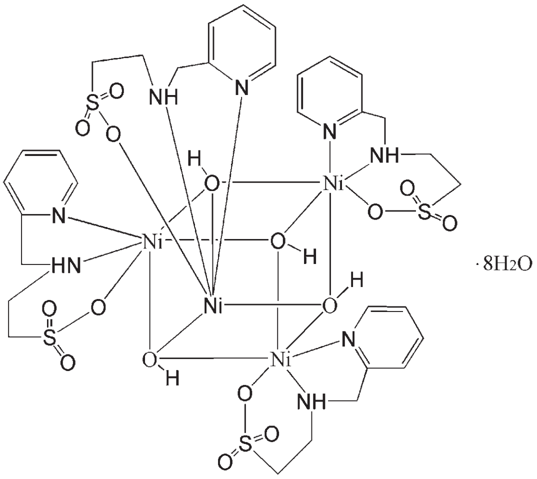

Figure 4. The scheme for **2**.

environment (figure 4 and figure 5), with distorted octahedral configuration, bonded to three donor atoms of the tridentate chelating pmt ligand [Ni1–N1 = 2.062(3) Å, Ni1–N2 = 2.095 (3) Å, Ni1–O1 = 2.129(2) Å; Ni2–N3 = 2.089(3) Å, Ni2–N4 = 2.106(3) Å, Ni2–O6 = 2.125(3) Å] and three O atoms from three hydroxides [Ni1–O7 = 2.038(2) Å, Ni1–O8 = 2.068(3) Å, Ni1–O7$^{\#1}$ = 2.072(2) Å; Ni2–O7 = 2.053(2) Å, Ni2–O8 = 2.066(3) Å, Ni2–O8$^{\#1}$ = 2.049(2) Å] (symmetry codes for #1: $-x+1$, y, $-z+1/2$). For Ni1, N2, O1, O7 and O7$^{\#1}$ atoms define the equatorial plane and N1 and O8 occupy axial positions. Ni1 deviates from the least-squares plane of the equatorial plane N2/O1/O7/O7$^{\#1}$ by 0.0553 Å towards N1. Four hydroxides are μ_3-bridges, joining four Ni^{II}'s to generate a Ni–O cubical framework (figure 6) similar to cubane. The distances

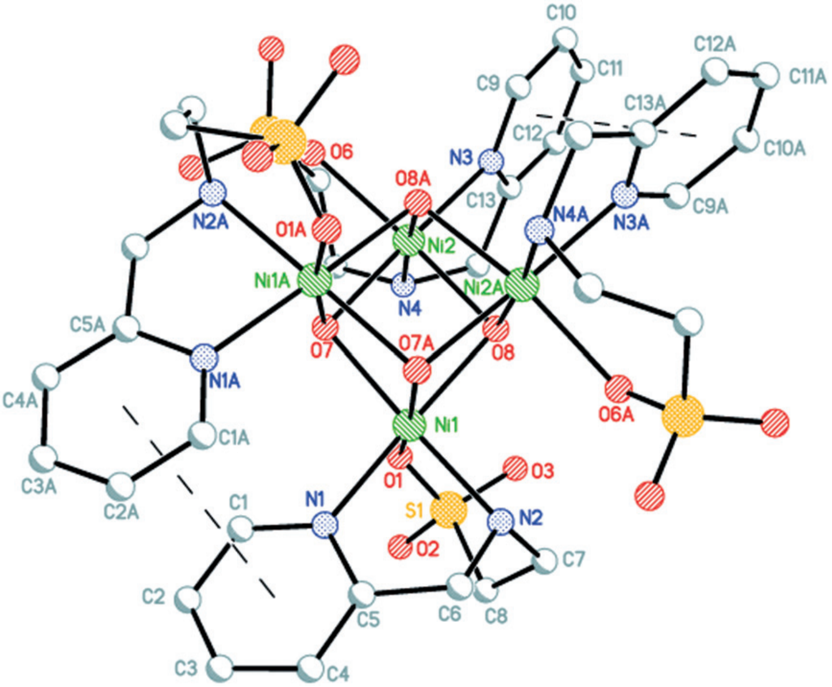

Figure 5. The molecular structure for **2** with atom numbering. Water molecules and H atoms have been omitted. The π–π stacking is shown as dashed lines.

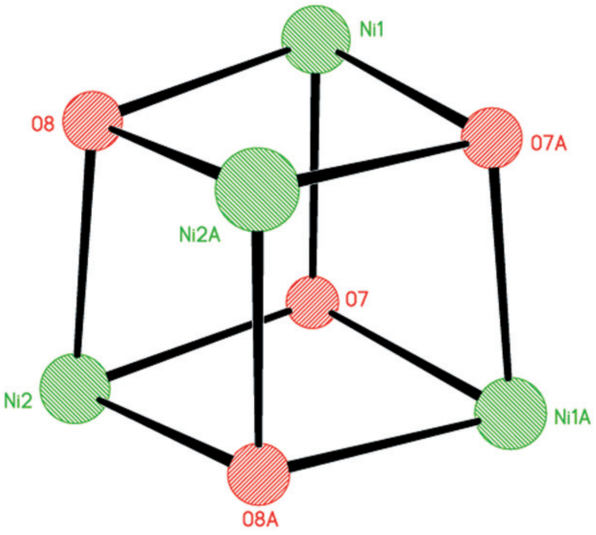

Figure 6. The cubic framework composed of Ni^{II} and O atoms in **2**.

of diagonal Ni^{II} atoms fall in the range 3.096 Å to 3.138 Å. This tetranuclear structure is similar to a reported tetranuclear cobalt complex tetrakis((μ_3-oxo)-N-(2-pyridylmethyl)glycinato cobalt(III)) hydrate [14]. The difference is that four O^{2-} ions act as μ_3-bridges for the latter complex; geometric parameters agree well.

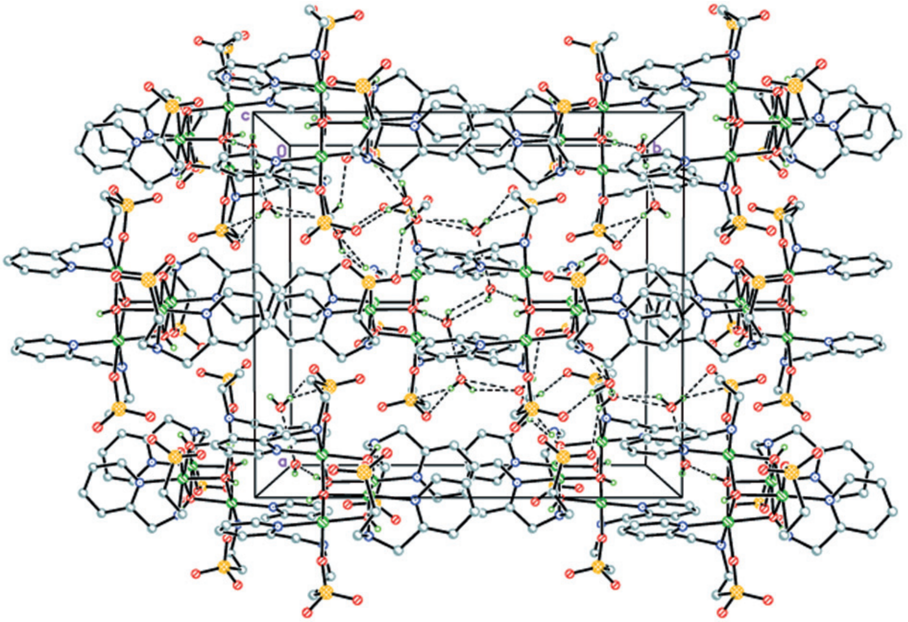

Figure 7. The hydrogen bonds in **2** (dashed lines). H atoms bound to C and N atoms have been omitted.

In **2**, there exist two kinds of π–π stacking interactions between pyridine rings: one is stronger between N1/C1/C2/C3/C4/C5 and N1A/C1A/C2A/C3A/C4A/C5A rings, the other is between N3/C9/C10/C11/C12/C13 and N3A/C9A/C10A/C11A/C12A/C13A rings (figure 5). The dihedral, average distance and ring-centroid separation distance are 5.34(6)°, 3.2571(1) Å, 3.9493(3) Å for the former, 20.60(6)°, 3.5147(1) Å, 4.5776(4) Å for the latter. It is through π–π stacking that the tetranuclear structure is stabilized.

The water molecules are not involved in coordination but form a variety of hydrogen bonding interactions with pmt ligands and bridging hydroxides (figure 7). These intermolecular hydrogen bonds further stabilize the complex connecting it into a three-dimensional network.

4. Conclusions

In this article, we report new nickel(II) complexes [Ni(pmt)(Cl)] bridged by chlorides and $[Ni_4(pmt)_4(OH)_4]\cdot 8H_2O$ bridged by hydroxides. Different experimental methods result in different components and different structures. The Ni–$O_{hydroxide}$ bond [length: 2.038(2) Å–2.072(2) Å] is much stronger than Ni–$Cl_{bridged}$ [length: 2.6873(8) Å] proving that hydroxide competes with chloride for coordination to metal.

Supplementary data

CCDC numbers 614218 and 613274 contain the supplementary crystallographic data for this article. 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; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

This work was funded by Guangxi Science Foundation (grant No.0731053) of the People's Republic of China. We also thank Luoyang Normal College and Nankai University for supporting this study.

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